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 $C_8^+MF_6^-$; $S_2O_6F_2$ 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^-, and FSO_3^- are intercalated in the galleries of the graphite have long been known.[1,2] Salts derived from well oriented graphite have been shown by Ubbelohde and his co-workers[3] to be excellent electrical conductors. We have prepared new graphite salts containing anions of high ionization potential (AsF_6^-, OsF_6^-, and SO_3F^-) and the salt $(BN)_4^+SO_3^-$ which is the first example of a first-stage boron nitride salt. Our findings also support salt formulations for the highly conducting graphite–AsF_5 materials.[4,5]

Treatment of graphite single crystals with OsF_6 yields, at room temperature, a material of approximate composition C_8OsF_6. This, like the MoF_6 and UF_6, salts[6] is blue. The magnetic susceptibility obeys the Curie–Weiss law over the temperature range 20—77 K with a Weiss constant of 40 K and μ_{eff} = 3·5 B.M.[7] This magnetic behaviour is like that of OsF_6^- salts, typified[8] by cubic $SF_3^+OsF_6^-$, for which the Weiss constant is 4 K 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. The a_0 [4·92(5) Å] values are consistent with those for 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 210 K, 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 case of osmium, 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[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

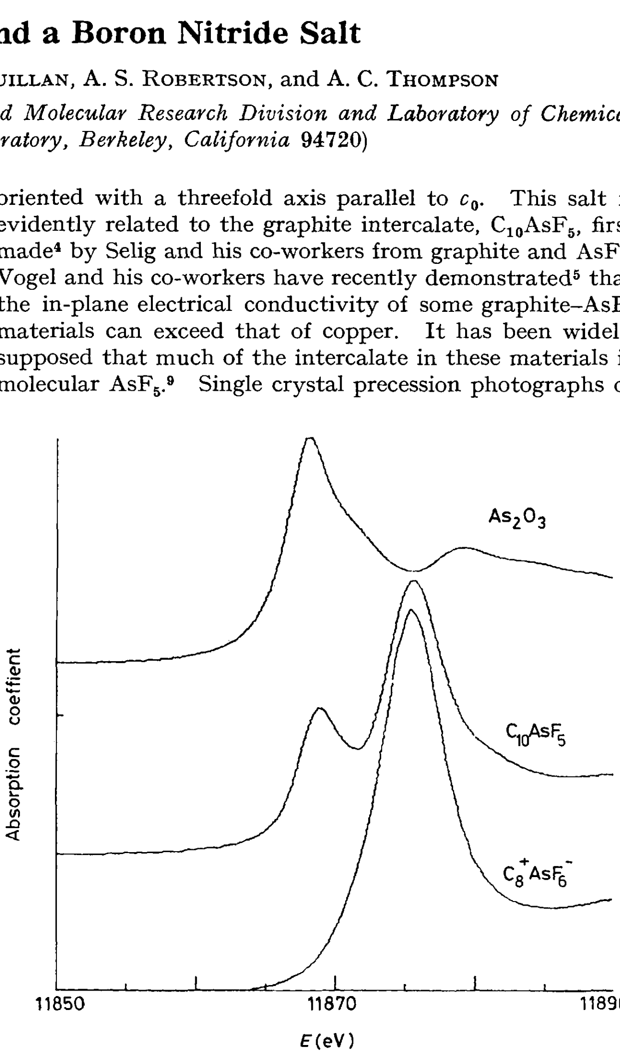

Figure. X-Ray K-shell absorption edge spectra of $C_8^+AsF_6^-$, $C_{10}AsF_5$, and As_2O_3.

the first-stage graphite compound, obtained by intercalating AsF_5 at *ca.* 293 K, are very similar to those of $C_8{}^+AsF_6{}^-$ and the unit cell parameters are not significantly different. Moreover, As atom *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 [equation (1)].

$$3AsF_5 + 2e^- \rightarrow 2AsF_6{}^- + AsF_3 \qquad (1)$$

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 *ca.* 293 K gives a second-stage material with a c_0 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 001 lines indicate $c_0 = 8{\cdot}02(5)$ Å. A bulk sample of the microcrystalline blue solid proved to be an electrical conductor in contrast with $(BN)_x$ which is an insulator. This behaviour is consistent with removal of electrons from the highest filled Brillouin zone of the $(BN)_x$. 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 *ca.* 313 K, detonations have occurred. Moreover boron trifluoride is detectable as a decomposition product of the solid. Glemser and his co-workers[14] had previously shown that elemental fluorine converts BN into BF_3 and N_2, and HF converts it into NH_4BF_4.

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