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CRYSTAL STRUCTURES OF HIGH-VALENT TRANSITION-METAL CHALCOGENIDE FLUORIDES

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The structures of high-valent transition-metal chalcogenide fluorides are of interest since it is not clear whether they will be related to those of their oxide-fluoride analogues or to those of the transition-metal chalcogenide chlorides and bromides. This will depend on the extent to which substitution of fluorine for chlorine or bromine or sulphur, or selenium for oxygen has the more significant effect.

The first single-crystal structure on a compound of this class, WSF_4, shows that it consists of octahedrally coordinated tungsten atoms linked by cis-bridged fluorine atoms into polymeric chains. This, together with work on the structure of $ReSF_4$, suggests that the tendency is to follow oxide-fluoride and fluoride structures.

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METAL HEXAFLUOROPHOSPHATE AND HEXAFLUOROARSENATE COMPLEXES WITH PYRAZINE

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PF_6^- and AsF_6^- are known to exhibit very weak coordinating tendencies towards transition metals and have been used as counter anions in the synthesis of a number of complex cationic species. We report here the synthesis of the complexes $[CuL_4](EF_6)_2$ (where L is pyrazine (pyz) or methylpyrazine and E is P or As). Spectroscopic and magnetic studies indicate the presence of $[CuL_4]^{2+}$ complex cations containing monodentate pyrazine ligands and non-coordinated EF_6^- anions. Thermal decomposition, under vacuum, of the $[CuL_4](AsF_6)_2$ complexes leads to the decomposition of the fluoroanion with the formation of donor-acceptor complexes, $L{\cdot}AsF_5$, plus mixtures of copper(II) fluoride complex species. Anion decomposition is avoided when the complexes are heated in an atmosphere of AsF_5. Under these conditions, complexes of composition $CuL_2(AsF_6)_2$ are obtained. Spectroscopic studies suggest that these complexes contain bridging pyrazine ligands and weakly coordinated AsF_6^- ions. Magnetic susceptibility studies on $Cu(pyz)_2(AsF_6)_2$ and a structurally related mixed anion complex, $Cu(pyz)_2(NO_3)(AsF_6)$, show the presence of significant antiferromagnetic coupling between metal centres. The role of the AsF_6^- anion in enhancing magnetic concentration in pyrazine complexes will be discussed. Some recent studies on related iron(II) complexes will also be reported.