Lawrence Berkeley National Laboratory
Recent Work

Title
STRUCTURE AND BONDING IN ORGANO-LANTHANIDE AND -ACTINIDE COMPOUNDS

Permalink
https://escholarship.org/uc/item/0nd424s3

Author
Eigenbrot, C.W.

Publication Date
1981-02-01
STRUCTURE AND BONDING IN ORGANO-LANTHANIDE AND ACTINIDE COMPOUNDS

Charles Weaver Eigenbrot, Jr.
(Ph.D. thesis)

February 1981

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
STRUCTURE AND BONDING IN ORGANO-LANTHANIDE AND -ACTINIDE COMPOUNDS

Charles Weaver Eigenbrot, Jr.
Ph.D. thesis

February 1981

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.

This manuscript was printed from originals provided by the author.
Structure and Bonding in Organo-Lanthanide and -Actinide Compounds

Charles Weaver Eigenbrot, Jr.

ABSTRACT

The reactions of U(C_5H_5)_3(THF) and U(C_5H_4CH_3)_3(THF) with pyrazine lead to the formation of dimeric, μ-bridged species of U^{3+} of formulae [U(C_5H_5)_3]_2C_4H_4N_2 and [U(C_5H_4CH_3)_3]_2C_4H_4N_2. The dimeric formulation of the two compounds is indicated by the X-ray powder pattern of [U(C_5H_5)_3]_2C_4H_4N_2, the mass spectra of both compounds, and the pmr spectrum of [U(C_5H_4CH_3)_3]_2C_4H_4N_2. Preliminary results indicate unusual magnetic behavior at low temperature.

New compounds have been prepared and characterized by their infra-red, visible-near IR, pmr, and mass spectra; and by single crystal X-ray diffraction.

The compound U(C_5H_5)_3(C_3H_3N_2) has been prepared by the reaction between U(C_5H_5)_3Cl and Na(C_3H_3N_2) in THF. The molecular structure consists of discrete U(C_5H_5)_3(C_3H_3N_2) molecules in which the U^{4+} ion is coordinated by three η^5-cyclopentadienide rings in a nearly trigonal array. Two additional coordination sites are occupied by the two nitrogen atoms of the pyrazolate anion, for a total coordination number of 11. This is the first example of an endo-bidentate
\( \eta^2 \) coordination for the pyrazolate anion. Red-brown crystals from toluene conform to space group P2\(_1\)/a, with \( a=14.295(1) \), \( b=8.383(1) \), \( c=14.282(1) \) Å, \( \beta=112.80(1) \) degrees, and 4 molecules per unit cell. The model refined to final weighted and unweighted \( R \) factors both of 3.14%. The U-N bond distances are 2.36(1) Å and 2.40(1) Å. The average U-C bond distance of 2.76 Å is consistent with that predicted for an 11-coordinate \( U^{4+} \) cyclopentadienide complex.

The reactions between \( U(C_5\text{Me}_5)_2\text{Cl}_2 \) and \( C_3\text{H}_4\text{N}_2 \) in THF have led to the isolation of three new compounds of formulae \( U(C_5\text{Me}_5)_2\text{Cl}_2(C_3\text{H}_4\text{N}_2) \), \( U(C_5\text{Me}_5)_2\text{Cl}(C_3\text{H}_3\text{N}_2) \), and \( U(C_5\text{Me}_5)_2(C_3\text{H}_3\text{N}_2)_2 \).

The crystal structure of \( U(C_5\text{Me}_5)_2\text{Cl}_2(C_3\text{H}_4\text{N}_2) \) consists of discrete molecular units at positions of \( \overline{mm} \) symmetry. The \( U^{4+} \) ion is coordinated by two \( \eta^5 \)-pentamethylcyclopentadienide rings, two chloride ions, and one nitrogen from the neutral pyrazole ring, for a total coordination number of 9. Red-brown crystals from hexane conform to space group Cmcm with \( a=13.697(4) \), \( b=11.496(2) \), \( c=15.555(2) \) Å, and 4 molecules per unit cell. The model refined to final weighted and unweighted \( R \) factors of 3.48% and 2.45% respectively. The average U-C bond distance is 2.74(2) Å, the U-N bond distance is 2.607(8) Å, and the U-Cl bond distance is 2.696(2) Å.

The crystal structure of \( U(C_5\text{Me}_5)_2\text{Cl}(C_3\text{H}_3\text{N}_2) \) consists of discrete \( U^{4+} \) ions coordinated by two \( \eta^5 \)-pentamethylcyclopentadienide rings.
pentadienide rings, one chloride ion, and both nitrogen atoms from the pyrazolate anion, for a total coordination number of 9. Red-brown crystals from hexane conform to space group P2_1/n with a=8.737(1), b=18.068(1), c=15.229(1) Å, \( \beta = 92.38(1) \) degrees, and 4 molecules per unit cell. The model refined to final weighted and unweighted R factors of 4.50% and 3.27% respectively. The average U-C bond distance is 2.73(3) Å, the U-N bond distances are 2.351(5) Å and 2.349(5) Å, and the U-Cl bond distance is 2.611(2) Å.

The crystal structure of \( \text{U(C}_{5}\text{Me}_{5})_{2}(\text{C}_{5}\text{H}_{3}\text{N}_{2})_{2} \) consists of discrete U\(^{4+}\) ions coordinated by two \( \eta^{5}\)-pentamethylcyclopentadienide rings and four nitrogen atoms from the two pyrazolate anions, for a total coordination number of 10. Red-brown crystals from hexane conform to space group C2/c with a=33.326(2), b=10.450(2), c=16.646(1) Å, \( \beta = 117.09(1) \) degrees, and 8 molecules per unit cell. The model refined to final weighted and unweighted R factors of 3.31% and 2.43% respectively. The U-C bond distances average 2.75(2) Å, and the U-N bond distances are 2.403(4) Å, 2.360(5) Å, 2.363(5) Å, and 2.405(5) Å.

The crystal and molecular structure of the known complex \([\text{Nd(N(C}_{2}\text{H}_{5}\text{NH}_{2})_{3})_{2}(\text{CH}_{3}\text{CN})](\text{ClO}_{4})_{3}\) has been determined by single crystal X-ray diffraction. Clear pink crystals from a mixture of acetonitrile and benzene conform to space group Cc, with a=15.044(1), b=17.729(1), c=11.088(1) Å, \( \beta = 95.079(5) \)
degrees, and 4 formula weights per unit cell. The structure of the molecular cation consists of a Nd$^{3+}$ ion coordinated by two tetradentate $\text{N(C}_2\text{H}_5\text{NH}_2)_3$ ligands and the nitrogen atom from an acetonitrile molecule for a total coordination number of 9. The model refined to final weighted and unweighted R factors of 3.19% and 2.94% respectively. The coordination polyhedron is a tri-capped trigonal prism.

Kenneth N. Raymond
For Knox Burger.

2 days older than I am,
he has been a very good father to me.
Acknowledgement

I wish to thank all the people who helped me in completing this work. Most prominent among them are Andy, Hoy, Sherry, Loc, Al, Cathy, and Lirmar from the shops and storerooms in the College. As Professor Raymond's secretary, June Smith was in charge of everything. Fred Hollander was of invaluable assistance with the crystallography, as was Geoff Wong with the nmr spectra. Out softball team, The Ducks on the Pond, brought me more joy than has even the completion of this dissertation. As for all the others, too numerous to mention, I've got $5 that says if you're reading this before December 1981, then you're among those I wish to thank. And, of course, thanks to Ken Raymond. He paid the bills.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract Number W-7405-ENG-48.
## TABLE OF CONTENTS

**INTRODUCTION** .............................................. 1  
Statement of Purpose ........................................... 12  
Tables .................................................................. 14  
Figures .................................................................. 18  
References ........................................................... 32

**CHAPTER ONE** – The Synthesis and Characterization of \((\text{UCp}_3)_2(\text{pyrazine})\) and \([\text{U(MeCp)}_3]_2(\text{purazine})\):

\(\mu\)-Bridged Dimers of \(\text{U}^{3+}\) ........................................ 38  
Tables .................................................................. 47  
Figures .................................................................. 49  
References ........................................................... 53

**CHAPTER TWO** – Synthesis and X-ray Structure of \(\text{UCp}_3(\text{C}_3\text{H}_3\text{N}_2)\). A New Mode of Pyrazolate Bonding ............................................. 54  
Tables .................................................................. 64  
Figures .................................................................. 70  
References ........................................................... 76

**CHAPTER THREE** – Synthesis and X-ray Structures of \(\text{U(C}_5\text{Me}_5)_2\text{Cl}_2(\text{C}_3\text{H}_4\text{N}_2)\), \(\text{U(C}_5\text{Me}_5)_2\text{Cl}(\text{C}_3\text{H}_2\text{N}_2)\), and \(\text{U(C}_5\text{Me}_5)_2(\text{C}_3\text{H}_3\text{N}_2)_2\) ........................................ 79  
Tables .................................................................. 100  
Figures .................................................................. 117  
References ........................................................... 131
CHAPTER FOUR - Crystal and Molecular Structure of $[\text{Nd(tren)}_2(\text{CH}_3\text{CN})]_2\text{ClO}_4$ .......................... 135

Tables ........................................................................... 144

Figures ........................................................................... 153

References ................................................................. 161
Introduction

Organometallic chemistry, while over 100 years old, has experienced fantastic growth since the 1950's. Today it is a large, diverse area of ongoing basic research and industrial application. As the number and types of such compounds has increased, theories have been developed that, by and large, satisfactorily explain the role d-electrons play in the bonding of the predominant members of this group of compounds, those formed by the d-transition metals$^{1,2}$. During this period of expansion, the first organometallic complexes of the f-transition elements were characterized. This subset of organometallic chemistry was largely ignored for its first 10 years or so—in part due to the fact that the addition of f-electrons to the electronic configurations made their interrelationships much more complex, and prevented the satisfying analyses performed on the d-metal organometallic compounds. To many, the predominant ionicity of the earliest compounds, the tris(cyclopentadienide)lanthanides$^3$, made them less interesting than d-metal metallocenes, where covalent interactions are common. Meanwhile the actinides, because they also possess f-electrons, were probably dismissed in the same breath as the "boring" lanthanides. And, of course, many of the actinides were unknown during this period. (Indeed, all the chemistry of the later (synthetic) actinides has been and probably will continue to be hampered by the time and
expense required in handling them safely.)

However, a resurgence of interest in the organometallic chemistry of the lanthanides and actinides was occasioned by Streitwieser and Muller-Westerhoff's synthesis of uranocene\(^4\) in 1968. The subsequent crystal structure\(^5\) offered initial confirmation of the elegance of Streitwieser's hypothesis—that the symmetry of the f-orbitals was appropriate for covalent bonding to the cyclooctatetraene dianion (COT) in much the same way that the d-orbitals of other metals bond to the cyclopentadienide (Cp) anion. Almost overnight chemists around the world set to the task of exploiting the apparent covalency of uranocene, and they have been working at it ever since.

During the last 12 or so years, the question of f-electron covalency has been one of intense interest. Some workers have been a little over-enthusiastic in concluding certain properties were the effects of covalency\(^6\), apparently due to the lingering opinion that covalent interactions are philosophically and intellectually more satisfying than ionic ones. Other workers have collected data that leave little doubt that some covalency exists, principally in COT complexes of uranium. These studies include Green's\(^7\) photoelectron spectra of uranocene and thoracene. The intensity variation of the observed peaks in going from He(I) irradiation to He(II) irradiation, and their interpretation based on the most plausible molecular
orbital scheme for the complexes, very strongly suggests that there is mixing of ligand and metal (f) orbitals. This is covalency by any definition. In addition, the nmr and the low temperature magnetic susceptibility of uranocene have been interpreted in terms of some degree of covalency. And, while there is generally less evidence of covalency in Cp complexes, the Mossbauer spectrum of \( \text{NpCp}_4 \) indicates the net charge on the metal ion is less than +4.0, consistent with some net donation of ligand electrons to the 4+ metal center.

Because intelligent interpretation of the data obtained in these various physical studies requires a detailed knowledge of the crystal and/or molecular symmetry of the compound in question, X-ray crystal structures have played a central role in bonding studies. In addition, the structures themselves can serve as a useful, albeit insensitive, probe of bonding, once a careful and limited structural definition of covalent/ionic bonding has been drawn.

A Structural Definition of Covalent/Ionic Bonding

For the question of the presence or absence of any property to have meaning, the property itself must be well defined. While there are certainly many definitions of covalent/ionic bonding, and various physical techniques lend themselves to each definition, the following two criteria provide a phenomenological definition based only on structure:
[1] The geometries of ionic compounds tend to be irregular and depend on the steric bulk, number, and charge of the ligands. The coordination number observed is the result of a balance between ionic attractive forces and non-bonded repulsions. This is in marked contrast to the regular, directional bonds which typify covalent compounds.

[2] Bond lengths for a series of structurally related compounds will follow systematically from their "ion size" and coordination number—that is, ionic radii can be used to predict bond lengths. In contrast, the structure of predominantly covalent compounds show pronounced departures from such predictions.

In simple ionic salts it is found that the difference between the cation-anion interatomic distances, $R$, is constant for a given ion. For example, $R$ equals 2.81 and 2.98 for NaCl and NaBr respectively, and their difference is .17 Å. Likewise for the analogous potassium salts the difference is .15 Å, and for the rubidium salts the difference is .15 Å. Then one can say that the radius of bromide ion is about .15 Å greater than that of chloride ion.

Following Pauling's approach\textsuperscript{10} one can write

$$R = r_+ + r_-$$

where $r_+$ and $r_-$ are radii of the cation and anion,
respectively, and

$$\frac{r_+}{r_-} = \frac{Z_+^*}{Z_-^*}$$

(2)

where $Z_+^*$ and $Z_-^*$ are the effective nuclear charges for the valence electrons of the cation and anion respectively. This gives the so-called "univalent radii", which tacitly assumes a $\pm 1$ charge on each ion. The decrease in effective size that accompanies higher charge for a salt $M^{+i}X^{-j+i}$ is given by

$$R_{ij} = R_{11} \left| \frac{1}{n-1} \right|$$

(3)

where $n$ is the Born exponent\(^{10}\) (12 for most of the cations we will consider). In a similar fashion, the increase in effective ion size with coordination number is given by

$$\left| \frac{R_{II}}{R_I} \right| = \left| \frac{CN_{II}}{CN_I} \right| \frac{1}{n-1}$$

(4)

where $R_{II}$ and $R_I$ are the interionic distances for coordination II and I respectively.
The most useful and complete tabulation of ionic radii today is that of Shannon\textsuperscript{11} who has produced a self-consistent set of ionic radii from over 900 structure reports. These radii will be used in the following discussion, with adjustments applied for changes in coordination number as described in equation (4), when appropriate. The definition of coordination number used here is: the number of electron pairs involved in ligand-to-metal coordination.

**Structural Types and Coordination Numbers of Organoactinides and -Lanthanides**

\[ \text{MCP}_3 X \quad \text{and} \quad \text{MCP}_3 \]

There is a large class of lanthanide and actinide compounds of the general formula MCP\textsubscript{3}X,\textsuperscript{12} where X is a donor ligand, anion, or \( \eta^1 \) bridging cyclopentadienyl ring. The structure of one such compound, tris(benzylcyclopentadienyl)chlorouranium(IV)\textsuperscript{13}, provided the first accurate determination of a cyclopentadienyl actinide complex. The cyclopentadienyl rings are pentahapto bound and the chloride anion is coordinated along the trigonal axis of the formally ten coordinate complex. The geometry is that of a trigonally compressed tetrahedron such that the Cl-U-(Cp centroid) bond angle is 100° (Fig. 1). This geometry remains essentially invariant throughout the class.

An introduction to compounds of the formula MCP\textsubscript{3} is provided by another member of this class. In tris(methyl-
cyclopentadienyl)neodymium(III), Nd(MeCp)$_3$, the metal ion (1.17 Å) is ten-coordinate through formation of a tetramer in which all three Cp rings form η$^5$ bonds to Nd and one of the rings also bridges to form an η$^1$ ring bridge to the adjacent metal ion. The smaller (1.13 Å) Sm$^{3+}$ ion in Sm(indenyl)$_3$ is 9-coordinate with three η$^5$ rings providing all of the coordination. The even smaller (.87 Å) Sc$^{3+}$ ion in ScCp$_3$ is eight-coordinate in a polymeric structure formed by 2 η$^5$ Cp rings and a third ring which forms an η$^1$,η$^1$ bridge. All of the Cp rings in these three compounds show undistorted pentagonal symmetry with no evidence of double-bond localization. Thus there is a monotonic decrease in coordination number with decreasing ionic radius of the metal ion. It is clear from these examples that the principal determinant of coordination numbers and geometries is the metal size, indicating that an ionic mode of bonding best describes these MCp$_3$ compounds.

In contrast, the structure of tris(cyclopentadienyl)-indium(III) (Fig. 2) is composed of indium atoms which achieve a relatively regular four-coordinate tetrahedral environment of σ bonds by bonding to 2 η$^1$ Cp rings with the third ring forming a η$^1$,η$^1$ bridge. The C-C bond lengths within the Cp rings show localized double bond character of the type

![InCp3](image)

In short, InCp$_3$ provides a classic example of the structural
effects of covalent bonding.

**MCp₄**

For the series **MCp₄** (Fig. 3) there is again a pronounced change in coordination number and structure as the metal ion size changes. In **TiCp₄** the coordination number of the Ti⁴⁺ ion (0.74 Å) is eight, from two η⁵ rings and two η¹ rings. For the larger Zr⁴⁺ ion (0.91 Å) in **ZrCp₄** there are three η⁵ rings and one η¹ ring to give a total coordination number of ten. In **UCp₄** all four Cp rings are η⁵ bound in a tetrahedral array to give a total coordination number of twelve around the U⁴⁺ ion (1.17 Å). Thus, these **MCp₄** compounds again demonstrate that metal ion size plays the dominant role in determining the coordination number and geometry, indicating an ionic mode of bonding.

**M(COT)₂**

The compounds **Ti(C₈H₈)₂** and **Ti₂(C₈H₈)₃** exhibit similar structures, involving one symmetrical η⁸-coordinated COT ring and one non-planar ring of lower hapticity per titanium. In the analogous zirconium complex, the metal's larger size is manifested in an additional coordination site being occupied by a THF molecule in the otherwise similar structure.

Cyclooctatetraene complexes of larger metal ions such as cerium, thorium, and uranium all exhibit two symmetr-
ical \eta^8\text{-coordinated} COT rings. The thorium and uranium compounds exhibit almost exact \(D_{8h}\) molecular symmetry while the cerium compound is very close to \(D_{8d}\). Structural parameters of these compounds are collected in Table 1.

The failure of the early metals to accept a uranocene-type structure can be explained in two ways. One way is to note that the lanthanide and actinide ions are substantially larger, thereby requiring more ligands to saturate their coordination sphere. Uranocene is formally ten-coordinate and coordination numbers of nine and ten are quite common for uranium complexes. The early metals cannot accommodate so large a coordination number and so one COT ring slips to the side—providing a total coordination number of seven or eight. This argument rests squarely on an ionic description of the bonding. Alternatively, one may note that two \(\eta^8\text{-coordinated}\) COT rings provide 20 \(\pi\)-electrons to the metal center—in violation of the effective atomic number rule. While actinide and lanthanide complexes do not in general follow this rule, Group IVB organometallic complexes almost invariably have 16 or 18 valence electrons. Thus the second COT ring slips to one side to reduce the number of valence electrons. This argument views the bonding in the early metals as predominantly covalent while recognizing the lack of anything resembling the effective atomic number rule to apply in the case of the lanthanide or actinide analogues. This recognition is tantamount to viewing the bonding in the later metals as ionic.
The Covalent/Ionic Structural Criterion and 3d Metalloccenes

Having seen the conclusions drawn by considering the general structural features (i.e. metal coordination number and ligand hapticity) of carbocyclic complexes of the actinides and lanthanides, we now turn to another structural criterion of the mode of bonding—the metal-to-carbon bond distance (R(M-C)). Table 2 contains structural data collected from X-ray and gas phase electron diffraction studies of first row metalloccenes\(^{25-36}\). If these compounds involved ionic bonding, the metal-to-carbon distances could be predicted as the sum of the ionic radii of the metal ion and the Cp anion. Another way of saying this is that the difference between the metal-to-carbon distance and the ionic radius of the metal (the effective ionic radius of the Cp ligand) would be constant. But in the d-transition metal metalloccenes, one cannot assign an effective ionic radius to the Cp anion. If we plot R(M-C) vs. the metal ion radius (Fig. 4) we see that this is not a smooth function.

The predominant covalency of these compounds can be illustrated in a graph of R(M-C) vs. electron imbalance as defined by Haaland\(^{27}\) (Fig. 5). Haaland's definition is based on a molecular orbital treatment of the bonding in these compounds, considers the effects of electron occupancy of bonding and antibonding orbitals -- and results in a linear correlation of R(M-C) and predicted bond order.

Table 3 collects corresponding structural data for
lantanide and actinide Cp complexes. We can see that the effective ionic radius for the Cp ligand is essentially invariant in structures of 23 complexes, and is 1.64(4) Å. This consistency is illustrated in Figure 6, where the plot of RM-C vs. the metal ion radius is presented for the available lanthanide complexes. The relatively high correlation coefficient and near unit slope (equation (1) requires that the slope, \( \frac{dR(M-C)}{dM-C} = 1 \)) shows that RM-C varies in direct proportion to metal ion size, a clear indication of ionic bonding.

**Bond Lengths in Metal COT Complexes**

Of all the lanthanide and actinide organometallic complexes, there is probably the most evidence of covalency in the COT complexes of the actinides (vide supra). For this reason, it is interesting to see how well the purely structural model described here applies to the systematics observed in the geometries of these compounds. Table 4 collects data from X-ray structures of COT complexes of 12 d, f, and s-block metals. Subtraction of the metal ionic radii from RM-C yields an effective ionic radius for COT, which will be constant if the ionic model is applicable. Indeed, The COT ionic radius is essentially invariant, averaging 1.56(4) Å. The graph of metal ionic radius vs. RM-C for these complexes appears in Figure 6. The slope and correlation coefficient indicate that, despite other evidence suggesting covalency, there is no structural evi-
dence for it.

Statement of Purpose

This analysis of structural data leads us to conclude that within the limited structural definition of covalent/ionic bonding, the bonding in organolanthanides and actinides is predominantly ionic. The usefulness of the analysis can be broadened by examination of new types of compounds; for instance, those with different ligands and/or new coordination numbers. It is possible that the structural definition can become less limited and allow for the consideration of compounds that are not so strictly members of a homologous series.

In addition, we know that other more sensitive techniques have detected some covalency. Among the more sensitive techniques that has not been fully exploited is the measurement of magnetic moments, especially at low temperatures. Such studies are most informative when applied to dimeric species where an opportunity exists for the spins of two paramagnetic metal ions to become coupled, which would result in a pronounced change in the magnetic moment. Few low temperature (below 77K) studies have been performed even on monomeric organolanthanides or actinides. One particularly thorough study has been made, however, on the compound of formula \((\text{YbCp}_3)_2(\text{pyrazine})\)\(^{38}\). The molecular unit of this compound is a dimer located about a crystallographic inversion center. Two ytterbium atoms, each with three
\( \eta^5 \)-cyclopentadienide rings, are nearly linearly bridged by a pyrazine ring coordinated through its nitrogens (Fig. 7). The magnetic susceptibility of the dinuclear complex exhibits simple Curie-Weiss behavior over the range 4 to 100 K, with \( \mu_{\text{eff}} = 3.48 \mu_B \). This result is typical of ionic Yb(III) complexes, and the conclusion can be drawn that the method detects no covalency.

The lack of covalent effects in this study is less than surprising, considering the large amount of evidence indicating that the \( \text{Ln}^{3+} \) compounds are very ionic in nature. This is attributable to the small radial extension of the 4f orbitals, with the result that they contain what are, chemically, core electrons. However, for the early actinides (before increasing nuclear charge dampens the effect), speculation persists that the greater radial extension of 5f orbitals might be sufficient to allow some 5f participation in covalent bonding.

Thus, this work was undertaken to use the magnetism of appropriate dimeric species of the early actinides as a sensitive probe for covalent effects and to examine novel ligand systems in the light of structural criteria for the mode of bonding. The exclusive use of compounds of uranium in these studies is due to the relative ease with which they can be handled safely.
### Table I. Crystal and Molecular Data for COT\(^a\) Complexes

<table>
<thead>
<tr>
<th>Space group</th>
<th>U(COT)(_2)</th>
<th>Th((COT)(_2))</th>
<th>[K(d)][Ce(COT)(_2)](^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>density, g/cm(^3)</td>
<td>2.29</td>
<td>2.22</td>
<td>1.56</td>
</tr>
<tr>
<td>molecules/cell</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Site symmetry</td>
<td>Ci</td>
<td>Ci</td>
<td>Cs</td>
</tr>
<tr>
<td>Mean M-C bond, (\text{Å})</td>
<td>2.647(4)</td>
<td>2.701(4)</td>
<td>2.742(8)</td>
</tr>
<tr>
<td>Mean C-C bond, (\text{Å})</td>
<td>1.392(7)</td>
<td>1.386(9)</td>
<td>1.388(28)</td>
</tr>
<tr>
<td>Inter-ring dist. (\text{Å})</td>
<td>3.847(10)</td>
<td>4.007(3)</td>
<td>4.151</td>
</tr>
<tr>
<td>Reference</td>
<td>5</td>
<td>5</td>
<td>24</td>
</tr>
</tbody>
</table>

\(^a\) COT = (C\(_8\)H\(_8\))\(^2-\)

\(^b\) d = (CH\(_3\)OCH\(_2\)CH\(_2\))\(_2\)\(^0\)
## Table II.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R(M-C)</th>
<th>Metal ion radius</th>
<th>Cp radius</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(\text{Cp}_2)</td>
<td>2.280(5)</td>
<td>0.79</td>
<td>1.49</td>
<td>25</td>
</tr>
<tr>
<td>Cr(\text{Cp}_2)</td>
<td>2.169(4)</td>
<td>0.73</td>
<td>1.44</td>
<td>25</td>
</tr>
<tr>
<td>Mn(\text{Cp}_2)</td>
<td>2.383(3)</td>
<td>0.83</td>
<td>1.55</td>
<td>26</td>
</tr>
<tr>
<td>Mn(Me(\text{Cp})^a_2</td>
<td>2.144(12)</td>
<td>0.67</td>
<td>1.47</td>
<td>27</td>
</tr>
<tr>
<td>Mn(Me(\text{Cp})^b_2</td>
<td>2.433(8)</td>
<td>0.83</td>
<td>1.60</td>
<td>27</td>
</tr>
<tr>
<td>Fe(\text{Cp}_2)</td>
<td>2.064(3)</td>
<td>0.61</td>
<td>1.45</td>
<td>28</td>
</tr>
<tr>
<td>Co(\text{Cp}_2)</td>
<td>2.119(3)</td>
<td>0.65</td>
<td>1.47</td>
<td>29-30</td>
</tr>
<tr>
<td>Ni(\text{Cp}_2)</td>
<td>2.196(4)</td>
<td>0.69</td>
<td>1.51</td>
<td>31</td>
</tr>
</tbody>
</table>

b. Single-Crystal X-ray Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>R(M-C)</th>
<th>Metal ion radius</th>
<th>Cp radius</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(\text{Cp}_2)</td>
<td>2.24</td>
<td>0.79</td>
<td>1.45</td>
<td>32</td>
</tr>
<tr>
<td>Cr(\text{Cp}_2)</td>
<td>2.14</td>
<td>0.73</td>
<td>1.41</td>
<td>32</td>
</tr>
<tr>
<td>Mn(\text{Cp}_2)</td>
<td>2.41</td>
<td>0.83</td>
<td>1.58</td>
<td>33</td>
</tr>
<tr>
<td>Fe(\text{Cp}_2)</td>
<td>2.045(4)</td>
<td>0.61</td>
<td>1.44</td>
<td>34</td>
</tr>
<tr>
<td>Co(\text{Cp}_2)</td>
<td>2.096(8)</td>
<td>0.65</td>
<td>1.45</td>
<td>35</td>
</tr>
<tr>
<td>Ni(\text{Cp}_2)</td>
<td>2.15</td>
<td>0.69</td>
<td>1.46</td>
<td>32</td>
</tr>
<tr>
<td>[Fe(Me(\text{Cp})_2]^-</td>
<td>2.05(2)</td>
<td>0.55</td>
<td>1.50</td>
<td>36</td>
</tr>
</tbody>
</table>

\(^a\) low spin \(^b\) high spin
Table III. Single-Crystal X-ray Diffraction Data

<table>
<thead>
<tr>
<th>compound</th>
<th>$R$(M-C)</th>
<th>metal ion radius $\AA$</th>
<th>Cp radius $\AA$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScCp$_3$</td>
<td>2.49(2)</td>
<td>0.87</td>
<td>1.62</td>
<td>16</td>
</tr>
<tr>
<td>Sm(indenyl)$_3$</td>
<td>2.75(5)</td>
<td>1.13</td>
<td>1.62</td>
<td>15</td>
</tr>
<tr>
<td>Nd(MeCp)$_3$</td>
<td>2.79(5)</td>
<td>1.17</td>
<td>1.62</td>
<td>14</td>
</tr>
<tr>
<td>PrCp$_3$CNC$<em>6$H$</em>{11}$</td>
<td>2.77(2)</td>
<td>1.18</td>
<td>1.59</td>
<td>37</td>
</tr>
<tr>
<td>(YbCp$_3$)$_2$(C$_4$H$_4$N$_2$)</td>
<td>2.68(1)</td>
<td>1.04</td>
<td>1.64</td>
<td>38</td>
</tr>
<tr>
<td>(ScCp$_2$Cl)$_2$</td>
<td>2.46(2)</td>
<td>0.87</td>
<td>1.59</td>
<td>39</td>
</tr>
<tr>
<td>[Yb(MeCp)$_2$Cl]$_2$</td>
<td>2.585(8)</td>
<td>0.985</td>
<td>1.60</td>
<td>40</td>
</tr>
<tr>
<td>(YbCp$_2$Me)$_2$</td>
<td>2.613(13)</td>
<td>0.985</td>
<td>1.63</td>
<td>41</td>
</tr>
<tr>
<td>GdCp$_3$(THF)</td>
<td>2.72(6)</td>
<td>1.11</td>
<td>1.61</td>
<td>42</td>
</tr>
<tr>
<td>Yb(Me$_5$C$_5$)$_2$(pyr)$_2$</td>
<td>2.741</td>
<td>1.14</td>
<td>1.60</td>
<td>43</td>
</tr>
<tr>
<td>UCp$_3$Cl</td>
<td>2.74</td>
<td>1.06</td>
<td>1.68</td>
<td>44</td>
</tr>
<tr>
<td>UCp$_3$F</td>
<td>2.74</td>
<td>1.06</td>
<td>1.68</td>
<td>45</td>
</tr>
<tr>
<td>U(benzylCp)$_3$Cl</td>
<td>2.733(1)</td>
<td>1.06</td>
<td>1.67</td>
<td>13</td>
</tr>
<tr>
<td>U(indenyl)$_3$Cl</td>
<td>2.78</td>
<td>1.06</td>
<td>1.72</td>
<td>46</td>
</tr>
<tr>
<td>UCp$_3$(C$_2$H)</td>
<td>2.73(5)</td>
<td>1.06</td>
<td>1.67</td>
<td>47</td>
</tr>
<tr>
<td>UCp$_3$(C$_2$6)</td>
<td>2.68</td>
<td>1.06</td>
<td>1.62</td>
<td>48</td>
</tr>
<tr>
<td>UCp$_3$(p-xylyl)</td>
<td>2.71(1)</td>
<td>1.06</td>
<td>1.65</td>
<td>49</td>
</tr>
<tr>
<td>UCp$_3$(n-butyl)</td>
<td>2.73(1)</td>
<td>1.06</td>
<td>1.67</td>
<td>49</td>
</tr>
<tr>
<td>UCp$_3$(2-Me-allyl)</td>
<td>2.74(1)</td>
<td>1.06</td>
<td>1.68</td>
<td>50</td>
</tr>
<tr>
<td>UCp$_4$</td>
<td>2.81(2)</td>
<td>1.17</td>
<td>1.64</td>
<td>20</td>
</tr>
<tr>
<td>(ThCp$_2$C$_5$H$_4$)$_2$</td>
<td>2.83</td>
<td>1.13</td>
<td>1.70</td>
<td>51</td>
</tr>
<tr>
<td>UCp$_3$(NCS)(MeCN)</td>
<td>2.763</td>
<td>1.08</td>
<td>1.68</td>
<td>52</td>
</tr>
<tr>
<td>U(MeCp)Cl$_3$(THF)$_2$</td>
<td>2.720</td>
<td>1.00</td>
<td>1.72</td>
<td>53</td>
</tr>
<tr>
<td>Compound</td>
<td>R(M-C) Å</td>
<td>Metal ion radius Å</td>
<td>Net COT² radius Å</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------</td>
<td>--------------------</td>
<td>-------------------</td>
<td>------</td>
</tr>
<tr>
<td>U(COT)₂</td>
<td>2.647</td>
<td>1.06</td>
<td>1.59</td>
<td>5</td>
</tr>
<tr>
<td>U(Me₄COT)₂</td>
<td>2.658</td>
<td>1.06</td>
<td>1.60</td>
<td>54</td>
</tr>
<tr>
<td>Th(COT)₂</td>
<td>2.701</td>
<td>1.13</td>
<td>1.57</td>
<td>5</td>
</tr>
<tr>
<td>K(dg)[Ce(COT)₂]</td>
<td>2.742</td>
<td>1.25</td>
<td>1.49</td>
<td>24</td>
</tr>
<tr>
<td>[Ce(COT)Cl(THF)₂]₂</td>
<td>2.710</td>
<td>1.20</td>
<td>1.51</td>
<td>55</td>
</tr>
<tr>
<td>[Na(COT)(THF)₂]</td>
<td>2.68</td>
<td>1.18</td>
<td>1.61</td>
<td></td>
</tr>
<tr>
<td>[Na(COT)₂]</td>
<td>2.79</td>
<td>1.18</td>
<td>1.61</td>
<td>56</td>
</tr>
<tr>
<td>Zr(COT)₂(THF)</td>
<td>2.461</td>
<td>0.89</td>
<td>1.57</td>
<td>23</td>
</tr>
<tr>
<td>Ti(COT)Cp</td>
<td>2.323</td>
<td>0.76</td>
<td>1.56</td>
<td>57</td>
</tr>
<tr>
<td>[K(dg)₂(Me₄COT)]</td>
<td>3.003</td>
<td>1.46</td>
<td>1.54</td>
<td>58</td>
</tr>
<tr>
<td>K₂(COT)(dg)</td>
<td>2.98</td>
<td>1.38</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.05</td>
<td>1.46</td>
<td>1.59</td>
<td>59</td>
</tr>
<tr>
<td>Rb₂(COT)(dg)</td>
<td>3.10</td>
<td>1.52</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.15</td>
<td>1.56</td>
<td>1.59</td>
<td>60</td>
</tr>
</tbody>
</table>

a COT = C₈H₈

b dg = (CH₃OCH₂CH₂)₂O.
Figure 1. Perspective drawing of $\text{U(benzylCp)}_2\text{Cl}$ from reference 13.
Figure 2. Perspective drawing of $\text{InCp}_3$ from reference 17.
Figure 3. Perspective drawings of tetrakis(Cp) complexes: TiCp₄ (left, reference 18), ZrCp₄ (middle, reference 19), and UCp₄ (right, reference 20).
Figure 4. A graph of $R(M-C)$ vs. metal ionic radius for complexes of the type $MCp_2$. 
Metal Ionic Radius for MCp$_2$ (Å)

slope = 1.18

correlation coeff. = 0.83
Figure 5. A graph of $R(M-C)$ vs. "electron imbalance", as defined by Haaland in reference 27.
Figure 6. Graphs of $R(M-C)$ vs. metal ionic radius for lanthanide Cp complexes and metal COT complexes.
Metal Ionic Radius for COT Complexes (Å)

Ln Cp₃ and Ln Cp₃·L
slope = 0.98
corr. coeff. = 0.98

Metal COT's
slope = 1.01
correlation coeff. = 0.97

XBL 7911-7288
Figure 7. Perspective drawing of \((\text{YbCp}_3)_2(\text{pyrazine})\) from reference 38.
References


505-562.


32. Wheatley, P.J.; "Perspectives in Structural Chemistry" 

33. Bunder, W.; Weiss, E.; 


43. Zalkin, A.; private communication.


Chapter One

The Synthesis and Characterization of \((\text{UCp}_3)_2\text{(pyrazine)}\) and \([\text{U(MeCp)}_3]_2\text{(pyrazine)}\) : \(\pi\)-Bridged Dimers of \(\text{U}^{3+}\).

Introduction

Since the resurgence of interest in the organometallic chemistry of the lanthanide and actinide elements in the late 1960's, occasioned by Streitweiser's synthesis of uranocene\(^1\), many people have investigated the role of \(f\)-electrons in the bonding in these compounds\(^2\). This chapter describes part of our effort\(^3\) to use magnetic studies as a probe for covalency in organouranium compounds. The Introduction summarizes a previous report on the synthesis and characterization of \((\text{YbCp}_3)_2\text{(pyrazine)}\), which led to the conclusion that as low as 4K no spin-pairing took place\(^4\). The behavior of pyrazine in \(d\)-metal dimers has demonstrated that, in the covalent extreme, it can facilitate spin-pairing between the \(4f^{13}\) paramagnets. The fact that no pairing was apparent is convincing evidence of the predominantly ionic bonding in this compound. However, since it is well-known that the \(4f\) electrons in the lanthanide elements make very little contribution to the chemical environment, this result was of little surprise.

It is also well-known, however, that early in the actinide series, the \(5f\) shell electrons make a greater
contribution to the chemical environment, and so it was thought some covalency might be involved in compounds of uranium, for instance. Other uranium dimers have been reported\(^5\), but their magnetic characterization has not been complete. This study represents an attempt to completely characterize a \(\mu\)-bridging uranium dimer.

**Experimental**

All manipulations were accomplished using a Schlenk or vacuum line with high purity Argon or in a Vacuum Atmospheres HE-93 glove box with a recirculating oxygen and moisture-free Argon atmosphere. All solvents were dried by distillation from potassium benzophenone ketyl and were degassed prior to use. Pyrazine (Aldrich 99+%\(^\dag\)) was dried over BaO at 60°C. Infra-red spectra were recorded on a Perkin-Elmer 597 spectrophotometer, the visible-near IR spectra on a Cary 14M spectrophotometer, nmr spectra on the UCB 250 MHz spectrometer, and mass spectra on an AEI-MS12 spectrometer. The magnetic behavior was measured using a PAR Model 155 vibrating magnetometer equipped with a 12 in. Varian electromagnet capable of producing a homogeneous field between 2.5 and 12.5 kG. A powdered sample was weighed into a calibrated, diamagnetic sample container machined from Kel-F rod. Sample temperatures between 4 and 80 K were measured with a calibrated GaAs diode approximately 12 mm. above the sample in a liquid helium dewar.

Elemental analyses were performed by the
Microanalytical Laboratory at U.C. Berkeley or Mallissa and Reuter Analytische Laboratorien, Engelskirchen, W. Germany. X-ray powder patterns were collected with Cu radiation. NaCp(DME)$_6$ (DME is 1,2-dimethoxyethane) and UCl$_4$ were prepared by the literature techniques. Napthalene was sublimed before use. K(MeCp) was produced by the reaction between the diene (after cracking) and KH in THF (tetrahydrofuran) at $0^\circ$C.

UCp$_3$(THF) and U(MeCp)$_3$(THF)

To small pieces of sodium weighing 0.30 g (13 mmol) in 100 ml THF was added 1.70 g (13 mmol) of napthalene. The resulting dark green mixture was stirred at room temperature overnight. It was then filtered through a glass frit onto 5.00 g (13 mmol) of UCl$_4$ in 150 ml THF. The mixture of green solutions turned immediately to a deep purple. This mixture was stirred at room temperature for one hour. Next, the NaCp(DME) or KMeCp (39.5 mmol) (solution and slurry, respectively) in 100 ml THF was added, the purple changing to brown immediately. This mixture was stirred at room temperature for another hour, at which time the THF was removed under vacuum. Care was taken to retain a slight dampness of THF. The brown residue was soxhlet extracted with benzene overnight. Next the benzene was removed under vacuum and the residue subjected to room temperature vacuum for 12 hours to remove the napthalene. The product thus obtained (90% based on UCl$_4$) is crystalline. Its composition was con-
firmed by the IR spectrum, pmr spectrum (for the methylated compound at 21°C in d8-toluene, shifts in 6 ppm vs. TMS: -8.1 (s, 7H, 102 Hz); -14.5 (s, 12H, 49 Hz); -21.4 (s, 8H, 73 Hz)), and elemental analysis.

UC22H29O: calculated– %C, 48.26; %H, 5.30; found– %C, 48.91; %H, 5.53.

(U Cp3)2(pyrazine)

This compound can be synthesized by the combination of stoichiometric amounts of UCp3(THF) and pyrazine in benzene, toluene, DME, or THF. The blue-grey product precipitates immediately upon addition of pyrazine to a brown solution of UCp3(THF). It is most soluble in THF, but only sparingly so. The supernatant from a THF preparation, if cooled quickly to -78°C and held there for a few days, yields black microcrystalline material. This material was used for the X-ray powder pattern. Analysis: U2C34H34N2. Calculated– %C, 43.13; %H, 3.59; %N, 2.96. Found– %C, 43.40; %H, 4.07; %N, 2.22.

Infra-red Spectrum (Nujol mull)(cm⁻¹)

3080, 1422, 1279, 1261, 1068,
1018, 960, 809, 782, 737,
619, 602, 470.

Mass spectral data (70 eV) are included in Table Ia.
The low solubility of this compound hampered further characterization.

\[
[U(\text{MeCp})_3]_2(\text{pyrazine})
\]

To a dark brown solution of \( U(\text{MeCp})_3(\text{THF}) \) in toluene was added a stoichiometric amount of pyrazine in a small volume of toluene. The color changed immediately to a deep blue-black. Stirring at room temperature for a few minutes, followed by filtration yielded a very strongly colored filtrate. Cooling to \(-15^\circ C\) overnight yielded black crystals shaped like needles. Analysis \( U_2C_{40}H_{46}N_2 \)-- calculated: \( \%C, 46.29, \%H, 4.28, \%N, 2.81 \); found: \( \%C, 46.60, \%H 4.47, \%N, 2.72 \).

Infra-red spectrum (Nujol mull) (cm.\(^{-1}\))

\begin{align*}
1420, 1279, 1057, 1048, 1030, \\
950, 880, 849, 840, 805, 770, \\
758, 742, 728, 694, 611, 463.
\end{align*}

PMR spectrum (20°C, d\(^8\)-toluene, 6 ppm vs. TMS)
-2.15 (s, 18H, 9 Hz, Me)

-11.5 (s, 11H, 15 Hz, ring)

-13.4 (s, 12H, 15 Hz, ring)

-67.0 (s, 4H, 15 Hz, pyrazine).

Mass spectral data (70 eV) are in Table Ib.

Electronic spectrum (in toluene vs. toluene)(nm.)

1510, 1360, 1220, 1180, 1020, 910, 680. The maxima are quite broad.

Single crystals suitable for diffraction studies have not been obtained. Both this and the previous compound sublime with some decomposition at $10^{-3}$ torr and $120^\circ$C.

Discussion

The dimeric formulation of these compounds is based primarily on;

(a) the X-ray powder pattern of $(\text{UCp}_3)_2(\text{pyrazine})$

(b) the mass spectra of both compounds, and

(c) the pmr of the methylated compound.
The crystal and molecular structure of (YbCp₃)₂⁻(pyrazine) has been determined⁴ and is illustrated in Figure 1. It consists of a dimer located about a crystallographic inversion center. Two ytterbium atoms, each with three η⁵-Cp rings, are nearly linearly bridged by a pyrazine ring coordinated through its nitrogens. Because (UCp₃)₂(pyrazine) exhibits low solubility, and [U(MeCp)₃]₂(pyrazine) forms only thin needles during crystal growth, a single crystal X-ray structure of these compounds has eluded us. However, it is reasonable to assume that substitution of U³⁺ for Yb³⁺ would lead to isomorphic structures, and if so, that powder patterns of the two compounds should be quite similar. Indeed this is so, the similarity of the patterns extending to the general pattern of the lines and their relative intensities (Fig 2).

The mass spectra of both compounds reveal the presence of dimeric species (Table I). Both spectra contain several prominent peaks that are not easily assigned, but that are included for completeness. The intensity of the high-mass peaks is rather low, consistent with the decomposition observed during sublimation. In the spectrum of the methylated compound, peaks appear that correspond to [U₂L₆₋ₓ(pyrazine) + 15]⁺, which suggests that perhaps uranium-methyl bonds are formed in the spectrometer.

The pmr spectrum of the methylated compound includes one singlet resonance for the four pyrazine protons. In any
reasonable monomeric formulation their chemical shifts would differ. This spectrum also exhibits resonances one expects for the mono-methylCp ligands—the methyl groups shifted the least, while the inequivalent sets of ring protons are shifted more by the uranium ion.

The infra-red spectra also confirm the presence of $\eta^5$-Cp rings, the spectrum of the methylated compound being predictably more complex due to the lowered symmetry the methyl groups impart. The electronic spectrum is consistent with the almost indescribable color, consisting as it does of nearly constant absorption throughout the range 1600-450 nm. With the structure thus confidently assigned, we address the magnetic behavior.

Our use of the liquid helium apparatus is predicated on the expectation that any covalent effects would be of particularly low energy and necessitate the use of very low temperatures. For this reason neither the room temperature moment nor the temperature dependence of the nmr spectrum has been determined. The magnetic behavior of the methylated compound has been investigated four times. Three times the data indicate the compound is only weakly paramagnetic, and that the paramagnetism varies slowly with temperature. The fourth investigation produced results that suggest an abrupt spin-state change at very low temperature. The magnetic behavior of this compound remains under investigation.
Acknowledgement

We wish to thank Helena Ruben for her assistance with the X-ray powder patterns.
<table>
<thead>
<tr>
<th>RA(%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>m/e</th>
<th>assignment&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>883</td>
<td>$U_2L_5X$</td>
</tr>
<tr>
<td>1.5</td>
<td>817</td>
<td>$U_2L_4X$</td>
</tr>
<tr>
<td>0.8</td>
<td>620</td>
<td>$U_2LX$</td>
</tr>
<tr>
<td>1.1</td>
<td>514</td>
<td>$UL_3X$</td>
</tr>
<tr>
<td>1.4</td>
<td>512</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>433</td>
<td>$UL_3$</td>
</tr>
<tr>
<td>16</td>
<td>403</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>387</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>368</td>
<td>$UL_2$</td>
</tr>
<tr>
<td>16</td>
<td>338</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>322</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>303</td>
<td>$UL$</td>
</tr>
<tr>
<td>72</td>
<td>80</td>
<td>X</td>
</tr>
<tr>
<td>73</td>
<td>66</td>
<td>L</td>
</tr>
<tr>
<td>100</td>
<td>44</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> Relative abundance

<sup>b</sup> $L = C_5H_5$ and $X = C_4H_4N_2$
Table Ib. Mass Spectrum of

\[ [\text{U(MeCp)}_3]_2(\text{pyrazine}) \]

<table>
<thead>
<tr>
<th>RA(%)^a</th>
<th>( \frac{m}{e} )</th>
<th>assignment^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>966</td>
<td>( \text{U}_2\text{L}_5\text{X} + 15 )</td>
</tr>
<tr>
<td>0.1</td>
<td>952</td>
<td>( \text{U}_2\text{L}_5\text{X} )</td>
</tr>
<tr>
<td>0.7</td>
<td>887</td>
<td>( \text{U}_2\text{L}_4\text{X} + 15 )</td>
</tr>
<tr>
<td>0.4</td>
<td>873</td>
<td>( \text{U}_2\text{L}_4\text{X} )</td>
</tr>
<tr>
<td>0.3</td>
<td>726</td>
<td>-</td>
</tr>
<tr>
<td>0.6</td>
<td>647</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>602</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>568</td>
<td>-</td>
</tr>
<tr>
<td>2.0</td>
<td>556</td>
<td>( \text{UL}_3\text{X} )</td>
</tr>
<tr>
<td>1.5</td>
<td>523</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>494</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>475</td>
<td>( \text{UL}_3 )</td>
</tr>
<tr>
<td>25</td>
<td>431</td>
<td>-</td>
</tr>
<tr>
<td>88</td>
<td>415</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>336</td>
<td>-</td>
</tr>
<tr>
<td>70</td>
<td>80</td>
<td>( \text{X} )</td>
</tr>
<tr>
<td>100</td>
<td>79</td>
<td>( \text{L} )</td>
</tr>
</tbody>
</table>

^a relative abundance

^b \( \text{L} = C_6\text{H}_7 \) and \( \text{X} = C_4\text{H}_4\text{N}_2 \)
Figure 1. Perspective drawing of \((\text{YbCp}_3)_2(\text{pyrazine})\) from reference 4.
Figure 2. X-ray powder patterns of \((\text{YbCp}_3)_2(\text{pyrazine})\) (A) and \((\text{UCp}_3)_2(\text{pyrazine})\) (B) in the forward-scattering region.
References


Chapter Two

Synthesis and X-ray Structure of UCp$_3$(C$_3$H$_3$N$_2$).

A New Mode of Pyrazolate Bonding.

Introduction

The search for new organoactinide and -lanthanide compounds for use in structural and magnetic analyses of their mode of bonding$^{1,2}$ has led to a new complex of uranium. The pyrazolate anion has been used extensively throughout transition metal chemistry$^3$, where its coordination is almost always exo-bidentate, i.e. an $\eta^2$ bridging ligand. Stucky and Fieselman recently reported that the reaction of TiCp$_2$Cl with Na(pyrazolate) yields a dimeric compound of formula [TiCp$_2$(pyrazolate)]$^4$. And, while the large class of MCp$_3$X compounds (M = lanthanide or actinide) are all formally ten-coordinate, R.D. Fischer and coworkers have reported the eleven-coordinate UCp$_3$(NCS)(CH$_3$CN)$^5$. Thus we anticipated that results similar to those with TiCp$_2$Cl would be obtained with UCp$_3$Cl. Instead, we report the first example of an endo-bidentate ($\eta^2$ non-bridging) pyrazolate anion in the formally 11-coordinate UCp$_3$(C$_3$H$_3$N$_2$).

Experimental

All reactions were carried out under an inert atmosphere of argon on a Schlenk or vacuum line. Transfer and some handling were facilitated by a Vacuum Atmospheres HE-
93-A glove box with recirculating moisture and oxygen-free argon atmosphere. Elemental analyses were performed by the U.C. Berkeley Analytical Laboratory. Infra-red spectra were recorded on a Perkin-Elmer Model 597 spectrophotometer (Nujol mull, reported in cm\(^{-1}\)), mass spectra were obtained on an AEI-MS12 mass spectrometer (70 eV, reported as m/e(relative abundance)), electronic spectra were recorded on a Cary 14 spectrophotometer, and pmr spectra obtained with a JEOL model FX90Q spectrometer (in d\(^8\)-toluene, shifts reported in \(\delta\) ppm vs. TMS). Crystalline samples for X-ray diffraction were mounted in glass capillaries under a He atmosphere in a horizontal-format inert atmosphere glove box equipped with a binocular microscope.

**Materials**

Toluene and tetrahydrofuran (THF) were distilled from potassium benzophenone ketyl. Pyrazole was obtained from Aldrich (98%) and recrystallized from toluene at \(-15^\circ\)C before use. Sodium pyrazolate was prepared from NaH and pyrazole in THF\(^6\). UCp\(_3\)Cl was prepared by the reaction between UC\(_{1.7}\) and NaCp(DME)\(^8\) in 1,2-dimethoxyethane (DME).

\[ \text{UCp}_3(\text{C}_3\text{H}_2\text{N}_2) \]

To a clear brown solution of 2.00 g UCp\(_3\)Cl (4.27 mmol) dissolved in 100 ml THF was added 0.38 g Na(\text{C}_3\text{H}_2\text{N}_2) (4.22 mmol) in 10 ml THF. A fine precipitate was visible after stirring for a few hours at room temperature. The mixture
was filtered through diatomaceous earth and the THF removed from the filtrate under vacuum. A saturated toluene solution was cooled to -15°C whereupon large crystals formed. Analysis calc. (found) for UC₁₈H₁₈N₂; %C, 43.20 (43.55), %H 3.60 (3.62), %N 5.60 (5.64).

Infra-red spectrum.

1469(w), 1440(w), 1409(w), 1343(w), 1280(s), 1070(s), 1022(s), 998(s), 970(m), 776(s), 616(m).

Mass spectrum.

500(21.7), 435(86.5), 370(18.7), 343(13.2), 317(28.8), 68(100).

Electronic spectrum (toluene solution, in nm.).

1640, 1600, 1520, 1370, 1325, 1290, 1260, 1230, 1160, 1110, 1080, 980, 892, 790, 760, 738, 690, 662, 587, 548.
Variable temperature pmr.

At 35°C: -9.51(s,Cp), 10.68(s,pyrazolate), 8.75(s,pyrazolate).
The respective peaks at other temperatures are;
-50°C: -14.22, 12.06, 9.69.
-75°C: -15.84, 12.53, 10.03.

Magnetic susceptibility measurements were made with a PAR model 155 vibrating sample magnetometer used with a homogeneous field produced by a Varian Associates 12 in. electromagnet capable of a maximum field strength of 12.5 kG. A 173 mg sample was weighed and transferred to a diamagnetic, calibrated sample holder machined from Kel-F rod. A variable temperature liquid helium dewar produced sample temperatures in the range 5-80 K which were measured by a calibrated GaAs diode approximately 12 mm above the sample. The magnetometer was calibrated with HgCo(CNS)₄. The resulting susceptibilities were corrected for underlying diamagnetism and yield a temperature independent paramagnetism from 7.5 to 37.1 K, above which \( \mu_{\text{eff}} \) calculated from the slope of \( \frac{1}{X} \) vs. T is equal to 2.67\( \mu_B \) (Table I).

Data Collection, Solution and Refinement

Suitable crystals for diffraction were obtained by
cooling an unsaturated toluene solution of UCp$_3$(C$_9$H$_3$N$_2$) to -75°C overnight. Several crystals were mounted in .2 mm glass capillaries under He, the capillaries sealed with grease, and later sealed in a flame. The crystal was mounted on a CAD4 automatic diffractometer with graphite monochromator and molybdenum tube. The lattice constants were determined from a least squares refinement on 25 automatically centered reflections with 20 values between 27 and 38 degrees. Data reduction and processing were carried out as described elsewhere$^9$. The intensities were corrected for Lorentz and polarization effects and converted to values of $F^2$. Crystal faces were identified with the help of the diffractometer, and the dimensions of the 9 faces found were measured at 7X magnification under a binocular microscope. Absorption corrections were then made using an analytical algorithm$^{10}$. Azimuthal scans on 6 reflections revealed an intensity variation of roughly +10%. Minor adjustments to the observed dimensions of the crystal were made to minimize the variation after the absorption correction was made ($\mu=97.50\text{cm}^{-1}$), and it was thus adjusted to +4%. The actual data were then subjected to an absorption correction which ranged from 2.76 to 3.84. No crystal decay was observed in the three reflections monitored throughout data collection. The data were averaged to yield the 3631 independent reflections with $F^2>3\sigma(F^2)$ used in the final refinement.

The calculated density agrees well with that observed for Z = 4. The initial Patterson map confirmed the space
group P2₁/a\textsuperscript{11}. The structure was then solved using heavy atom methods\textsuperscript{12-15}. In the final refinement all non-hydrogen atoms were treated anisotropically and hydrogen atoms were fixed in calculated positions with a C-H distance of 0.95Å\textsuperscript{16} and an isotropic temperature factor of 8.0 Å\textsuperscript{2}. The model converged to give weighted and unweighted R factors both of 3.14%. On the final cycle all parameters shifted by less than 0.10 sigma. The variation of residuals with both \(\frac{\sin \theta}{\lambda}\) and \(F_0\) showed no abnormalities. In the final difference Fourier, the only peaks of greater than 1.\(Oe\textsuperscript{-}A^{-3}\) were within 1.4 Å of the uranium, and the most negative electron density at a grid point was -0.95\(e\textsuperscript{-}A^{-3}\). Positional and thermal parameters are listed in Table II.

**Description of the Structure**

The crystal structure consists of discrete mononuclear units at general positions in the unit cell (Figure 1). A perspective drawing of the complex is shown in Fig 2. The molecular structure consists of a uranium ion coordinated by three \(η^5\)-coordinated cyclopentadienyl rings and by the two nitrogens of the pyrazolate ion. If the coordination polyhedron is considered to be formed by the centers of the Cp rings and the midpoint of the N-N bond, the coordination about the uranium can be considered roughly \(C_{3v}\) in symmetry; with the Cp rings at the base, and the N-N midpoint at the apex of a flattened tetrahedron (Figure 3). The angles for
this polyhedron are [(Cp centroid)-U-(N-N)]
106.3°, 108.4°, and 97.1° for rings 1 to 3 respectively. The
angles between centroids are 114.2°, 115.0°, and 113.8°
(1-U-2, 1-U-3, 2-U-3).

The pyrazolate ring exhibits local C2v symmetry as in
[TiCp2(pyrazolate)]2-4. The pyrazolate ring and the Cp rings
are planar with average deviations from their least squares
planes of 0.075, 0.0055, 0.0044, and 0.0134 Å
(Cp1,2,3,pyrazolate) (Table III). The angle between the
U-N-N plane and the pyrazolate plane is 10.4°. The N-U-N
angle is 32.19°. Cp 3 and the pyrazolate are nearly paral-
lel, the angle between their least squares planes being
5.7°. The Cp C-C distances average 1.388(19) Å, and the
internal angles average 108.0°(1.0). The Cp's are symmetri-
cally bound to the uranium with average U-C distance of
2.762(12) Å. The U-N distances are 2.40(1) and 2.36(1) Å.
The closest intramolecular contact is 2.91 Å between N(2)
and C(10), and the closest intermolecular contact is 3.53 Å
between C(16) and C(6). Pertinent bond distances are listed
in Table IV.

Discussion

The endo-bidentate coordination of the pyrazolate ion
in this structure is surprising, and the failure to adopt a
bridging geometry is best attributed to the highly ionic
character of the U-N bond. In numerous pyrazolate complexes
of the d-block transition metals, the pyrazolate bridges two
metal ions. This is the appropriate geometry for directional covalent bonding involving the nitrogen lone pair electrons, and substantial overlap seems to be implied by the observation of magnetic interaction mediated by such bridging pyrazolates\textsuperscript{17,18}. In the present compound, the ionic character of the U-N bond dominates, with the coordination being a non-directional association of the N-N bond (the more negative side of the pyrazolate ring) with the uranium cation.

The geometry of the large class of compounds of the type $\text{MCp}_3\text{X}$, where $\text{X}$ is a monodentate Lewis base, anion or $\eta^1$ bridging Cp ring, is best described as a flattened tetrahedron\textsuperscript{19}. The Cp rings are shifted towards the sterically less bulky X ligand, decreasing the $\text{X-M-Cp}(\text{centroid})$ angles, and increasing the $\text{Cp-M-Cp}$ angles. This is also the case with our compound. The Cp-U-Cp angles are nearly identical and greater than 109°, while the Cp-U-(N-N) angles are all less than 109°.

The placement of the pyrazolate ring divides the Cp's into two classes. Cp1 and Cp2 are non-parallel with the pyrazolate, (the angles are 62.0° and 73.2°), while Cp3 is nearly parallel to the pyrazolate. In addition, the angle from the Cp3 centroid to the midpoint of the N-N bond is much less than for the other two Cp rings (\textit{vide supra}).

The average U-C distance of 2.76 Å is a little longer than those typically found in the 10-coordinate, $\text{UCp}_3\text{X}$-type structures, and is a reflection of the increased effective
ionic radius of the uranium in a formally 11-coordinate complex. The compound UCp₃(NCS)(MeCN)⁵ is also formally 11-coordinate. It exists in a trigonal-bipyramidal geometry with the Cp rings occupying the equatorial sites. Table V contains angles and distances for a comparison of some representative uranium Cp complexes. The compounds U(benzylCp)₃Cl²⁰, UCp₃(2-Me-allyl)²¹, and UCp₃(C₄H₉)²² all exhibit the flattened tetrahedral geometry described above. In UCp₃(NCS)(CH₃CN) however, the Cp-U-Cp angles are close to 120° and the Cp-U-N angles are close to 90°. Clearly, this represents a unique geometry — different from the flattened tetrahedron characterizing the MCp₃X compounds including the present one.

While the angles and geometries of the thiocyanato and pyrazolate complexes are distinctly different, there are marked similarities in their bond lengths, which are in turn consistent with the ionic radius calculated for an eleven-coordinate uranium(IV) complex. The average U-C distances (2.76 Å) for both compounds and the U-N distances (2.40 and 2.36 for the pyrazolate versus 2.40 for the thiocyanate) agree well. The reason for the 0.04 Å difference in the U-N distances of the pyrazolate is unclear; the closest intramolecular contact (between N(2) and C(10)) must be expected to make U-N(2) the longer bond, but the opposite is true.

The structure of Cu(β-N=N-β)(CNCMe₃)²₃ reveals a
roughly analogous, endo-bidentate coordination of an $N_2$ moiety. Structural evidence for a covalent $\sigma$-bond includes a lengthening of the N-N bond vs. uncoordinated azobenzene (from an average of 1.20 Å to 1.38 Å). However, one can expect the N-N bond in the pyrazolate anion to be less susceptible to such an effect by virtue of its incorporation in an aromatic π-system. In this light, we mention that in $[\text{TiC}_2\text{p}_2(\text{pyz})]_2$ the N-N distance (1.312(6) Å) is quite similar to that in our compound (1.318(10) Å).
Table I. Molar Susceptibilities for UCp$_3$ (pyrazolate)

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$x_m^{corr}$(cm$^3$/mole)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>12.92</td>
</tr>
<tr>
<td>10.7</td>
<td>12.80</td>
</tr>
<tr>
<td>18.3</td>
<td>12.62</td>
</tr>
<tr>
<td>27.2</td>
<td>12.23</td>
</tr>
<tr>
<td>37.1</td>
<td>13.14</td>
</tr>
<tr>
<td>50.0</td>
<td>11.55</td>
</tr>
<tr>
<td>56.7</td>
<td>10.94</td>
</tr>
<tr>
<td>77.3</td>
<td>8.57</td>
</tr>
</tbody>
</table>

$^a$ times 10$^3$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>U(1)</td>
<td>0.23092(2)</td>
<td>0.22422(1)</td>
<td>0.24961(2)</td>
<td>42.42(18)</td>
<td>75.5(4)</td>
<td>35.79(17)</td>
<td>4.9(3)</td>
<td>15.33(13)</td>
<td>4.2(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>0.3752(8)</td>
<td>0.3632(14)</td>
<td>0.4215(9)</td>
<td>63.8(18)</td>
<td>196.2(23)</td>
<td>-67.4(9)</td>
<td>-18.10(16)</td>
<td>16.6(6)</td>
<td>-49.11(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2)</td>
<td>0.3091(9)</td>
<td>0.2799(13)</td>
<td>0.4551(7)</td>
<td>101.9(18)</td>
<td>149.1(18)</td>
<td>37.6(6)</td>
<td>-8.11(11)</td>
<td>25.5(5)</td>
<td>-16.10(10)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3)</td>
<td>0.2171(9)</td>
<td>0.3602(15)</td>
<td>0.4201(9)</td>
<td>68.9(19)</td>
<td>207.2(23)</td>
<td>78.9(4)</td>
<td>-26.12(16)</td>
<td>52.8(8)</td>
<td>-52.12(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4)</td>
<td>0.2550(10)</td>
<td>0.4082(13)</td>
<td>0.3624(9)</td>
<td>90.10(10)</td>
<td>148.21(21)</td>
<td>75.9(9)</td>
<td>24.11(11)</td>
<td>27.7(7)</td>
<td>-32.11(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5)</td>
<td>0.3206(11)</td>
<td>0.4924(13)</td>
<td>0.3634(9)</td>
<td>117.12(12)</td>
<td>178.21(21)</td>
<td>77.10(12)</td>
<td>-34.12(12)</td>
<td>42.8(8)</td>
<td>-12.11(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6)</td>
<td>0.1581(10)</td>
<td>0.2577(14)</td>
<td>0.0425(7)</td>
<td>110.11(11)</td>
<td>190.26(21)</td>
<td>49.7(6)</td>
<td>-2.12(11)</td>
<td>19.6(6)</td>
<td>9.11(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)</td>
<td>0.1061(9)</td>
<td>0.3735(18)</td>
<td>0.0726(9)</td>
<td>70.9(9)</td>
<td>305.33(33)</td>
<td>73.9(9)</td>
<td>51.14(11)</td>
<td>11.7(7)</td>
<td>69.14(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(8)</td>
<td>0.1782(12)</td>
<td>0.4912(14)</td>
<td>0.1243(10)</td>
<td>127.13(13)</td>
<td>144.22(22)</td>
<td>85.10(10)</td>
<td>46.13(11)</td>
<td>41.9(9)</td>
<td>44.12(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9)</td>
<td>0.2702(10)</td>
<td>0.4428(18)</td>
<td>0.1242(10)</td>
<td>78.10(10)</td>
<td>274.31(11)</td>
<td>85.10(10)</td>
<td>-27.14(16)</td>
<td>26.8(8)</td>
<td>78.15(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(10)</td>
<td>0.2568(10)</td>
<td>0.3004(18)</td>
<td>0.0723(9)</td>
<td>107.11(11)</td>
<td>266.29(29)</td>
<td>60.8(8)</td>
<td>16.14(11)</td>
<td>47.7(7)</td>
<td>21.13(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(11)</td>
<td>0.0486(8)</td>
<td>0.1293(13)</td>
<td>0.2550(9)</td>
<td>56.7(7)</td>
<td>200.20(20)</td>
<td>86.9(9)</td>
<td>-15.10(10)</td>
<td>42.7(8)</td>
<td>9.11(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(12)</td>
<td>0.0467(8)</td>
<td>0.0751(15)</td>
<td>0.1609(9)</td>
<td>66.9(9)</td>
<td>225.25(25)</td>
<td>75.9(9)</td>
<td>44.11(11)</td>
<td>8.7(7)</td>
<td>22.12(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(13)</td>
<td>0.1169(10)</td>
<td>-0.0476(15)</td>
<td>0.1786(11)</td>
<td>100.11(11)</td>
<td>165.24(24)</td>
<td>115.13(13)</td>
<td>-57.12(16)</td>
<td>46.10(10)</td>
<td>-36.14(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(14)</td>
<td>0.1627(9)</td>
<td>-0.0720(12)</td>
<td>0.2801(12)</td>
<td>73.9(9)</td>
<td>100.19(19)</td>
<td>144.14(14)</td>
<td>-24.9(9)</td>
<td>34.9(9)</td>
<td>33.13(13)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(15)</td>
<td>0.1203(9)</td>
<td>-0.0357(13)</td>
<td>0.3291(9)</td>
<td>91.10(10)</td>
<td>176.22(22)</td>
<td>85.9(9)</td>
<td>37.11(11)</td>
<td>36.9(8)</td>
<td>27.12(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)</td>
<td>0.3722(6)</td>
<td>0.0455(9)</td>
<td>0.3204(6)</td>
<td>62.6(6)</td>
<td>140.15(15)</td>
<td>58.6(6)</td>
<td>18.7(7)</td>
<td>19.5(5)</td>
<td>-13.7(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)</td>
<td>0.3472(6)</td>
<td>0.0597(10)</td>
<td>0.2213(6)</td>
<td>69.6(6)</td>
<td>175.16(16)</td>
<td>52.6(6)</td>
<td>21.7(7)</td>
<td>20.5(5)</td>
<td>-25.8(8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(16)</td>
<td>0.4015(10)</td>
<td>-0.0660(16)</td>
<td>0.1986(11)</td>
<td>85.10(10)</td>
<td>265.29(29)</td>
<td>110.12(12)</td>
<td>7.13(7)</td>
<td>49.9(9)</td>
<td>-72.15(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(17)</td>
<td>0.4575(9)</td>
<td>-0.1468(13)</td>
<td>0.2826(11)</td>
<td>82.10(10)</td>
<td>121.19(19)</td>
<td>140.13(13)</td>
<td>23.13(13)</td>
<td>35.10(10)</td>
<td>-26.14(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(18)</td>
<td>0.4369(9)</td>
<td>-0.0777(14)</td>
<td>0.3576(10)</td>
<td>95.10(10)</td>
<td>185.24(24)</td>
<td>80.10(10)</td>
<td>45.12(12)</td>
<td>14.8(8)</td>
<td>34.12(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table IIb. Calculated Hydrogen Atom Positions\(^a\) for UCp\(_3\) (pyrazolate)

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(1)</td>
<td>0.4439</td>
<td>0.3370</td>
<td>0.4354</td>
</tr>
<tr>
<td>H(2)</td>
<td>0.3245</td>
<td>0.1854</td>
<td>0.4949</td>
</tr>
<tr>
<td>H(3)</td>
<td>0.1589</td>
<td>0.3325</td>
<td>0.4334</td>
</tr>
<tr>
<td>H(4)</td>
<td>0.1718</td>
<td>0.5611</td>
<td>0.3276</td>
</tr>
<tr>
<td>H(5)</td>
<td>0.3456</td>
<td>0.5697</td>
<td>0.3303</td>
</tr>
<tr>
<td>H(6)</td>
<td>0.1289</td>
<td>0.1629</td>
<td>0.0067</td>
</tr>
<tr>
<td>H(7)</td>
<td>0.0359</td>
<td>0.3735</td>
<td>0.0608</td>
</tr>
<tr>
<td>H(8)</td>
<td>0.1656</td>
<td>0.5863</td>
<td>0.1356</td>
</tr>
<tr>
<td>H(9)</td>
<td>0.3326</td>
<td>0.4982</td>
<td>0.1547</td>
</tr>
<tr>
<td>H(10)</td>
<td>0.3078</td>
<td>0.2422</td>
<td>0.0596</td>
</tr>
<tr>
<td>H(11)</td>
<td>0.0091</td>
<td>0.2131</td>
<td>0.2657</td>
</tr>
<tr>
<td>H(12)</td>
<td>0.0044</td>
<td>0.1149</td>
<td>0.0960</td>
</tr>
<tr>
<td>H(13)</td>
<td>0.1308</td>
<td>-0.1043</td>
<td>0.1276</td>
</tr>
<tr>
<td>H(14)</td>
<td>0.2143</td>
<td>-0.1483</td>
<td>0.3128</td>
</tr>
<tr>
<td>H(15)</td>
<td>0.1378</td>
<td>0.0425</td>
<td>0.4002</td>
</tr>
<tr>
<td>H(16)</td>
<td>0.4003</td>
<td>-0.0861</td>
<td>0.1327</td>
</tr>
<tr>
<td>H(17)</td>
<td>0.5013</td>
<td>-0.2340</td>
<td>0.2882</td>
</tr>
<tr>
<td>H(18)</td>
<td>0.4641</td>
<td>-0.1103</td>
<td>0.4263</td>
</tr>
</tbody>
</table>

\(^a\) isotropic thermal parameters equal 8.0 e\(^{-}\)/\(\AA\(^2\))
<table>
<thead>
<tr>
<th>Table III. Least-Squares Planes for UCp₃(C₃H₃N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>atom</strong></td>
</tr>
<tr>
<td>C1</td>
</tr>
<tr>
<td>C2</td>
</tr>
<tr>
<td>C3</td>
</tr>
<tr>
<td>C4</td>
</tr>
<tr>
<td>C5</td>
</tr>
</tbody>
</table>

**Parameters from Equation of Plane**

| A | 1.140 |
| B | 2.59  |
| C | 5.93  |
| D | 3.39  |

**Cp3** pyrazolate

<table>
<thead>
<tr>
<th><strong>atom</strong></th>
<th><strong>dist(Å)</strong></th>
<th><strong>atom</strong></th>
<th><strong>dist(Å)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>C11</td>
<td>0.005(10)</td>
<td>N1</td>
<td>0.013(8)</td>
</tr>
<tr>
<td>C12</td>
<td>-0.001(10)</td>
<td>N2</td>
<td>-0.013(8)</td>
</tr>
<tr>
<td>C13</td>
<td>-0.003(11)</td>
<td>C16</td>
<td>0.015(13)</td>
</tr>
<tr>
<td>C14</td>
<td>0.006(10)</td>
<td>C17</td>
<td>0.004(12)</td>
</tr>
<tr>
<td>C15</td>
<td>-0.007(10)</td>
<td>C18</td>
<td>-0.022(13)</td>
</tr>
</tbody>
</table>

**Parameters from Equation of Plane**

| A | 10.5 |
| B | 5.52 |
| C | 3.32 |
| D | .37  |
Table IV. Bond Distances (Å) for UCp$_3$(pyrazolate)

<table>
<thead>
<tr>
<th></th>
<th>U-C(1)</th>
<th>U-C(2)</th>
<th>U-C(3)</th>
<th>U-C(4)</th>
<th>U-C(5)</th>
<th>ave. U-C</th>
<th>C(16)-N(2)</th>
<th>C(16)-C(17)</th>
<th>C(17)-C(18)</th>
<th>C(18)-N(1)</th>
<th>N(1)-N(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.78</td>
<td>2.75</td>
<td>2.76</td>
<td>2.76</td>
<td>2.78</td>
<td>2.76</td>
<td>1.36</td>
<td>1.34</td>
<td>1.35</td>
<td>1.35</td>
<td>1.32</td>
</tr>
</tbody>
</table>
Table V. Bond Angles (°) and Distances (Å) for Representative Uranium Cp Complexes

<table>
<thead>
<tr>
<th>formula</th>
<th>Cp-U-Cp</th>
<th>Cp-U-X</th>
<th>ave. U-C(Cp)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(benzylCp)₃Cl</td>
<td>117,118,116</td>
<td>100,101,99</td>
<td>2.73</td>
<td>18</td>
</tr>
<tr>
<td>UC₃py(2Me-allyl)</td>
<td>119,115,118</td>
<td>102,100,98</td>
<td>2.74</td>
<td>19</td>
</tr>
<tr>
<td>UC₃py(n-but)</td>
<td>118,116,116</td>
<td>98,102,101</td>
<td>2.74</td>
<td>20</td>
</tr>
<tr>
<td>UC₃py(C₃H₅N₂)</td>
<td>114,115,114</td>
<td>106,108,97</td>
<td>2.76</td>
<td>herein</td>
</tr>
<tr>
<td>UC₃py(NCS)(MeCN)</td>
<td>121,119,119</td>
<td>92,95,90</td>
<td>2.76</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>86,89,88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Stereoscopic packing diagram for \( \text{UCp}_3(\text{pyrazolate}) \). The view is down the \( b \) axis.
Figure 2. Perspective drawing of UCp₃(pyrazolate).
Figure 3. Perspective drawing of UCp$_3$(pyrazolate) looking down the pseudo-threefold axis.
References


11. The symmetry operations for this non-standard setting of P2₁/c are: x, y, z; -x, -y, -z; 1/2 + x, 1/2 - y, z; 1/2 - x, 1/2 + y, -z.

12. Full matrix least-squares refinement on F was used in which the function minimized was \( \sum_w (|F_o| - |F_c|)^2 \),
where $F_o$ and $F_c$ are the observed and calculated structure factors and the weighting factor, $w$, is

$$\frac{4F_o^2}{\sigma^2(F_o^2)}$$. The atomic scattering factors for neutral U, C, and N were taken from the tables of Cromer and Mann\(^{13}\), and those for neutral H from Stewart, Davidson, and Simpson\(^{14}\). Corrections for anomalous dispersion using both $\Delta f'$ and $\Delta f''$ were included for all atoms except H\(^{15}\).


Chapter Three

Synthesis and X-ray Structures of
\[ \text{U(C}_5\text{Me}_5 \text{)}_2 \text{Cl}_2(\text{pyrazole}), \]
\[ \text{U(C}_5\text{Me}_5 \text{)}_2 \text{Cl}(\text{pyrazolate}), \text{ and} \]
\[ \text{U(C}_5\text{Me}_5 \text{)}_2(\text{pyrazolate})_2 \]

Introduction

The synthesis and structure of \( \text{UCp}_3(\text{pyrazolate}) \), reported in chapter 2, revealed that our attempt to form a dimer based on a precedent in titanium chemistry, \( [\text{TiCp}_2(\text{pyrazolate})]_2 \), resulted instead in the formation of a monomeric species, allowing us to characterize a new mode of pyrazolate bonding. To investigate what role, if any, steric factors played in the formation of the monomeric compound, and to learn more about the pyrazolate ion as a ligand, we have adjusted the size and number of the \( \text{Cp}(\text{C}_5\text{H}_5) \) ligands. We anticipated that a reduction in the total steric bulk of the other ligands might lead to the formation of one or more dimeric species. The compound \( \text{UCp}''_2\text{Cl}_2 \) (\( \text{Cp}''=\text{C}_5\text{Me}_5 \)) has proven to be a useful starting material for other studies \(^3,4\), and now our own. We have not, however, succeeded in forming dimeric compounds. The compounds \( \text{U(C}_5\text{Me}_5 \text{)}_2 \text{Cl}(\text{pyrazolate}) \) and \( \text{U(C}_5\text{Me}_5 \text{)}_2(\text{pyrazolate})_2 \) are formed by the reaction between \( \text{U(C}_5\text{Me}_5 \text{)}_2\text{Cl}_2 \) and stoichiometric amounts of \( \text{Na(pyrazolate)} \). In the course of this study, an adduct of neutral pyrazole, \( \text{U(C}_5\text{Me}_5 \text{)}_2\text{Cl}_2(\text{pyrazole}) \) was also characterized.
Experimental

All reactions were carried out under an inert atmosphere of argon on a Schlenk or vacuum line. Transfer and some handling were facilitated by a Vacuum Atmospheres HE-93-A glove box with recirculating moisture and oxygen-free argon atmosphere. Elemental analyses were performed by the Microanalytical Laboratory UC Berkeley. Infra-red spectra were recorded on a Perkin-Elmer 597 spectrophotometer (Nujol mulls, reported in cm⁻¹), mass spectra were obtained on an AEI-MS12 mass spectrometer (reported as m/e(relative abundance (%)), electronic spectra were recorded on a Cary 14 spectrophotometer (in toluene vs. toluene reported in nm.), and pmr spectra obtained with the UCB-250 nmr spectrometer (in d⁸-toluene, shifts in ppm vs. TMS). Magnetic susceptibilities were determined with a PAR 155 vibrating magnetometer equipped with a 12 inch Varian electromagnet capable of producing homogeneous fields up to 12.5 kilogauss. Weighed samples were loaded into calibrated, diamagnetic sample containers machined from Kel-F rod. Sample temperatures between 4 K and 80 K were measured with a GaAs diode approximately 12 mm. above the sample in the variable temperature liquid helium dewar. The instrument was calibrated with Hg[Co(NCS)₄]. The reported susceptibilities are the average of those obtained at 5.0, 7.5, 10.0, and 12.5 kG., and are corrected for underlying diamagnetism.⁵ Crystalline samples for X-ray diffraction were mounted in glass capillaries under a He atmosphere in a horizontal-format
inert atmosphere glove box equipped with a binocular microscope.

**Materials**

Toluene and tetrahydrofuran (THF) were distilled from potassium benzophenone ketyl. Pyrazole was obtained from Aldrich (98%) and recrystallized from toluene at -15°C before use. Sodium pyrazolate was prepared from NaH and pyrazole in THF. UCl₄ was prepared by the literature procedure.

$\text{UCp}^\text{"n"}_2\text{Cl}_2$

To a green solution of 5.00 g (13.2 mmol) UCl₄ in THF was added 6.87 g (39.5 mmol) $K(C_5\text{Me}_5)$ (prepared by the reaction between KH and $HC_5\text{Me}_5$ in THF). The total of 200 ml THF was maintained at reflux under argon for 24 h. After removal of solvent, the residue was extracted several times with a total of 200 ml of toluene. The separation of suspended particulate and solvent was facilitated by centrifugation. The volume of toluene was reduced and cooling overnight to -15°C yielded crystals of U(C₅Me₅)$_2$Cl₂ in moderate yield.
To a red-brown solution of 0.55 g (0.9 mmol) \( \text{UCp}^\text{II}_2\text{Cl}_2 \) in 75 ml THF was added 0.06 g (0.9 mmol) pyrazole. The solution was stirred overnight at room temperature. After solvent removal, the red-brown residue was washed with hexane, then dissolved in toluene and this solution cooled to \(-15^\circ\text{C}\). After 12 hours, the large crystals that had formed were filtered and an IR spectrum clearly revealed an \( \text{N-H} \) stretch at 3100 cm\(^{-1}\). Analysis—found: \%C, 43.26; \%H, 5.55; \%N, 4.38; calculated: \%C, 42.66; \%H, 5.29; \%N, 4.33.

**Infra-red spectrum**

3265(s), 3115, 2720, 1424(s), 1337(s), 1149(sh), 1132(s), 1052(sh), 1040(s), 1018(s), 930, 910, 776(s), 723(sh), 598.

**Mass spectrum**

624(9.5), 622(7.4), 578(93.4), 542(34.3), 443(98.6), 407(73.1), 403(79.3), 308(100), 135(37.6), 119(75.1), 105(42.5).

**Electronic spectrum**

1607, 1590, 1423, 1400, 1168, 1133, 1118, 1095, 1049, 990, 908, 880, 858, 817, 790, 730, 718, 708, 691, 680.
PMR spectrum

At 22°C. 11.49 (s, ~40 Hz, 30H, methyl) ; -9.85 (s, ~200 Hz, 2H, pyrazole) ; -28.63 (~1500 Hz, 1H, N-H).

At -10°C. 12. ; -16. ; -47. ; -65.

At -25°C. 13. ; -17. ; -19. ; -52. ; -72.

At -40°C. 13.9 (s, ~40 Hz, 30H, methyl) ; -20.0 (s, ~80 Hz, 1H, pyrazole) ; -21.2 (s, ~90 Hz, 1H, pyrazole) ; -58.1 (s, ~205 Hz, 1H, pyrazole) ; -80.2 (s, ~250 Hz, 1H, pyrazole).

Magnetic susceptibility

This compound exhibits Curie-Weiss behavior with C=1.46 and θ = 42.34K. Table Ia includes $x_M^{corr}$ versus T. The slope of $1/x_M^{corr}$ versus T yields $\mu_{eff} = 3.42 \mu_B$.

\[
\text{U(C}_5\text{Me}_5)_2\text{Cl(pyrazolate).}
\]

About 150 ml THF was vacuum distilled from potassium benzophenone ketyl onto a mixture of 1.00g (1.7 mmol) UCp\textsubscript{2}Cl\textsubscript{2} and 0.16g (1.8 mmol) Na(pyrazolate). The reaction was warmed to room temperature and stirred 12 hours. The THF was distilled away under vacuum. A hexane solution was filtered through diatomaceous earth, concentrated, and cooled to -15°C overnight yielding large crystals. Analysis

UC\textsubscript{23}H\textsubscript{33}N\textsubscript{2}Cl -- calculated: %C, 45.21 ; %H, 5.44 ; %N, 4.58 ; %Cl, 5.80 ; found: %C, 45.35 ; %H, 5.57 ; %N, 4.54 ; %Cl, 6.06.
Infra-red spectrum

2730(w), 1418, 1348(w), 1286(s), 1066(w), 1023(w), 968(s), 922, 782(s), 771, 726(w), 609.

Mass spectrum

610(6.8), 542(1.0), 475(38.7), 407(5.6), 403(4.8), 340(7.3), 137(19.6), 121(28.2), 105(63.3), 91(57.0), 77(31.3), 68(100).

Electronic spectrum

1648, 1635, 1562, 1440, 1290, 1259, 1175, 1122, 1095, 1040, 967, 920, 907, 872, 855, 826, 773, 721, 713, 700, 660, 600.

PMR spectrum

12.956 (s, 84Hz, 2H, pyrazolate); 8.098 (s, 30Hz, 3H, Me).

Magnetic susceptibility

This compound exhibits Curie-Weiss behavior with C = 0.73 and θ = 5.95K. Table Ib. includes $x^\text{corr}_M$ versus T. The slope of $1/x^\text{corr}_M$ versus T yields $\mu_{\text{eff}} = 2.42\mu_B$. 
Onto a mixture of 1.35 g (2.3 mmol) $\text{U(C}_5\text{Me}_5\text{)}_2\text{Cl}_2$ and 0.42 g (4.7 mmol) Na(pyrazolate) was distilled about 200 ml THF from potassium benzophenone ketyl. The resulting red-brown solution was stirred at room temperature for 24 hours with the development of a fine precipitate. The solvent was removed under vacuum and the residue extracted with a small volume of hexane (ca. 30 ml). The volume was reduced and the solution cooled overnight to -15 °C, whereupon large crystals formed. Analysis: calculated—%C, 48.59; %H, 5.65; %N, 8.72; found—%C, 48.72; %H, 5.71; %N, 8.80.

**Infra-red spectrum**

3125(w), 3100(w), 2720(w), 1731(w), 1696(w), 1590(w), 1410, 1349, 1280(s), 1230(w), 1052, 1018, 985(s), 921(s), 866, 800(w), 759(s), 725(w), 616(s), 591(w), 550(w), 382.

**Mass spectrum**

$642(67.35), 575(3.13), 508(73.93), 507(91.79), 412(66.92), 372(42.65), 136(34.74), 119(57.09), 105(32.69), 91(27.69), 77(15.02); 68(99.15).$

**Electronic spectrum**

1464, 1317, 1262, 1183, 1124, 1089, 982, 950, 930, 855, 834, 745, 691, 661.

**PMR spectrum**
\[ 29.09(s, \sim 30 \text{ Hz}, \text{2H, pyrazolate}); 27.44(s, \sim 200 \text{ Hz}, \text{4H, pyrazolate}); -0.20(s, \text{30H, \sim 7 Hz, methyl}). \]

**Magnetic susceptibility**

This compound does not exhibit simple behavior. Table Ic includes \( x_M^{\text{corr}} \) vs. \( T \), and Figure 1 illustrates \( 1/x_M^{\text{corr}} \) vs. \( T \).

**Data Collection, Solution, and Refinement**

**UCp\(^{\prime}\)\_2Cl\(_2\)(pyrazole)**

Suitable crystals for diffraction were grown by cooling a saturated hexane solution to \(-15^\circ\text{C}\). Precession photographs revealed mm symmetry, indicating orthorhombic or higher symmetry. For reflections \( hkl, h + k = 2n \) indicated a C-centered unit cell. A glide plane was indicated by the condition for \( h0l, l = 2n \). These data left as possible space groups Cmcm, Cmc2\(_1\), and Ama2\(^{\prime}\).

The crystal was oriented and lattice parameters accurately determined by 25 automatically centered reflections with values of \( 2\theta \) between 26\(^\circ\) and 40\(^\circ\) (Table II).

One octant \((+h+k+l)\), for a total of 1071 data, was collected between 4\(^\circ\) and 52\(^\circ\) \( 2\theta \) by ignoring those reflections not satisfying the C-centering condition. During data collection, one reorientation was required.

Azimuthal scans on 5 reflections with \( \theta \) between 7\(^\circ\) and
21° revealed an intensity variation of ±17%. The crystal faces were identified with the help of the diffractometer, and their dimensions measured at 7X under a binocular microscope. The distances of the 8 planes identified from a common center were adjusted incrementally until the calculated edge lengths agreed most closely with those observed. An absorption correction ranging between 2.15 and 2.67 was then applied ($\mu = 65.82 \text{ cm}^{-1}$). No crystal decay was observed during data collection.

There were 58 reflections collected that were weak and were excluded from the least squares refinement. Inspection of the 56 reflections of the type h0l that were collected revealed almost all were less than 3σ. Those 9 such reflections for which the intensity exceeded 3σ were finally excluded on the grounds that some of their intensity could be attributed to contamination of the X-ray beam with $\frac{1}{2}$. We therefore were left with the 924 reflections used in the final refinement.

The initial Patterson map confirmed the space group Cmcm, and the structure was solved by heavy-atom techniques (p factor = .03). The pyrazole was found to be lying across the mirror-plane at $x = 0$, disordering the NH and CH ortho to the metal-bound nitrogen. The structure was refined with only the carbon atom position varied (at .25 occupancy), with the parameters of the mirror-related nitrogen being reset to those of the carbon after each least-squares cycle.
This is a reasonable approximation considering how close to one another these two elements are in the Periodic Chart. The model converged to weighted and unweighted R factors of 3.48% and 2.45% respectively. During the final least-squares cycle the largest parameter shift was 0.18°. The largest peak in the final difference Fourier was $\frac{4}{2\pi}^2$ and was less than one Angstrom from the uranium. Hydrogen atoms were not found, nor were calculated positions included in the final calculations. The residuals showed no anomalies. Positional and thermal parameters appear in Table III.

UC$\text{p}^\text{II}_2\text{Cl}$(pyrazolate)

Crystals suitable for diffraction studies were obtained by cooling a concentrated hexane solution at -15°C overnight. The large polycrystalline solids that formed were fractured into single crystal fragments. Precession photographs revealed systematic absences $h0l$, $h + l = 2n$, and $0k0$, $k = 2n$ indicating space group $P2_1/n$. Cell parameters were determined from 25 automatically centered reflections between 27° and 30° in 2θ (Table II).

A total of 3513 $hl + 1$ data were collected between 4° and 45° in θ. Azimuthal scans on 6 reflections between 5° and 22° in θ revealed an intensity variation of ±17%. Because the data crystal was of a particularly irregular shape, an empirical absorption correction was applied; it ranged from 1.00 to 1.49 ($\mu=66.00\text{cm}^{-1}$). No decay was
observed during data collection.

Of the 138 absent reflections that were collected, 3 had an intensity greater than 3σ; these were rejected with the rest on the grounds that their intensity resulted from contamination of the X-ray beam with \( \frac{1}{2} \) (low θ). The averaging of equivalent reflections left 3134 unique data, 2566 of which were greater than 3σ and were used in the least-squares refinement.

The initial Patterson map confirmed the space group and revealed the positions of the uranium and the chloride ion. The p factor for weighting was set at 0.03. Subsequent difference Fourier-least-squares cycles revealed the pyrazolate and the two Cp" rings. Residual electron density and some poor atomic relationships suggested a second orientation for both the Cp" rings, so primed carbon atom positions and isotropic thermal parameters were refined. The relative occupancy factors of the two orientations refined to about 50/50 for Cp"2 and about 60/40 for Cp"1. Fourier maps showed these ligands consisted of diffuse rings of electron density. This observation led us to conclude that further attempts to improve the moderately poor atomic relationships in the ring were unwarranted. In the final refinements, only the thermal parameters of uranium and chlorine were treated anisotropically.

The model converged to weighted and unweighted R factors of 4.50% and 3.27% respectively. On the final
least-squares cycle, the largest parameter shift was $0.29\sigma$, while for those 7 atoms not involved in the disorder the largest shift was $0.02\sigma$. The residual peaks in the final difference Fourier (largest = $0.525\sigma^2$) were near the methyl carbons of the Cp" rings. Hydrogen atoms were not found, nor were calculated positions included in the final calculations. The residuals showed no anomalies. Positional and thermal parameters appear in Table IV.

\[ \text{UCp}^{\text{"}}_{2} (\text{pyrazolate})_{2} \]

Crystals suitable for diffraction experiments were obtained by slow cooling of a hexane solution to $-15^\circ$C. Precession photographs revealed systematic absences indicating space groups Cc or C2/c ($hkl$, $h + k = 2n$, and $h0l$, $l = 2n$).

The crystal was oriented and lattice parameters accurately determined by 25 automatically centered reflections with values of 2\(\theta\) between $26^\circ$ and $35^\circ$ (Table II). A total of 3737 $hk+l$ data were collected between $4^\circ$ and $45^\circ$ 2\(\theta\) by ignoring those reflections not satisfying the C-centering condition. Twice during data collection reorientation of the crystal was required.

Azimuthal scans on 7 reflections with \(\theta\) between $5^\circ$ and $22^\circ$ revealed an intensity variation of $\pm 10\%$. The crystal faces were identified with the help of the diffractometer, and their dimensions measured at 7X under a binocular
microscope. The distance of the 8 planes used to approximate the true shape of the crystal from a common center were adjusted incrementally until calculated edge lengths agreed most closely with those observed. The absorption correction applied ranged from 1.91 to 2.77 ($\mu = 60.52 \text{cm}^{-1}$). No crystal decay was observed during data collection.

Inspection of the 223 reflections of the type $h0l$, $l = 2n$ that were collected revealed 12 reflections where $F_{\text{obs}}$ was about or greater than $1\sigma$, but all of these were rather weak and were rejected with the rest of the 223. Symmetry equivalent reflections were averaged leaving 3363 reflections of which 2706 were greater than $3\sigma$ and were used in the least-squares refinements.

The initial Patterson map confirmed the space group $C2/c$, and the structure was solved by heavy-atom techniques. (The $p$ factor for weighting was set to 0.03.) In the final refinements, the temperature factors of all atoms were treated anisotropically, the model converging to weighted and unweighted $R$ factors of 3.31% and 2.43% respectively. On the final cycle, the largest parameter shift was $0.63\sigma$ for one of the methyl carbons on $\text{Cp}^\text{"2}$. This ring has generally greater thermal motion than the other parts of the molecule. In the final difference Fourier map the largest peak at a grid point was $0.36e^{-A^2}$, and was more than 1.6 $\AA$ from any atom or other peak. Hydrogen atoms were not found, nor were calculated positions included in the final calculations. The
residuals showed no anomalies. Positional and thermal parameters are listed in Table V.

**Description of the Structures**

**UCp"<sub>2</sub>Cl<sub>2</sub>(pyrazole)**

The crystal structure consists of discrete mononuclear units at positions of \textit{mm} symmetry (Fig 2). The closest intermolecular contact is 3.68(1)\text{
\AA} between C(60) and C(71). The molecular structure consists of a uranium ion bound by two \eta^5-pentamethylcyclopentadienide rings, two chloride ions, and one nitrogen from the pyrazole ring, for a formal coordination number of 9. Both the uranium and the bound nitrogen lie at the intersection of mirror planes, while the chlorides, C(3), C(6), and the remaining atoms of the pyrazole ring lie in mirror planes. All the other atoms are in general positions. A perspective drawing of the molecular unit is illustrated in Figure 3.

The uranium-carbon distances average 2.74(2)\text{
\AA}, the U-Cl bond is 2.696(2)\text{
\AA}, and the U-N bond is 2.607(8)\text{
\AA} long. The closest intramolecular non-bonded contact is 3.07(1)\text{
\AA} between Cl and C(80). Data on the least-squares planes of the ligand rings appears in Table VI. The Cl-U-Cl angle of 148.29(8)^\text{o} is by symmetry bisected by the U-N bond. The Cl-U-Cp"(centroid) angle is 95.7^\text{o}, and the Cp"-U-Cp" angle is 137.1^\text{o}. The Cp"-U-N angle is 111.4^\text{o}. Pertinent bond angles and distances are listed in Table VII.
The crystal structure consists of discrete mononuclear units at general positions in the unit cell (Fig 4). The closest intermolecular contact is 3.41(3)Å between C(17) and C(20'). The molecular structure consists of a uranium ion coordinated by two η⁵-pentamethyl cyclopentadienide rings, one chloride ion, and two nitrogens from the pyrazolate ion for a formal coordination number of 9. The coordination geometry is very roughly tetrahedral when considering the chloride, the Cp" centroids, and the midpoint of the N-N bond as the ligands. The angles from both the N-N midpoint and the chloride to each of the other three ligands are approximately equal; either serves as the apex of a tetrahedron in which the basal angles are distorted by the 136° angle between the Cp" centroids. Figure 5 illustrates the molecular structure utilizing one nominal orientation for each Cp" ring.

The uranium-carbon distances range between 2.69(1)Å and 2.78(1)Å, averaging 2.73(3)Å. The U-N distances are 2.351(5)Å and 2.349(5)Å. The U-Cl distance is 2.611(2)Å. Within a molecule, the closest inter-ligand non-bonded contact is 3.00(2)Å between N(1) and C(16'). Selected bond lengths and angles appear in Table VIII.

Least-squares planes for the 4 Cp" rings show all but that of C's 11-15 are planar to about one sigma; C's 13 and 14 are about two sigma from their least-squares plane (Table
The methyl carbons generally are tilted away from the uranium by tenths of an Angstrom (5-15 sigma); one methyl carbon from each ring, however, is much more nearly coplanar with the internal carbons of the ring to which it belongs. The pyrazolate ring is planar to within one sigma, and the three pyrazolate carbon atoms are about one sigma from the UN$_2$ plane.

$\text{UCp}^\mu_2(\text{pyrazolate})_2$

The crystal structure consists of discrete mononuclear units at general positions in the unit cell (Fig 6). The closest intermolecular contacts are 3.638(8) and 3.637(9)Å between C(10) and C(2) and C(7) respectively. The molecular structure consists of the uranium ion coordinated by two $\eta^5$-pentamethylcyclopentadienide rings and 4 nitrogens from the two pyrazolate rings, for a total formal coordination number of 10. The pyrazolates are adjacent and nearly coplanar while they oppose the two Cp" rings, whose least-squares planes are about 40° from each other (vide infra). A perspective drawing of the molecule appears in Figure 7, where one can see relatively high thermal motion in Cp"2.

The U-carbon distances range from 2.724(6)Å to 2.786(5)Å, averaging 2.75(2)Å. The U-N distances are 2.403(4)Å, 2.360(5)Å, 2.363(5)Å, and 2.405(5)Å. The closest intramolecular non-bonded contact is 3.006(6)Å between N’s 2 and 3. Selected bond lengths and angles appear in Table X.
The internal carbons of both Cp" rings are essentially planar, deviations from the least squares plane being on the order of one sigma. Also, the methyl carbons are all bent out away from the uranium ion by a few tenths of an Angstrom. Both pyrazolates are planar. The average deviation from the UN₄ least squares plane is 0.003 Å (ca. 5 σ). The angles between the least squares planes of the Cp" rings is 41.4°, between the pyrazolates is 5.6°, and between the Cp"s and the pyrazolates 20.2°, 25.3°, 21.6°, and 16.1° (Cp"1-pyz1,2; Cp"2-pyz1,2). Complete data on the least squares planes appear in Table XI.

Discussion

These structures constitute the first formal reports of bis-pentamethylCp uranium 4+ compounds. Marks has presented unpublished results on the structure of UCp"₂(CONMe₂)₁⁷ and has published structural results on [UCp"₂Cl]₃, [ThCp"₂H₂]₁⁸, and [ThCp"₂O₂C₂Me₂]₁⁹. More unpublished results include the structures of ThCp"₂Cl(COCH₂CMe₃) and ThCp"₂Cl(CONEt₂)¹⁷. In addition, the structures of numerous Ti⁴⁺ and Zr⁴⁺ compounds of the type MCp₂X₂ have been reported²⁰,²¹.

The larger size of the methylated Cp rings means fewer of them are able to share a coordination sphere, relative to the numerous compounds with unsubstituted Cp rings of general formula MCp₃X²². The Cp-U-Cp angles in these compounds is less than 120°, whereas the present compounds share a
value for this angle of about 137°. All the Cp" ligands characterized here exhibit the bending outward of the methyl groups as is quite common for the ligand. The U-Cl distance in UCp"\textsubscript{2}Cl(pyzr) (2.611 \AA) is similar to those found in other U\textsuperscript{4+} organometallics\textsuperscript{23–26}, but the U-Cl distance in UCp"\textsubscript{2}Cl\textsubscript{2}(pyrazole) (2.696(2) \AA) is considerably longer. This is probably best attributed to the relatively greater crowding the chloride in UCp"\textsubscript{2}Cl\textsubscript{2}(pyrazole) experiences.

The average U-C(ring) distances are nearly identical for the three compounds, and the two rings bear a constant relationship to each other of 137°. In UCp"\textsubscript{2}Cl\textsubscript{2}(pyrazole), the two Cp" centroids and N(1) are coplanar by symmetry. The 137° angle between centroids leaves 111.5° between each of the centroids and N(1). We also see that the Cp"-U-Cl angle is 95° (Table XII).

In moving to UCp"\textsubscript{2}Cl(pyzr), the angles from the Cp"'s to the other ligands is raised from 95° by the removal of one ligand. Also as a result of there being fewer ligands, the Cl-U-(N-N) angle relaxes to 103° from the 148° for the Cl-U-Cl angle in UCp"\textsubscript{2}Cl\textsubscript{2}(pyrazole). In going to UCp"\textsubscript{2}(pyrazolate)\textsubscript{2}, substitution of a sterically larger pyrazolate for the remaining chloride results in an increase in the (N-N)-U-(N-N) angle relative to the Cl-U-(N-N) angle in UCp"\textsubscript{2}Cl(pyzr), while also the Cp"-U-(N-N) angles decrease slightly on average. This behavior is the same as that seen in the thorium compounds (Table XIII). The Cp"-
Th-Cp" angle decreases in going from the small bridging hydride ligands to the larger bridging enediolate ligands, and the monomeric species, where crowding is decreased, exhibit the largest angles. We see, then, that the inter-ligand relationships in these compounds can be explained with steric arguments.

In UCp"_2(pyrazolate)_2, Cp"(2) exhibits much more thermal motion than Cp"(1). This is probably the result of the fact that Cp"(2) has fewer non-bonded neighbors than Cp"(1). For instance, the closest intermolecular contact in this compound is 3.64 Å and involves atoms of Cp"(1) (vide supra). The closest such contact for Cp"(2) is 3.72 Å (C(19)-C(19)). In addition, Cp"(1) has 33 intermolecular contacts within 4.5 Å, while Cp"(2) has only 29.

The disorder in UCp"_2Cl(pyrazolate) can also be explained in terms of intermolecular contacts. Although the closest intermolecular contact is shorter than in UCp"_2(pyrazolate)_2 (3.413(3)Å vs. 3.638(8)Å), in UCp"_2Cl(pyrazolate)), Cp"(2) and Cp"(2') have only 34 contacts within 4.5 Å, or 17 contacts per 5 methyl carbons. The occupancy factors for Cp"(1) refined to .62/.38, while for Cp"(2) they refined to .50/.50. The fact that Cp"(1) has many more contacts (32 per 5 methyl carbons) explains its greater preference for one orientation over the other, inasmuch as the orientation is determined by the intermolecular environment.
The U-N distance in UCp"2Cl2(pyrazole) is much longer than those reported in UCp3(pyrazolate)\(^1\), and this is undoubtedly due to the electrical neutrality of the pyrazole ligand. In UCp"2(pyrazolate)\(_2\), we see the same U-N distances found in UCp3(pyrazolate), i.e. 2.36 Å and 2.40 Å. The origin of 0.04 Å difference in UCp3(pyrazolate) is difficult to explain, but even more mystifying is the pattern of the U-N bond lengths in UCp"2(pyrazolate)\(_2\). The shorter bonds are those from uranium to the "internal" nitrogens where the crowding is greatest (vide supra), while the longer bonds are those to the "external" nitrogens where the crowding is less. However, in UCp"2Cl(pyrazolate) the U-N distances are identical, as one would expect by almost any argument.

Of the other physical properties of these compounds, a couple are worthy of mention. The pmr spectrum of UCp"2Cl2(pyrazole) reveals a fluxionality of the pyrazole ligand. At low temperature, four resonances are resolved that can be assigned to the pyrazole. Those most strongly shifted can be assigned to the C-H and N-H adjacent to the metal-bound nitrogen, while those less strongly shifted are the protons further from the uranium. By room temperature, the four resonances have collapsed into a broad singlet and a very broad resonance, indicative of a fluxional U-N bond that makes all the carbon bound protons nearly equivalent and leaves the remaining proton's resonance quite broad and less strongly shifted than previously.
The magnetic behavior of both UCp"2Cl2(pyrazole) and UCp"2Cl(pyrazolate) is as one expects for U4+ ions. However, UCp"2(pyrazolate)2 does not exhibit similar magnetic behavior. Instead of decreasing with increasing temperature from an initial high value as the others, the susceptibility of UCp"2(pyrazolate)2 has its minimum at low temperature and increases as the temperature increases, until it becomes relatively invariant with temperature. While temperature independent paramagnetism is common in U4+ compounds, the behavior seen for UCp"2(pyrazolate)2 remains a matter for conjecture.
Table Ia. Magnetic Susceptibility for UCp₂Cl₂(pyrazole)

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$x_M^{corr} \times 10^3$ (cm³/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4</td>
<td>30.26</td>
</tr>
<tr>
<td>9.0</td>
<td>27.16</td>
</tr>
<tr>
<td>17.9</td>
<td>23.83</td>
</tr>
<tr>
<td>27.8</td>
<td>21.46</td>
</tr>
<tr>
<td>37.4</td>
<td>52.18</td>
</tr>
<tr>
<td>46.4</td>
<td>58.52</td>
</tr>
<tr>
<td>60.2</td>
<td>73.69</td>
</tr>
</tbody>
</table>
Table Ib. Magnetic Susceptibility for UCp$^2$Cl(pyrazolate)

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$x_M^{corr} \times 10^3$ (cm$^3$/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>93.17</td>
</tr>
<tr>
<td>9.1</td>
<td>57.89</td>
</tr>
<tr>
<td>17.9</td>
<td>31.47</td>
</tr>
<tr>
<td>27.8</td>
<td>21.23</td>
</tr>
<tr>
<td>37.4</td>
<td>16.20</td>
</tr>
<tr>
<td>46.4</td>
<td>12.81</td>
</tr>
<tr>
<td>60.2</td>
<td>10.69</td>
</tr>
<tr>
<td>77.6</td>
<td>9.34</td>
</tr>
</tbody>
</table>
Table Ic. Magnetic Susceptibility for UCp"₂(pyrazolate)₂

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$x_M^{\text{corr}} \times 10^3$ (cm$^3$/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>2.57</td>
</tr>
<tr>
<td>8.6</td>
<td>4.37</td>
</tr>
<tr>
<td>17.9</td>
<td>7.56</td>
</tr>
<tr>
<td>27.5</td>
<td>9.29</td>
</tr>
<tr>
<td>37.2</td>
<td>9.42</td>
</tr>
<tr>
<td>46.3</td>
<td>8.82</td>
</tr>
<tr>
<td>60.2</td>
<td>8.58</td>
</tr>
<tr>
<td>77.6</td>
<td>8.73</td>
</tr>
</tbody>
</table>
### Table II. Cell Parameters for UCP\(^{2}\)Cl\(_{2}\)(pyrazole), UCP\(^{2}\)Cl(pyrazolate), and UCP\(^{2}\)(pyrazolate)\(_{2}\)

<table>
<thead>
<tr>
<th></th>
<th>HPYZ</th>
<th>1:1</th>
<th>1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>space group</td>
<td>Cmcm</td>
<td>P2(_{1}/n)</td>
<td>C2/c</td>
</tr>
<tr>
<td>a(Å)</td>
<td>13.697(4)</td>
<td>8.737(1)</td>
<td>33.326(2)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>11.496(2)</td>
<td>18.068(1)</td>
<td>10.450(2)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>15.555(2)</td>
<td>15.229(2)</td>
<td>16.646(1)</td>
</tr>
<tr>
<td>β(°)</td>
<td>90</td>
<td>92.38(1)</td>
<td>117.09(1)</td>
</tr>
<tr>
<td>Vol.(Å(^{3}))</td>
<td>2449.4(14)</td>
<td>2401.9(6)</td>
<td>5160.8(17)</td>
</tr>
<tr>
<td>molecules/cell</td>
<td>4</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>d(_{calc})(g/cm(^{3}))</td>
<td>1.756</td>
<td>1.690</td>
<td>1.654</td>
</tr>
<tr>
<td>d(_{obs})(g/cm(^{3}))</td>
<td>1.77</td>
<td>1.68</td>
<td>1.66</td>
</tr>
<tr>
<td>observations</td>
<td>924</td>
<td>2566</td>
<td>2706</td>
</tr>
<tr>
<td>parameters</td>
<td>75</td>
<td>201</td>
<td>280</td>
</tr>
<tr>
<td>R</td>
<td>2.45%</td>
<td>3.27%</td>
<td>2.43%</td>
</tr>
<tr>
<td>R(_{w})</td>
<td>3.48%</td>
<td>4.50%</td>
<td>3.31%</td>
</tr>
</tbody>
</table>

HPYZ is UCP\(^{2}\)Cl\(_{2}\)(pyrazole)  
1:1 is UCP\(^{2}\)Cl(pyrazolate)  
1:2 is UCP\(^{2}\)(pyrazolate)\(_{2}\)
<table>
<thead>
<tr>
<th>ATOM</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>B(1,1)</th>
<th>B(2,2)</th>
<th>B(3,3)</th>
<th>B(1,2)</th>
<th>B(1,3)</th>
<th>B(2,3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.0000(8)</td>
<td>0.2632(3)</td>
<td>0.2588(8)</td>
<td>0.0042(2)</td>
<td>0.0053(2)</td>
<td>0.0076(2)</td>
<td>0.0000(8)</td>
<td>0.0000(8)</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.1893(2)</td>
<td>0.2504(2)</td>
<td>0.2580(8)</td>
<td>0.0040(9)</td>
<td>0.0131(3)</td>
<td>0.0076(1)</td>
<td>-0.0004(3)</td>
<td>0.0000(8)</td>
<td>0.0000(8)</td>
</tr>
<tr>
<td>N1</td>
<td>0.0000(8)</td>
<td>0.4831(8)</td>
<td>0.2588(8)</td>
<td>0.0009(7)</td>
<td>0.0041(7)</td>
<td>0.0076(7)</td>
<td>0.0000(8)</td>
<td>0.0000(8)</td>
<td>0.0000(8)</td>
</tr>
<tr>
<td>N2</td>
<td>0.0776(8)</td>
<td>0.6222(8)</td>
<td>0.2588(8)</td>
<td>0.0066(8)</td>
<td>0.0082(8)</td>
<td>0.0121(8)</td>
<td>-0.0035(8)</td>
<td>0.0000(8)</td>
<td>0.0000(8)</td>
</tr>
<tr>
<td>C11</td>
<td>0.0616(6)</td>
<td>0.2273(6)</td>
<td>0.0010(4)</td>
<td>0.0077(4)</td>
<td>0.0144(6)</td>
<td>0.0030(3)</td>
<td>-0.0020(7)</td>
<td>0.0017(6)</td>
<td>0.0010(6)</td>
</tr>
<tr>
<td>C21</td>
<td>0.0035(6)</td>
<td>0.1176(6)</td>
<td>0.1191(4)</td>
<td>0.0006(4)</td>
<td>0.0123(6)</td>
<td>0.0042(3)</td>
<td>0.0076(9)</td>
<td>0.0012(6)</td>
<td>0.0000(7)</td>
</tr>
<tr>
<td>C31</td>
<td>0.0000(8)</td>
<td>0.0516(8)</td>
<td>0.1287(6)</td>
<td>0.0180(9)</td>
<td>0.0077(7)</td>
<td>0.0036(3)</td>
<td>0.0000(8)</td>
<td>0.0000(8)</td>
<td>-0.0021(9)</td>
</tr>
<tr>
<td>C41</td>
<td>0.0496(8)</td>
<td>0.1397(9)</td>
<td>0.2588(8)</td>
<td>0.0181(7)</td>
<td>0.0069(8)</td>
<td>0.0156(11)</td>
<td>0.0022(14)</td>
<td>0.0000(8)</td>
<td>0.0000(8)</td>
</tr>
<tr>
<td>C51</td>
<td>0.0776(12)</td>
<td>0.5222(16)</td>
<td>0.2588(8)</td>
<td>0.0066(18)</td>
<td>0.0002(16)</td>
<td>0.0121(16)</td>
<td>-0.0035(23)</td>
<td>0.0000(8)</td>
<td>0.0000(8)</td>
</tr>
<tr>
<td>C61</td>
<td>0.1136(6)</td>
<td>0.3265(9)</td>
<td>0.0422(8)</td>
<td>0.0124(6)</td>
<td>0.0050(9)</td>
<td>0.0067(4)</td>
<td>-0.0128(13)</td>
<td>0.0001(8)</td>
<td>0.0071(10)</td>
</tr>
<tr>
<td>C71</td>
<td>0.0000(8)</td>
<td>-0.0791(10)</td>
<td>0.1467(7)</td>
<td>0.0412(25)</td>
<td>0.0063(9)</td>
<td>0.0081(6)</td>
<td>0.0000(8)</td>
<td>0.0000(8)</td>
<td>-0.0034(12)</td>
</tr>
<tr>
<td>C81</td>
<td>0.1091(6)</td>
<td>0.0728(9)</td>
<td>0.1146(6)</td>
<td>0.0121(5)</td>
<td>0.0030(12)</td>
<td>0.0008(5)</td>
<td>0.0015(11)</td>
<td>0.0013(9)</td>
<td>-0.0063(13)</td>
</tr>
</tbody>
</table>

The form of the anisotropic thermal parameter is:

\[ \text{Exp}(-B(1,1)H^2 + B(2,2)K^2 + B(3,3)L^2 + B(1,2)HK + B(1,3)HL + B(2,3)KL)]. \]
### Table IV. UC$_2$Cl$_7$(pyrazolate)

**Positional and Thermal Parameters and Their Estimated Standard Deviations.**

<table>
<thead>
<tr>
<th>ATOM</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>B(1,1)</th>
<th>B(2,2)</th>
<th>B(3,3)</th>
<th>B(1,2)</th>
<th>B(1,3)</th>
<th>B(2,3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.4095(3)</td>
<td>0.1836(2)</td>
<td>0.2834(2)</td>
<td>0.0076(4)</td>
<td>0.0022(1)</td>
<td>0.0037(1)</td>
<td>0.0053(4)</td>
<td>0.0044(4)</td>
<td>-0.0001(2)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.4456(3)</td>
<td>0.1856(1)</td>
<td>0.3375(2)</td>
<td>0.0123(1)</td>
<td>0.0062(1)</td>
<td>0.0073(1)</td>
<td>-0.0016(3)</td>
<td>-0.0043(4)</td>
<td>0.0024(2)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.2119(8)</td>
<td>0.2393(4)</td>
<td>0.3307(5)</td>
<td>4.5(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.3419(8)</td>
<td>0.3051(4)</td>
<td>0.3755(6)</td>
<td>9.2(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.79(1)</td>
<td>-0.8228(7)</td>
<td>0.1671(9)</td>
<td>4.2(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.310(2)</td>
<td>0.0352(8)</td>
<td>0.1147(10)</td>
<td>5.6(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.430(1)</td>
<td>0.0771(7)</td>
<td>0.0082(8)</td>
<td>3.1(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.560(1)</td>
<td>0.0526(7)</td>
<td>0.1262(9)</td>
<td>4.1(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.535(2)</td>
<td>-0.0099(8)</td>
<td>0.1766(9)</td>
<td>4.9(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.258(2)</td>
<td>-0.0828(11)</td>
<td>0.1089(14)</td>
<td>3.0(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.158(4)</td>
<td>0.0527(13)</td>
<td>0.0709(15)</td>
<td>9.6(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.458(2)</td>
<td>0.1379(12)</td>
<td>0.0132(14)</td>
<td>0.8(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.740(3)</td>
<td>0.0655(13)</td>
<td>0.1201(16)</td>
<td>9.9(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.626(3)</td>
<td>-0.0659(17)</td>
<td>0.2384(16)</td>
<td>11.3(7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.287(2)</td>
<td>0.2118(9)</td>
<td>0.3818(10)</td>
<td>3.6(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.276(2)</td>
<td>0.2364(9)</td>
<td>0.2198(10)</td>
<td>3.6(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.430(2)</td>
<td>0.2636(9)</td>
<td>0.2378(10)</td>
<td>3.3(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.454(2)</td>
<td>0.2453(9)</td>
<td>0.3311(10)</td>
<td>3.0(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.328(2)</td>
<td>0.2176(9)</td>
<td>0.3657(10)</td>
<td>3.5(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.021(3)</td>
<td>0.1955(15)</td>
<td>0.2633(10)</td>
<td>9.2(7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.224(3)</td>
<td>0.2569(13)</td>
<td>0.1284(16)</td>
<td>7.6(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.555(3)</td>
<td>0.2980(12)</td>
<td>0.1946(16)</td>
<td>6.9(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.576(3)</td>
<td>0.2583(14)</td>
<td>0.3801(17)</td>
<td>8.5(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.253(4)</td>
<td>0.1938(19)</td>
<td>0.4497(24)</td>
<td>12.7(10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.186(1)</td>
<td>-0.8210(6)</td>
<td>0.4458(7)</td>
<td>7.8(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.154(1)</td>
<td>-0.8347(8)</td>
<td>0.4421(7)</td>
<td>6.2(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.187(1)</td>
<td>0.0001(6)</td>
<td>0.3744(7)</td>
<td>7.8(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.464(2)</td>
<td>-0.383(2)</td>
<td>0.1650(11)</td>
<td>2.1(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.322(2)</td>
<td>-0.0840(11)</td>
<td>0.1445(12)</td>
<td>3.3(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.346(3)</td>
<td>0.0524(12)</td>
<td>0.0942(15)</td>
<td>4.2(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.510(2)</td>
<td>0.0665(12)</td>
<td>0.1810(14)</td>
<td>4.8(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.561(2)</td>
<td>0.0176(12)</td>
<td>0.1508(14)</td>
<td>4.2(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.230(2)</td>
<td>0.2876(9)</td>
<td>0.3463(11)</td>
<td>4.8(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.197(1)</td>
<td>0.2142(7)</td>
<td>0.2499(9)</td>
<td>2.7(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.326(2)</td>
<td>0.2428(8)</td>
<td>0.2851(13)</td>
<td>3.6(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.434(2)</td>
<td>0.2525(10)</td>
<td>0.2785(11)</td>
<td>4.6(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.399(2)</td>
<td>0.2328(10)</td>
<td>0.3228(12)</td>
<td>5.2(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.475(6)</td>
<td>-0.1019(10)</td>
<td>0.2369(18)</td>
<td>9.0(11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.157(5)</td>
<td>-0.3952(22)</td>
<td>0.1312(28)</td>
<td>18.0(11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.327(1)</td>
<td>0.1123(19)</td>
<td>0.8111(38)</td>
<td>10.1(11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.484(4)</td>
<td>0.1087(15)</td>
<td>0.0652(24)</td>
<td>7.4(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.739(4)</td>
<td>-0.7235(20)</td>
<td>0.2827(23)</td>
<td>9.1(19)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.182(3)</td>
<td>0.1028(13)</td>
<td>0.4875(16)</td>
<td>7.9(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.821(3)</td>
<td>0.1969(12)</td>
<td>0.2892(14)</td>
<td>6.6(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.324(3)</td>
<td>0.2695(13)</td>
<td>0.1140(16)</td>
<td>9.2(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.585(3)</td>
<td>0.2934(18)</td>
<td>0.2684(22)</td>
<td>11.7(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.466(4)</td>
<td>0.2375(17)</td>
<td>0.4458(28)</td>
<td>11.2(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The form of the anisotropic thermal parameter is:

$$\exp(-B(1,1)x^2 - B(2,2)y^2 - B(3,3)z^2 + B(1,2)xy + B(1,3)xz + B(2,3)yz).$$
### Table V. DCP₂(pyrazolate)₂

<table>
<thead>
<tr>
<th>ATOM</th>
<th>X (Å)</th>
<th>Y (Å)</th>
<th>Z (Å)</th>
<th>B(1,1) (Å²)</th>
<th>B(2,2) (Å²)</th>
<th>B(3,3) (Å²)</th>
<th>B(1,2) (Å²)</th>
<th>B(1,3) (Å²)</th>
<th>B(2,3) (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.12999(1)</td>
<td>0.294(2)</td>
<td>0.974(1)</td>
<td>0.000(3)</td>
<td>0.0004(2)</td>
<td>0.0037(1)</td>
<td>0.0001(1)</td>
<td>0.00002(1)</td>
<td>0.00002(1)</td>
</tr>
<tr>
<td>Cl1</td>
<td>0.1729(1)</td>
<td>0.475(1)</td>
<td>0.82(1)</td>
<td>0.0035(1)</td>
<td>0.0005(1)</td>
<td>0.0005(1)</td>
<td>0.0007(1)</td>
<td>0.002(2)</td>
<td>0.002(2)</td>
</tr>
<tr>
<td>Cl2</td>
<td>0.163(1)</td>
<td>0.432(1)</td>
<td>0.69(1)</td>
<td>0.0105(1)</td>
<td>0.007(2)</td>
<td>0.0005(1)</td>
<td>0.015(3)</td>
<td>0.025(2)</td>
<td>0.029(3)</td>
</tr>
<tr>
<td>Cl3</td>
<td>0.182(1)</td>
<td>0.2849(5)</td>
<td>0.58(1)</td>
<td>0.0004(1)</td>
<td>0.004(2)</td>
<td>0.004(2)</td>
<td>0.004(4)</td>
<td>0.018(2)</td>
<td>0.014(1)</td>
</tr>
<tr>
<td>Cl4</td>
<td>0.088(4)</td>
<td>0.119(5)</td>
<td>0.489(3)</td>
<td>0.0125(6)</td>
<td>0.0044(3)</td>
<td>0.0044(3)</td>
<td>0.0091(3)</td>
<td>0.019(2)</td>
<td>0.004(1)</td>
</tr>
</tbody>
</table>

**The form of the anisotropic thermal parameter is:**

\[ \exp(-B(1,1)x^2 - B(2,2)y^2 - B(3,3)z^2 - B(1,2)xy - B(1,3)yz - B(2,3)zx) \]
<table>
<thead>
<tr>
<th>atom</th>
<th>dist(Å)</th>
<th>parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(11)</td>
<td>0.003(6)</td>
<td>A -0.0001</td>
</tr>
<tr>
<td>C(21)</td>
<td>-0.009(6)</td>
<td>B -0.3480</td>
</tr>
<tr>
<td>C(31)</td>
<td>0.011(9)</td>
<td>C -0.9375</td>
</tr>
<tr>
<td>C(12)</td>
<td>0.003(6)</td>
<td>D -2.0935</td>
</tr>
<tr>
<td>C(22)</td>
<td>-0.008(6)</td>
<td></td>
</tr>
<tr>
<td>Bond Distances (Å) and Angles (°) for ( \text{UCp}^2\text{Cl}_2(\text{pyrazole}) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Bond</td>
<td>Distance (Å)</td>
<td>Angle (°)</td>
</tr>
<tr>
<td>U-Cl</td>
<td>2.696(2)</td>
<td>C(11)-C(12) 1.410(11)</td>
</tr>
<tr>
<td>U-C(11)</td>
<td>2.722(5)</td>
<td>C(11)-C(21) 1.422(7)</td>
</tr>
<tr>
<td>U-C(21)</td>
<td>2.737(5)</td>
<td>C(11)-C(41) 1.525(8)</td>
</tr>
<tr>
<td>U-C(31)</td>
<td>2.756(7)</td>
<td>C(21)-C(31) 1.396(7)</td>
</tr>
<tr>
<td>U-N(1)</td>
<td>2.607(8)</td>
<td>C(21)-C(51) 1.535(7)</td>
</tr>
<tr>
<td>C(31)-C(61)</td>
<td>1.525(12)</td>
<td>Cl-U-Cl 148.29(8)</td>
</tr>
<tr>
<td>N(1)-C(80)</td>
<td>1.327(14)</td>
<td>Cl-U-N(1) 74.14(4)</td>
</tr>
<tr>
<td>C(80)-C(71)</td>
<td>1.401(17)</td>
<td>Cl-U-Cp 95.73(1)</td>
</tr>
<tr>
<td>C(71)-C(72)</td>
<td>1.384(16)</td>
<td>Cp-U-N(1) 111.44(1)</td>
</tr>
<tr>
<td>U-C(ave)</td>
<td>2.74(2)</td>
<td>Cp-U-Cp 137.1</td>
</tr>
<tr>
<td>C(12)-C(11)-C(21)</td>
<td>108.0(3)</td>
<td></td>
</tr>
<tr>
<td>C(12)-C(11)-C(41)</td>
<td>123.9(4)</td>
<td></td>
</tr>
<tr>
<td>C(41)-C(11)-C(21)</td>
<td>127.8(6)</td>
<td></td>
</tr>
<tr>
<td>C(11)-C(21)-C(51)</td>
<td>126.6(6)</td>
<td></td>
</tr>
<tr>
<td>C(11)-C(21)-C(31)</td>
<td>107.0(5)</td>
<td></td>
</tr>
<tr>
<td>C(51)-C(21)-C(31)</td>
<td>125.9(6)</td>
<td></td>
</tr>
<tr>
<td>C(21)-C(31)-C(61)</td>
<td>124.5(3)</td>
<td></td>
</tr>
<tr>
<td>C(21)-C(31)-C(22)</td>
<td>110.1(7)</td>
<td></td>
</tr>
<tr>
<td>N(2)-N(1)-C(80)</td>
<td>106.1(1)</td>
<td></td>
</tr>
<tr>
<td>N(1)-C(80)-C(71)</td>
<td>111.1(1)</td>
<td></td>
</tr>
<tr>
<td>C(80)-C(71)-C(72)</td>
<td>105.4(6)</td>
<td></td>
</tr>
</tbody>
</table>
Table VIIIa. Bond Distances (Å) and Angles (°) for UCp$^2$Cl(pyrazolate)

<table>
<thead>
<tr>
<th>U-X distances</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1),C(1')</td>
<td>2.72(1), 2.75(1)</td>
<td>C(11),C(11')</td>
</tr>
<tr>
<td>C(2),C(2')</td>
<td>2.69(1), 2.75(2)</td>
<td>C(12),C(12')</td>
</tr>
<tr>
<td>C(3),C(3')</td>
<td>2.72(1), 2.77(2)</td>
<td>C(13),C(13')</td>
</tr>
<tr>
<td>C(4),C(4')</td>
<td>2.72(1), 2.76(2)</td>
<td>C(14),C(14')</td>
</tr>
<tr>
<td>C(5),C(5')</td>
<td>2.70(1), 2.73(2)</td>
<td>C(15),C(15')</td>
</tr>
<tr>
<td>N(1),N(2)</td>
<td>2.351(5), 2.349(5)</td>
<td>Cl</td>
</tr>
<tr>
<td>U-C(av)</td>
<td>2.73(3)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pyrazolate distances and angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(23)</td>
</tr>
<tr>
<td>C(23)-C(22)</td>
</tr>
<tr>
<td>C(22)-C(21)</td>
</tr>
<tr>
<td>C(21)-N(2)</td>
</tr>
<tr>
<td>N(2)-N(1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>interligand angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp$^n$-U-Cp$^m$</td>
</tr>
<tr>
<td>Cp$^n$(1)-U-Cl</td>
</tr>
<tr>
<td>Cp$^n$(1)-U-(N-N)</td>
</tr>
<tr>
<td>Cp$^n$(2)-U-Cl</td>
</tr>
<tr>
<td>Cp$^n$(2)-U-(N-N)</td>
</tr>
<tr>
<td>Cl-U-(N-N)</td>
</tr>
<tr>
<td>N(1)-U-N(2)</td>
</tr>
<tr>
<td>Bond</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
</tr>
<tr>
<td>C(5)-C(1)</td>
</tr>
<tr>
<td>C(5)-C(1)-C(2)</td>
</tr>
<tr>
<td>C(2)-C(3)-C(4)</td>
</tr>
<tr>
<td>C(4)-C(5)-C(1)</td>
</tr>
<tr>
<td>C(5)-C(4)-C(9)</td>
</tr>
<tr>
<td>C(5)-C(1)-C(6)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(6)</td>
</tr>
<tr>
<td>C(3)-C(2)-C(7)</td>
</tr>
<tr>
<td>C(4)-C(3)-C(8)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>( \text{C}(11) - \text{C}(12) )</td>
</tr>
<tr>
<td>( \text{C}(12) - \text{C}(13) )</td>
</tr>
<tr>
<td>( \text{C}(13) - \text{C}(14) )</td>
</tr>
<tr>
<td>( \text{C}(14) - \text{C}(15) )</td>
</tr>
<tr>
<td>( \text{C}(15) - \text{C}(11) )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( \text{A} )</th>
<th>( \text{A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}(15) - \text{C}(11) - \text{C}(12) )</td>
<td>104(1)</td>
<td>103(1)</td>
</tr>
<tr>
<td>( \text{C}(11) - \text{C}(12) - \text{C}(13) )</td>
<td>109(1)</td>
<td>110(1)</td>
</tr>
<tr>
<td>( \text{C}(12) - \text{C}(13) - \text{C}(14) )</td>
<td>106(1)</td>
<td>100(1)</td>
</tr>
<tr>
<td>( \text{C}(13) - \text{C}(14) - \text{C}(15) )</td>
<td>110(1)</td>
<td>116(2)</td>
</tr>
<tr>
<td>( \text{C}(14) - \text{C}(15) - \text{C}(11) )</td>
<td>112(1)</td>
<td>113(2)</td>
</tr>
<tr>
<td>( \text{C}(13) - \text{C}(14) - \text{C}(19) )</td>
<td>131(2)</td>
<td>121(2)</td>
</tr>
<tr>
<td>( \text{C}(15) - \text{C}(14) - \text{C}(19) )</td>
<td>119(2)</td>
<td>122(2)</td>
</tr>
<tr>
<td>( \text{C}(14) - \text{C}(15) - \text{C}(20) )</td>
<td>146(2)</td>
<td>132(2)</td>
</tr>
<tr>
<td>( \text{C}(15) - \text{C}(11) - \text{C}(16) )</td>
<td>146(2)</td>
<td>141(2)</td>
</tr>
<tr>
<td>( \text{C}(12) - \text{C}(11) - \text{C}(16) )</td>
<td>110(2)</td>
<td>116(2)</td>
</tr>
<tr>
<td>( \text{C}(11) - \text{C}(12) - \text{C}(17) )</td>
<td>140(2)</td>
<td>123(1)</td>
</tr>
<tr>
<td>( \text{C}(13) - \text{C}(12) - \text{C}(17) )</td>
<td>111(2)</td>
<td>127(1)</td>
</tr>
<tr>
<td>( \text{C}(12) - \text{C}(13) - \text{C}(18) )</td>
<td>136(2)</td>
<td>129(2)</td>
</tr>
<tr>
<td>( \text{C}(14) - \text{C}(13) - \text{C}(18) )</td>
<td>117(2)</td>
<td>129(2)</td>
</tr>
<tr>
<td>( \text{C}(11) - \text{C}(15) - \text{C}(20) )</td>
<td>103(2)</td>
<td>117(2)</td>
</tr>
<tr>
<td></td>
<td>Cp'(1)</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>---------</td>
</tr>
<tr>
<td>atom</td>
<td>dist(Å)</td>
<td>atom</td>
</tr>
<tr>
<td>C(1)</td>
<td>.019(13)</td>
<td>C(11)</td>
</tr>
<tr>
<td>C(2)</td>
<td>-.023(15)</td>
<td>C(12)</td>
</tr>
<tr>
<td>C(3)</td>
<td>.019(12)</td>
<td>C(13)</td>
</tr>
<tr>
<td>C(4)</td>
<td>-.006(13)</td>
<td>C(14)</td>
</tr>
<tr>
<td>C(5)</td>
<td>-.008(14)</td>
<td>C(15)</td>
</tr>
<tr>
<td>A</td>
<td>.15</td>
<td>B</td>
</tr>
<tr>
<td>C</td>
<td>-.80</td>
<td>D</td>
</tr>
</tbody>
</table>

**pyrazolate**

<table>
<thead>
<tr>
<th>atom</th>
<th>dist(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(21)</td>
<td>.010(11)</td>
</tr>
<tr>
<td>C(22)</td>
<td>-.012(10)</td>
</tr>
<tr>
<td>C(23)</td>
<td>.010(11)</td>
</tr>
<tr>
<td>N(1)</td>
<td>-.004(7)</td>
</tr>
<tr>
<td>N(2)</td>
<td>-.004(8)</td>
</tr>
</tbody>
</table>

Table IX. Least-Squares Planes for UCp'2Cl(pyrazolate)
### Table X. Bond Distances (Å) and Angles (°) for UCp$_2$(pyrazolate)$_2$

<table>
<thead>
<tr>
<th>U-X distances</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1) 2.753(5)</td>
<td>C(11) 2.753(6)</td>
</tr>
<tr>
<td>C(2) 2.740(5)</td>
<td>C(12) 2.738(6)</td>
</tr>
<tr>
<td>C(3) 2.759(5)</td>
<td>C(13) 2.735(6)</td>
</tr>
<tr>
<td>C(4) 2.786(5)</td>
<td>C(14) 2.724(6)</td>
</tr>
<tr>
<td>C(5) 2.763(5)</td>
<td>C(15) 2.757(6)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pyrazolate distances</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-N(2) 1.349(6)</td>
<td>N(3)-N(4) 1.348(7)</td>
</tr>
<tr>
<td>N(1)-C(21) 1.362(8)</td>
<td>N(3)-C(24) 1.352(8)</td>
</tr>
<tr>
<td>C(21)-C(22) 1.411(9)</td>
<td>C(24)-C(25) 1.388(11)</td>
</tr>
<tr>
<td>C(22)-C(23) 1.386(10)</td>
<td>C(25)-C(26) 1.380(11)</td>
</tr>
<tr>
<td>C(23)-N(2) 1.373(8)</td>
<td>C(26)-N(4) 1.31(8)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angles of interest</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp&quot;(1)-U-Cp&quot;(2) 137.2</td>
<td>Cp&quot;(2)-U-N(3,4) 101.7</td>
</tr>
<tr>
<td>Cp&quot;(1)-U-N(1,2) 101.2</td>
<td>N(1,2)-U-N(3,4) 112.2</td>
</tr>
<tr>
<td>Cp&quot;(1)-U-N(3,4) 103.1</td>
<td>N(1)-U-N(2) 32.9</td>
</tr>
<tr>
<td>Cp&quot;(2)-U-N(1,2) 100.9</td>
<td>N(3)-U-N(4) 32.8</td>
</tr>
<tr>
<td></td>
<td>Cp&quot;(1)</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
</tr>
<tr>
<td>atom</td>
<td>dist(Å)</td>
</tr>
<tr>
<td>C(1)</td>
<td>-.008(6)</td>
</tr>
<tr>
<td>C(2)</td>
<td>.006(6)</td>
</tr>
<tr>
<td>C(3)</td>
<td>-.002(7)</td>
</tr>
<tr>
<td>C(4)</td>
<td>-.004(7)</td>
</tr>
<tr>
<td>C(5)</td>
<td>.008(7)</td>
</tr>
<tr>
<td>A= -.53</td>
<td>B= .57</td>
</tr>
<tr>
<td>C= -.62</td>
<td>D= -3.32</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pyrazolate(1)</th>
<th></th>
<th>pyrazolate(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>atom</td>
<td>dist(Å)</td>
<td>atom</td>
</tr>
<tr>
<td>N(1)</td>
<td>.005(5)</td>
<td>N(3)</td>
</tr>
<tr>
<td>N(2)</td>
<td>-.004(6)</td>
<td>N(4)</td>
</tr>
<tr>
<td>C(21)</td>
<td>-.009(8)</td>
<td>C(24)</td>
</tr>
<tr>
<td>C(22)</td>
<td>.003(9)</td>
<td>C(25)</td>
</tr>
<tr>
<td>C(23)</td>
<td>.004(9)</td>
<td>C(26)</td>
</tr>
<tr>
<td>A= -.75</td>
<td>B= .57</td>
<td>A= -.81</td>
</tr>
<tr>
<td>C= -.35</td>
<td>D= -1.44</td>
<td>C= -.29</td>
</tr>
</tbody>
</table>
Table XII. Comparisons Between UC\(_2\)Cl\(_2\)(pyrazole), UC\(_2\)Cl(pyrazolate), and UC\(_2\)(pyrazolate)\(_2\).

<table>
<thead>
<tr>
<th>coord. number</th>
<th>HPYZ</th>
<th>1:1</th>
<th>1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-C (ave) (\A)</td>
<td>2.74(2)</td>
<td>2.73(3)</td>
<td>2.75(2)</td>
</tr>
<tr>
<td>U-Cl (\A)</td>
<td>2.696(2)</td>
<td>2.611(2)</td>
<td>---</td>
</tr>
<tr>
<td>U-N (\A)</td>
<td>2.607(8)</td>
<td>2.351(5)</td>
<td>2.403(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.349(5)</td>
<td>2.360(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.363(5)</td>
<td>2.405(5)</td>
</tr>
<tr>
<td>C(_p^\prime)-U-C(_p^\prime) ((^{\circ}))</td>
<td>137</td>
<td>136</td>
<td>137</td>
</tr>
<tr>
<td>C(_p^\prime)-U-N ((^{\circ}))</td>
<td>111.4</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C(_p^\prime)-U-(N-N) ((^{\circ}))</td>
<td>---</td>
<td>107.4</td>
<td>101.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>104.6</td>
<td>103.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>101.7</td>
<td></td>
</tr>
<tr>
<td>X-U-N (-N) ((^{\circ}))</td>
<td>X=Cl</td>
<td>X=Cl</td>
<td>X=(N-N)</td>
</tr>
<tr>
<td></td>
<td>74.14</td>
<td>103.2</td>
<td>112.2</td>
</tr>
<tr>
<td>C(_p^\prime)-U-Cl ((^{\circ}))</td>
<td>95.7</td>
<td>102.5</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>98.4</td>
<td></td>
</tr>
</tbody>
</table>

HPYZ is UC\(_2\)Cl\(_2\)(pyrazole)
1:1 is UC\(_2\)Cl(pyrazolate)
1:2 is UC\(_2\)(pyrazolate)\(_2\)
**Table XIII. Distances (Å) and Angles (°) from some reported structures**

<table>
<thead>
<tr>
<th>compound</th>
<th>Cp&quot;-M-Cp&quot;</th>
<th>M-C(ring)</th>
<th>coord.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ThCp&quot;(_2)H(_2))(_2)</td>
<td>130</td>
<td>2.83(1)</td>
<td>9</td>
</tr>
<tr>
<td>(ThCp&quot;(_2)O(_2)C(_2)Me(_2))(_2)</td>
<td>129</td>
<td>2.83(6)</td>
<td>8</td>
</tr>
<tr>
<td>ThCp&quot;(_2)Cl(COCH(_2)CMe(_3))</td>
<td>138</td>
<td>2.80(3)</td>
<td>9</td>
</tr>
<tr>
<td>ThCp&quot;(_2)Cl(CONEt(_2))</td>
<td>138</td>
<td>2.78(4)</td>
<td>9</td>
</tr>
<tr>
<td>UCp&quot;(_2)(CONMe(_2))(_2)</td>
<td>138</td>
<td>2.79(1)</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 1. Graph of $\frac{1}{x_{\text{corr}}} \text{ vs. } T$ for UCp$^2$(pyrazolate)$_2$. 
$\frac{1}{X_M^{\text{corr}}} \text{ vs. } T$ for $\text{UCp}_2''(\text{pyrazolate})_2$
Figure 2. Stereoscopic drawing of the unit cell of UCP"2Cl2(pyrazole).
Figure 3. ORTEP drawing of the molecular unit of UCp"_2Cl_2(pyrazole).
Figure 4. Stereoscopic drawing of the unit cell of UCp"₂Cl(pyrazolate).
Figure 5. ORTEP drawing of the molecular unit of UCp"\textsubscript{2}Cl(pyrazolate).
Figure 6. Stereoscopic drawing of the unit cell of UCp"_2(pyrazolate)_2.
Figure 7. ORTEP drawing of the molecular unit of UCP\(^{2+}\)(pyrazolate)\(_2\).
References


8. Molybdenum Kα radiation was used throughout. The intensity of three standard reflections was measured every 7200 seconds of X-ray exposure, and the position of three orientation standards was checked every 250 reflections.

10. All calculations were performed on a PDP 11/60 equipped with 128 kilowords of memory, twin RK07 28 MByte disk drives, Versatec printer/plotter, and a TU10 tape drive using locally-modified Nonius-SDP\textsuperscript{11} software operating under RSX-11M.


12. The data reduction formulae are;
\[
F_0^2 = \frac{w(C-2B)}{L_p} \\
F_0 = (F_0^2)^{1/2} \\
\sigma_0(F_0^2) = \frac{w(C + 4B)^{1/2}}{L_p} \\
\sigma_0(F_0) = \frac{\sigma_0(F_0^2)}{2F_0}
\]
where \( C \) is the total count in the scan, \( B \) is the sum of the 2 background counts, \( w \) is the scan speed in degrees per minute, and
\[
\frac{1}{L_p} = \frac{\sin 2\theta (1 + \cos^2 2\theta_m)}{1 + \cos^2 2\theta_m - \sin^2 2\theta}
\]
is the correction for Lorentz and polarization effects for a reflection with scattering angle \( 2\theta \) and radiation monochromatized with a 50% perfect single-crystal monochromator with scattering angle \( 2\theta_m \).
13. \[ R = \frac{\sum |Fo| - |Fc|}{\sum |Fo|} \]

\[ wR = \sqrt{\frac{\sum w(|Fo| - |Fc|)^2}{\sum wFo^2}} \]

\[ GOF = \sqrt{\frac{\sum w(|Fo| - |Fc|)^2}{(n_o - n_v)}} \]

where \( n_o \) is the number of observations and \( n_v \) is the number of variable parameters, and the weights \( w \) were given by \[ w = \frac{4Fo^2}{\sigma^2(Fo^2)} \]
and \[ \sigma^2(Fo^2) = \sigma_0^2(Fo^2) + (pF^2)^2 \]
where \( p \) is the factor used to lower the weight of intense reflections.


15. Instrumentation at the University of California Chemistry Department X-ray Crystallography Facility (CHEXRAY) consists of two Enraf-Nonius CAD-4 diffractometers, one controlled by a DEC PDP 8/a with an RK05 disk and the other by a DEC PDP 8/e with an RL01 disk. Both use Enraf-Nonius software as described in the CAD-4 Operation Manual, Enraf-Nonius, Delft, November 1977, updated January 1980.

17. Marks, T.J.; Manriquez, J.M.; Fagan, P.J.; Day, V.W.;
   Day, C.S.; Vollmer, S.H.; "Lanthanide and Actinide Chem-
   istry and Spectroscopy," N. Edelstein, Ed., ACS Sympo-
   sium Series 131, American Chemical Society,
   Washington, D.C., pp 1, 29.

   Manriquez, J.M.; Fagan, P.J.; Marks, T.J.; Science (1979),
   203, 172.


   (1973), 12, 1329.

24. Fronczek, F.R.; Halstead, G.W.; Raymond, K.N.;

   2789.

Chapter 4

Crystal and Molecular Structure of

\[ \text{[Nd(tren)\textsubscript{2}(CH\textsubscript{3}CN)](ClO\textsubscript{4})\textsubscript{3}} \]

Introduction

Lanthanide coordination chemistry is dominated by oxygen donor ligands, especially by chelate ligands like β-diketonates or EDTA. The number of well-characterized nitrogen-bonded complexes has been increasing recently, however. As with the oxygen donating ligands, amine complexes are generally more stable when they involve chelate ligands. For example, pyridine complexes exist only in solution, while complexes with ethylenediamine or 1,10-phenanthroline can be isolated\(^1\). As another example, Forsberg and co-workers have recently added compounds of the type \(\text{Ln(tren)X\textsubscript{3}}\) and \(\text{Ln(tren)\textsubscript{2}X\textsubscript{3}}\) to the list of lanthanide amine complexes\(^2,3\).

The other general characteristic of lanthanide coordination complexes is their kinetic lability, which results from the negligible contribution the crystal field stabilization energy makes to the free energy of activation. The work reported here expands the present knowledge of lanthanide amine complexes, while at the same time laying the groundwork for the isolation of substitutionally inert lanthanide complexes.

In addition to an interest in lanthanides and actinides
based on the chemical effects of their unique position in the Periodic Table, there has been a continuing interest in the use of lanthanide ions as shift reagents in nmr spectroscopy. During the last decade, lanthanide shift reagents have been actively investigated and utilized in simplifying complex nmr spectra. The effective use of these reagents, and subsequent assignments in the expanded spectrum, requires consideration of the shift reagent properties.

In general, lanthanide shift reagents operate through a predominantly dipole-dipole interaction between the paramagnetic lanthanide ion and certain nuclei on the substrate. The magnitude of the interaction, and hence of the induced shift, is a sensitive function of geometry. It is understood that intermittent coordination of a functional group on the substrate molecule (O or N donors) to an unsaturated coordination sphere around the lanthanide ion produces new perturbations on the magnetic environment at substrate nuclei, leading to altered chemical shifts. The sensitive radial and geometric functions of these lanthanide-induced shifts are responsible for simplifying the substrate spectrum. The most elegant applications require several assumptions to be made. Typically they include;
1. the observed shifts are totally dipolar
2. only one lanthanide-substrate complex is in equilibrium
3. only one geometric isomer of the complex exists
4. the magnetic field of the complex is axially symmetric
5. the principal magnetic axis has only one, known orientation with respect to the ligands
6. there is one conformation per substrate or at least a time-averaged conformation.

As one might guess, the necessity of making some rather rough assumptions has hampered the development and popularity of lanthanide shift reagents. For this reason we have endeavored to design and synthesize lanthanide shift reagents that circumvent the geometry problem. We reasoned that a substitutionally inert lanthanide complex, once such a novelty were isolated, would prevent actual coordination of functional groups but still impart to the substrate an altered magnetic field. This research was undertaken to determine what, if any, advantages might result from this new type of shift reagent.

This chapter reports the crystal structure of a Nd$^{3+}$ compound that will serve as the starting material for the
synthetic work. We analyzed a known N-bonded complex 
\([\text{Nd(tren)}_2(\text{CH}_3\text{CN})](\text{ClO}_4)_3\) to determine the appropriate 
number of methylene units to use in linking the tren 
ligands, thereby encapsulating the metal ion.

Experimental

Manipulation of moisture-sensitive materials was accom-
ploished with Schlenk techniques and the use of a Vacuum 
Atmospheres HE-93-A glove box with recirculating moisture 
free argon atmosphere. Elemental analyses were performed by 
the Microanalytical Laboratory, U.C. Berkeley. Infra-red 
spectra were obtained on a Perkin-Elmer 597 spectrophotome-
ter (Nujol mulls, reported in wavenumbers).

Materials

Acetonitrile, CH$_3$CN, was distilled from P$_2$O$_5$, benzene 
from potassium benzophenone ketyl. The tren (N(EtNH$_2$)$_3$) 
was extracted from triethylenetetramine$^2$. Crystalline 
16-cyclam was a generous gift from William Smith$^6$.

Neodymium perchlorate, Nd(ClO$_4$)$_3$, was prepared by addi-
tion of excess Nd$_2$O$_3$ to 70% HClO$_4$. The excess Nd$_2$O$_3$ was fil-
tered off and the solution evaporated to dryness. Residual 
H$_2$O was removed by heating to ~250°C under vacuum for three 
days. Some reversion to the oxide was evidenced by the 
presence of blue amongst the pink perchlorate. This contam-
inant was conveniently left behind during an extraction into 
acetonitrile. Evaporation of the solution left a compound of
formula \( \text{Nd}(\text{ClO}_4)_3(\text{CH}_3\text{CN})_4 \).

Analysis: calculated—\%C, 15.83; \%H, 1.98; \%N, 9.27; \%Nd, 23.78; found—\%C, 16.23; \%H, 2.26; \%N, 9.23; \%Nd, 24.88.

\( \text{Nd(tren)}_2(\text{ClO}_4)_3 \) was prepared after Forsberg. Crystals suitable for diffraction were obtained by the addition of benzene to a concentrated acetonitrile solution. After standing at room temperature for 2 days, the clear pink solution yielded several large, well-formed crystals. Infra-red spectroscopy revealed the presence of acetonitrile (\( \nu_{\text{CN}} = 2262 \text{ cm}^{-1} \)).

**Data Collection, Solution, and Refinement**

The absences identified with the precession camera (\( hkl, h+k = 2n \); \( h0l, l = 2n \)) indicated the space group was either Cc or C2/c. The cell parameters were determined using 25 automatically centered reflections with 2\( \theta \) between 27 and 43 degrees. They are;

\[
\begin{align*}
a &= 15.0442(11) \text{ Å} \\
b &= 17.7290(14) \text{ Å} \\
c &= 11.0880(6) \text{ Å} \\
\beta &= 95.079(5)^\circ
\end{align*}
\]

These data, in conjunction with the measured density (1.751–6 \( \text{g cm}^{-3} \)), yield \( Z = 4 \) (\( d_{\text{calc}} = 1.750–6 \text{ g cm}^{-3} \)).
The initial Patterson map confirmed space group Cc. The structure was then solved using heavy atom techniques. The model refined to weighted and unweighted R factors of 3.19 and 2.94% respectively\(^1\). (The initial polarity refined to 3.58 and 3.24%). Final positional and thermal parameters appear in Table I. Pertinent bond distances and angles appear in Table II.

**Discussion**

The crystal structure consists of discrete mononuclear cations at general positions in the unit cell (Fig. 1), and immersed in a three dimensional network of hydrogen bonds. The structure of the molecular cation (Fig. 2) consists of Nd coordinated by 8 tren nitrogens and an acetonitrile nitrogen, to form a tri-capped trigonal prismatic coordination geometry. The inclusion of two tetradeinate tren ligands in the coordination sphere of one neodymium ion is a reflection of the lanthanide's relatively large size. Table IIb reveals that, as in other tren structures ( vide infra ), the intraligand bond angles indicate the ligand molecules are essentially unstrained. The capping nitrogens are the two tertiary tren nitrogens and that of the acetonitrile. Data on the various planes and their interrelationship can be found in Table III. These data confirm the tri-capped trigonal prismatic coordination geometry (Fig. 2) and suggest a two-fold axis along the acetonitrile (Fig. 3). A two-fold axis was then defined as the vector from Nd to a point 'X'
whose coordinates were obtained by the summation of all pseudo-two-fold related atoms (C's and N's). Rotation by 180° about this axis and calculation of the difference between the new atom positions and the old ones yields the results tabulated in Table IV. Here we see that the average difference is 0.21 Å with a standard deviation of 0.16 Å, and that the major aberrations from the two-fold symmetry are the carbon atoms of the acetonitrile. The remaining atoms have an average difference of 0.16 Å with a standard deviation of 0.06 Å. When considering only the nitrogen atoms that constitute the coordination sphere, the average difference is 0.11 Å with a standard deviation of 0.03 Å.

Figure 4 illustrates the hydrogen bonding around a cation, between perchlorate oxygens and some of the primary amine nitrogen atoms. The lengths of these bonds are tabulated in Table V. Among the other metal tren structures published is another example of a perchlorate salt, [Co(tren)(glycinato)]Cl(ClO₄), where a more extensive hydrogen bonding network was found¹². The network in this compound involves the perchlorate oxygens, the chloride ion, and glycinate oxygen atoms. Of the remaining tren structures that have been reported, the majority are tetraphenyl borate salts reported by Hendrickson and coworkers. The compounds [Ni₂(tren)₂(OCN)₂](BO₄)₁³ and [Cu₂(tren)₂X₂](BO₄)₁⁴₋₁⁶ have been characterized. The tren ligands in all the above compounds are tetradentate. In the Cu²⁺ systems, the ligand forms part of a trigonal bipyramidal coordination
environment, with the primary nitrogens in equatorial sites. In the Ni\(^{2+}\) and Co\(^{3+}\) structures, the tren contributes to an octahedral environment.

Although the past 10 years have seen a notable increase in the number of lanthanide amine complexes, very few of these involve nitrogen coordination exclusively. In addition to the Ln(tren)\(_2\)X\(_3\) complexes analogous to that described here (vide supra), lanthanide tris-terpyridine complexes have been reported\(^1\). The structure of one of these, [Eu(terpy)\(_3\)](ClO\(_4\))\(_3\)\(^{17}\), is the only other lanthanide structure in which all coordination sites are occupied by nitrogen atoms. The M-N bond distances in lanthanide amine complexes are in general agreement with those predicted from the metal ionic radii, a reflection of the predominantly ionic bonding lanthanide complexes exhibit. While there are no strict analogues with which to compare such distances in the present compound, one may note that the M-N distances in [Eu(terpy)\(_3\)](ClO\(_4\))\(_3\) are about 0.05 Å shorter than those found in the present compound. This difference is about what one would expect for the difference between an sp\(^3\) and an sp\(^2\) hybridized nitrogen atom. In this light, we mention that the metal ionic radii in these compounds differ by about 0.04Å\(^{18}\).

This crystal structure was carried out in part to determine the appropriate number of carbon atoms needed to bridge across the tren ligands in order to encapsulate the
metal ion. The proposed encapsulation would bridge N's 3 and 7, 6 and 4, and 2 and 8; Table VI reveals these are the closest ones. In the structure of 16-cyclam, non-bonded nitrogens are separated by 2.9 Å and bridged by propyl chains. Because such linkages are somewhat flexible, and because the present configuration is subject to adjustment, it appears a C₃ linkage would be appropriate in the encapsulating reaction.
<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B(11)</th>
<th>B(22)</th>
<th>B(12)</th>
<th>B(13)</th>
<th>B(23)</th>
<th>B(33)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ND</td>
<td>-0.25000</td>
<td>-0.23576</td>
<td>0.131</td>
<td>0.4913</td>
<td>0.2212</td>
<td>0.6091</td>
<td>2.121</td>
<td>0.3112</td>
</tr>
<tr>
<td>CL1(1)</td>
<td>-0.16500</td>
<td>-0.576</td>
<td>0.143</td>
<td>0.4249</td>
<td>0.9812</td>
<td>0.5175</td>
<td>0.3512</td>
<td>0.3212</td>
</tr>
<tr>
<td>CL1(2)</td>
<td>-0.05706</td>
<td>0.07716</td>
<td>-0.3088</td>
<td>0.5017</td>
<td>0.4941</td>
<td>1.147</td>
<td>0.8212</td>
<td>0.2771</td>
</tr>
<tr>
<td>CL1(3)</td>
<td>-0.38070</td>
<td>-0.15150</td>
<td>-0.4311</td>
<td>0.3759</td>
<td>0.9812</td>
<td>0.3215</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>N(1)</td>
<td>-0.24531</td>
<td>-0.37813</td>
<td>-0.0893</td>
<td>0.4513</td>
<td>0.3215</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>N(2)</td>
<td>-0.41261</td>
<td>-0.12354</td>
<td>-0.2046</td>
<td>0.3143</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>N(3)</td>
<td>-0.24531</td>
<td>-0.25044</td>
<td>-0.2184</td>
<td>0.5114</td>
<td>0.3215</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>N(4)</td>
<td>-0.32935</td>
<td>-0.09314</td>
<td>0.2246</td>
<td>0.3433</td>
<td>0.8812</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>N(5)</td>
<td>-0.19521</td>
<td>-0.12573</td>
<td>0.16015</td>
<td>0.3214</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>N(6)</td>
<td>-0.37071</td>
<td>-0.18239</td>
<td>0.20697</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>N(7)</td>
<td>-0.26810</td>
<td>-0.10926</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
<td></td>
</tr>
<tr>
<td>N(8)</td>
<td>-0.24705</td>
<td>-0.4896</td>
<td>0.3146</td>
<td>0.2234</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>N(9)</td>
<td>-0.08095</td>
<td>-0.01837</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>-0.17675</td>
<td>-0.13829</td>
<td>-0.2069</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(2)</td>
<td>-0.39210</td>
<td>-0.31401</td>
<td>-0.5198</td>
<td>0.9219</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(3)</td>
<td>-0.21447</td>
<td>-0.35735</td>
<td>-0.6710</td>
<td>0.11</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(4)</td>
<td>-0.12477</td>
<td>-0.42096</td>
<td>-0.8880</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(5)</td>
<td>-0.60501</td>
<td>-0.14028</td>
<td>-0.4427</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(6)</td>
<td>-0.10421</td>
<td>-0.60826</td>
<td>-0.2851</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(7)</td>
<td>-0.10436</td>
<td>-0.02946</td>
<td>-0.4732</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(8)</td>
<td>-0.20905</td>
<td>-0.04715</td>
<td>-0.3472</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(9)</td>
<td>-0.04306</td>
<td>-0.12581</td>
<td>-0.5321</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(10)</td>
<td>-0.41499</td>
<td>-0.11415</td>
<td>-0.3288</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(11)</td>
<td>-0.41416</td>
<td>-0.22486</td>
<td>-0.4504</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>O(12)</td>
<td>-0.31917</td>
<td>-0.1344</td>
<td>-0.4881</td>
<td>0.41</td>
<td>0.7012</td>
<td>0.41</td>
<td>0.3212</td>
<td>0.3212</td>
</tr>
<tr>
<td>C11</td>
<td>-0.2151(6)</td>
<td>-0.3663(5)</td>
<td>-0.1983(8)</td>
<td>24.5(5)</td>
<td>70.13(3)</td>
<td>92.8(3)</td>
<td>2.13(3)</td>
<td>22.5(5)</td>
</tr>
<tr>
<td>C12</td>
<td>-0.3131(6)</td>
<td>-0.3235(6)</td>
<td>-0.2122(9)</td>
<td>52.5(5)</td>
<td>50.15(3)</td>
<td>57.15(3)</td>
<td>3.1(3)</td>
<td>33.5(5)</td>
</tr>
<tr>
<td>C13</td>
<td>-0.3655(7)</td>
<td>-0.3960(6)</td>
<td>-0.1191(9)</td>
<td>55.15(3)</td>
<td>33.14(4)</td>
<td>102.5(5)</td>
<td>-10.13(3)</td>
<td>2.6(3)</td>
</tr>
<tr>
<td>C14</td>
<td>-0.4132(6)</td>
<td>-0.3352(6)</td>
<td>-0.1904(8)</td>
<td>51.5(5)</td>
<td>44.14(4)</td>
<td>113.19(9)</td>
<td>-14.13(3)</td>
<td>-11.15(5)</td>
</tr>
<tr>
<td>C15</td>
<td>-0.2343(8)</td>
<td>-0.4307(4)</td>
<td>0.0666(14)</td>
<td>54.13(3)</td>
<td>25.12(3)</td>
<td>119.5(8)</td>
<td>9.1(3)</td>
<td>9.1(6)</td>
</tr>
<tr>
<td>C16</td>
<td>-0.4127(7)</td>
<td>-0.4135(6)</td>
<td>0.0534(10)</td>
<td>68.16(6)</td>
<td>32.13(3)</td>
<td>127.11(11)</td>
<td>8.13(3)</td>
<td>-2.1(7)</td>
</tr>
<tr>
<td>C17</td>
<td>-0.3037(7)</td>
<td>-0.0930(5)</td>
<td>0.2073(8)</td>
<td>85.17(7)</td>
<td>30.13(3)</td>
<td>96.18(8)</td>
<td>-4.13(3)</td>
<td>26.16(6)</td>
</tr>
<tr>
<td>C18</td>
<td>-0.2025(10)</td>
<td>-0.1043(7)</td>
<td>-0.2126(12)</td>
<td>114.11(10)</td>
<td>51.16(6)</td>
<td>161.11(15)</td>
<td>-27.16(6)</td>
<td>-1.1(9)</td>
</tr>
<tr>
<td>C19</td>
<td>-0.3890(6)</td>
<td>-0.6629(5)</td>
<td>0.0147(8)</td>
<td>57.15(5)</td>
<td>34.13(3)</td>
<td>106.10(1)</td>
<td>13.13(3)</td>
<td>26.15(4)</td>
</tr>
<tr>
<td>C20</td>
<td>-0.3206(7)</td>
<td>-0.0465(5)</td>
<td>-0.0537(9)</td>
<td>51.17(7)</td>
<td>26.13(3)</td>
<td>111.19(1)</td>
<td>3.13(3)</td>
<td>27.16(4)</td>
</tr>
<tr>
<td>C21</td>
<td>-0.4256(6)</td>
<td>-0.1764(5)</td>
<td>0.1614(8)</td>
<td>65.14(4)</td>
<td>37.13(3)</td>
<td>113.18(1)</td>
<td>8.13(3)</td>
<td>39.15(5)</td>
</tr>
<tr>
<td>C22</td>
<td>-0.3556(7)</td>
<td>-0.2431(5)</td>
<td>0.2334(8)</td>
<td>67.15(5)</td>
<td>39.13(3)</td>
<td>98.18(1)</td>
<td>0.13(3)</td>
<td>46.15(5)</td>
</tr>
<tr>
<td>C23</td>
<td>-0.0226(6)</td>
<td>-0.1466(5)</td>
<td>-0.0203(7)</td>
<td>49.14(4)</td>
<td>31.13(3)</td>
<td>53.18(1)</td>
<td>-2.13(3)</td>
<td>11.15(5)</td>
</tr>
<tr>
<td>C24</td>
<td>0.0592(7)</td>
<td>-0.1033(6)</td>
<td>-0.0405(10)</td>
<td>53.15(5)</td>
<td>47.14(4)</td>
<td>132.11(11)</td>
<td>-14.14(4)</td>
<td>19.16(6)</td>
</tr>
</tbody>
</table>
Table Ib. Calculated Hydrogen Atom Positions\(^a\) for \([\text{Nd(tren)}_2(\text{CH}_3\text{CN})(\text{ClO}_4)_3\]

<table>
<thead>
<tr>
<th></th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(1A)</td>
<td>-0.18764</td>
<td>-0.43271</td>
<td>-0.19362</td>
</tr>
<tr>
<td>M(1B)</td>
<td>-0.26082</td>
<td>-0.34673</td>
<td>-0.26808</td>
</tr>
<tr>
<td>M(2A)</td>
<td>-0.12453</td>
<td>-0.33067</td>
<td>-0.28414</td>
</tr>
<tr>
<td>M(2B)</td>
<td>-0.12565</td>
<td>-0.52322</td>
<td>-0.14437</td>
</tr>
<tr>
<td>M(3A)</td>
<td>-0.36991</td>
<td>-0.44139</td>
<td>-0.16444</td>
</tr>
<tr>
<td>M(3B)</td>
<td>-0.39258</td>
<td>-0.40258</td>
<td>-0.64553</td>
</tr>
<tr>
<td>M(4A)</td>
<td>-0.47465</td>
<td>-0.34907</td>
<td>-0.20444</td>
</tr>
<tr>
<td>M(4B)</td>
<td>-0.36697</td>
<td>-0.32913</td>
<td>-0.26465</td>
</tr>
<tr>
<td>M(5A)</td>
<td>-0.27123</td>
<td>-0.42764</td>
<td>0.01900</td>
</tr>
<tr>
<td>M(5B)</td>
<td>-0.23668</td>
<td>-0.48039</td>
<td>-0.02523</td>
</tr>
<tr>
<td>M(6A)</td>
<td>-0.30469</td>
<td>-0.42246</td>
<td>-0.04557</td>
</tr>
<tr>
<td>M(6B)</td>
<td>-0.12572</td>
<td>-0.44603</td>
<td>0.11988</td>
</tr>
<tr>
<td>M(7A)</td>
<td>-0.31226</td>
<td>-0.04152</td>
<td>0.15618</td>
</tr>
<tr>
<td>M(7B)</td>
<td>-0.31543</td>
<td>-0.10983</td>
<td>0.26227</td>
</tr>
<tr>
<td>M(8A)</td>
<td>-0.17636</td>
<td>-0.26342</td>
<td>0.28551</td>
</tr>
<tr>
<td>M(8B)</td>
<td>-0.18679</td>
<td>-0.07860</td>
<td>0.14579</td>
</tr>
<tr>
<td>M(9A)</td>
<td>-0.42098</td>
<td>-0.04450</td>
<td>0.05243</td>
</tr>
<tr>
<td>M(9B)</td>
<td>-0.42897</td>
<td>-0.10693</td>
<td>-0.04882</td>
</tr>
<tr>
<td>M(10A)</td>
<td>-0.24247</td>
<td>-0.01664</td>
<td>-0.00633</td>
</tr>
<tr>
<td>M(10B)</td>
<td>-0.34462</td>
<td>-0.01959</td>
<td>-0.11570</td>
</tr>
<tr>
<td>M(11A)</td>
<td>-0.45424</td>
<td>-0.14299</td>
<td>-0.21231</td>
</tr>
<tr>
<td>M(11B)</td>
<td>-0.46725</td>
<td>-0.19275</td>
<td>0.05709</td>
</tr>
<tr>
<td>M(12A)</td>
<td>-0.44527</td>
<td>-0.26753</td>
<td>0.26153</td>
</tr>
<tr>
<td>M(12B)</td>
<td>-0.35608</td>
<td>-0.22729</td>
<td>0.30063</td>
</tr>
<tr>
<td>M(13A)</td>
<td>-0.44792</td>
<td>-0.26290</td>
<td>-0.07102</td>
</tr>
<tr>
<td>M(13B)</td>
<td>-0.41036</td>
<td>-0.22602</td>
<td>-0.17401</td>
</tr>
<tr>
<td>M(14A)</td>
<td>-0.24704</td>
<td>-0.25210</td>
<td>-0.27164</td>
</tr>
<tr>
<td>M(14B)</td>
<td>-0.16592</td>
<td>-0.21351</td>
<td>-0.23618</td>
</tr>
<tr>
<td>M(15A)</td>
<td>-0.02156</td>
<td>-0.31863</td>
<td>0.07690</td>
</tr>
<tr>
<td>M(15B)</td>
<td>-0.13723</td>
<td>-0.33375</td>
<td>0.17105</td>
</tr>
<tr>
<td>M(16A)</td>
<td>-0.15633</td>
<td>-0.26769</td>
<td>0.26760</td>
</tr>
<tr>
<td>M(16B)</td>
<td>-0.11565</td>
<td>-0.18683</td>
<td>0.29655</td>
</tr>
<tr>
<td>M(17A)</td>
<td>-0.21247</td>
<td>-0.08624</td>
<td>-0.11276</td>
</tr>
<tr>
<td>M(17B)</td>
<td>-0.29123</td>
<td>-0.11255</td>
<td>-0.18214</td>
</tr>
<tr>
<td>M(18A)</td>
<td>-0.38656</td>
<td>-0.32568</td>
<td>0.12132</td>
</tr>
<tr>
<td>M(18B)</td>
<td>-0.31194</td>
<td>-0.32363</td>
<td>0.20526</td>
</tr>
</tbody>
</table>

\(^a\) isotropic thermal parameters equal 7.0 \(\AA^2\).
### Table IIa. Pertinent Bond Distances (Å) for \([\text{Nd(tren)}_2(\text{CH}_3\text{CN})](\text{ClO}_4)_3\)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd-N(1)</td>
<td>2.717(6)</td>
</tr>
<tr>
<td>Nd-N(2)</td>
<td>2.666(7)</td>
</tr>
<tr>
<td>Nd-N(3)</td>
<td>2.607(6)</td>
</tr>
<tr>
<td>Nd-N(4)</td>
<td>2.615(7)</td>
</tr>
<tr>
<td>Nd-N(5)</td>
<td>2.701(6)</td>
</tr>
<tr>
<td>Nd-N(6)</td>
<td>2.629(7)</td>
</tr>
<tr>
<td>Nd-N(7)</td>
<td>2.625(7)</td>
</tr>
<tr>
<td>Nd-N(8)</td>
<td>2.628(7)</td>
</tr>
<tr>
<td>Nd-N(9)</td>
<td>2.692(7)</td>
</tr>
<tr>
<td>Nd-N(ave)</td>
<td>2.65(4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)</td>
<td>1.49(1)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.51(1)</td>
</tr>
<tr>
<td>C(2)-N(3)</td>
<td>1.48(1)</td>
</tr>
<tr>
<td>N(1)-C(3)</td>
<td>1.49(1)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.48(1)</td>
</tr>
<tr>
<td>C(4)-N(2)</td>
<td>1.49(1)</td>
</tr>
<tr>
<td>N(1)-C(5)</td>
<td>1.48(1)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.46(2)</td>
</tr>
<tr>
<td>C(6)-N(4)</td>
<td>1.48(1)</td>
</tr>
<tr>
<td>N(9)-C(13)</td>
<td>1.14(1)</td>
</tr>
<tr>
<td>C(13)-C(14)</td>
<td>1.45(1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(1)-O(1)</td>
<td>1.416(8)</td>
</tr>
<tr>
<td>Cl(1)-O(2)</td>
<td>1.432(12)</td>
</tr>
<tr>
<td>Cl(1)-O(3)</td>
<td>1.416(8)</td>
</tr>
<tr>
<td>Cl(1)-O(4)</td>
<td>1.361(8)</td>
</tr>
<tr>
<td>Cl(3)-O(9)</td>
<td>1.371(10)</td>
</tr>
<tr>
<td>Cl(3)-O(11)</td>
<td>1.327(10)</td>
</tr>
<tr>
<td>Cl(2)-O(5)</td>
<td>1.391(11)</td>
</tr>
<tr>
<td>Cl(2)-O(6)</td>
<td>1.396(7)</td>
</tr>
<tr>
<td>Cl(2)-O(7)</td>
<td>1.396(8)</td>
</tr>
<tr>
<td>Cl(2)-O(8)</td>
<td>1.444(8)</td>
</tr>
<tr>
<td>Cl(3)-O(10)</td>
<td>1.412(10)</td>
</tr>
<tr>
<td>Cl(3)-O(12)</td>
<td>1.344(10)</td>
</tr>
</tbody>
</table>
Table IIb. Ligand Bond Angles for
\([\text{Nd(tren)}_2(\text{CH}_3\text{CN})]\text{(ClO}_4\text{)}_3 (\pm 2^\circ)\)

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-N(1)-C(3)</td>
<td>110.6</td>
</tr>
<tr>
<td>C(3)-N(1)-C(5)</td>
<td>107.6</td>
</tr>
<tr>
<td>C(5)-N(1)-C(1)</td>
<td>110.4</td>
</tr>
<tr>
<td>N(1)-C(1)-C(2)</td>
<td>113.4</td>
</tr>
<tr>
<td>C(1)-C(2)-N(3)</td>
<td>109.2</td>
</tr>
<tr>
<td>N(1)-C(3)-C(4)</td>
<td>112.2</td>
</tr>
<tr>
<td>C(3)-C(4)-N(2)</td>
<td>110.8</td>
</tr>
<tr>
<td>N(1)-C(5)-C(6)</td>
<td>113.1</td>
</tr>
<tr>
<td>C(5)-C(6)-N(4)</td>
<td>110.9</td>
</tr>
<tr>
<td>C(7)-N(5)-C(9)</td>
<td>110.1</td>
</tr>
<tr>
<td>C(9)-N(5)-C(11)</td>
<td>109.9</td>
</tr>
<tr>
<td>C(7)-N(5)-C(11)</td>
<td>108.7</td>
</tr>
<tr>
<td>N(5)-C(7)-C(8)</td>
<td>115.1</td>
</tr>
<tr>
<td>C(7)-C(8)-N(6)</td>
<td>112.9</td>
</tr>
<tr>
<td>N(5)-C(9)-C(10)</td>
<td>113.9</td>
</tr>
<tr>
<td>C(9)-C(10)-N(7)</td>
<td>110.0</td>
</tr>
<tr>
<td>N(5)-C(11)-C(12)</td>
<td>113.3</td>
</tr>
<tr>
<td>C(11)-C(12)-N(8)</td>
<td>111.1</td>
</tr>
</tbody>
</table>
Table III. Relationships Between Planes for $[\text{Nd}(\text{tren})_2(\text{CH}_3\text{CN})](\text{ClO}_4)_3$

<table>
<thead>
<tr>
<th>plane no.</th>
<th>N's</th>
<th>ave. $d$-Nd (Å)</th>
<th>d-cap (Å)</th>
<th>angle with planes 1,2,3,4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,3,7</td>
<td>--</td>
<td>1.83</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>4,6,8</td>
<td>--</td>
<td>1.80</td>
<td>12.58</td>
</tr>
<tr>
<td>3</td>
<td>2,3,4,8</td>
<td>.18</td>
<td>.95</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>84.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>91.91</td>
</tr>
<tr>
<td>4</td>
<td>3,4,6,7</td>
<td>.09</td>
<td>.90</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>84.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>96.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>62.68</td>
</tr>
<tr>
<td>5</td>
<td>2,7,6,8</td>
<td>.16</td>
<td>.96</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>89.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>93.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>54.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>62.88</td>
</tr>
<tr>
<td>related atom pairs</td>
<td>difference (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>----------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd, Nd</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1), N(5)</td>
<td>0.156</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2), N(8)</td>
<td>0.113</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3), N(6)</td>
<td>0.105</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(4), N(7)</td>
<td>0.129</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(9), N(9)</td>
<td>0.064</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>average</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>std. dev.</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X, X</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1), C(7)</td>
<td>0.152</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2), C(8)</td>
<td>0.242</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(3), C(11)</td>
<td>0.173</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4), C(12)</td>
<td>0.122</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5), C(9)</td>
<td>0.242</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6), C(10)</td>
<td>0.265</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>average</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>std. dev.</td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(13), C(13)</td>
<td>0.304</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(14), C(14)</td>
<td>0.687</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>average</td>
<td>0.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>std. dev.</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen Bond Lengths for</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>--------------------------</td>
<td>-------</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(<a href="%5Ctext%7BClO%7D_4">\text{Nd(tren)}_2(\text{CH}_3\text{CN})</a>_3) (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)-O(1)</td>
<td>3.18(1)</td>
<td>N(7)-O(6)</td>
<td>3.25(1)</td>
<td></td>
</tr>
<tr>
<td>N(4)-O(1)</td>
<td>3.19(1)</td>
<td>N(7)-O(10)</td>
<td>3.17(1)</td>
<td></td>
</tr>
<tr>
<td>N(4)-O(3)</td>
<td>3.17(1)</td>
<td>N(8)-O(3)</td>
<td>3.16(1)</td>
<td></td>
</tr>
<tr>
<td>N(6)-O(1)</td>
<td>3.11(1)</td>
<td>N(8)-O(5)</td>
<td>3.25(1)</td>
<td></td>
</tr>
</tbody>
</table>
Table VI. Interatomic Distances (Å) for

\[ \text{[Nd(tren)$_2$(CH$_2$CN)](ClO}_4)_3 \]

<table>
<thead>
<tr>
<th>nitrogens</th>
<th>distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,7</td>
<td>3.06</td>
</tr>
<tr>
<td>6,4</td>
<td>3.06</td>
</tr>
<tr>
<td>2,8</td>
<td>3.24</td>
</tr>
<tr>
<td>7,2</td>
<td>3.51</td>
</tr>
<tr>
<td>6,8</td>
<td>3.27</td>
</tr>
<tr>
<td>2,3</td>
<td>3.38</td>
</tr>
<tr>
<td>4,8</td>
<td>3.42</td>
</tr>
<tr>
<td>3,4</td>
<td>3.81</td>
</tr>
<tr>
<td>6,7</td>
<td>3.90</td>
</tr>
</tbody>
</table>
Figure 1. Stereoscopic drawing of the unit cell of

$[\text{Nd(tren)}_2(\text{CH}_3\text{CN})](\text{ClO}_4)_3$. 
Figure 2. ORTEP drawing of the molecular cation of $\text{[Nd(tren)$_2$(CH$_3$CN)](ClO}_4$)}_3$ emphasizing the pseudo-threefold symmetry. The nitrogen atoms are drawn at the 50% contour. For clarity, the carbon atoms are drawn at the 10% contour.
Figure 3. ORTEP drawing of the molecular cation of [Nd(tren)$_2$(CH$_3$CN)](ClO$_4$)$_3$ emphasizing the pseudo-twofold symmetry. The nitrogen atoms are drawn at the 50% contour. For clarity, the carbon atoms are drawn at the 10% contour.
Figure 4. ORTEP drawing of the hydrogen-bonding experienced by one molecular cation of \([\text{Nd(tren)}_2(\text{CH}_3\text{CN})](\text{ClO}_4)_3\).
References


8. A total of 3819 hk+l data were collected between 4° and 56° in 2θ, monitoring three intensity standards every 7200 seconds of X-ray exposure, and checking three orientation standards every 250 reflections. Azimuthal scans were collected on 4 reflections with 2θ between 11 and 33 degrees. Data reduction and processing were carried out as described elsewhere. The intensity
standards underwent decay of 14%, 14%, and 17% during data collection. A decay correction of 14% was applied. The six crystal faces were identified with the help of the diffractometer and their dimensions measured at 7X under a binocular microscope. The absorption correction ($\mu = 21.09 \text{ cm}^{-1}$) applied ranged between 1.212 and 1.498. The data were then averaged ($R = 2.6\%$) to yield the 3553 independent reflections used in refinement.


10. After a difference Fourier revealed most of the hydrogens, their positions were calculated with a C-H distance of .95Å and an N-H distance of .87Å. The temperature factors of all atoms were refined anisotropically except for those of the hydrogens, where the isotropic $B$'s were set at 7.0 Å$^2$ and not refined. On the final least-squares cycle, all parameters shifted by less than 0.06 sigma. In the final difference Fourier, the largest peak at a grid point was $55e^{-} \text{Å}^{-3}$ and the most negative electron density was $-38e^{-} \text{Å}^{-3}$. The residuals showed no abnormalities.


This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.