Journal of Fluorine Chemistry, 24 (1984) 319–325

THE STRUCTURE OF SOME TRANSITION METAL FLUORIDES

O. GLEMSER

Institut für Anorganische Chemie der Universität Göttingen
Tammannstraße 4, D-3400 Göttingen (F.R.G.)

SUMMARY

The structures of the solid fluorides MF_2, MF_3, MF_4 and MF_5, in which M has the coordination number 6 and belongs to the 3*d*, 4*d*- and 5*d*-periods and the Vb to VIII groups, can be divided into 3 types: (a) cubic close packing (*ccp*) of F with an M-F-M bridging angle of 180°; (b) hexagonal close packing (*hcp*) with an M-F-M-bonding angle of 132°; (c) intermediate packing between (a) and (b). The linear bridging is assumed to be a consequence of π-back bonding (or charge transfer) between *p*F-orbitals and *d*-orbitals of the metal. If such bonding is not possible then *hcp* with the bridging angle of 132° will result. Weaker π-interactions give the intermediates (c).

INTRODUCTION

The structures of the solid fluorides MF_2, MF_3, MF_4 and MF_5, in which M is octahedrally coordinated and belongs to the 3d-, 4d- and 5d-periods and the Vb and VIII groups of the Periodic Table, can be considered from a general point of view as shown below. To a first approximation three types of structure may be distinguished:

0022-1139/84/$3.00

1) Cubic close packing (<u>ccp</u>) with a M-F-M bridging angle of 180°
2) Hexagonal close packing (<u>hcp</u>) with a M-F-M-bridging angle of 132°
3) A packing intermediate between 1) and 2) with a M-F-M bond angle of ca. 150°.

RESULTS AND DISCUSSION

How do these packing variants apply to the species considered?

Pentafluorides

In the solid state the transition metal pentafluorides form cyclic tetramers $(MF_5)_4$ and polymeric chains $(MF_5)_n$. Two different molecular structures are found for the tetramers (Fig. 1):

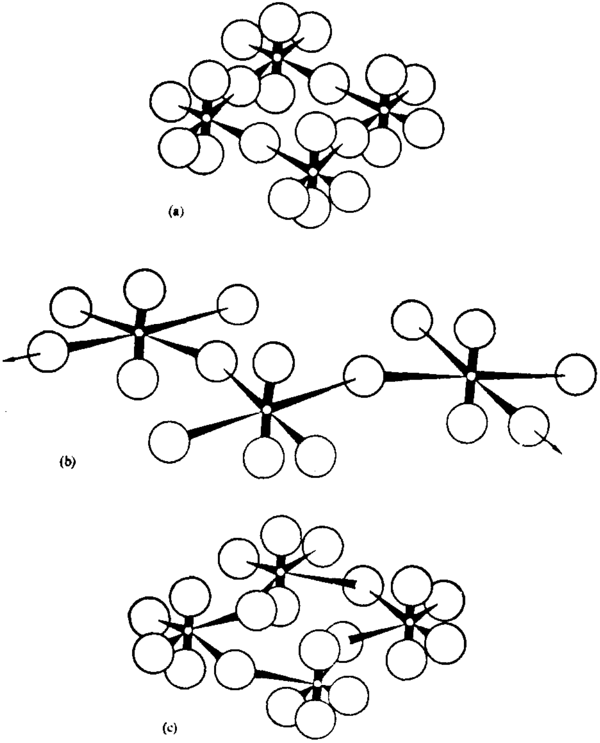

Fig. 1. Structures of the transition metal pentafluorides. From J.H. Canterford, R. Colton and T.A. O'Donnell, Rev. Pure and Appl. Chem. <u>17</u> (1967) 23. Small circles represent metal, large circles fluorine.

(a) In the Nb, Ta, Mo and W species the four metal atoms are located at the corners of a square, linked via linear M-F-M bridges: The coordination octahedra are distorted.

(c) The cyclic structure of the $(MF_5)_4$ fluorides of the noble metals Ru, Rh, Os, Ir and Pt resembles that of (a), but the M-F-M bridges are non-linear with an angle of ca. 132°. The metal atoms are located at the corners of a rhombus and the octahedral coordination is distorted. In the other pentafluorides (b), i.e. those of V, Cr, Tc and Re, the coordination octahedra are linked via cis-fluorine bridges to form endless chains [1].

Tetrafluorides, trifluorides and difluorides

The polymeric solid tetrafluorides $(MF_4)_n$ exhibit layer structures or three dimensional networks. The ccp arrangement with an M-F-M bridging angle of ca. 180° has so far only been found in the layer structure of NbF_4 which is iso-structural with SnF_4 and PbF_4. $(NbF_4)_n$ has the same arrangement of layers as in NiF_4^{2-}. A remarkable structure is found for IrF_4 (isostructural with RhF_4, PdF_4 and probably PtF_4): each IrF_6 octahedron shares four corners with other octahedra; the two cis corners remain unshared. The packing of the F atoms closely approaches hcp, and the M-F-M bridging angle is ca. 134°. The only known representative of an intermediate type of packing is probably polymeric VF_4 [2] with a layer structure [3].

Amongst the trifluorides NbF_3 and probably TaF_3 are known with ccp (ReO_3 type) and an M-F-M bridging angle of ca. 180°. On the right-hand side of the periodic table we find RhF_3 and IrF_3 approaching hcp, and an M-F-M bridging angle of ca. 132°. RuF_3 can also be included, with a bridging angle of 136° and a structure resembling that of VF_3. PdF_3 is $Pd^{2+}Pd^{4+}F_6$. Once again the F atoms approach hcp. As three-dimensional polymers, the structures of TiF_3, VF_3, CrF_3, MnF_3, FeF_3, CoF_3, MoF_3 lie between these two extremes.

Finally, the difluorides MF_2 should also be mentioned. Except for Ti, all 3d metals are known to form difluorides with the rutile structure (hcp with an M-F-M bridging angle of 132° as ideal case. CrF_2 and CuF_2 have Jahn - Teller distortion). Apart from ZrF_2 [4] and PdF_2 and AgF_2 [5] (rutile structure) there are no known 4d and 5d difluorides. Since fluorine is trigonally coordinated in the rutile structure, a direct comparison with the higher binary fluorides (in which F always has a coordination number of two or two an one in MF_5) is not possible.

Explanation of the occurrence of the various packing structures

In his book 'Structural Inorganic Chemistry' [1], A.F. Wells remarks: "There is an interesting connection, which is not understood, between the structures of these compounds and the position of M in the Periodic Table". This refers to MF_3 species, but also applies to MF_4 and MF_5 types. It is possible to understand this "interesting connection" by assuming the following model:

In transition metal fluorides with α ccp arrangement of F atoms and an M-F-M bridging angle of 180°, the linear bridge is consistent with π-back bonding of occupied p-orbitals of fluorine with t_{2g} orbitals on the metal. If such bonding is not possible, the hcp with an M-F-M bridging angle of 132° will result. In the case of weaker π-back bonding interactions, we should have 'intermediate packing' with M-F-M bridging angles between 180° and 132°. The π-bonding reduces the stereochemical effect of the two lone-pairs on fluorine, and simultaneous π-bonding with both metal atoms is optimised when the M-F-M angle is 180°.

Some years ago it was suggested that this π-back bonding should play a role in the occurrence of linear M-F-M bridges in $(NbF_5)_4$ and $(MoF_5)_4$ [6], and has also been assumed in some 5d-hexafluorides such as WF_6 [7]. On the other hand it is possible to consider the π-back bonding as a charge transfer from F-p orbitals to metal d-orbitals as was deduced from electron impact excitation spectra of WF_6 and UF_6 [8]. Bearing in mind that ccp and hcp do not differ much energetically, then even weak π-back bonding contributions will influence the packing of the F atoms. These weak back-bonding effects (or charge transfers) should not be ruled out for lower fluorides.

In order to improve our understanding of the bonding, let us examine Fig. 2, showing the 1-electron level diagram for

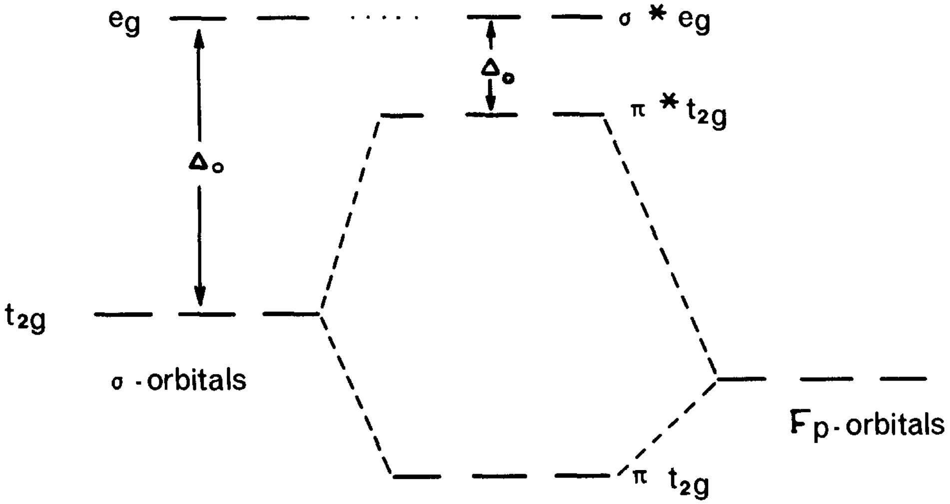

Fig. 2. One-electron energy-level diagram for a system with π-donor ligands.

a π-system with a donor ligand. Electrons of the $\underline{t}_{2g}$ orbitals are now in $\underline{t}^*_{2g}$ orbitals, and hence at a higher energy level. Since the level of the $\underline{e}_g$ orbitals remains unaffected by π-interaction, Δ_0 is lowered. In other words F → M π-back bonding destabilizes the $\underline{t}^*_{2g}$ orbitals. The energy level diagram applies only to discrete molecules or complex ions. In the case of oligomers such as $(MF_5)_4$ or polymers like $(MF_5)_n$, $(MF_4)_n$, $(MF_3)_n$ and $(MF_2)_n$, the energy levels become energy bands. Their calculation is however difficult.

The contribution of this kind of π-back bonding to the overall bonding decreases by the same extent as the occupation of the antibonding $\underline{t}^*_{2g}$ orbitals increases. It should further be noted that for a given group of transition metals Δ_0 increases from 3<u>d</u> via 4<u>d</u> to 5<u>d</u> by about 40% each time. Δ_0 further increases as the oxidation number of a given metal atom increases. This is why high-spin species are expected in the 3<u>d</u>-series and low-spin species in the 4<u>d</u>- and <u>5</u>-series.

π-F → M back bonding is anticipated at low occupations of $\underline{t}^*_{2g}$ orbitals with electrons, i.e. at the beginning of the <u>d</u>-series of the periodic classification (it should be remembered that we are considering only fluorine species with coordination number 6 for the metal). π-F → M back bonding is most favorable in the 5<u>d</u>-series, and far less so in the 3<u>d</u>-series; the 4<u>d</u>-series occupy an intermediate position.

The model of π-F → M back bonding presented here is in accord with species occurring in the various groups and <u>d</u>-series. We can understand why NbF_3 is <u>ccp</u> with the ReO_3 structure, and why MoF_3 is not. However, as soon as MoF_3 contains a little oxygen, as was apparently the rule in earlier preparations, then the population of the electrons in the $\underline{t}^*_{2g}$ orbital decreases and the charge on the central atom becomes higher; Δ_0 increases and the occurrence of the ReO_3-type may be accounted for. Let us again consider the niobium fluorides $(NbF_3)_n$, $(NbF_4)_n$ and $(NbF_5)_4$ in Group V, and the iridium fluoride $(IrF_3)_n$, $(IrF)_n$ and $(IrF_5)_4$ in Group VIII. The niobium fluorides mentioned all have approximately <u>ccp</u> F-atoms with a bridging angle Nb-F-Nb of ca. 180°, and the iridium fluorides approximately <u>hcp</u> F-atoms with a bridging angle of ca. 132°. In both groups the structural arrangement occurs despite the different charge of the metal atoms.

CONCLUSION

"The precise nature of the anion packing is of interest, since it determines the M-F-M angle", Wells writes in his book cited above [1]. But it may well be the M-F-M angle which determines the anion packing.

ACKNOWLEDGEMENT

I thank Prof. Sheldrick, Göttingen, for helpful discussions and the Herbert-Quandt Stiftung for support.

REFERENCES

1 A.F. Wells, Structural Inorganic Chemistry, 4th ed., Clarendon Press, Oxford 1975, p. 350 ff.

2 A.J. Edwards, P. Taylor, Chem. Commun. 1970, 1474

3 MnF_4: trigonal: a = 34.1; c = 9.09 Å.
B.G. Müller, Abstracts 6. Europ. Fluor-Symp. Dortmund 1977, J 51
The structure of CrF_4 is probably similar to the tetrafluorides of titanium and vanadium, that is, chains of CrF_6 units joined by shared edges: R. Colton and J.H. Canterford, Halides of the First Row Transition Metals, Wiley Interscience, London, New York, Sidney, Toronto,1969

4 F.K. Taggert, A.G. Turnbull, Austral. J. Chem. 17, 727 (1964)

5 P. Fischer, D. Schwarzenbach, H.M. Rietveld, J. Phys. Chem. Solids 32, 543 (1971)

6 J.H. Canterford, R. Colton and T.A. O'Donnell, Rev. Pure and Appl. Chem. 17, 123 (1967)

7 N. Bartlett, Angew. Chem. Intern. Ed. 7, 433 (1965)

8 R. Rianda, R.P. Frueholz and A. Kuppermann, J. Chem. Phys. 70, 1056 (1979)