SOME REACTIONS OF METAL-HEXAFLUORO-ARSENATES WITH SILYL AMINES

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Metal-hexafluoroarsenates (M=Ni, Cu [1,2], Mn, Fe, Co [2], Zn, Mg) are readily prepared by oxidation of the appropriate metals with AsF_{5} in liquid SO_{5}

M +
$$3AsF_5 \xrightarrow{SO_2} M (SO_2)_2 (AsF_6)_2 + AsF_3$$

The structure of the Mg-salt was determined, in the solid the Mg-atoms are surrounded by two O-coordinated SO_2 -ligands and 4 F-atoms from 4 different AsF₆-anions. The Mg-and AsF₆-ions form eight-membered cycles, connected to infinite chains.

Weak donor ligands, e.g. silylamines ($R_3SiNSOF_2$, R_3SiNSO , $R_3SiNSNSiR_3$, $R_3SiNSF_2NSiR_3$) displace the SO -ligands, by coordination the reactivity of the Si -N-bond is greatly enhanced, it is cleaved even by the AsF_6^- - anion; e.g.

$$\underset{(SO_2)_2}{\operatorname{Ni}(SO_2)_2} (\operatorname{AsF}_{6})_2 + \operatorname{R}_3 \operatorname{SINSOF}_2 \xrightarrow{SO_2} \left[\operatorname{Ni}(SO_2)_2 [\operatorname{AsF}_4 (\operatorname{NSOF}_2)_2] \right] + \operatorname{R}_3 \operatorname{SINSOF}_2 \rightarrow [\operatorname{Ni} (\operatorname{NSOF}_2)_2]_n$$

Reaction mechanisms and structures of the reaction products will be discussed.

1 C.D. Desjardins, J.Passmore J.Fluor.Chem. <u>6</u>, 379 (1975)[2]P.A.W.Dean, ibid. <u>5</u> 499 (1975)

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REACTIONS OF $A_{s}F_{s}$ AND SbF_{s} WITH ELEMENTAL SELENIUM AND TELLURIUM AND WITH TeF_{4} AND $Te(OTeF_{5})_{4}$

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Arsenic and antimony pentafluorides are versatile oxidizing agents that have been used to prepare a variety of new species. The reactions of these reagents with Se and Te and with mixtures of these two elements have been studied in some detail and a variety of cationic species of these elements have been prepared. Among the species containing both selenium and tellurium these include $Te_2Se_2^{2+}$, $Te_2Se_4^{2+}$, $Te_2Se_6^{2+}$ and $Te_2Se_8^{2+}$. The reactions have been followed using ⁷⁷Se nnd ¹²STe nmr spectros copy and the structures of the hexafluorarsenate and hexafluorantimonate salts that have been isolated have been determined by X-ray crystallography.

During the course of the work on the oxidation of Te with AsF₅ it became of interest to study the reaction of TeF₄ with AsF₅ and the results of this study and a similar study of the analogous reaction with Te(OTeF₅)₄ will be reported. Among the products of the latter reaction new ionic species such as Te_x(OTeF₅)_{3-x}⁺ and AsF_x(OTeF₅)_{6-x}⁻ have been observed.