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Structures of some transition metal fluorides and oxofluorides and the VSEPR model

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The work reported here is part of an investigation into the reasons why some transition metal molecules appear to be exceptions to the VSEPR model [1–3]. It was first suggested over 20 years ago that if the core of an atom in a molecule is not spherical, deviations from the VSEPR predictions might be observed [1,2]. A core may not be spherical because it has an incomplete d shell as is the case for many transition metal molecules or because it is polarized by the ligands.

In the present work we have studied the Laplacian of the electron density of several of chromium(VI) and molybdenum(VI) molecules whose structures are not in accord with the predictions of the VSEPR model. $CrOF_4$ and $MoOF_4$ have square pyramidal structures whereas the analogous main group molecule SOF_4 and essentially all other five-coordinated main group element molecules have trigonal bipyramidal structures [1–3]. CrO_2F_2 is also an apparent exception to the VSEPR model. Although it has the predicted approximately tetrahedral structure, the angle between the double-bonded oxygen atoms OCrO is smaller than the FCrF angle, whereas the VSEPR model predicts that the OCrO angle should be the largest just as the OSO angle is the largest in SO_2F_2.

The Laplacian of the electron density [4] reveals features of the electron density distribution that are not evident in the electron density distribution itself. In particular, for free atoms it shows spherical regions of concentration of electron density separated by regions of electron density depletion corresponding to the shell structure of the atom. In a covalent molecule, the spherical region of charge concentration corresponding to the valence shell is distorted to give several separate regions of charge concentration that in almost all cases correspond in number and position to the bonding and non-bonding electron pairs of the VSEPR model [4,5]. In a transition metal molecule, the valence shell charge concentration is missing but distortions are observed in the outer shell of the core resulting from the polarization of the core by the ligands. In the case of $CrOF_4$ and $MoOF_4$, there is a charge concentration in the outer shell of the core opposite each of the bonds, but that opposite the doubly bonded oxygen atom is larger than that opposite each fluorine atom giving the core an approximate egg shape [6]. This non-spherical core stabilizes the square pyramid structure with respect to the trigonal bipyramidal structure predicted by the VSEPR model for atoms with spherical cores. The Laplacian of the Cr core in CrO_2F_2 is also distorted to produce large charge concentrations opposite each O atom, which in turn causes the OCrO angle to be smaller than the FCrF angle [6].

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