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On the Bond Length Variation in the Dihalides of the First Series Transition Metals

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A few years ago Hargittai and Tremmel [1] called attention to the similarity in the variation of the relative ionic radii (in octahedral environment) and in that in the dihalide bond lengths in the first transition metal series. Curve A in Fig. 1 reproduces the variation of ionic radii according to Cotton and Wilkinson [2]. The points are connected for Ca, Mn, and Zn, *i.e.* for atoms with spherically symmetrical distribution of d electrons. As the shielding of one d electron by another is imperfect, a contraction in the ionic radii is expected. This in itself would account only for a steady decrease in the radii, whereas the ionic radii of all the other atoms are smaller than interpolation would suggest from the Ca–Mn–Zn curve. As is well known, the non-uniform distribution of d electrons around the nuclei is the reason for this phenomenon. The d orbitals split in the octahedral environment into orbitals with t_{2g} and e_g symmetry. The electrons added gradually occupy t_{2g} orbitals in Sc^{2+}, Ti^{2+}, and V^{2+} as well as in Fe^{2+}, Co^{2+}, and Ni^{2+}.* Since these orbitals are not oriented towards the ligands, the shielding between the ligands and the positively charged atomic cores decreases and so does the ionic radius. The fourth electron in Cr^{2+} as well as the ninth in Cu^{2+} occupy e_g orbitals so the shielding increases somewhat and, accordingly, there is a smaller relative decrease in the ionic radii.

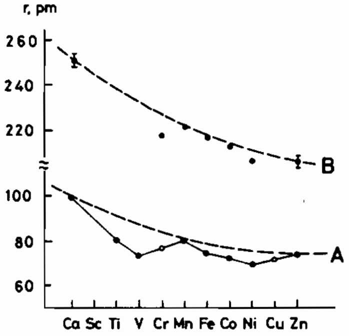

Fig. 1. The variations of octahedral ionic radii according to Cotton and Wilkinson (Curve A) and of the bond length of some dihalides (Curve B) in the first transition metal series.

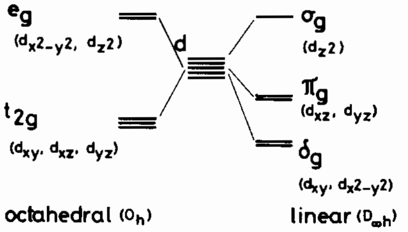

Fig. 2. d orbital splitting in octahedral and linear environment (arbitrary scale).

Figure 1 curve B demonstrates the available experimental data on the bond length in the vapour-phase dichlorides of the first series transition metals. The decrease of the bond lengths is even more pronounced here than that in the ionic radii. Although the experimental data are scarce, it seems to be challenging to account for the emerging pattern that could also facilitate the prediction of unknown features in the bond length variations. The splitting of the d orbitals differs in these $D_{\infty h}$ symmetry linear molecules from that in the octahedral environment, as is shown in Fig. 2. Here the d_{z^2} orbital is the only one oriented towards the ligands. Since this is the least favourable orbital, it will be occupied by the fifth and the tenth electrons only. Thus the least shielding occurs with four and nine electrons. Accordingly, the largest deviations from the Ca–Mn–Zn line are anticipated for the bond lengths in $CrCl_2$ and $CuCl_2$. Preliminary data on $CrCl_2$ are consistent with this prediction.

As for the steeper slope of the bond length variation as compared with the ionic radius variation, the following may be a possible interpretation. The coordination number is smaller in the dihalides than in the octahedral environment. The van der Waals repulsion of the ligands may counter the attraction by the central atom in the octahedral environment and thus may partially compensate the imperfect shielding. On the other hand, the van der Waals repulsion of the ligands have probably not large influence on the metal–halogen bond length in the dihalides.

In the above oversimplified picture, the geometrical variations in the gas phase MX_2 molecules were compared to the variation of the M^{2+} ionic radii as if only electrostatic forces would operate in these systems, whereas their bonds do have an essential amount of covalent character. How can this simple electrostatic argument be valid if the overlap of different molecular orbitals can not be ignored?

The results of a recent He^1 photoelectron spectroscopic study of a series of MX_2 gas phase transition metal dihalides [3] show this more quantitative description of the electronic structure to agree nicely with the above highly qualitative but descriptive

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*Here and later high spin configurations are supposed.

picture. According to ref. [3], the highest occupied molecular orbitals in the series of dihalides from manganese towards nickel are essentially metal 3d orbitals, *viz.* $1\delta_g$, $3\pi_g$, and $9\sigma_g$, that are occupied by electrons in exactly the same sequence as in the high spin description used in our reasoning. These metal d orbitals were found to have progressively increasing binding energies that accounts for the systematic decrease in their radii. This is invariant to the relative amount of ionic and covalent character in their bonding. However, the ionic character is most probably increasing as going towards nickel as also indicated by the calculated charge distribution [3].

References

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