Submitted to Journal of the Chemical Society, Chemical Communications (In press)

LBL-6948
Preprint

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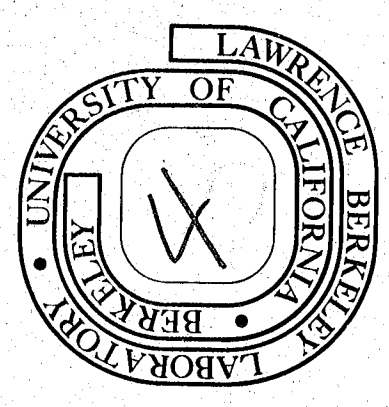
December 1977

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



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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.[1,2] and those derived from well oriented graphite have been shown by Ubbelohde and his coworkers[3] 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.[4,5]

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,[6] is blue. The magnetic susceptibility obeys the Curie-Weiss law over the

temperature range 20 → 77° K with a Weiss constant of 40° and μ_{eff} = 3.5 B.M.[7] This magnetic behavior is like that of OsF_6^- salts, typified[8] by cubic $SF_3^+OsF_6^-$, for which the Weiss constant is 4° and μ_{eff} = 3.44 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_o = 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 $\underline{c}_o$.

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 $\underline{c}_o$. This salt is evidently related to the graphite intercalate, $C_{10}AsF_5$, first made[4] by Selig and his co-workers from graphite and AsF_5. Vogel and his co-workers have recently demonstrated[5] 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.[9] 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 significently different. Moreover, As atom $\underline{K}$-shell

absorption edge spectra,[10] shown in the Figure, indicate only one As species in C_8AsF_6, with absorption edge characteristics similar to those for the As atom in $Cs^+AsF_6^-$, $Xe_2F_3^+AsF_6^-$ and $XeF^+AsF_6^-$ salts.[11] For $C_{10}AsF_5$, 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 As_2O_3. Evidently the AsF_5 intercalation by graphite is following a course common[12] to AsF_5 oxidations: $3\ AsF_5 + 2\ e^- \rightarrow 2\ AsF_6^- + AsF_3$.

Graphite is quickly oxidized by liquid $S_2O_6F_2$ at room temperature to give a blue first-stage compound of composition $C_{12}SO_3F$. X-ray precession photography shows the graphite interplanar spacing to be 7.86(8) Å and loss of $S_2O_6F_2$ at ~20° gives a second stage material with a c_o 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 $(BN)_4SO_3F$ is obtained. X-ray powder photographs show a close similarity to photographs of known first stage graphite salts and the 00ℓ lines indicate c_o = 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 Brilloin zone of the BN. We believe that this

is the first example of a first-stage boron nitride salt.[13] CAUTION: The boron nitride salt appears to be thermodynamically unstable since on occasions when the $BN/S_2O_6F_2$ 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[14] had previously shown that elemental fluorine converts BN to BF_3 and N_2 and HF converts it to NH_4BF_4.

We acknowledge support from the Energy Research and Development Authority and an I.B.M. fellowship to R. N. Biagioni.

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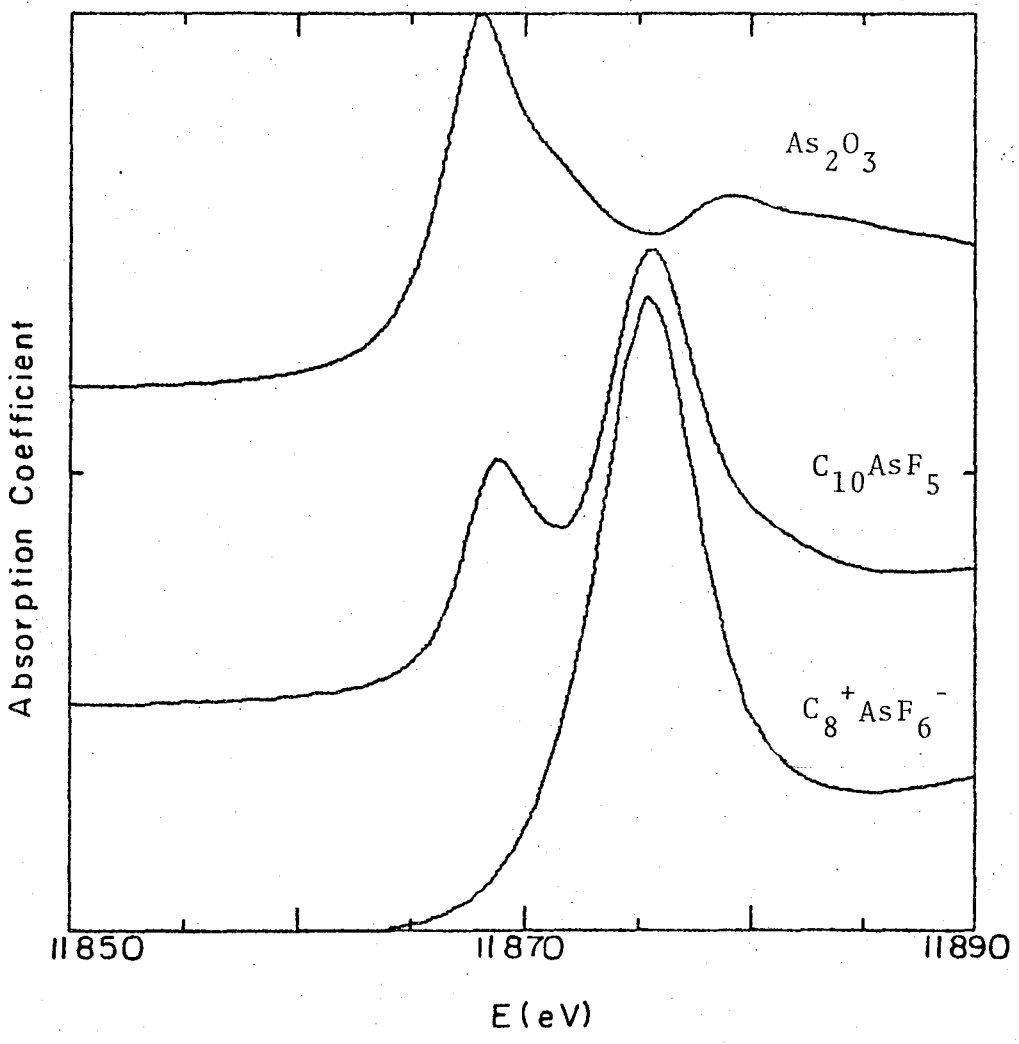

Figure. X-Ray K-Shell absorption edge spectra of $C_8^+AsF_6^-$, $C_{10}AsF_5$ and As_2O_3.

XBL 7710-6305

This report was done with support from the United States Energy Research and Development Administration. 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 United States Energy Research and Development Administration.