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LETTER

On the bond length variation of first-series transition metal di- and trihalides. A comment on the bond length of FeF_3

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Some time ago it was predicted [1] that the variation of the M–X bond lengths in MX_2 linear first-series transition metal dihalides is different from that of the metal octahedral ionic radii because of different d orbital splittings in the two environments. New or improved experimental data have recently become available for several transition metal dihalides including CrF_2 [2], MF_2 (M = Mn, Fe, Co, Ni) [3], CuF_2 [4], ZnF_2 [5], MCl_2 (M = Mn, Fe, Co, Ni) [6], MBr_2 (M = Fe, Ni) [6], CaX_2 [7] and ZnX_2 [8] (X = Cl, Br, I)*. These data support our prediction.

The variation of octahedral ionic radii was discussed in the third edition of Cotton and Wilkinson's *Advanced Inorganic Chemistry* [9]. Curve A in Fig. 1 presents such a diagram using the ionic radii (coordination number 6) of Shannon [10].

A steady decrease of the radii is expected with increasing atomic number because of the imperfect shielding of d electrons by each other. Thus all points could be expected somewhere along the dashed line which connects the points for Ca, Mn and Zn, i.e. ions with spherically symmetrical (d^0, d^5, d^{10}) distribution of d electrons. In practice, however, further contraction of the metal ionic radii is observed, which is the consequence of the non-uniform distribution of d electrons around the nuclei. The d orbital splitting in an octahedral environment is depicted in Fig. 2. With building up the energetically favorable t_{2g} orbitals, relatively less and less shielding and, consequently, further contraction of the ionic radii is observed. This situation culminates with d^3 and d^8 configurations, i.e. with V^{2+} and Ni^{2+} in the series. Supposing only high spin configurations, further electrons will occupy the energetically unfavorable e_g orbitals and this will increase the ionic radii.

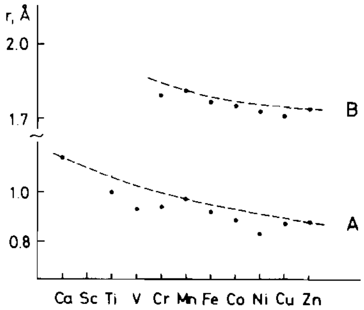

Fig. 1. The variation of octahedral M^{2+} ionic radii according to Cotton and Wilkinson [9] with the ionic radii of Shannon [10] (curve A) and of the bond lengths of difluorides [2–5] (curve B) in the first transition metal series.

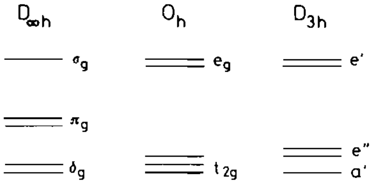

Fig. 2. d Orbital splitting in linear, octahedral and trigonal planar environment (arbitrary scale).

It was noted in our previous paper [1] that the d orbital splitting in a linear MX_2 molecule will be different from that in an octahedral environment as illustrated in Fig. 2. In the linear environment the d_{z^2} (σ_g) orbital is the only unfavorable orbital, in contrast to the two e_g orbitals of the octahedral case, therefore, here the least shielding can be expected for d^4 and d^9 configurations, i.e. for chromium and copper. Accordingly, the largest deviation from the Ca–Mn–Zn interpolation was predicted for chromium and copper in their respective neighborhoods, among the gas-phase MX_2 bond lengths.

There is now a full set of difluoride bond lengths from manganese to zinc illustrated in curve B in Fig. 1, and the shortest bond, indeed, occurs for copper difluoride, in agreement with our prediction. The deviation of the chromium difluoride bond length is conspicuously large from the continuation of the Mn–Zn line which is consistent with the prediction. Note that the bond lengths for the preceding difluorides are not shown on the Figure. CaF_2, in

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*r_g bond lengths (Å): Cr–F 1.795(3) [2], Mn–F 1.811(4) [3], Fe–F 1.769(4) [3], Co–F 1.754(3) [3], Ni–F 1.729(4) [3], Cu–F 1.713(12) [4], Zn–F 1.742(4) [5], Mn–Cl 2.202(4) [6], Fe–Cl 2.151(5) [6], Co–Cl 2.113(4) [6], Ni–Cl 2.076(4) [6], Fe–Br 2.294(7) [6], Ni–Br 2.201(4) [6], Ca–Cl 2.483(7) [7], Ca–Br 2.616(16) [7], Ca–I 2.840(10) [7], Zn–Cl 2.072(4) [8], Zn–Br 2.204(5) [8], Zn–I 2.401(5) [8].

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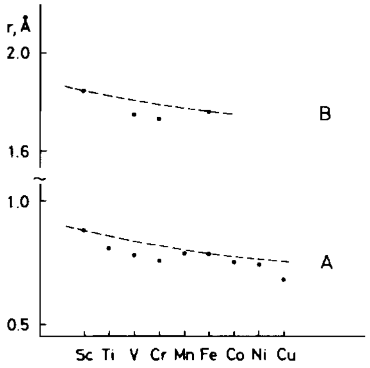

Fig. 3. The variation of octahedral M^{3+} ionic radii with the ionic radii of Shannon [10] (curve A) and of the bond lengths of trifluorides [13, 14] (curve B) in the first transition metal series.

contrast to the other calcium dihalides, is believed to be bent [11, 12]*, while the molecular shape and bond lengths of ScF_2, TiF_2 and VF_2 are not known.

Recently the molecular geometry of several transition metal trifluorides has also been determined, viz. ScF_3 [13], VF_3 [13], CrF_3 [13] and FeF_3 [14]**. This raised the possibility of a similar discussion of bond length variations in transition metal trihalides to that of the dihalides. Figure 3 shows analogous data to those of Fig. 1. The ionic radii of transition metal ions with three positive charges (coordination number 6) are depicted around curve A again after Shannon [10]. In this case $Sc^{3+}(d^0)$ and $Fe^{3+}(d^5)$ have spherical d subshells, and there is no third such ion (d^{10}). The experimental bond lengths for the planar gas-phase trifluorides are depicted in curve B of Fig. 3 and the points for ScF_3 and FeF_3 are connected.

The d orbital splitting in a trigonal planar environment is shown in Fig. 2, displaying a qualitative similarity to that of octahedral environment although the degeneracy and the symmetry of the orbitals are different. There are two unfavorable orbitals in the trigonal planar situation just as in the octahedral situation. Consequently the same qualitative trend can be expected in the bond length variation of MX_3 molecules as in the corresponding M^{3+} ions.

The available experimental data fully support this reasoning. The difference between the ionic radii and the bond lengths of the trifluorides is nearly constant. Accordingly, we predict CrF_3 to have the shortest bond in its vicinity. The overall shortest bond may be similarly predicted for CuF_3.

This rudimentary discussion of geometrical variations implies the following three assumptions for the gaseous dihalides and trihalides that needs further scrutiny: (i) the nature of bonding was supposed to be predominantly ionic, (ii) the electronic configurations were assumed to be high spin, (iii). the metal d orbitals were assumed to be filled in the order shown in Fig. 2.

According to ESR studies of transition metal mono-, di- and trifluoride molecules [15] they all have high spin electronic configuration, indeed, with less than 5% of the free electron density residing on the fluorines. This means that the unpaired electrons are in metal non-bonding orbitals and the bonding is highly ionic. The electron absorption spectra of gaseous transition metal dichlorides are in accordance with high spin configurations and with the order of orbitals δ_g, π_g, σ_g [16]. Photoelectron spectroscopic studies of gas-phase transition metal dihalides [17–19] are also in agreement with all the above. Incidentally, the gas-phase and solid-phase PES spectra of transition metal difluorides and dichlorides are markedly similar [19]. The ligand orbitals in the fluorides are largely separated from the metal d shell in both phases. *Ab initio* MO calculations of several transition metal dichlorides [20] show the same picture. In view of all this our reasoning about the bond length variation seems reasonable. At the same time, we feel that any model, qualitative as it might be, can be useful for such systems for which actual experimental information is scarce.

A final note concerns the relationship of the bond lengths of chromium and iron di- and trifluorides, depicted below:

CrF_2		CrF_3
1.795(3)	$\gg$	1.732(2)
$\vee$		$\wedge$
FeF_2		FeF_3
1.769(4)	$\approx$	1.763(4)

The bond of CrF_2 is much longer than that of CrF_3 while the analogous iron fluorides have the same bond lengths within experimental error. Due to the highly ionic bonding, the larger nuclear charge in CrF_3 means stronger nuclear attraction and accordingly shorter bonds as compared with CrF_2. This seems to be the prevailing effect since the contractions due to the non-spherical d subshell are comparable for CrF_2 and CrF_3; both were predicted to show the largest deviations from the Ca–Mn and Sc–Fe lines, respectively. The larger nuclear charge and stronger attraction in FeF_3 as compared with FeF_2 is as valid here as is the analogous observation for the chromium fluorides. However, a special feature of the FeF_3/FeF_2 comparison is that iron has a spherical d^5 subshell in FeF_3. Thus there is no extra contraction here and this seems to compensate for the stronger

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*The computed Ca–F bond length is 2.030 Å.

**r_g bond lengths (Å): Sc–F 1.847(2), V–F 1.751(3), Cr–F 1.732(2) [13], Fe–F 1.763(4) [14].

attraction due to larger nuclear charge. Hence there is no considerable difference in the bond lengths of the two iron fluorides.

Comparison of bond lengths in the difluoride and trifluoride pairs CrF_2/FeF_2 and CrF_3/FeF_3 is also straightforward on the basis of the curves of Figs. 1 and 3. The decrease of bond length from CrF_2 to FeF_2 is interpreted as a result of general contraction along the series; both metals occupy a position lower than the Ca–Mn–Zn line in their vicinities. For the CrF_3/FeF_3 pair the situation is reversed; Fe–F is longer than Cr–F. Here FeF_3 has no contraction due to the spherical d^5 subshell of iron whereas the largest contraction is expected for chromium with its d^3 electronic configuration.

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