

V. SUMMARY

Although the VSEPR model has a central role in structural chemistry of main group compounds, it has become clear by theoretical and experimental works, that many transition metal complexes favour other structures than those predicted by this model. The geometry of high-valent transition metal complexes depends on the nature of the ligands. Electronegative, π -donating ligands, such as halides and alkoxides, favour the octahedron, whereas σ -bonding ligands, like methyl groups, prefer non-octahedral structures. From this point of view it is of interest to synthesize and to examine novel homoleptic methyl compounds of molybdenum and some derivatives.

This work covers the preparation and characterization of the hexacoordinated, neutral molybdenum compounds $\text{Mo}(\text{CH}_3)_6$, $\text{Mo}(\text{CH}_3)_5\text{OCH}_3$, $\text{Mo}(\text{CH}_3)_4(\text{OCH}_3)_6$ and of the tungsten compound $\text{W}(\text{CH}_3)_3\text{Cl}_3$. The structures of all of these molecules were determined by single-crystal X-ray diffraction. They all have a distorted trigonal prismatic coordination geometry with overall C_{3v} -symmetry. The idea behind these syntheses was to create a transition between the trigonal prism and octahedral geometries. Beginning with trigonal prismatic $\text{Mo}(\text{CH}_3)_6$ every methyl group was exchanged successively by π -donor ligands, to observe when the trigonal prismatic system begins to distort towards an octahedral system. In this context $\text{Mo}(\text{OCH}_3)_6$ was chosen as the octahedral reference system, synthesized and structurally investigated. $\text{Mo}(\text{OCH}_3)_6$ appears to have a disordered structure and therefore it was necessary to have Raman spectroscopic data, besides the crystal structure analysis, to confirm the O_h -symmetry of the MoO_6 -core. The comparison with the tungsten compound $\text{W}(\text{OCH}_3)_6$ led to the same result.

Unfortunately it was not possible to synthesize the two compounds $\text{M}(\text{CH}_3)(\pi\text{-L})_5$ and $\text{M}(\text{CH}_3)_2(\pi\text{-L})_4$ [$\text{M} = \text{Mo}, \text{W}$], which would have been decisive for observing the distortion toward O_h -symmetry. Only WCH_3Cl_5 proved to be easy to synthesize. The synthesis and characterization of the twice methylated species of both metals can be regarded as an important challenge for further works in this area.

The heptacoordinated anion $[\text{Mo}(\text{CH}_3)_7]^-$ was also prepared and structurally determined by X-ray diffraction. The anion has a capped octahedral geometry with overall C_{3v} -symmetry, which is influenced by the contact of the lithium ion to the three basal methyl groups.

$\text{Mo}(\text{CH}_3)_5$ has also been prepared. Single crystal structure determination gives a full account of the molecular structure. $\text{Mo}(\text{CH}_3)_5$ has a square pyramidal C_{4v} -geometry. Pentamethylmolybdenum(V) is paramagnetic and gives a very weak e.p.r. signal which is in full agreement with its structure.

Molecular orbital calculations confirm that the trigonal prismatic, the capped octahedron and the square pyramid are favoured structures, which avoid 180° arrangements of ligands. The same predictions were obtained by the extended VSEPR model, which considers the core electrons. The core electrons are polarized by the covalent M-CH₃-bonds and it appears impossible for the ligands to occupy an 180° arrangement. This corresponds to *Pauling's* valence bond theory which predicts that in case of sd^n -hybridization, angles of 180° do not exist. Only if the contribution of p-orbitals to the hybrid orbitals increases, then 180° arrangements occur. Even if the capped octahedron of [Mo(CH₃)₇]⁻ and the square pyramid in d^1 -Mo(CH₃)₅ are the structures with the lowest mutual ligand repulsion, it can be concluded that the VSEPR model is not the definitive model for the geometry of homoleptic methyl compounds.