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Novel Salts of Graphite and a Boron Nitride Salt

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Summary: Graphite is oxidized by $O_2^+AsF_6^-$ and by $OsF_6$ to give first-stage graphite salts $C_8^+MF_6^-$ and $S_2O_6F_2$ oxidizes both graphite and boron nitride to yield the salts $C_{12}^+SO_3F^-$ and $(BN)_4^+SO_3F^-$, the latter being the first example of a first-stage boron nitride salt.

Salts of graphite in which stable anions such as $NO_3^-, HSO_4^-, ClO_4^-, FSO_3^-$ are intercalated in the galleries of the graphite have long been known and those derived from well oriented graphite have been shown by Ubbelohde and his coworkers to be excellent electrical conductors. We have prepared new graphite salts containing anions of high ionization potential ($AsF_6^-, OsF_6^-, SO_3F^-$) and the first example of a first-stage boron nitride salt. Our findings support salt formulations also for the highly conducting graphite/AsF_5 materials.

Treatment of graphite single crystals with OsF_6 yields, at room temperature, material of approximate composition $C_8OsF_6$. This, like, MoF_6 and UF_6 relatives, is blue. The magnetic susceptibility obeys the Curie-Weiss law over the
temperature range 20 - 77° K with a Weiss constant of 40° and \( \mu_{\text{eff}} = 3.5 \text{ B.M.} \). This magnetic behavior is like that of OsF_6^- salts, typified by cubic SF_3^+OsF_6^-, for which the Weiss constant is 4° and \( \mu_{\text{eff}} = 3.44 \text{ B.M.} \). Evidently the intercalated osmium species is OsF_6^-.

Single crystals of C_8OsF_6, are hexagonal and the spacing of the carbon sheets is 8.06(10) Å and \( a_0 = 4.92(5) \) Å - values consistent with C_8X. The former dimension is in harmony with the location of the OsF_6^- species with a threefold axis parallel to \( c_0 \).

Oxidation of graphite single crystals by O_2^+AsF_6^-, in suspension in SO_2ClF at -63°, yields a blue first stage salt. The crystals are hexagonal with \( a = 4.90(5) \), \( c = 8.06(6) \) Å. This is in harmony with the composition C_8AsF_6 and, as in the osmium case, suggests that the anions may be oriented with a threefold axis parallel to \( c_0 \). This salt is evidently related to the graphite intercalate, C_{10}AsF_5, first made by Selig and his co-workers from graphite and AsF_5. Vogel and his co-workers have recently demonstrated that the in-plane electrical conductivity of some graphite/AsF_5 materials can exceed that of copper. It has been widely supposed that much of the intercalate in these materials is molecular AsF_5.

Single crystal precession photographs of the first stage graphite compound, obtained by intercalating AsF_5 at ~20°, are very like those for C_8^+AsF_6^- and the unit cell parameters are not significantly different. Moreover, As atom K-shell
absorption edge spectra, shown in the Figure, indicate only one As species in C₈AsF₆, with absorption edge characteristics similar to those for the As atom in Cs⁺AsF₆⁻, Xe₂F₃⁺AsF₆⁻ and XeF⁺AsF₆⁻ salts. For C₁₀AsF₅, however, there are two As K-shell absorption edge peaks, one consistent with As(V) and the other, shifted to lower energy by 7.4 eV, and coincident with that of As(III) in As₂O₃. Evidently the AsF₅ intercalation by graphite is following a course common to AsF₅ oxidations: 3 AsF₅ + 2 e⁻ → 2 AsF₆⁻ + AsF₃.

Graphite is quickly oxidized by liquid S₂O₆F₂ at room temperature to give a blue first-stage compound of composition C₁₂SO₃F. X-ray precession photography shows the graphite interplanar spacing to be 7.86(8) Å and loss of S₂O₆F₂ at ~20° gives a second stage material with a c₀ axis of 11.3(1) Å. Layer form boron nitride (white) is also oxidized by this oxidant and a deep blue material of approximate composition (BN)₄SO₃F is obtained. X-ray powder photographs show a close similarity to photographs of known first stage graphite salts and the 00k lines indicate c₀ = 8.02(5) Å. A bulk sample of the microcrystalline blue solid proved to be an electrical conductor in contrast with BN which is an insulator. This behavior is consistent with removal of electrons from the highest filled Brillouin zone of the BN. We believe that this
The boron nitride salt appears to be thermodynamically unstable since on occasions when the BN/S$_2$O$_6$F$_2$ reaction mixture has been heated to ~40°, detonations have occurred. Moreover boron trifluoride is detectable as a decomposition product of the solid. Glemser and his coworkers had previously shown that elemental fluorine converts BN to BF$_3$ and N$_2$ and HF converts it to NH$_4$BF$_4$.

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References


7. Below 16°C, the C80sF6 samples show evidence of antiferromagnetic coupling.

References (Contd.)


10. The X-ray absorption experiments at the Stanford Synchrotron Facility were carried out with the help of N. Kafka, J. A. Kirby, M. Klein, J. P. Smith, and T. P. Walker.


Figure. X-Ray K-Shell absorption edge spectra of $C_8^+AsF_6^-$, $C_{10}AsF_5$ and $As_2O_3$. 

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