Coordination Chemistry Reviews, 30 (1979) 379–385

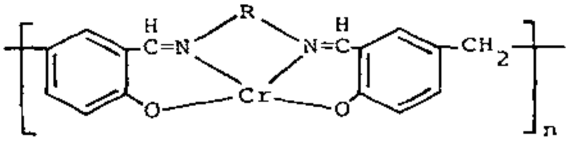
Chapter 8

THE NOBLE GASES

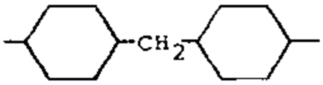
M.F.A.Dove

8.1 THE ELEMENTS

The solubilities of He,Ne,Ar and Kr in n-octane, n-decane, 1-octanol, 1-decanol and in octamethylcyclotetrasiloxane have been determined for 1 atm. pressure and over the temperature range 292 to 313K.[1] Riederer and Sawodny[2] have reported that the novel polymeric Schiff-base complex (1) can be used as the stationay phase in molecular sieve chromatography; Ar, Kr and Xe can be separated from one another and from a mixture of He and Ne at 28°C on this phase. Following an extraction with toluene low levels of ^{220}Rn and ^{222}Rn, such as are found in natural waters and in gases from geothermal wells, can conveniently be measured by γ-ray spectrometry.[3]



(1), R =



The synthesis and microwave spectrum of the very weakly bound complex $ArBF_3$ have been reported:[4] the Ar–B distance is 3.33Å and the stretching frequency is $44cm^{-1}$. Webb and Bernstein[5] have reported that new electronic transitions arise when MF_6 (M=W,Mo,U,Re and Ir) is dissolved in liquid Xe (molar ratio 1:12). They have assigned them to intermolecular charge transfer transitions in complexes which are not strongly bound, being completely dissociated in the vapour at room temperature. Estimates of the electron affinity of these hexafluorides were obtained and were compared with that of PtF_6 (215 kcal mol^{-1}) which is known to react with Xe.

A green xenon species, which is stable in solution at 300K under a pressure of xenon gas, has been identified as Xe_2^+ on the basis of e.s.r., Raman and u.v.-visible spectroscopy.[6] The cation was produced in antimony pentafluoride either by the action of O_2^+ salts on Xe or by the reduction of XeF^+. The ultimate product of oxidation of Xe by dioxygenyl salts is the XeF^+ cation(equation (1)). An intense e.s.r. spectrum produced by the u.v. irradiation of Kr in CF_3OF at 10K has been attributed to the linear radical, KrFKr.[7]

$$Xe + 2O_2^+SbF_6^- \longrightarrow XeF^+Sb_2F_{11}^- + 2O_2 \quad (1)$$

Artem'ev et al have investigated the conditions appropriate for the combustion of Xe/F_2 mixtures.[8] The minimum pressure for ignition is 8×10^5 Pa at a F_2 (96% pure) concentration of ca. 30 mass % in a spherical vessel at 20°C. When excess F_2 was used the products were found to consist of XeF_2 and XeF_4, but never XeF_6.

New and revised ^{129}Xe chemical shift data have been reported for compounds ranging from XeO_6^{4-} to $FXeN(SO_2F)_2$, 2077 to -2016ppm, relative to $XeOF_4$, respectively.[9] The chemical shifts have been discussed empirically and are found to provide a sensitive probe for assessing the degree of ionic character in the Xe-F bond. ^{19}F n.m.r. spectroscopy of xenon compounds intercalated in graphite has shown that reduction of XeF_4 and XeF_6 occurs on intercalation, whereas XeF_2 and $XeOF_4$ intercalate without change of oxidation state.[10]

8.2 KRYPTON AND XENON(II)

From a photoionization mass spectrometric study of process (2) a value for $\Delta H_f^o(KrF_2)$ of 15.5 kcal mol^{-1} has been derived :[11]

$$KrF_2 + h\nu \longrightarrow Kr^+ + F^- + F \quad (2)$$

this implies an average Kr-F bond energy of 0.46eV in KrF_2. in the presence of certain fluoride ion acceptors (including SbF_5,NbF_5,PF_5, TiF_4 and BF_3) KrF_2 reacts with NF_3 in anhydrous HF to form the appropriate NF_4^+ salts.[12]

Krypton difluoride has been shown to intercalate in graphite even at 0°C.[13] A typical product composition is $C_{44.5}KrF_{9.5}$, showing that lattice fluorination accompanies intercalation. Decomposition of the product in a mass spectrometer yields no KrF^+ fragment. Under the conditions of a glow discharge (1-10 torr) when Kr, F_2 and SbF_5 react to form $KrF_2.SbF_5$, no reaction could be detected when Ar was used in the place of Kr.[14]

Using monochromatized Al-K_α radiation Bancroft _et al_.[15] have made a detailed gas-phase ESCA study of the valence levels and Xe 3d and 4d core levels in XeF_2 (and XeF_4): several previous experimental and theoretical assignments were shown to be incorrect. An unstable adduct, probably $(FO_2S)_2NXe^+AsF_6^-$, has been observed in the reaction of AsF_5 and $FXeN(SO_2F)_2$ which decomposes under dynamic vacuum to give $2FXeN(SO_2F)_2.AsF_5$.[16] Raman and ^{19}F n.m.r. spectroscopy of the 2:1 adduct are in agreement with the formulation $[(FO_2S)_2NXe]_2F^+AsF_6^-$. The X-ray diffraction data from $XeF^+AsF_6^-$ have been refined to R=0.033.[17] The structure consists of ion pairs connected by a bridging F atom, see Figure 1, into $FXeFAsF_5$ units, which are very similar in shape to the RuF_5 analogue. The Raman spectra of the weakly bound complexes of XeF_2

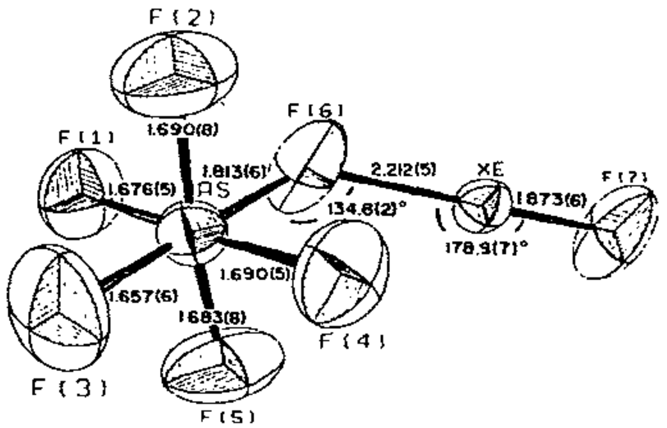


Figure 1. The formula unit of $XeF_2.AsF_5$. (Reproduced by permission from Inorg. Chem.,17(1978)1318.)

with MF_6, M=Mo, W, and U, have been recorded at 77K.[18] The only unexpected features occur with the UF_6 adduct and these were assigned to Xe-F-U vibrational modes.

Xenon difluoride dissolved in anhydrous HF is a moderately strong oxidant which can be used selectively in many situations to prepare a wide range of inorganic fluorine-containing compounds, such as binary and ternary fluorides.[19] Diphenyl and t-butylphenyl sulphides are oxidised by XeF_2 in MeCN to the corresponding S(IV) difluorides.[20] However the presence of an α-H substituent leads to α-fluorination and even to olefin formation. Stavber and Zupan[21] have shown that XeF_2 in the presence of BF_3 causes fluorine addition to 1-substituted (H, Cl, Br, or C_6F_5)pentafluorobenzene regiospecifically, i.e. forming 1-substituted heptafluorocyclohexa-1,4-dienes, and in high yields.

8.3. XENON(IV)

The first xenon(IV) compound in which there are no Xe-F bonds has been reported by Lenz and Seppelt.[22] The preparation of xenon tetrakis(pentafluoroorthotellurate) from XeF_4 is summarized by equation (3). The crystalline

$$3XeF_4 \quad + \quad 4B(OTeF_5)_3 \xrightarrow{0^{\circ}C} 3Xe(OTeF_5)_4 \quad + \quad 4BF_3 \qquad (3)$$

product (dec. 72°C) sublimes in vacuum at 50°C and shows a ^{129}Xe chemical shift of 4694ppm relative to Xe. The stability of the new compound helps to substantiate the claim that the $OTeF_5$ group is more electronegative than F. The crystal structure of trifluoroxenon(IV) hexafluorobismuthate resembles closely that of the hexafluoroantimonate salt : a significant difference is that the bridging fluorine is more strongly associated with Xe in $[XeF_3][BiF_6]$ indicating that BiF_5 is a weaker fluoride ion acceptor than SbF_5. Apart from the bridging fluorine F(5), Figure 2, there are four longer contacts which are disposed symmetrically about the lone pair of the XeF_4 unit, Figure 3.

The isolation of pure $XeOF_2$ has now been claimed : the Raman spectrum is consistent with the planar C_{2v} geometry (2) expected for the monomer. It was synthesised by the hydrolysis of XeF_4 in HF at -63°C for 24h. The light yellow compound decomposes explosively at *ca*. 0°C. Reaction with CsF.xHF generates the Cs salt of the new anion $XeOF_3^-$, for which a planar structure (3) was proposed. The reaction of $XeOF_2$ with CsF *in solution* in HF produces the xenon(VI) anion, XeO_2F_3(4) in a disproportion reaction.

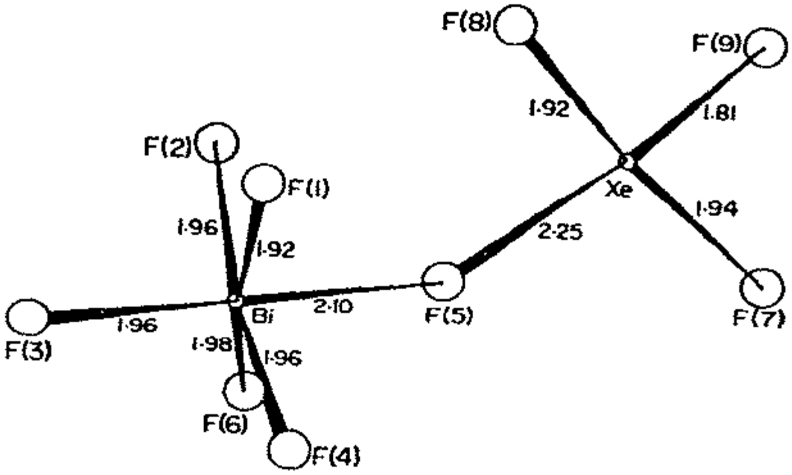


Figure 2. The $[XeF_3][BiF_6]$ structural unit. (Reproduced by permission from J.Chem.Soc. Dalton, (1977) 2234)

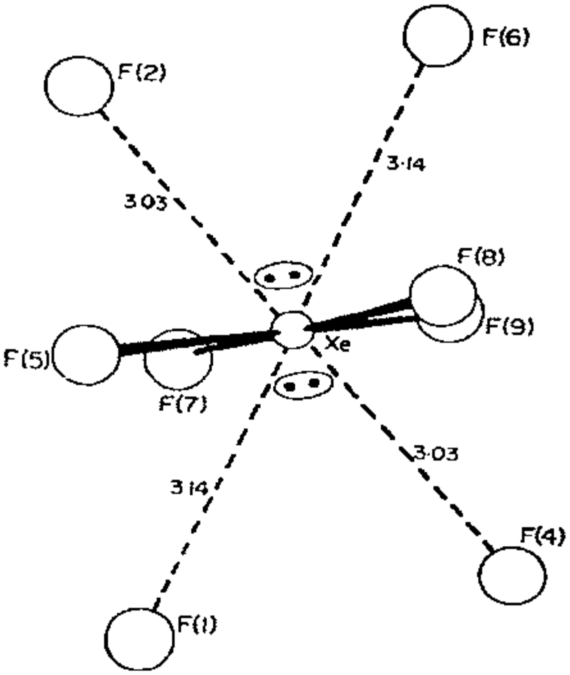
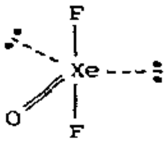
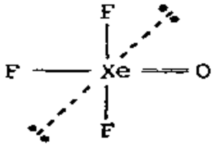


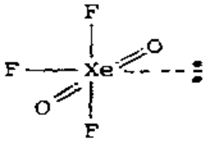
Figure 3. The complete coordination about the xenon atom. (Reproduced by permission from J.Chem.Soc.,Dalton,(1977) 2234)



(2)



(3)



(4)

8.4 XENON(VI)

Kepert[25] has pointed out that the structure of XeF_6 in the gas-phase may be derived by minimising the repulsion energy between electron pairs and by assuming an r^{-6} repulsion law, with the non-bonding electron pair situated close to the xenon. The ^{19}F n.m.r. spectrum of ^{129}Xe-enriched XeF_6 in CF_3Cl at -140°C consists of 9 broad resonances showing the 325Hz coupling and thus confirming the tetrameric nature of the solute. Adams and Bartlett[27] have reported additional Raman spectra of salts of the XeF_5^+ and $Xe_2F_{11}^+$ cations in solution in HF as well as in the solid state. Solutions of XeF_6 in WF_6 appear to consist of tetramer and monomer, whereas in liquid HF the major solute species in concentrated solutions is the tetramer, at intermediate concentrations $Xe_2F_{11}^+$ is dominant, and in dilute solutions XeF_5^+ is more important.

REFERENCES

1 R.J.Wilcock, J.L.McHale, R.Battino, and E.Wilhelm, Fluid Phase Equilibria, 2(1978)225; R.J.Wilcock, R.Battino, W.F.Danforth, and E.Wilhelm, J. Chem. Thermodyn., 10(1978)817.

2 M.Riederer and W.Sawodny, Angew. Chem. Int. Ed. Engl., 17(1978)610.

3 M.Yanokura, K.Horiuchi, H.Nakahara, and Y.Murakami, Chem. Lett., (1978)1131.

4 K.C.Janda, L.S.Bernstein, and J.M.Steed, J. Am. Chem. Soc., 100 (1978)8074.

5 J.D.Webb and E.R.Bernstein, J. Am. Chem. Soc., 100(1978)483.

6 .Stein, J.R.Norris, A.J.Downs, and A.R.Minihan, J. Chem. Soc. Chem. Commun., (1978)502.

7 A.R.Boate, J.R.Morton and K.F.Preston, Chem. Phys. Lett., 54(1978) 579.

8 K.K.Artem'ev, V.A.Legasov, G.S.Kolenta, A.S.Marinin, and B.B. Chaivanov, Russ. J. Inorg. Chem., 22(1977)1434.

9 G.J.Schrobilgen, J.H.Holloway, P.Granger, and C.Brevard, Inorg. Chem., 17(1978)980.

10 L.B.Ebert and H.Selig, Mater. Sci. Eng., 31(1977)177.

11 J.Berkowitz and J.H.Holloway, J. Chem. Soc. Faraday Trans. II, 74(1978)2077.

12 A.A.Artyukhov and S.S.Khoroshev, Koord. Khim., 3(1977)1478.

13 H.Selig, P.K.Gallagher, and L.B.Ebert, Inorg. Nucl. Chem. Lett., 13(1977)427.

14 V.D.Klimov, V.A.Legasov, and S.S.Khoroshev, Russ. J. Phys. Chem., 52(1978)1037.

15 G.M.Bancroft, P.-Å.Malmquist, S.Svensson, E.Basilier, U.Gelius, and K.Siegbahn, Inorg. Chem., 17(1978)1595.

16 D.D.DesMarteau, J. Am. Chem. Soc., 100(1978)6270.

17 A.Zalkin, D.L.Ward, R.N.Biagioni, D.H.Templeton, and N.Bartlett, Inorg. Chem. 17(1978)1318.

18 V.K.Ezhov and S.S.Khoroshev, Russ. J. Phys. Chem., 52(1978)772.

19 R.C.Burns, I.D.MacLoed, T.A.O'Donnell, T.E.Peel, K.A.Phillips, and A.B.Waugh, J. Inorg. Nucl. Chem., 39(1977)1737.

20 R.K.Marat and A.F.Janzen, Can. J. Chem., 55(1977)3031.

21 S.Stavber and M.Zupan, J. Chem. Soc.,Chem. Commun., (1978)969.

22 D.Lenz and K.Seppelt, Angew. Chem., Int. Ed. Engl., 17(1978)356.

23 R.J.Gillespie and D.Martin, J. Chem. Soc. Dalton Trans., (1977)2234.

24 R.J.Gillespie and G.J.Schrobilgen, J. Chem. Soc. Chem. Commun., (1977)595.

25 D.L.Kepert, Aust. J. Chem., 31(1978)1917.

26 K.Seppelt and N.Bartlett, Z. Anorg. Allg. Chem., 436(1977)122.

27 C.J.Adams and N.Bartlett, Israel J. Chem., 17(1978)114.