

## Electronic Mechanisms Associated with Bond-Stretch Isomerism in Transition Metal Complexes

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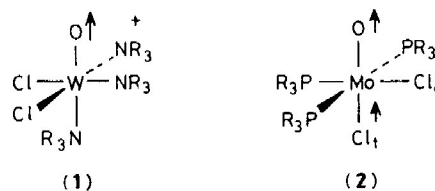
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Two electronic mechanisms are presented which can explain the existence of bond-stretch isomerism in transition metal complexes: the first entails a real level crossing, and the second, best regarded as a second-order Jahn–Teller effect, has links with bond localization problems in allyl anion and benzene.

It has become clear over the past few years that a new type of isomerism exists. There are now molecules in the solid state and also in solution which interconvert with varying degrees of ease, and whose only structural difference is a dramatic difference in the length of one or several bonds. We call this bond-stretch isomerism after earlier theoretical work dealing with main group systems.<sup>1</sup> (1) and (2) show some relevant bond lengths in two sets of molecules studied by Wieghardt and colleagues,<sup>2</sup> and by Chatt, Manojlović-Muir, and Muir, respectively.<sup>3</sup> The second group used the term 'distortional isomerism' to describe the effect which so far is restricted to transition metal examples as far as crystallographic characterization is concerned. Notice in (1) and (2) the large difference in M–O distance. These molecules are representatives of a class of M<sup>IV,V</sup> (M = Mo, W) compounds which may be made in 'blue' and 'green' forms, and show different  $\nu(\text{MO})$  frequencies. Also known are some isoelectronic rhenium nitrides which show large differences in their <sup>15</sup>N chemical shifts.<sup>4</sup> In this communication we describe two mechanisms which may give rise to this effect, and how the nature of the other ligands, co-ordinated to the metal, influences the electronic picture.

One possibility is the crossing of two electronic states, with different bonding properties, as the M–O linkage is stretched. Figure 1 shows how this may occur in the *cis*-(WOC<sub>2</sub>H<sub>4</sub>)<sup>3-</sup> model complex in an idealized octahedral geometry. The *xy* orbital is not involved in interaction with any orbital located on the moving oxygen atom, and so remains unchanged in energy on distortion. However *y*<sub>2</sub> and *x*<sub>2</sub> orbitals are involved



(1-a)	(1-b)	(2-a)	(2-b)		
W–O	1.719 (18)	1.893 (20) Å	Mo–O	1.676 (7)	1.803 (11) Å
			Mo–Cl <sub>c</sub>	2.551 (3)	2.426 (6) Å

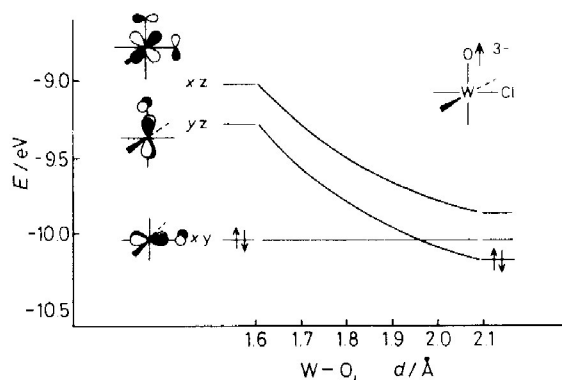


Figure 1. Energy of the low-lying d orbitals in the model complex  $\text{cis}-(\text{WOClH}_4)_3^-$  as a function of W-O bond stretching.

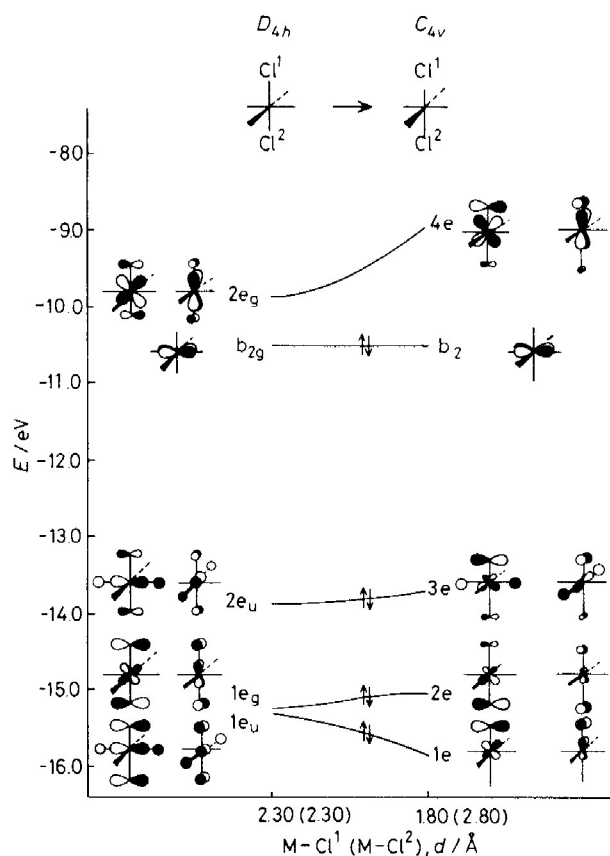
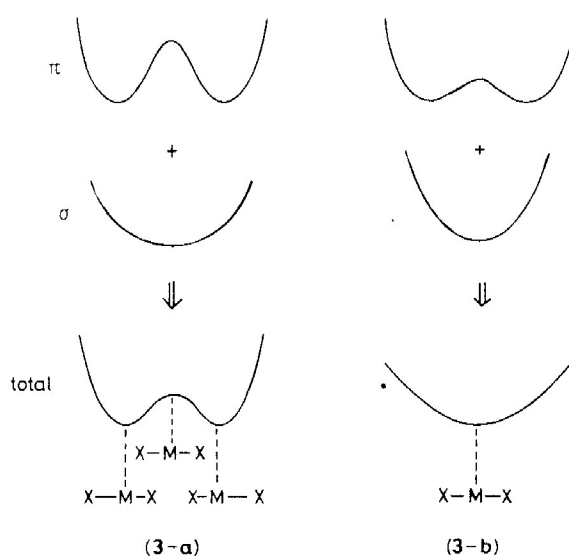


Figure 2. Orbital diagram for the asymmetric distortion of the two Mo-Cl bonds in the model complex  $\text{trans}-(\text{MoCl}_2\text{H}_4)_2^-$ .

in  $\pi$ -antibonding interactions with the oxygen, and therefore decrease in energy on M-O bond stretching. Since there are initially two electrons in the M-O non-bonding orbital before the crossing, and two in an M-O antibonding orbital ( $yz$ ) after the crossing, the metal-oxygen linkages are formally described as  $\text{M}=\text{O}$  and  $\text{M}=\text{O}$ , respectively (all the known examples are  $d^1$  or  $d^2$  systems). At the same time, the two electrons which were M-Cl antibonding in  $xy$  become M-Cl non-bonding in  $yz$  after the crossing, so that the M-Cl bond should be reinforced in an analogous way. In fact this bond formally has multiple bond character, an area which we believe requires further examination.



Since the  $xy$  orbital is involved in  $\pi$ -interactions with the ligands *cis* to oxygen,  $\pi$ -donor ligands in this position favour an orbital crossing by reducing the HOMO-LUMO separation at the left-hand side of Figure 1. Conversely  $\pi$ -acceptor ligands at these sites disfavour the crossing. Similar considerations show that  $\pi$ -acceptors and not  $\pi$ -donors *trans* to the oxygen should encourage a crossing. Application of these ideas to (1) and (2) suggests that (2) is probably a poor candidate for a crossing but (1) is a possibility. These conclusions are confirmed by molecular orbital calculations of the extended Hückel type [replacing  $\text{PR}_3$  by  $\text{PH}_3$  in (2) and using three  $\text{NH}_3$  molecules in (1)]. Our models for (1-a) and (1-b) are found to have different electronic configurations. Their interconversion is thus forbidden. No crossing is found in our model for (2) upon M-O stretching.

The distortion in (2) is, in fact, of a different type from that in (1), since there is significant motion of the ligand (chlorine) *trans* to oxygen. The actual motion appears to be an asymmetric one at the metal centre. We may view such a distortion in terms of a second-order Jahn-Teller effect which mixes symmetric and antisymmetric orbitals of  $\pi$ -type<sup>†</sup> on distortion. Figure 2 shows the results of a calculation for the hypothetical species,  $\text{trans-MoCl}_2\text{H}_4^{2+}$ , where  $1e_u$  and  $2e_g$  orbitals mix strongly on distortion. If the d manifold ( $b_{2g}$  and  $2e_g$ ) contains one or two electrons, then the asymmetric distortion is clearly favoured on  $\pi$  grounds. It is interesting that in the molecule  $\text{MoCl}_2(\text{TTP})$  (TTP = dianion of 5,10,15,20-tetra-*p*-tolylporphyrin) an asymmetric distortion is actually observed,<sup>5</sup> with  $\text{Mo-Cl} = 2.276(4), 2.347(4)$  Å.

The actual energetics of the distortion are, however, a superposition, not only of this  $\pi$ -effect (which gives rise to a double minimum Cl-M-Cl and Cl-M-Cl), but of a  $\sigma$ -contribution, with a minimum at the symmetric geometry, which resists distortion (3). If the  $\pi$ -effect dominates, (3-a), as is calculated in the model complex  $\text{trans-MoCl}_2\text{H}_4^{2+}$ , then two minima result. If the  $\sigma$ -effect dominates, only one minimum will be found, (3-b). It is that which is found in  $\text{CO}_2$  (but here the effect we have discussed manifests itself as a positive bond-bond interaction force constant<sup>6</sup>), allyl anion,<sup>7</sup> and benzene.<sup>8</sup> (3-a) applies to perovskite distortions<sup>9</sup> and is behind the non-existence of a cyclic  $\text{N}_6$  structure.<sup>8</sup> Although

<sup>†</sup>  $\pi$ -orbitals are those involving chlorine lone pairs perpendicular to the Mo-Cl bonds. Some of them ( $1e_u$  and  $2e_u$ ) mix with the  $\sigma$  Mo-H bonds (whose lengths are held fixed on distortion), but not with the  $\sigma$  Mo-Cl bonds whose lengths are varied.

we are reaching here the limits of the extended Hückel method, which is not expected to give consistently the exact balance between two effects working in opposite directions, we think (3a) should describe the bond-stretch isomerism in some of these transition metal systems where no crossing is found.

We also believe that the metrical details of this type of isomerism are not yet fully revealed and that these systems deserve extremely careful crystallographic examination.

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