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RATIONALIZING STRUCTURES OF TRANSITION METAL FLUORIDES

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SUMMARY

Engel's theory of intermetallic bonding which differentiates transition metals into acid and bases about a Group VII dividing line is used to rationalize transition metal fluoride structures. Some chemical consequences are indicated.

INTRODUCTION

Glemser [1] has provided a plausible explanation for the structural variation in fluorides across transition metal series in terms of the back-bonding from fluorine to metal straightening M-F-M bridging bonds.

We should like to present an alternative view of these structural variations which is compatible with the back-bonding postulate, and to indicate some interesting corollaries arising therefrom.

DISCUSSION

Metallurgists have long known that the most stable and refractory alloys are formed between metals at opposite ends of the transition metal series. Engel [2] has combined Pauling's ideas on metallic bonding [3] with those of Hume-Rothery [4] - the occurrence of stable phases around distinctive valence electron/atom ratios - to rationalize metallic and intermetallic structures. Brewer [5] has supplied much supporting evidence for Engel's ideas. It is suggested that long range order in b.c.c., h.c.p. and c.c.p. metal lattices are controlled by the s and p valence electron/atom ratios around 1, 2 and 3 respectively. Hence some ground state atoms of transition elements are promoted before bonding to

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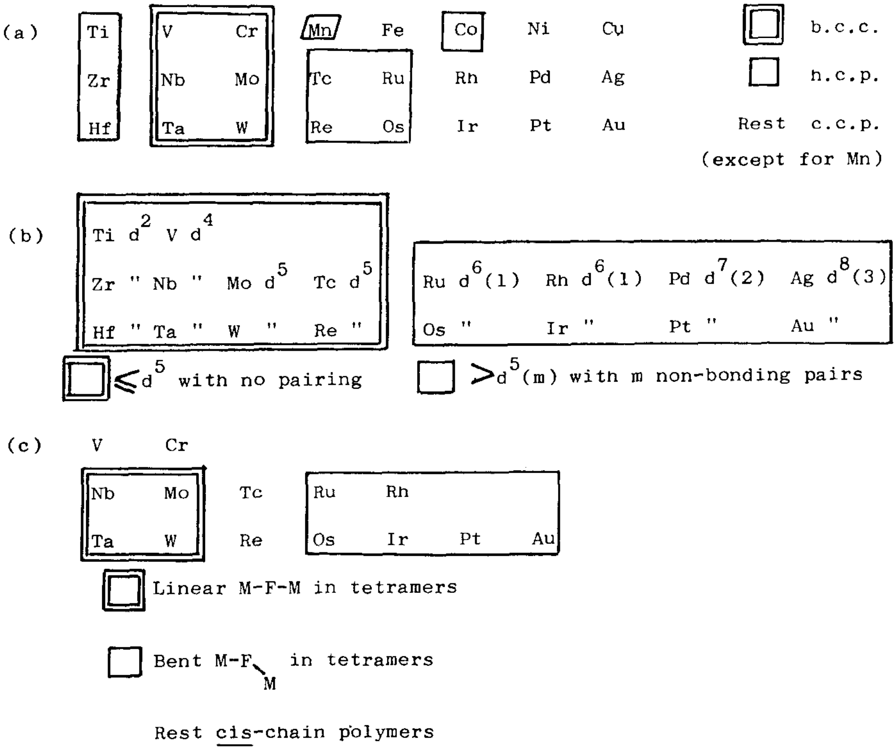

Fig. 1. Metal classification according to: (a) crystal structures; (b) Engel d-electron configurations; (c) pentafluoride structures.

excited states appropriate to the metal structures with, for example, $d^{n-1}s$ and $d^{n-2}sp$ configurations (n = number of valence electrons) if such configurations are not available initially. The same type of promotion is accepted with main-group elements. For example the $s^2p^2 \rightarrow sp^3$ excitation of C or Si provides increased bonding capabilities which more than compensate for the extra promotion energies. If this configuration matching with metal structure is carried out on the atoms of the third transition series the number of unpaired d electrons rises from one in Lu to five in Re and then drops from four in Os to only two in Au. The physical properties such as melting points or hardness reflect the maximum in the unpaired d-electron count. Hence for the transition metals up to Re the electrons are all unpaired and available for bonding, but incomplete use is made of bonding orbitals in metal structures. After Group VII the d-electrons are not all available because of necessary electron pairing, but the bonding orbitals are fully used. If metals from opposite sides of the Group VII division are brought together, then, according to Engel's theory, electrons flow from the post- to the pre-Group VII element to fill orbital vacancies and fully utilize the available electrons forming very stable structures. This interaction can be regarded as a Lewis acid-base interaction in the Usanovitch sense. The transition metals show increased basicity to the right, or increased acidity to the left. It is recognized that irregularities occur in the first transition series from Cr to Ni because of the differing penetrations of d into s and p electron density. The occurrence of ferromagnetism indicates that some 3d-electrons resist pairing in the metallic state, unlike the corresponding 4d and 5d ones.

It can be seen from Figure 1 that the enclosure of metal configurations beyond Group VII according to Engel's theory, corresponds with the distinctive platinum-metal pentafluoride structures. The borderline structures at Tc and Re are not clearly separated unless higher excited states are also considered. Fluorine can be regarded as intermediate in basicity or acidity with respect to metals on each side of the Group VII divide, i.e. it can be amphoteric.

Hence the alternative to Glemser's viewpoint is that an electron flow from fluorine to unfilled d-orbitals on Group IV - VI can occur, whereas the electron flow is reversed from incompletely used d-electrons on Group VII - X metals to the low lying unfilled p-orbitals on fluorine. It should be noted that the series can be extended to gold compounds, which as expected, have bent Au-F-Au bonds. A full crystal structure on AuF_3 [6] shows a helical chain of cis-joined square-planar units $AuF_2(2F/2)$ with the small bridging fluorine angle of 116°. A powder diffraction pattern on AuF_5 suggests a similar structure to RuF_5 and an electron diffraction study on AuF_5 vapour gave bridging angles of 92° and 75° in a dimer and 80° and 116° in the trimer [7].

The electron flow in Group IV - VI fluorides is counter to the flow expected from electronegativity principles, i.e. towards fluorine, the most electronegative element. A similar counter-flow also occurs in intermetallic compounds from the more electronegative post-Group VII to the less electronegative pre-Group VII elements. This provides further support to those who maintain that electronegativity considerations alone cannot be used to argue against the concept of positive fluorine [8].

Structural differences in pentafluorides should also be reflected in differences in chemical behaviour. However, since the overall difference depends both on the central metal atom as well as the bonded ligand it would be difficult to apportion the chemical relevance of each element. The depolymerisation of pentafluorides with a weak base such as sulphur dioxide might be a suitable reaction for a comparative study.

A possible way to accentuate any chemical difference would be to make combined pentafluorides of Group V and X, e.g. $[TaF_5.PtF_5]_n$. One would expect, at the very least, a Raoultian non-ideality in the liquid phase compared with components and possibly enhanced electrical conductivity over that of TaF_5 [9]. In the solid state there may be an ordering of metal sites and conceivably there could be an electron flow from Pt to Ta via linear bridging fluorines - a super-exchange phenomenon. There could also be interesting phenomena with mixed tetrafluorides or even combinations of acidic and basic metal pentafluoride with basic or acidic tetrafluorides.

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