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Preliminary communication

The Electronic Factors Governing the Relative Stabilities of Geometric Isomers of Octahedral Complexes with π-acceptor and π-donor Ligands

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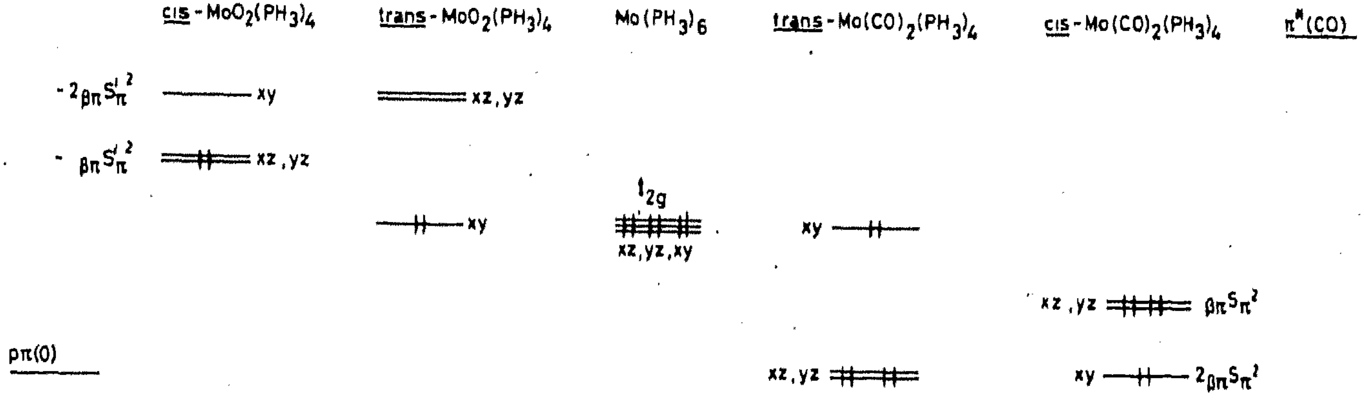
Summary

Extended Hückel molecular orbital calculations have shown that the relative stabilities of geometric isomers in 16, 17 and 18 electron octahedral complexes containing strong π-acid or π-donor ligands depend on the number of valence electrons and in a complementary fashion on whether the ligands are π-donors or π-acceptors.

Chemical and electrochemical studies, particularly by Bond and Colton (1), have given rise to the interesting observation that although in the 18 electron complexes $M(CO)_2(diphos)_2$ (M = Cr, Mo or W) and $Mn(CO)_3(diphos)X$(2) the more stable isomer is that which has mutually cis- carbonyl ligands, in the related 17 electron complexes it is the trans- and mer- isomers which are thermodynamically preferred. For octahedral dioxo-complexes it has been noted that it is trans- isomer which is more stable when the electron count is 18, e.g.



Stabilization Energies

18 electron	$6\beta_{\pi}S'^{2}_{\pi}$	<	$8\beta_{\pi}S'^{2}_{\pi}$	$8\beta_{\pi}S^{2}_{\pi}$	~	$8\beta_{\pi}S^{2}_{\pi}$
17 electron	$7\beta_{\pi}S'^{2}_{\pi}$	<	$8\beta_{\pi}S'^{2}_{\pi}$	$8\beta_{\pi}S^{2}_{\pi}$	>	$7\beta_{\pi}S^{2}_{\pi}$
16 electron	$8\beta_{\pi}S'^{2}_{\pi}$	~	$8\beta_{\pi}S'^{2}_{\pi}$	$8\beta_{\pi}S^{2}_{\pi}$	>	$6\beta_{\pi}S^{2}_{\pi}$

Figure 1

Stabilisation and destabilisation effects of π-acceptor and π-donor ligands on the metal t_{2g} set in an octahedral complex, expressed in terms of the angular overlap functions.

$[MoO_2Cl_4]^{4-}$ (3), and the cis- isomer in 16 electron complexes such as $[MoO_2(CN)_4]^{2-}$(4).

Extended Hückel molecular orbital calculations(5) which have been completed on $Mo(CO)_2(PH_3)_4$, $Mo(CO)_3(PH_3)_3$, $MoO_2(PH_3)_4$ and the related cationic species not only have shown that this phenomenon has a simple explanation in terms of the occupancies of the highest occupied molecular orbitals, but also indicated that the complementary nature of the effects observed for π-acceptor ligands such as CO and π-donor ligands such as O^{2-} leads to a reversal of the preferred stability order for 16 and 18 complexes of these ligands.

Table I

Sum of occupied 1 electron energy levels for some carbonyl and oxo-complexes

Compound	No. of Valence Electrons	Energy (eV)	Stable Isomer	Energy Diff. (eV)
cis-$Mo(CO)_2(PH_3)_4$	18	-950.852	cis-	0.377
trans-$Mo(CO)_2(PH_3)_4$	18	-950.475		
cis-$Mo(CO)_2(PH_3)_4^+$	17	-957.664	trans-	0.134
trans-$Mo(CO)_2(PH_3)_4^+$	17	-957.798		
cis-$MoO_2(PH_3)_4$	18	-815.932	trans-	0.560
trans-$MoO_2(PH_3)_4$	18	-816.492		
cis-$MoO_2(PH_3)_4^{2+}$	16	-795.365	cis-	0.473
trans-$MoO_2(PH_3)_4^{2+}$	16	-794.892		
mer-$Mo(CO)_3(PH_3)_3$	18	-1054.265	fac-	0.712
fac-$Mo(CO)_3(PH_3)_3$	18	-1054.977		
mer-$Mo(CO)_3(PH_3)_3^+$	17	-1054.442	mer-	0.145
fac-$Mo(CO)_3(PH_3)_3^+$	17	-1054.297		

Table I summarises the results of the molecular orbital calculations and demonstrates that this type of calculation accurately reflects the observed stability order for 18 and 17 electron carbonyl and 18 and 16 electron oxo-complexes. Figure I represents schematically the energies and orbital occupations of the highest occupied molecular orbitals for *cis-* and *trans-* $Mo(CO)_2(PH_3)_4$ and $MoO_2(PH_3)_4$. The molecular orbitals are localised predominantly on the metal and are derived from the t_{2g} set of the parent octahedron, $Mo(PH_3)_6$, and their energies reflect the extent of overlap, S_π, between the linear combinations of the ligand π-orbitals and the appropriate component of the metal t_{2g} set. In the conventional fashion the $\pi^*(CO)$ interaction leads to a stabilization and $\pi(O)$ a destabilization of the t_{2g} orbitals. Furthermore, the extent of this interaction can be estimated approximately from the angular overlap model expression(6), $\Delta e = \beta_\pi S_\pi^2$, and is given in the Figure for each isomer and for 16, 17 and 18 electron configurations. These suggest that in the 18 electron carbonyl complex, and 16 electron dioxo-complex the *cis-* and *trans-* isomers are equally stable, which is at variance with the results of the more detailed calculations in Table I which predicts the *cis-* isomer to be more stable for both complexes. This difference arises because of the neglect of the ligand-ligand overlaps in the angular overlap model, which can result in a significant stabilization for *cis-* ligands with short metal-ligand bond lengths. With this correction added the correct stability order is predicted by both models, and the complementary nature of the relative stabilities of the isomeric possibilities for π-acceptor and π-donor ligands is accounted for.

Figure 2 illustrates that similar arguments may be used to account for the relative stabilities of the *mer-* and *fac-* isomers of $Mo(CO)_3(PH_3)_3$. More detailed calculations have also demonstrated that the barrier for the intramolecular interconversion of the isomeric possibilities is reduced in the 17 electron carbonyl complexes compared with those for the 18 electron complexes,

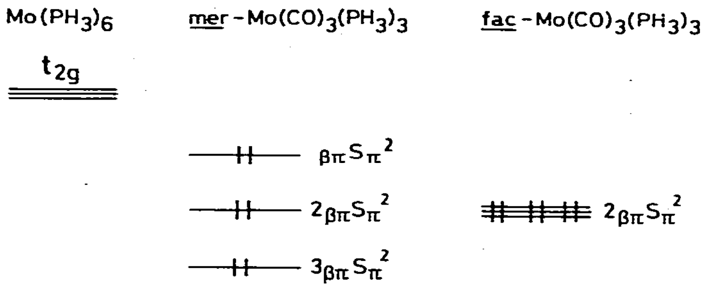


Figure 2 Stabilisation of the t_{2g} set in mer- and fac- $Mo(CO)_3(PH_3)_3$.

thereby accounting for the observed facile isomerisation of complexes such as cis-$Cr(CO)_2(diphos)_2^+$ and $Mn(CO)_3(diphos)X^+$.

Although for 16 and 18 electron complexes the geometric preferences for the π-donor and π-acceptor ligands are in conflict, for 17 electron complexes the trans- isomer is preferred for both ligand types, and this leads to the interesting prediction the complexes of the type trans- $Mo(CO)_2O_2L_2^+$, having both π-donor and acceptor ligands, may have exceptional stabilities.

In addition the calculations suggest that in the case of the neutral carbonyl complexes the splittings within the t_{2g} set of orbitals is sufficiently large, especially in the trans- complexes, to be detected by UV photoelectron spectral studies.

Acknowledgement

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