A General Method for the Synthesis of Polymeric Binary Fluorides Exemplified by AgF_3, NiF_4, RuF_4, and OsF_4

Boris Zemva,[a] Karel Lutar,[a] Adolf Jesih,[a] William J. Casteel, Jr.,[b] and Neil Bartlett*[b]
[a] *'Jozef Stefan' Institute, 'Edward Kardelj' University, 6100 Ljubljana, Yugoslavia*
[b] *Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, CA 94720, U.S.A.*

Fluoride-ion capture from their anion relatives in anhydrous hydrogen fluoride solution by strong fluoride ion acceptors such as AsF_5 provides a general approach to the synthesis of polymeric binary fluorides and is particularly advantageous in the synthesis of highest-oxidation-state transition metal polymeric fluorides.

The highest attainable oxidation state of an element is usually obtained in anionic species. This is commonly so for fluorides. Thus salts of NiF_6^{2-} have long been known[1] but the parent binary fluoride, NiF_4, has not been described in spite of repeated efforts[2,3] to establish its existence. Similarly, the fluoroargentates(III) were described more than twenty years ago by Hoppe and his co-workers[4] but although a synthesis of AgF_3 has been recently given, by Bougon and his co-workers,[5] the structure has remained unknown. The low thermal stability of both NiF_4 and AgF_3 has been an obstacle to their identification. This has been overcome with the novel low temperature synthesis described here. This approach uses a strong acceptor fluoride, such as AsF_5, to abstract F^- from anionic relatives of the binary fluoride, dissolved in anhydrous hydrogen fluoride (AHF). With appropriately chosen soluble salts the reaction temperature can be kept at −60 °C or lower and the synthesis is generally applicable to the high purity synthesis of polymeric and AHF-insoluble fluorides having an anion stable in AHF.

A brown precipitate appeared as gaseous AsF_5 was bubbled through a deep red solution of $(XeF_5)_2NiF_6$ (ref. 6) in AHF. This precipitate redissolved in the solution on mixing, up to a 1 : 1 stoicheiometry of AsF_5 to $(XeF_5)_2NiF_6$, but persisted with more AsF_5. At a stoicheiometry of 2 : 1 the supernatant liquid was colourless. Fluorine gas, evolved by the brown solid (which then became black) was measured tensimetrically and, on the assumption that the brown solid was NiF_4, was in accord with the equation (1). The brown solid dissolved in AHF on addition of two equivalents of KF, to yield a deep red solution from which K_2NiF_6 was recovered quantitatively.

$$NiF_4 \rightarrow 1/2\ F_2 + NiF_3 \qquad (1)$$

Addition of AsF_5 gas to a yellow solution of XeF_5AgF_4 (ref. 7) in AHF at ~20 °C quantitatively precipitated AgF_3 as a bright red diamagnetic solid. *X*-Ray powder photographs closely resemble those of AuF_3 (ref. 8) and the pattern was indexed on the basis of a hexagonal unit cell: $a_0 = 5.088(10)$; c_0

= 15.43(3) Å; $V = 346$ Å^3; $Z = 6$, with extinctions conforming to the space group appropriate for AuF_3, *i.e.*, $P6_122\text{–}D_6^2$ or $P6_522\text{–}D_6^3$. For AuF_3, $a_0 = 5.149$; $c_0 = 16.26$; $V = 373$ Å^3. Evidently the Ag–F–Ag bridge bonding of the approximately square $[AgF_4]$ units, spiralling hexagonally along c_0, is shorter than in the AuF_3 structure. To account for this and for the close packing of the AgF_3 chains (measured by a_0) the steric activity of the d_{z^2} electron pair (normal to $[MF_4]$) must be ~4 Å^3 less in Ag^{III} than in Au^{III}. This suggests that the d_{z^2} pair is more strongly bound in AgF_3 than in AuF_3, which is consistent with our failure to prepare Ag^V species.[6] The bright red AgF_3 is quantitatively restored to XeF_5AgF_4 on addition of one equivalent of XeF_6 in AHF. The red AgF_3 transforms, at ~20 °C, in several hours to a brown solid which possesses the same *X*-ray powder diffraction pattern as that given by Bougon and his co-workers.[5] This brown solid does not dissolve completely in AHF in the presence of XeF_6 and this could signify some loss of fluorine in the transformation of bright red AgF_3 to the brown solid.

The tetrafluorides, RuF_4 or OsF_4, prepared reductively[9,10] from Ru_4F_{20} and Os_4F_{20} or OsF_6, are difficult to obtain in high purity, being commonly contaminated with trifluoride or metal, from which they cannot be easily separated.[11] Precipitation at ~20 °C with AsF_5, from AHF solutions of the K_2MF_6 salts (M = Ru or Os)[12] affords each of the tetrafluorides in high purity and quantitatively [reaction (2)]. The RuF_4

$$MF_6^{2-}\,(s) + 2\,AsF_5\,(g) \xrightarrow{\sim 20\,°C} MF_4\downarrow + 2\,AsF_6^-\,(s) \qquad (2)$$

prepared in this way is a pink solid which gives the same *X*-ray diffraction pattern as the major phase resulting from the reduction of Ru_4F_{20} with Ru metal at 310 °C (ref. 11). OsF_4 is a yellow–orange solid and is isomorphous with RhF_4 but not with RuF_4. The OsF_4 unit cell is orthorhombic with $a_0 = 9.85(3)$; $b_0 = 9.28(3)$; $c_0 = 5.69(2)$ Å; $V = 520$ Å^3; $Z = 8$ and the observed extinctions conform to the space group *Fdd*2, which is the one adopted by the isostructural tetrafluorides MF_4 (M = Rh, Pd, Ir, and Pt).[13,14] The OsF_4 structure thus appears to involve approximately octahedral co-ordination of the osmium atoms with two *cis* related F atoms non-bridging and each of the other four F atoms symmetrically bridging to another osmium atom, to produce the three-dimensional array that is related to a rutile structure, in which every other metal atom is omitted.[14]

The authors gratefully acknowledge support of the U.S.–Yugoslav Joint Fund for Scientific and Technological Co-operation, in co-operation with the National Science Foundation under Grant No. 552, and the Research Community of Slovenia. That part of the work carried out at Berkeley was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-ACO3-76SF00098.

Received, 19th September 1988; Com. 8/03563F

References

1 W. Klemm and E. Huss, *Z. Anorg. Chem.*, 1949, **258**, 221.
2 T. L. Court and M. F. A. Dove, *Chem. Commun.*, 1971, 726; *J. Chem. Soc., Dalton Trans.*, 1973, 1955.
3 L. Stein, J. M. Neil, and G. R. Alms, *Inorg. Chem.*, 1969, **8**, 2472.
4 R. Hoppe, *Z. Anorg. Chem.*, 1957, **292**, 28.
5 R. Bougon, and M. Lance, *C. R. Seances Acad. Sci., Ser. 2*, 1983, **297**, 117.
6 A. Jesih, K. Lutar, I. Leban, and B. Zemva, *Inorg. Chem.*, submitted for publication.
7 K. Lutar, A. Jesih, and B. Zemva, *Revue de Chimie Minérale*, 1986, **23**, 565.
8 F. W. B. Einstein, P. R. Rao, J. Trotter, and N. Bartlett, *J. Chem. Soc. (A)*, 1967, 478.
9 O. Ruff and E. Vidic, *Z. Anorg. Chem.*, 1925, **143**, 163; J. H. Holloway and R. D. Peacock, *J. Chem. Soc.*, 1963, 3892.
10 R. T. Paine, and L. B. Asprey, *Inorg. Chem.*, 1975, **14**, 1111.
11 N. Bartlett, B. Zemva, and A. Tressaud, 7th International Symposium on Fluorine Chemistry, Santa Cruz, July, 1973, I-49.
12 M. A. Hepworth, P. L. Robinson, and G. J. Westland, *J. Chem. Soc.*, 611.
13 P. R. Rao, A. Tressaud, and N. Bartlett, *J. Inorg. Nucl. Chem.*, 1976, Supplement, 23; N. Bartlett and A. Tressaud, *Compt. Rend. Acad. Sci., Ser. C.*, 1974, **278**, 1501.
14 A. F. Wright, B. E. F. Fender, N. Bartlett, and K. Leary, *Inorg. Chem.*, 1978, **17**, 748.