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# Electronic mechanisms associated with bond-stretch isomerism in transition metal complexes

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## Bond-Stretch Isomerism in Transition-Metal Complexes

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**Abstract:** The occurrence of bond-stretch isomers is now experimentally established via X-ray crystal structure determination. These are molecules, also called distortion isomers, whose only structural difference is a dramatic difference in the length of one (usually M–O) or several bonds. In this paper we provide two electronic mechanisms by which this may occur. One involves a real electronic crossing of filled and empty orbitals (a first-order Jahn–Teller effect) and the other a second-order Jahn–Teller distortion of the type important in other bond localization problems (allyl anion, benzene, etc.). The electronic conditions for optimal observation of each process are described for  $d^1$  and  $d^2$  transition-metal complexes. The ideas are extended to  $d^9$   $\text{Cu}^{\text{II}}$  systems.

Isomerism is a concept that is close to the intellectual center of chemistry. Even when little was known about the details of molecular geometry, the ideas of linkage, and optical and geometrical isomerism provided much of the richness of organic and inorganic chemistry. Molecules differing in the way atoms were linked up to each other, or, once connected in a specified manner, distinct in the way that they were arranged in space, provided a remarkable fine tuning of the physical, chemical, and biological properties of molecules.<sup>1</sup>

With time the idea of a conformation has emerged. We have many examples: boat versus chair cyclohexane, staggered versus eclipsed ethane,  $\text{Fe}(\text{CO})_4$  (ethylene) with the ethylene in the equatorial plane of a trigonal bipyramid or rotated  $90^\circ$  away from that equilibrium geometry, etc. Whether two molecules are considered to be related as isomers or as different conformations was recognized as a question of the available thermal energy: cis- and trans-substituted ethylenes are separated by less than 70 kcal/mol, staggered and eclipsed ethane by less than 3 kcal/mol. If ambient conditions, i.e., room temperature, are to be taken as a standard, then it is still possible to define a border between isomers and conformers—isolation at room temperature and persistence for a few minutes requires a barrier typically greater than 30 kcal/mol between two interconvertible but different equilibrium geometries.<sup>2</sup>

We now have available molecules that illustrate the whole gamut of energy barriers or time scales for interconversion, from 0 to >100 kcal/mol. Even the hitherto sacrosanct optical isomerism of four-coordinate carbon is recognized as just being due to a large barrier to the tetrahedral-square-planar interconversion. It has become the target of substitutional strategy to subvert that barrier.<sup>3</sup> Almost any geometrical preference can, by design or chance, be turned upside down. Push–pull stabilized or sterically hindered ethylenes twisted near  $90^\circ$  and eclipsed ethanes<sup>4</sup> are just two of them.

One fundamental idea however has seemed to have survived—to have isomerism a “real” difference in the three-dimensional arrangement of atoms in a molecule is needed. Some internal rotation of one part of a molecule relative to another, a topological change, is required. Just stretching bonds alone is not good enough. Chemists have not been willing to admit the complete rupture of a bond (for example,  $\text{H}_2 \rightarrow 2\text{H}^\bullet$  or cyclobutane  $\rightarrow \text{CH}_2\text{CH}_3\text{CH}_3\text{CH}_2^\bullet$ ) as an example of isomerism. This they have chosen to call a chemical reaction. At another extreme of energy, the small differences in the structures of distinct (but constitutionally identical) molecules in the unit cell of a crystal with several molecules in the asymmetric unit are usually viewed as just being due to the small influence of packing forces and not as isomerism.

But this last bastion of isomerism has been quietly disappearing. There are now molecules in the solid state, and even in solution, which interconvert with varying ease, and whose *only* structural difference is a relatively small increment in the length of one or several bonds. We initially exclude from this category several Jahn–Teller distorted systems. In the extraordinary structural chemistry of  $\text{Cu}^{\text{II}}$ , we find examples of Cu–X linkages spread over an enormous range (2.3–3.2 Å for X = Cl, for example). Here the potential surface is a very soft one and the actual Cu–X distances that are found appear to be very much determined by the crystal environment.<sup>5</sup> We will, however, return to these systems later.

## Bond-Stretch Isomerism

The term “distortional isomerism” was first proposed by Chatt, Manojlovic-Muir, and Muir<sup>6a</sup> in 1971 to characterize metallic complexes that differ only by the length of one or several bonds. The term has gained some currency. However, in this paper we will describe the phenomenon as bond-stretch isomerism. This term both describes more precisely the particular sort of distortion that is observed in these compounds and connects up to an existing theoretical description of the phenomenon. There are, as yet, a very limited number of well-established examples of this new type of isomerism. Two structures of *cis-mer*-( $\text{MoOCl}_2(\text{R})_3$ ) have been isolated<sup>6,7</sup> in the solid phase, mainly differing in the lengths of Mo–O and Mo–Cl bonds, with Cl<sub>l</sub> trans to oxygen (structures **1a** and **1b**). In **1a** Mo–O is short and Mo–Cl<sub>l</sub> long, the reverse being true in **1b**. However, in solution, only isomer **1a** is observed<sup>6a</sup>

(1) Mislow, K. *Introduction to Stereochemistry*, W. A. Benjamin: New York, 1966, and references therein. Slanina, Z. *Contemporary Theory of Chemical Isomerism*; D. Reidel: Dordrecht 1986.

(2) E. L. Muettterties (*Inorg. Chem.* **1965**, *4*, 769) gives a clear influential early statement of the importance of time scales in discussing isomerism.

(3) (a) Hoffmann, R.; Alder, R. W.; Wilcox, C. F. *J. Am. Chem. Soc.* **1970**, *92*, 4992–4993. (b) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeyer, R.; Pople, J. A. *Ibid.* **1976**, *98*, 5419–5427 and subsequent papers.

(4) Seiler, P.; Weisman, G. R.; Glendening, E. G.; Weinhold, F.; Johnson, V. B.; Dunitz, J. D. *Angew. Chem., Int. Ed. Engl.*, in press.

(5) (a) Gazo, J.; Bersuker, I. B.; Garaj, J.; Kabesova, M.; Kohout, J.; Langfelderova, H.; Melnik, M.; Serator, M.; Valach, V. *Coord. Chem. Rev.* **1976**, *19*, 253–297. (b) Dunitz, J. D.; Orgel, L. E. *J. Phys. Chem. Solids* **1957**, *3*, 20–29, 318–323. (c) Orgel, L. E.; Dunitz, J. D. *Nature (London)* **1957**, *179*, 462–465. (d) Dunitz, J. D.; Orgel, L. E. *Adv. Inorg. Chem., Radiochem.* **1960**, *2*, 1–60. (e) Dyachkov, P. N.; Levin, A. A. *Vibrational Theory of the Relative Stability of Isomers in Inorganic Molecules and Complexes* VINITI, Moscow, 1987.

(6) (a) Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1971**, 655–656. (b) Butcher, A. V.; Chatt, J. *J. Chem. Soc. A* **1970**, 2652–2656. (c) Manojlovic-Muir, L. *Ibid.* **1971**, 2796–2800. (d) Manojlovic-Muir, L. *J. Chem. Soc., Chem. Commun.* **1971**, 147. (e) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1972**, 686–690.

(7) In fact the identity of these molecules is slightly different. **1a** contains the phosphine  $\text{PMe}_2\text{Ph}$  but **1b** contains  $\text{PEt}_2\text{Ph}$ . The green isomer with R =  $\text{PMe}_2\text{Ph}$  has been characterized later ( $\text{M}=\text{O} = 1.80 \text{ \AA}$ ): Haymore, B. L.; Goddard, W. A., III; Alison, J. C. *Proc. Int. Conf. Coord. Chem.*, **23rd** **1984**, 535.

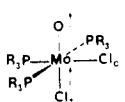
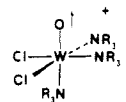
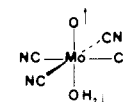
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<sup>§</sup> Cornell University.

so that it is not clear whether the existence of two bond-stretch isomers in the solid state is simply due to a packing effect or reveals some more fundamental phenomenon.

					
1		2		3	
1-a	1-b	2-a	2-b	3-a	3-b
Mo-O	1.676 (7) 1.803 (11)	W-O	1.719 (18) 1.893 (20)	Mo-O	1.60 (2) 1.72 (2)
Mo-Cl <sub>1</sub>	2.551 (3) 2.426 (6)			Mo-(OH <sub>2</sub> )	2.48 (3) 2.96 (8)
				Mo-(CN) <sub>av</sub>	2.19 2.13

Actually compounds **1a** and **1b** are not quite as unique as we make them out to be. They are members of a class of compounds<sup>8</sup> which come in blue and green variants. Cotton and co-workers<sup>8c</sup> have recently reported the structure of green  $\text{MoOCl}_2(\text{PMePh}_2)_3$ . The "blue" or "green" color characterization of course reflects a real but relatively small difference in the visible absorption spectrum of the isomers. Other physical properties also differ, for instance the Mo-O stretch is at  $954\text{ cm}^{-1}$  in **1a** and at  $943\text{ cm}^{-1}$  in **1b**. Bond-stretch isomerism has also been reported in a bimetallic complex<sup>9</sup> and in rhenium nitride compounds.<sup>10</sup>

Chemists appear not to have been very excited over this striking new kind of isomerism but interest has been recently renewed by the work<sup>11</sup> of Wiegardt and co-workers on  $(\text{LWOCl}_2)^+$  complexes ( $\text{L} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane). Both in the solid state and in solution, two isomers are stable, which differ mainly in the length of the W-O bond (**2a** and **2b**). For these species, a packing effect is thus excluded. A barrier of at least 20 kcal/mol has to be cleared to transform one isomer to the other. This value seems very large with respect to the rather small geometrical change in going from **2a** to **2b**. Finally, two bond-stretch isomers are also found<sup>12</sup> for the  $(\text{MoO}(\text{OH}_2)(\text{CN})_4)^{2-}$  complex in the solid phase: both Mo-O and Mo-OH<sub>2</sub> bonds are lengthened while the mean value of the four Mo-CN bond lengths decreases (**3a** and **3b**).

There are so far really few well-characterized bond-stretch isomers, so it is difficult to generalize as to the origin of the phenomenon. There are, however, some common characteristics in compounds **1-3**. First there is always a large change in the metal-oxygen bond length between isomers (0.12 to 0.17 Å), accompanied by more or less apparent variations of the other metal-ligand bond lengths. The M-O bond length is in the range expected for multiple bonding. All the complexes are relatively high oxidation states of Mo or W, octahedral, and electron deficient. The electron counts are  $d^2$  for **1** and **3** and  $d^1$  for **2**. The relative paucity of electrons, coupled to the availability of orbitals and variety of ligands to tune the energy of these orbitals, will eventually turn out to be important. But first let us say something about the bond lengths in these compounds, because they are the main variable.

(8) (a) Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347-352. (b) Backes-Dahmann, G.; Wiegardt, K. *Inorg. Chem.* **1985**, *24*, 4044-4049. (c) Young, C. G.; Enemark, J. H. *Ibid.* **1985**, *24*, 4416-4419. (d) There is a suggestion of a similar isomerism in  $(\text{WOCl}_2)^{2-}$ : Sharp, C.; Hills, E. F.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.*, in press. (e) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 2848-2852.

(9) Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594-1602.

(10) Considerable work has been performed on rhenium nitrides isoelectronic with the molybdenum oxides described here. (a) B. Haymore, private communication. (b) Dilworth, J. R.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *Inorg. Chim. Acta* **1983**, *71*, 21.

(11) Wiegardt, K.; Backes-Dahmann, G.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 777-778.

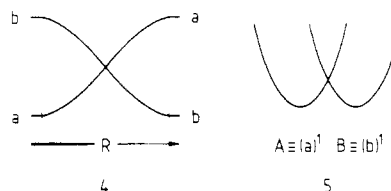
(12) Wiegardt, K.; Backes-Dahmann, G.; Holzbach, W.; Swiridoff, W. J.; Weiss, J. *Z. Anorg. Allg. Chem.* **1983**, *499*, 44-58. Note, however, that the M-OH<sub>2</sub> bond length value found in **3b** (2.96 Å) is probably unrealistic and that the shortening of the mean value of the Mo-CN bond lengths is hardly significant (K. Wiegardt, private communication).

The bond-stretch isomers must be distinguished from the many cases where in the solid state (and probably in liquid crystals too) there are two or more molecules in the asymmetric unit. These *always* differ in dimensions in small ways—typically by less than 0.03 Å in any bond length, often by much more in internal rotations, etc. The nonequivalence of the detailed geometrical structures of such molecules is traceable to the consequences of the 1-5 kcal/mol that is the typical result of the balance of packing forces in the crystal. That nonequivalence is a wonderful indicator of the persistence of molecular geometry, including conformation, in any environment, and, at the same time, a nice internal *test* of the accuracy and precision of the crystallographic structure determination. We know that molecules in slightly different environments will have slightly different bond lengths.<sup>13</sup> If the crystal structure shows that such differences are too large, there is often something wrong with the quality of the structure determination. Here though, we must add our qualifier concerning the structural chemistry of Cu<sup>II</sup>. Structural differences for that ion are often enormous.<sup>14</sup>

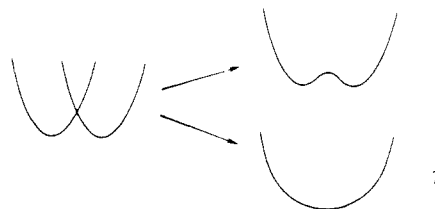
The bond-stretch isomers are different. They really have substantially different bond lengths, though it seems that the variation is mainly restricted to the M-O distance. Since the bond lengths are the critical differentiating factor, we must rely on the accuracy of the experimental structure determinations. The structural parameters cited in **1-3** are presented "neutrally", with the number of significant figures given in the original paper.<sup>15</sup> The determinations are of varying quality and, as we will see below, we have some reason to propose a greater variation in the metal-ligand (other than oxygen) bond length than that which is observed. The phenomenon of bond-stretch isomerism is so interesting that it merits analysis and reanalysis by the very best structural techniques available to the profession.

If we accept the experimental demonstration of such isomerism, how can it be explained? There are two possibilities, which may merge with each other:

(1) Along a simple bond stretch (or some other deformation) coordinate there might be a level crossing of a set of levels which are less than fully occupied. This is shown schematically in **4** for a configuration containing one electron and leads to a configuration diagram in **5**. If the states A and B resulting from configurations (a)<sup>1</sup> and (b)<sup>1</sup> are of the same symmetry, configuration interaction



will mix them and from the large experience of molecular calculations it is unlikely that two minima will survive (**6**) if the geometrical excursion is small. More often a surface such as **7** will result, perhaps carrying a memory of its origins in its anharmonicity. But if the states A and B are of different spatial

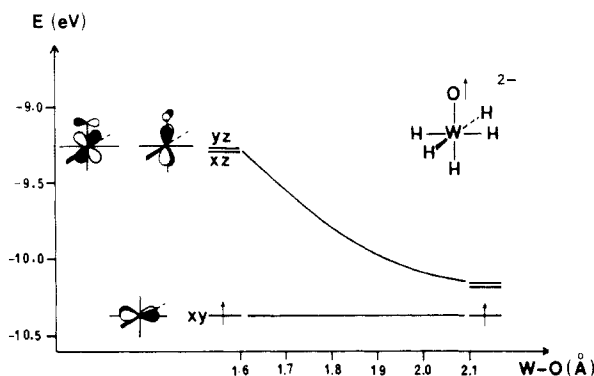


geometry, two minima are likely to survive, and a large barrier arises for their interconversion. This is clearly more likely for

(13) The existence of such effects has had an impact in the area of structural correlation (Bürgi, H.-B. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 460-473).

(14) Bersuker, I. B. *The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry*; Plenum: New York, 1984.

(15) We do not wish to try to evaluate these structure determinations in terms of "quality" here. It is, however, quite clear that some are better than others.

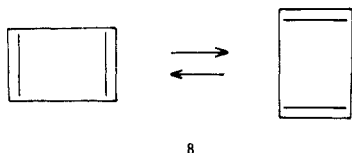


**Figure 1.** Energy of the low-lying d orbitals in the model  $d^1$  complex  $(WOH_3)^{2-}$  as a function of W-O stretching.

odd rather than even electron systems if the levels a and b are of different symmetry.

The phenomenon here is of course related to the presence of different potential energy curves for the different electronic states (ground and excited) of molecules. In that sense the phenomenon is trivial—one surface is the ground state, the others are excited states. The problem of bond-stretch isomers is then that of the coexistence of difficultly interconvertible electronic states of molecules, perhaps quite a common occurrence. But then let us think. How many crystals are known that contain an excited state molecule? We have, however, recently predicted<sup>16</sup> that there are two structures, linear and bent, for the triatomic  $P_3^-$  which are close in energy and correspond to two different electronic states.

Much rarer indeed would be case 6, conformational curves of the same symmetry which after CI still give a double minimum. Actually this case has been discussed in the literature previously, perhaps first, for [2.2.2] propellane by Stohrer and Hoffmann,<sup>17</sup> who coined the term "bond-stretch isomerism". The same picture also describes many Jahn-Teller systems such as the distortion of the cyclobutadiene singlet,<sup>18</sup> 8.



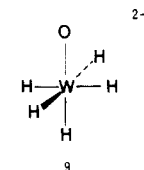
(2) A second, still more intriguing possibility is that there is no real level crossing, no forbidden reaction, but there is still a double minimum. Behind every such case is an intended crossing of valence configurations, if not levels. These cases are often better expressed in the language of valence bond theory, and the phenomenon is tied to recent important discussions of bond localization in allyl, benzene, and other systems.<sup>19</sup>

We will show that even the small number of bond-stretch isomers observed to date illustrate *all* of these hypothetical cases. They are a microcosm of configuration and state changes. Our ideas will be supported by molecular orbital calculations of the extended Hückel type with the parameters given in the Appendix. Although such computations are not going to be reliable in a numerical sense, the insight they will provide will prove to be valuable.

### Orbital Crossing in the d Block

**M-O Lengthening Alone.** As noticed above, the main geometrical distortion common to complexes 1–3 is the lengthening of the M–O bond. Let us first consider the electronic consequences of such a bond stretch in the model  $d^1$  complex  $(MOH_3)^{2-}$  (M

= W, 9), in which the hydrides model pure  $\sigma$ -donor ligands. One



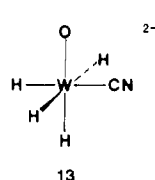
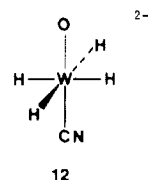
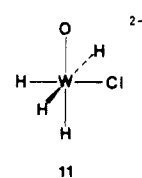
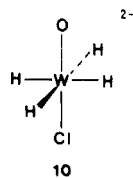
obtains, of course, a classical three below two level pattern of an octahedral complex. Figure 1 shows only the three-level block (what would be  $t_{2g}$  in a pure octahedral complex). Throughout the first part of this paper we will continue to show only that block, because we are dealing with low electron counts, typically one or two electrons on the metal.

$\pi$  bonding with oxygen induces a splitting of the  $t_{2g}$  block:  $xy$  is purely nonbonding, while  $xz$  and  $yz$  are destabilized by antibonding mixing with oxygen lone pairs. The splitting between  $xy$  and  $(xz, yz)$  is calculated to be 0.80 eV for M–O = 1.7 Å. The filled bonding counterpart to these antibonding orbitals, mainly oxygen p orbitals mixed with  $xz, yz$ , is of course what is responsible for the  $\pi$  bonding and short M–O length. A typical M–O triple bond is 1.60 Å and a single bond 1.95 Å; the observed bond lengths in the bond-stretch isomers are all in the intermediate region.

Upon lengthening of the M–O bond,  $xz$  and  $yz$  are stabilized since the antibonding interactions with the oxygen lone pairs decrease, while the energy of  $xy$  is unaffected. For an infinite M–O distance the three orbitals would be degenerate, so that no crossing in the d block can be expected in the range of experimental M–O distances (Figure 1). However, this simple scheme can be modified by introducing ligands able to interact with the other d orbitals on the metal. As a matter of fact, all the characterized bond-stretch isomers carry  $\pi$ -acceptor or  $\pi$ -donor ligands.

**Influence of  $\pi$ -Donor Ligands.** Consider first a  $\pi$ -donor ligand (chlorine atom) either trans (10) or cis (11) with respect to oxygen. In 10,  $xy$  does not interact with the chlorine lone pairs and remains a purely nonbonding d orbital (at the left-hand side of Figure 2a). On the other hand,  $xz$  and  $yz$  are destabilized by one chlorine and one oxygen lone pair. Therefore, the energy gap between  $xy$  and  $(xz, yz)$  increases (from 0.80 eV in 9 to 1.11 eV in 10), a factor which works against an orbital crossing in the d block (Figure 2a).

If the chlorine atom is now located cis with respect to oxygen, 11, the chlorine lone pairs destabilize  $xy$  and  $xz$  and leave  $yz$  unaffected. Consequently, the energy gap between the frontier molecular orbitals  $xy$  and  $yz$  (at the left-hand side of Figure 2b) is reduced from 0.80 eV in 9 to 0.47 eV in 11, so that a crossing occurs in the d block as the M–O bond is lengthened. We calculate the crossing point to occur at M–O  $\approx$  1.95 Å. At longer distances an antibonding M–Cl orbital ( $xy$ ) is depopulated while an antibonding M–O orbital ( $yz$ ) is populated. In other words, the crossing results in reduced bonding between M and O and stronger bonding between M and Cl, thus the lengthening of the M–O bond should be accompanied by simultaneous shortening of the M–Cl one. An interesting consequence of this viewpoint, one to which we will return, is that substituents other than oxygen (or nitrogen, in other compounds) can show in their structures explicit  $\pi$ -bonding capability.

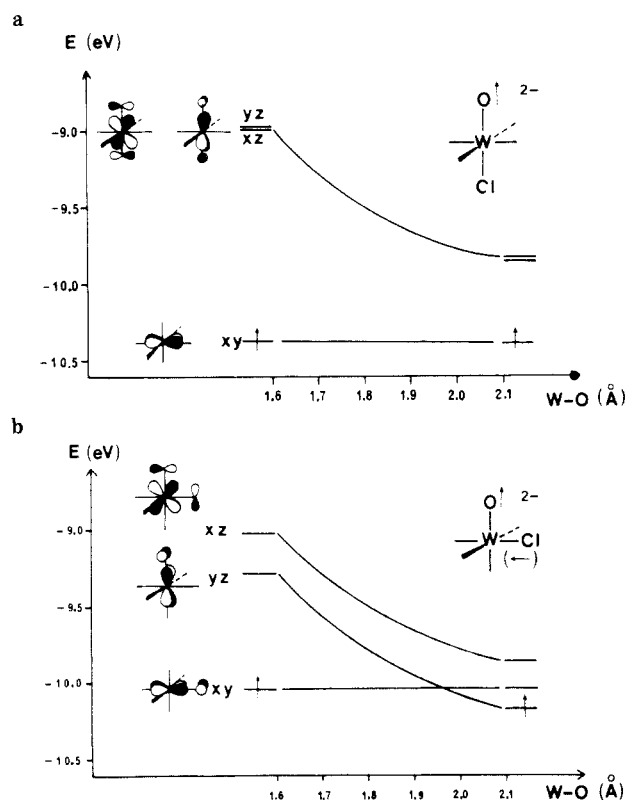


(16) Burdett, J. K.; Marsden, C. J. *New J. Chem.*, in press.

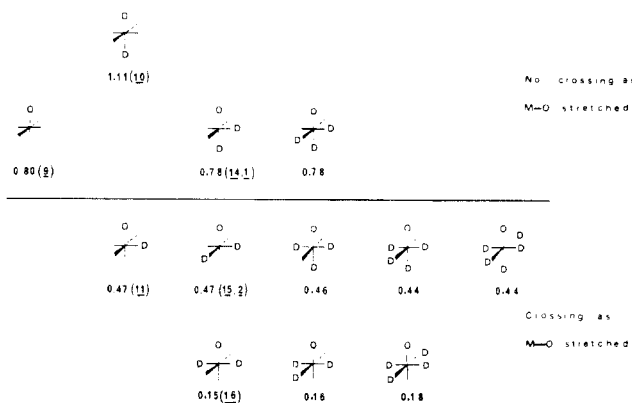
(17) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 1661–1668.

(18) Salem, L. In *Electrons In Chemical Reactions*; Wiley: New York, 1982.

(19) (a) Shaik, S. S.; Bar, R. *Nouv. J. Chim.* **1984**, *8*, 411–420. (b) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J. M. *Ibid.* **1985**, *9*, 385–388. (c) Hiberty, P. C.; Shaik, S. S.; Lefour, J. M.; Ohanessian, G. *J. Org. Chem.* **1985**, *50*, 4659–4661. (d) Shaik, S. S.; Hiberty, P. C.; Lefour, J. M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363–374.

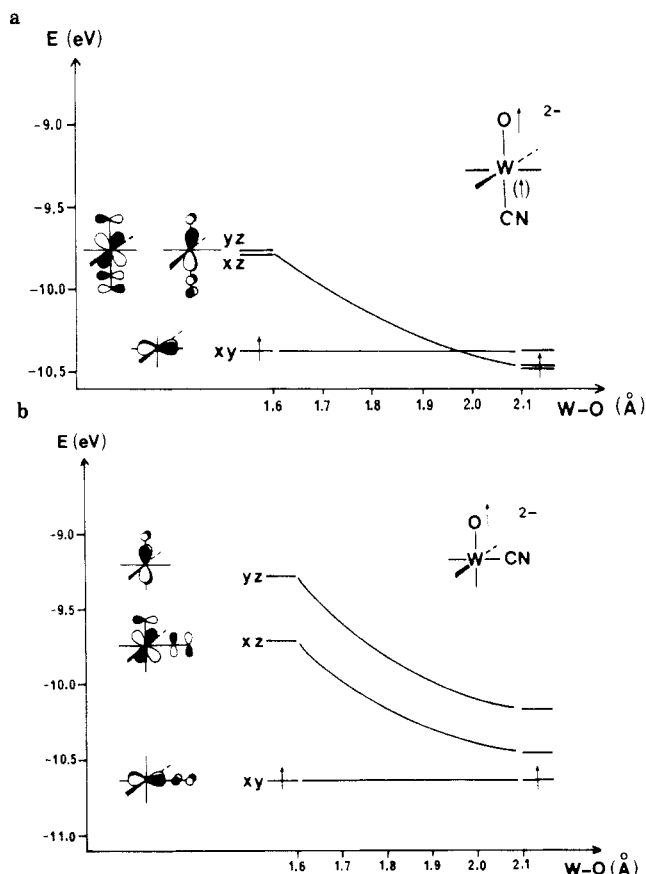


**Figure 2.** Energy of the low-lying d orbitals in the model  $d^1$  complex  $(\text{WOClH}_4)^{2-}$ , with oxygen and chlorine atoms either trans (**10**, Figure 2a) or cis (**11**, Figure 2b) as a function of W–O bond stretching alone. The arrow in parentheses in Figure 2b shows the way in which the W–Cl bond length should vary after the crossing. Note that orbitals  $xy$  and  $yz$  in 2-b are both antisymmetric with respect to the  $xz$  plane, so that their crossing should be avoided. However, these orbitals remain essentially orthogonal on W–O stretching, and the crossing is so barely avoided that their energetic behavior is identical with that expected for orbitals of different symmetry. The same remark applies to Figure 8.

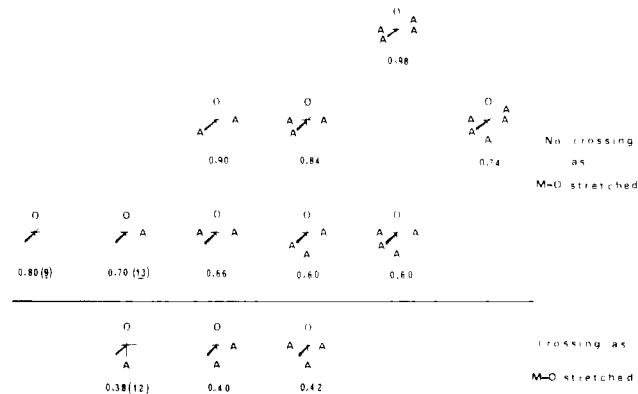


**Figure 3.** Energy gap ( $\Delta E$ , in eV) between the frontier MOs in the model  $d^1$  complexes  $(\text{WO}A_n\text{H}_{5-n})^{2-}$ , as a function of  $n$  (W–O = 1.7 Å). D is a  $\pi$ -donor ligand (D = Cl). Upon W–O stretching, an orbital crossing occurs in the d block for complexes with  $\Delta E \cong 0.45$  eV (W–O  $\cong 1.95$  Å) or  $\Delta E \cong 0.15$  eV (W–O  $\cong 1.80$  Å). No crossing takes place in the other complexes upon W–O stretching alone.

This analysis can be extended in a straightforward manner to complexes carrying 2 to 5  $\pi$ -donor ligands (Figure 3), the general trend being always that  $\pi$ -donor ligands *cis* to oxygen favor an orbital crossing in the d block while a  $\pi$ -donor *trans* to oxygen works against this crossing. The computed energy gap between the frontier MOs for M–O = 1.7 Å gives a measure of the ease of the crossing. For values around 0.45 eV, it occurs for M–O  $\cong 1.95$  Å. In the most favorable cases ( $\Delta E \cong 0.15$  eV), the crossing takes place for M–O  $\cong 1.80$  Å. Again some M–Cl bond lengths are expected to vary after the crossing point, in a way easily



**Figure 4.** Energy of the low-lying d orbitals in the model  $d^1$  complex  $(\text{WO}(\text{CN})\text{H}_4)^{2-}$ , with oxygen and cyanide ligand either trans (**12**, Figure 4a) or cis (**13**, Figure 4b) as a function of W–O bond stretching alone. The arrow in parentheses in Figure 4a shows the way in which the W–CN bond length should vary after the crossing.



**Figure 5.** Energy gap ( $\Delta E$ , in eV) between the frontier MOs in the model  $d^1$  complexes  $(\text{WO}A_n\text{H}_{5-n})^{2-}$  as a function of  $n$  (W–O = 1.7 Å). A is a  $\pi$ -acceptor ligand (A = CN). Upon W–O stretching, an orbital crossing occurs in the d block for complexes with  $\Delta E \cong 0.40$  eV (W–O between 2.0 and 2.1 Å). No crossing takes place in the other complexes upon W–O stretching alone.

found from examination of the character of the molecular orbitals involved in the crossing.

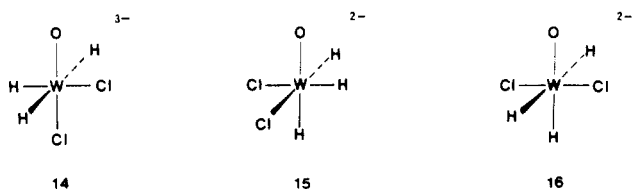
**Influence of  $\pi$ -Acceptor Ligands.** For  $\pi$ -acceptor ligands, the major interaction involves the  $\pi^*$  orbitals of the ligands, so that the conclusion is exactly the opposite to that reached for  $\pi$ -donor ligands: the orbital crossing upon M–O lengthening is favored by a  $\pi$ -acceptor ligand *trans* to the oxygen (**12**, Figure 4a), while  $\pi$ -acceptor ligands *cis* are not favorable (**13**, Figure 4b). In **12**,  $xy$ , which is purely nonbonding, is depopulated while  $xz$  (or  $yz$ ), M–(CN) bonding and M–O antibonding, is populated (Figure 4a). Again the crossing entails a swap of a bond, from the M–O to M–(CN) linkage.

Figure 5 shows the energy gap between the frontier MOs in a series of complexes with 1 to 5  $\pi$ -acceptor ligands modeled by cyanide. The three complexes in which the d orbitals could cross ( $M-O \cong 2.0$  Å) carry a  $\pi$ -acceptor trans to the oxygen. In each case, the  $M-(CN)_{trans}$  bond is predicted to be shortened after the crossing point.

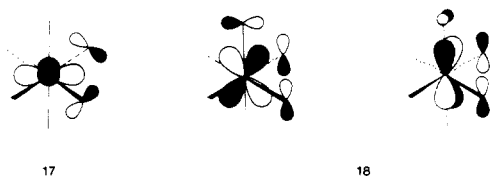
Finally, in mixed ligand complexes, the best candidates for an orbital crossing are those carrying a  $\pi$ -acceptor trans to the oxygen, and one or several  $\pi$ -donors cis to it.

**Comparison with the Known Complexes 1–3.** Let us now return to the known complexes 1–3 to see whether their substitution patterns favor an orbital crossing upon *lengthening of the M–O bond alone*. It is clear that complex 3 carries a substitution pattern which is the *worst* one for a crossing: there is a  $\pi$ -donor ligand trans to the oxygen and four  $\pi$ -acceptors cis to it! On the other hand, complex 1 which carries two chlorine atoms (one cis and one trans with respect to O) also belongs to a class of complexes we have predicted to be unfavorable for an orbital crossing ( $\Delta E = 0.78$  eV in the model complex 14 of Figure 3). Calculations on the complex  $MoOCl_2(PH_3)_3$  confirm the absence of an orbital crossing. Therefore, this first analysis fails to rationalize the existence of bond-stretch isomers in complexes 1 and 3. Note, however, that these two complexes are precisely those in which the structures reveal some variation in metal–ligand bond lengths other than M–O. Could it be that these, coupled to M–O elongation, could produce level crossings? We will see.

In contrast to 1 and 3, 2, which we have modeled by 15, is a good candidate for an orbital crossing, since it carries two  $\pi$ -donor ligands cis to the oxygen. Calculations on  $WOCl_2(NH_3)_3^+$  confirm our previous analysis; a crossing in the d block occurs for  $M-O \cong 1.90$  Å. Therefore going from 2a to 2b is a forbidden reaction and this may explain the stability of both isomers, even in solution.



Although the lengthening of the M–O bond is the only large geometrical difference between 2a and 2b, it is interesting to analyze how the strength of the other metal–ligand bonds is affected. In Figure 6 we plot the reduced overlap population associated with the W–Cl and W–N bonds calculated for  $WOCl_2(NH_3)_3^+$  as a function of W–O distance. The bonds most strongly affected are W–Cl, which are strengthened as W–O is lengthened. In the MOs where  $xz$  and  $yz$  mix in a *bonding* way with the oxygen and chlorine lone pairs, the coefficient on the oxygen atom is reduced and that on the chlorines increased, as the W–O bond is stretched, so that there is an increase in the W–Cl overlap population. The orbital crossing too helps to reinforce the W–Cl bonds. Note the discontinuity in the reduced overlap population at the crossing point in Figure 6. It can be understood by looking at the orbital composition of the MOs involved in the crossing. The reason why the HOMO becomes less W–Cl antibonding after the crossing point appears more clearly if the  $x$  and  $y$  axes are rotated by  $45^\circ$  so that  $xy$  becomes  $x^2-y^2$  (17). In 17, the antibonding interaction with the chlorine lone pairs is large since they lie in the plane of  $x^2-y^2$ . It is smaller in  $xz$  or  $yz$  (18), where the chlorine lone pairs now lie out of the plane of maximum density of the d orbitals. This effect, rather



small since both 17 and 18 are W–Cl antibonding, suggests that the lengthening of the W–O bond should be accompanied by a shortening of the W–Cl ones. The experimental structures appear

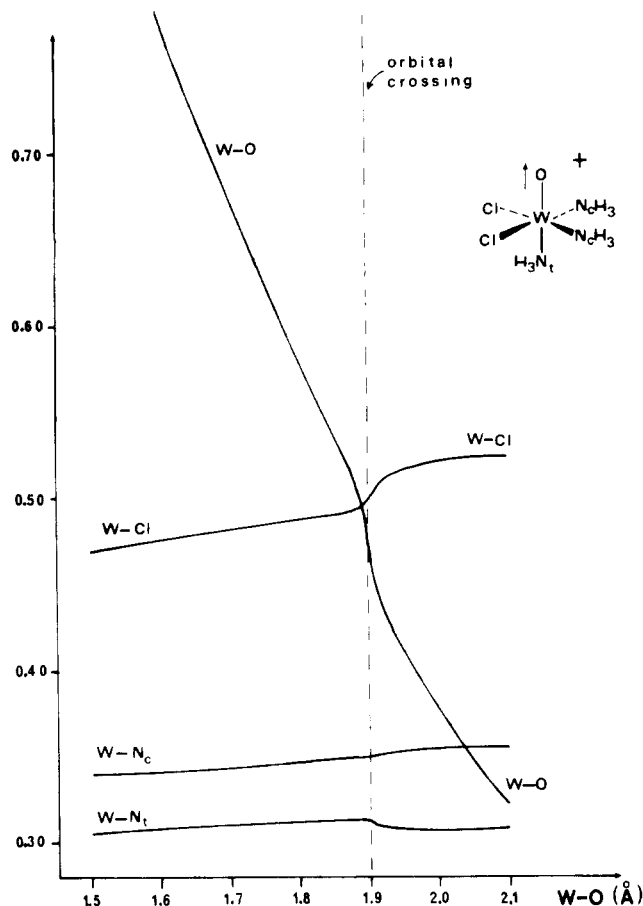
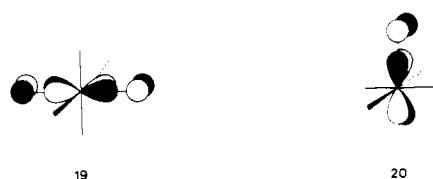


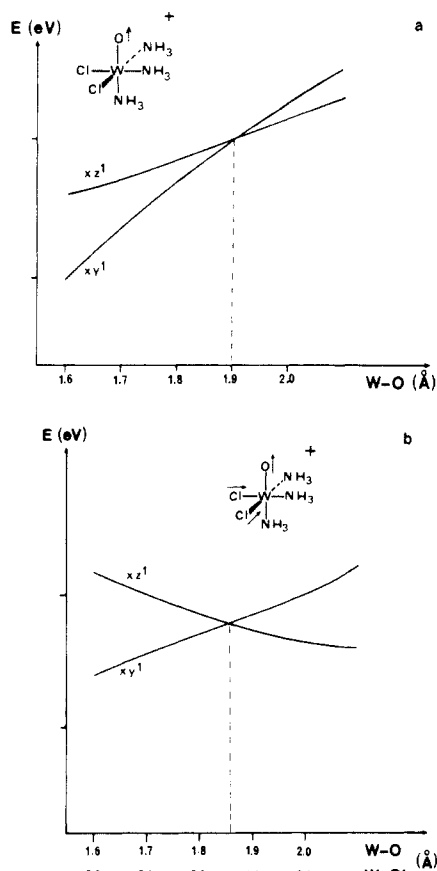
Figure 6. Reduced overlap populations as a function of W–O stretching in  $(WOCl_2(NH_3)_3)^+$  used as a model for 2.

to reflect this expectation,<sup>11</sup> the W–Cl bond lengths being reduced from 2.322 (5) Å in 2a to 2.295 (6) Å in 2b (although the effect is hardly statistically significant). It is noteworthy that larger W–Cl bond shortening could take place in a complex like 16, the geometrical isomer of 15, with two chlorine atoms cis to the oxygen but trans to each other. The crossing now involves one W–Cl antibonding orbital ( $xy$ , 19) and one W–Cl nonbonding orbital ( $yz$ , 20).



Finally if one looks at the total energy of complex 2 given by the extended Hückel calculations, one obtains at first a rather disappointing result. Despite the expected crossing between the electronic configurations  $xy^1$  and  $xz^1$ , a single minimum is found for a short W–O bond (Figure 7a). The orbitals of lower energy, in particular those characterizing the  $\sigma$  W–O bond, resist the distortion and dominate, after the crossing point, the stabilization of the single electron in the d orbitals. However, if simultaneous shortening of the W–Cl bonds is allowed, the structure with a long W–O is stabilized and a double minimum appears (Figure 7b). The extended Hückel method is not at all good for actually mimicking changes in bond lengths, especially when trying to weigh the effects of (say) lengthening a M–O bond and simultaneously contracting a M–Cl bond. Our ideas in this paper therefore can only be exploratory ones, making use of the importance of one-electron changes in the energy.

**Concerted Variation of Several Bond Lengths.** Starting from the basic diagram of Figure 1, we have shown that one way to force an orbital crossing in the d block upon M–O stretching is to put ligands carrying a  $\pi$  system in a position that makes use

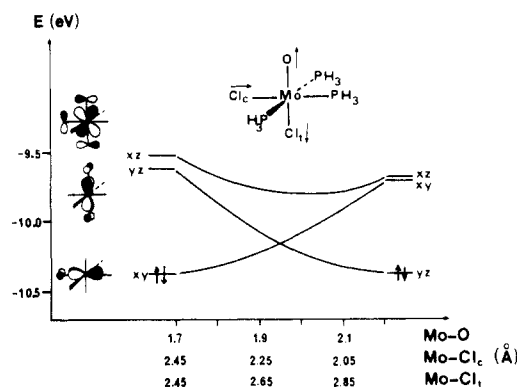


**Figure 7.** Potential energy curves associated with the electronic configurations  $xy^1$  and  $xz^1$  in  $(WOCl_2(NH_3)_3)^+$ : (a) stretching of the W-O bond alone (W-Cl fixed at 2.31 Å); (b) simultaneous stretching of W-O and shortening of W-Cl bonds.

of their  $\pi$ -donor or  $\pi$ -acceptor properties. We have also shown that, when M-O stretching alone leads to an orbital crossing, some reorganization of the other metal-ligand bonds takes place. One can now ask whether there is a way to favor an orbital crossing in complexes where it is not predicted to occur by M-O stretching alone, by simultaneously varying the other metal-ligand bond lengths. We note that in complexes **1** and **3** such variations actually take place. The general strategy consists of destabilizing the highest occupied molecular orbital, i.e.,  $xy$ , and/or stabilizing the lowest unoccupied molecular orbital ( $xz$  or  $yz$ , depending on the substitution pattern).

In all of the cases described above, the energy of  $xy$  remained constant as M-O was stretched because (i) the oxygen lone pairs do not interact with  $xy$  and (ii) the other bond lengths were fixed at a constant value. One way to destabilize  $xy$  is to increase antibonding interactions with the  $\pi$ -donor (D) ligands and/or to decrease the bonding interactions with the  $\pi$ -acceptors (A). Since the  $\pi$  system of a ligand trans to the oxygen cannot mix by symmetry with  $xy$ , the destabilization of  $xy$  upon M-O stretching can be achieved by simultaneous *shortening of M-D bonds and/or lengthening of M-A bonds cis to the M-O one*.

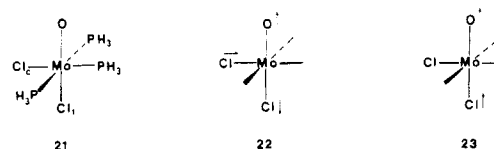
To stabilize  $xz$  or  $yz$  we have to decrease the antibonding interactions and/or to increase the bonding ones in the lowest unoccupied molecular orbital (LUMO). This can be realized by *lengthening the M-D bonds and/or shortening the M-A bonds involved in these interactions*. Since the  $\pi$  system of a ligand such as Cl or CN trans to the oxygen can interact with  $xz$  and  $yz$ , the length of the bond trans to M-O influences the energy levels of these orbitals: M-D<sub>trans</sub> bond has to be lengthened, M-A<sub>trans</sub> one shortened. For bonds cis to M-O, only those involved in d- $\pi$  interactions in the LUMO have to be varied in the same way. Note that sometimes, for ligands cis to the oxygen, the distortion required to destabilize  $xy$  is just the opposite to that found for  $xz$  or  $yz$  stabilization, so that these particular metal-ligand bond



**Figure 8.** Evolution of low-lying d orbital energy in the  $d^2$  complex  $MoOCl_2(PH_3)_3$  as a function of Mo-O and Mo-Cl<sub>trans</sub> bond stretching and Mo-Cl<sub>cis</sub> bond shortening.

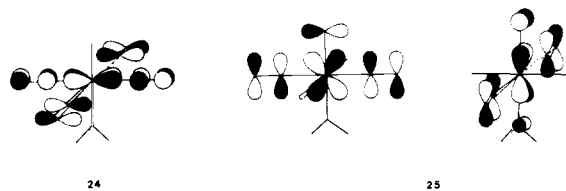
lengths should remain almost constant.

It would be tedious to apply these general conclusions to all the possible substitution patterns by  $\pi$ -donor and/or  $\pi$ -acceptor ligands. Let us simply derive the consequences of this analysis for **1** (modeled by **21**) and **3**. The orbital splitting in **21** is given in Figure 8 (left-hand side). The best way to force an orbital crossing is (i) to raise the energy of  $xy$  by shortening the Mo-Cl<sub>c</sub>

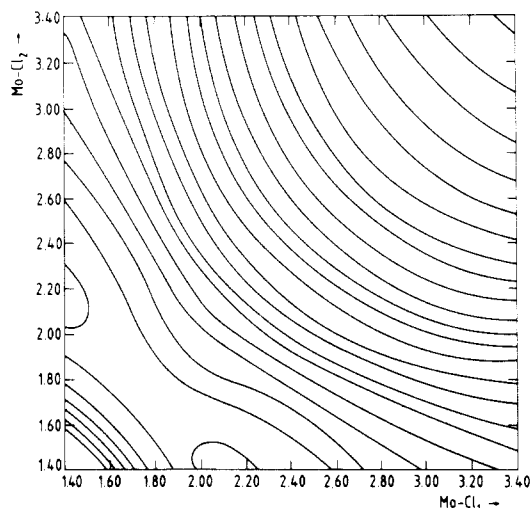


bond (increasing antibonding interaction between  $xy$  and a chlorine lone pair) and (ii) to decrease the energy of  $yz$  by lengthening both Mo-O and Mo-Cl<sub>c</sub> bonds. The crossing actually occurs along this concerted distortion, **22**, of the three bonds (Figure 8), leading to a double minimum on the potential energy surface.

Now we come to a point of difficulty. The distortion predicted to be the most favorable for an orbital crossing is *not* that experimentally observed on going from **1a** to **1b** (**23**). In **23** the M-Cl<sub>c</sub> bond length is shortened (the opposite of **22**) while the M-Cl<sub>c</sub> bond length remains unchanged. We have carried out a calculation on the observed distortion mode **23**, and it does *not* lead to a level crossing, in agreement with our general analysis. Thus the bond-stretch isomerism in **1** cannot be traced to the electronic mechanism at work in **2**. We will find a reason for it in the next section, but it is surprising to us that distortion **22**, apparently favorable for a level crossing, is not observed. Perhaps it will be seen, but in some related system.



As we noted above, complex **3** is extremely unfavorable for an orbital crossing along with Mo-O stretching alone, since it carried a  $\pi$ -donor ligand trans to the oxygen and four  $\pi$ -acceptor ones cis to it. The energy gap between the frontier MOs is large:  $xy$  (**24**) is stabilized by four  $\pi^*_{CN}$  orbitals lying in its plane, and there are no antibonding interactions with the  $\pi$ -donor ligands. On the other hand,  $xz$  and  $yz$  are destabilized by oxygen lone pairs and stabilized by  $\pi^*_{CN}$  orbitals (**25**), but less so than  $xy$ . A way to reduce the energy gap between  $xy$  and  $xz$  ( $yz$ ) is to lengthen the Mo-O and at least two Mo-CN bonds, those not involved in the bonding interactions in  $xz$  ( $yz$ ). However, no crossing can be expected,  $xy$  and  $xz$  ( $yz$ ) becoming only degenerate for infinite stretchings. As for complex **1**, the origin of the bond-stretch isomerism in **3** cannot be related to an orbital crossing in going from one isomer to the other.



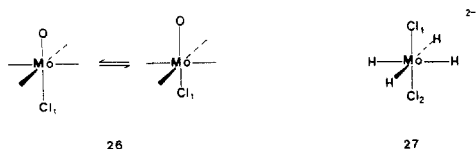
**Figure 9.** Potential energy surface as a function of Mo-Cl<sub>1</sub> and Mo-Cl<sub>2</sub> bond lengths in the model complex MoCl<sub>2</sub>H<sub>4</sub><sup>2-</sup> ( $\Delta E = 0.25$  eV between two equipotentials).

There is, however, the possibility to get two isomers in d<sup>2</sup> complexes even without an orbital crossing: a low-spin isomer for short M-O bond length and a high-spin isomer for a longer M-O bond (small energy gap between frontier MOs). However, this mechanism does not account for the existence of bond-stretch isomers in complex **1** (MoOCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>), both blue and green isomers being diamagnetic.<sup>6b</sup>

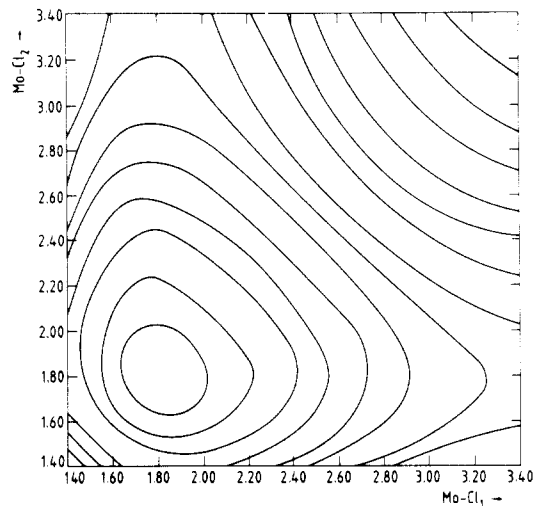
We now investigate the possibility of getting bond-stretch isomers without orbital crossing in the d block.

#### No Orbital Crossing in the d Block

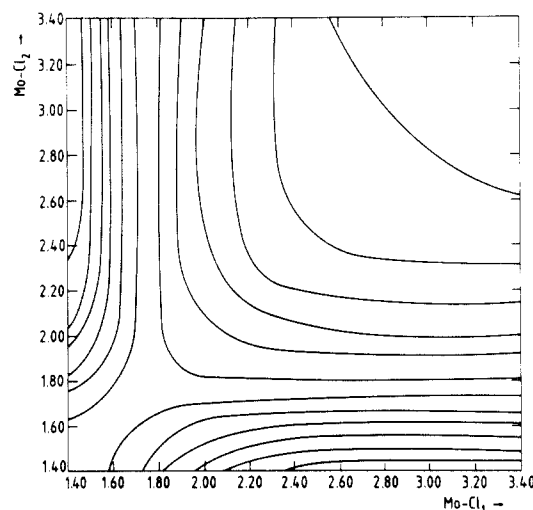
**Muir's Complex 1.** In Muir's complex<sup>6a</sup> **1**, the distortion that converts **1a** into **1b** is an antisymmetric motion of the Mo-O and Mo-Cl<sub>i</sub> bonds. Along with the stretching of Mo-O, Mo-Cl<sub>i</sub> is shortened by approximately the same amount, so that one bond is weakened while the other is strengthened. This, of course, is just an ally anion-like situation, summarized by **26**. According to this scheme, a double minimum could result from a reorganization of the d- $\pi$  bonding, developed mainly between Mo and O in **1a**, and between Mo and Cl<sub>i</sub> in **1b**.



In order to test the role of d- $\pi$  bonding in such compounds, we have first studied the d<sup>2</sup> model complex **27**, with two identical double faced  $\pi$ -donor ligands (Cl), trans to each other. The total energy ( $E_{\text{tot}}$ ) as a function of Mo-Cl bond lengths is reported in Figure 9: two unsymmetrical minima are found (Mo-Cl<sub>1,2</sub>  $\approx$  2.20 Å, Mo-Cl<sub>2,1</sub>  $\approx$  1.40 Å), the geometrical distortion converting one to the other being actually the antisymmetric motion observed in **1**. The bond lengths we compute at the minima are obviously unrealistic, a result that is not very surprising given our comments above concerning our one-electron model. More important is that whatever the common value chosen for the Mo-Cl bond lengths in the symmetrical structure, a stabilization of the total energy results from an antisymmetric motion of these two atoms, i.e., there is a driving force which disfavors structures with equal Mo-Cl bond lengths. We can locate the origin of this by decomposing the total energy into two components: (i) the first is the " $\pi$ " component ( $E_{\pi}$ ), involving all the MOs in which the chlorine lone pairs orthogonal to M-Cl bonds participate. These orbitals mainly characterize the d- $\pi$  bonding between the metal and the  $\pi$ -donor ligands. 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. (ii) The second is the " $\sigma$ " component ( $E_{\sigma}$ ), made of the remaining MOs



**Figure 10.**  $\sigma$  component of the energy ( $E_{\sigma}$ ) in the model complex MoCl<sub>2</sub>H<sub>4</sub><sup>2-</sup> as a function of Mo-Cl<sub>1</sub> and Mo-Cl<sub>2</sub> bond lengths ( $\Delta E = 0.25$  eV between two equipotentials).



**Figure 11.**  $\pi$  component of the energy ( $E_{\pi}$ ) in the model complex MoCl<sub>2</sub>H<sub>4</sub><sup>2-</sup> as a function of Mo-Cl<sub>1</sub> and Mo-Cl<sub>2</sub> bond lengths ( $\Delta E = 0.25$  eV between two equipotentials).

and responsible for the  $\sigma$  metal-ligand bonds. Figures 10 and 11 show the potential energy surfaces relative to each component ( $E_{\sigma}$  and  $E_{\pi}$ , respectively). Although we should treat the computed numbers of the problem with great care, it is clear to see that  $E_{\sigma}$  favors a single minimum with equal Mo-Cl bond lengths (Mo-Cl<sub>1</sub> = Mo-Cl<sub>2</sub> = 1.80 Å, Figure 10), while  $E_{\pi}$  exhibits two strongly asymmetrical minima (Mo-Cl<sub>1,2</sub> = 3.20 Å, Mo-Cl<sub>2,1</sub> = 1.40 Å, Figure 11). Therefore, the electronic factors that tend to make complexes such as **27** unsymmetrical lie in the  $\pi$  component of the energy. The behavior of the total energy ( $E_{\pi} + E_{\sigma}$ ) as a function of distance is the result of opposite trends found for  $E_{\sigma}$  (single minimum) and  $E_{\pi}$  (double minimum). In **27**,  $E_{\pi}$  dominates and the potential energy for  $E_{\text{tot}}$  exhibits two unsymmetrical minima (Figure 9). This is shown schematically in **28**.

The picture we have obtained is very much analogous to the case of allyl anion.<sup>19</sup> Here a single symmetrical structure is favored by the  $\sigma$  system, while the  $\pi$  electrons wish to localize one double bond, i.e., favor two unsymmetrical minima. In the case of allyl the  $\sigma$  component dominates (**29**). In general four-electron three-orbital systems, be they X-M-X, allyl, or the S<sub>N</sub>2 transition state, will be faced with similar choices and balances.

We can obtain a detailed understanding of the behavior of the  $\pi$  energy in **27** by examining the MO diagram in Figure 12. On the left-hand side are shown the MOs involved in  $E_{\pi}$  for a symmetrical ( $D_{4h}$ ) structure with Mo-Cl<sub>1</sub> = Mo-Cl<sub>2</sub> = 2.30 Å. There is a set of two pairs of degenerate orbitals,  $1e_g$  and  $2e_g$ , which result



from the bonding ( $1e_g$ ) and antibonding ( $2e_g$ ) interactions between ( $xz, yz$ ) and the lone pair combinations of proper symmetry on the chlorine atoms. In a hypothetical low-spin  $d^2$  complex, the  $2e_g$  set is unoccupied. In-phase combinations of the chlorine lone pairs mix with the  $\sigma$  M-H bonds parallel to it, either in a bonding ( $1e_u$ ) or antibonding ( $2e_u$ ) manner. Finally, the highest occupied molecular orbital ( $b_{2g}$ ), purely  $xy$  on the metal, is also shown. Consider now the antisymmetric motion ( $D_{4h} \rightarrow C_{4v}$ ) of the two M-Cl bonds. The symmetry of this distortion ( $u$ ) is such that it induces mixings between  $e_g$  and  $e_u$  levels (the  $b_{2g}$  level remaining unaffected). As expected from the analysis developed in the first section, no orbital crossing occurs in the  $d$  block along this distortion. For a given set of degenerate orbitals, the orbital mixings upon  $D_{4h} \rightarrow C_{4v}$  distortion are either stabilizing or destabilizing, depending on the relative energy of the interacting levels. The net result which emerges from Figure 12 is that the lowest orbitals ( $1e_u \rightarrow 1e$ ) are much stabilized because they interact only with levels of higher energy ( $1e_g$  and  $2e_g$ ). On the other hand, the highest set of degenerate orbitals ( $2e_g \rightarrow 4e$ ) is strongly raised in energy by mixing with more stable orbitals ( $1e_u$  and  $2e_u$ ). Orbitals of intermediate energy ( $1e_g$  and  $2e_u$ ) are less affected. Since the  $2e_g$  set is unoccupied in low-spin  $d^2$  complexes, the large stabilization of  $1e_u$  dominates and here lies the driving force which favors unsymmetrical structures in the  $E_\pi$  component of the total energy. This mixing between MOs during a geometrical distortion

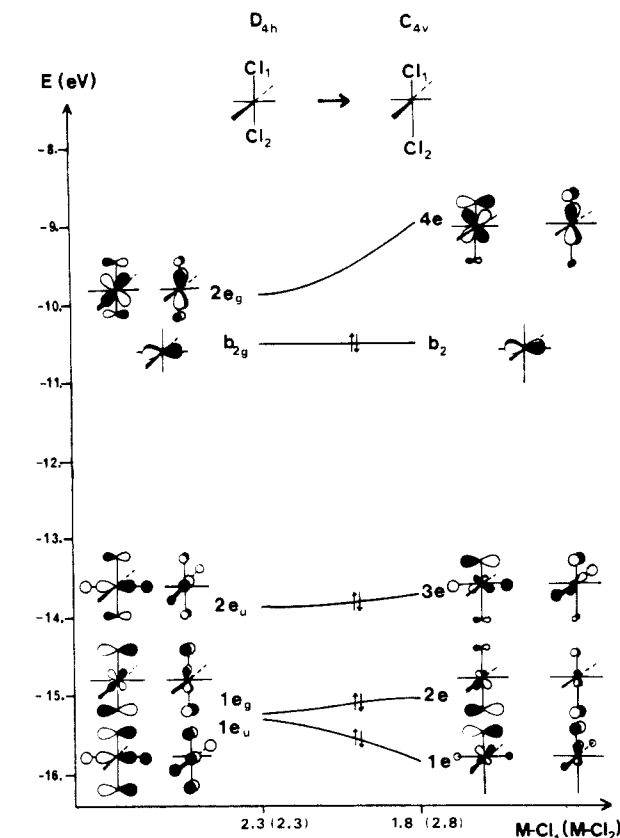
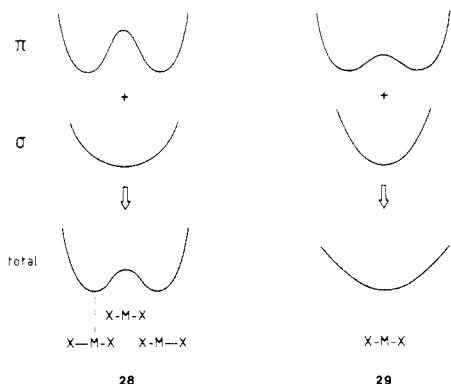


Figure 12. Orbital diagram for the asymmetric distortion of the two Mo-Cl bonds in the  $d^2$  model complex  $(\text{MoCl}_2\text{H}_4)^{2-}$ .

Table I. Energy Variations (eV) upon Asymmetric Distortion of Two Mo-Cl Bonds Trans to Each Other in the Model Complexes  $\text{MoCl}_2\text{L}_4^{2-}$  ( $\text{L} = \text{H, CN, Cl}$ ), from  $\text{Mo-Cl}_1 = \text{Mo-Cl}_2 = 2.30 \text{ \AA}$  to  $\text{Mo-Cl}_1 = 1.80 \text{ \AA}$  and  $\text{Mo-Cl}_2 = 2.80 \text{ \AA}$ <sup>a</sup>

	$\Delta E_\pi$	$\Delta E_\sigma$	$\Delta E_{\text{total}}$
<i>trans</i> - $\text{MoCl}_2\text{H}_4^{2-}$	-0.64	0.24	-0.40
<i>trans</i> - $\text{MoCl}_2(\text{CN})_4^{2-}$	-0.64	0.33	-0.31
$\text{MoCl}_6^{2-}$	-0.12	0.33	+0.21

<sup>a</sup>  $\Delta E_\pi$  and  $\Delta E_\sigma$  are the  $\pi$  and  $\sigma$  components of the total energy variation  $\Delta E_{\text{total}}$ .

leading to a stabilization of filled MOs and a destabilization of empty ones is typical of a second-order Jahn-Teller (SOJT) effect.<sup>20</sup> The distortion allows ( $xz, yz$ ) orbitals to participate more in the bonding in the complex: their occupation increases from 0.142 to 0.328 for the distortion reported in Figure 12.

The main conclusions reached from the study of the model complex **27** apply to more realistic models of complex **1**. Both in **10** and **21**, no orbital crossing is found upon antisymmetrical motion of Mo-O and Mo-Cl<sub>i</sub> bonds. The evolution of the MOs is similar to that reported in Figure 12 and the preference for a distorted structure can always be traced to the reorganization of the  $d$ - $\pi$  bonding through a SOJT effect. However, there is a change in the shape of the total energy potential energy surface. A single minimum appears, for Mo-O "short" and Mo-Cl<sub>i</sub> "long". The decomposition of  $E_{\text{tot}}$  in  $E_\pi$  and  $E_\sigma$ , which is possible in **10**, reveals that the trends found in the model complex **27** are still valid: double minimum for  $E_\pi$ , single minimum for  $E_\sigma$ , but the balance between the two components is now governed by  $E_\sigma$ . This is shown schematically in **29**.

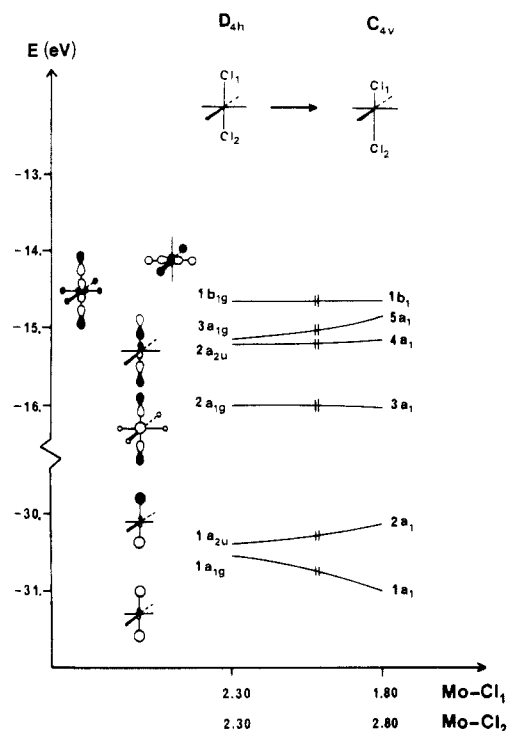
The computational result of a single minimum is not as much in contradiction with the experimental data as it might seem, since isomers **1a** and **1b** are isolable only in the solid state, the single isomer prevailing in liquid phase being that with the "short" Mo-O bond. This behavior is consistent with the greater stability of isomer **1a**, associated with a low-energy barrier between **1a** and **1b**. Also we are reaching here the limits of the extended Hückel method. Even if the trends found for  $E_\pi$  and  $E_\sigma$  are correct, one cannot expect this type of calculation to give consistently the exact balance between two effects that are working in opposite directions.

**$\sigma$  versus  $\pi$  Effects.** We have stressed above the importance of  $\pi$  bonding in this problem. From our calculations we find that in **27**  $E_\pi$  dominates and a double well is found as in **28**, but in the analogous ammonia case, *trans*- $\text{Mo}(\text{NH}_3)_2\text{H}_4$ , the  $\pi$  effect is tiny and  $\sigma$  dominates (**29**). Ammonia is a very poor  $\pi$  ligand and although chlorine is better, it is by no means superlative. Obviously the effect will be larger (on our model by a factor 2) if the ligands involved are double-faced  $\pi$ -donors, since both orthogonal  $\pi$  systems can be effectively used.

The ideas of the second-order Jahn-Teller approach suggest that the effect should be larger, the smaller the energy gap between the interacting orbitals of the problem. As we have described above, one way to stabilize the  $4e$  orbitals of Figure 12 is to place acceptor ligands at the equatorial position. Table I shows in fact that the  $\pi$  effect is computed to be very similar in *trans*- $\text{MoCl}_2(\text{CN})_4^{2-}$  and in  $\text{MoCl}_2\text{H}_4^{2-}$ . This occurs as a result of the competing effects of  $d\pi$  depression (leading to a decrease in the denominator of the second-order stabilization energy) and  $\pi$  delocalization (which leads to a decrease in the numerator). However, a strong effect is shown with  $\pi$ -donors ( $\text{MoCl}_6^{2-}$ ) where both effects work in the same direction. Many of the results from previous work on bond asymmetry in the perovskites,<sup>21</sup> solid oxides of stoichiometry  $\text{ABO}_3$ , carry over to the present molecular sit-

(20) (a) Bader, R. F. W. *Mol. Phys.* **1960**, *3*, 137-151. (b) Burdett, J. K. In *Molecular Shapes*; Wiley: New York, 1980.

(21) Wheeler, R. A.; Whangbo, M.-H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222-2236.



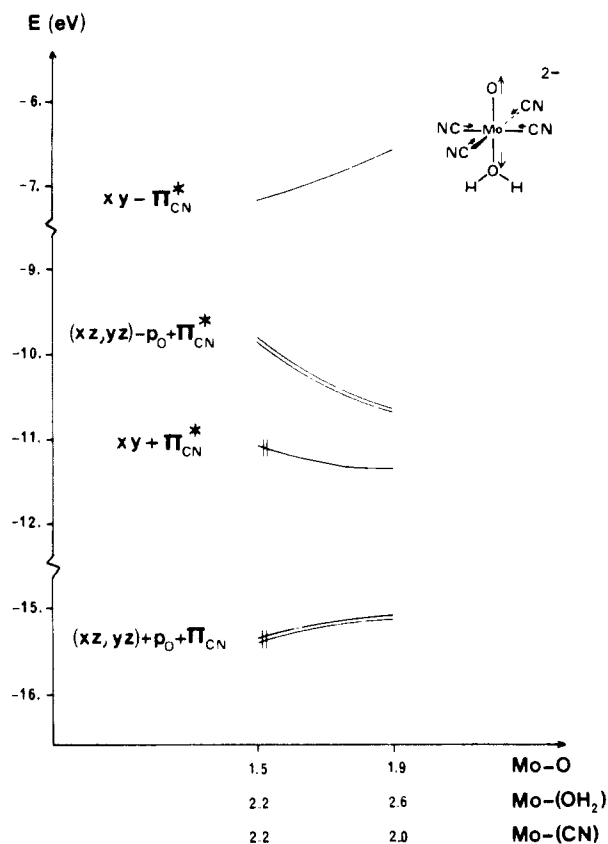
**Figure 13.** Energy of the  $\sigma$  orbitals in  $\text{trans-MoCl}_2\text{H}_4^{2-}$  upon an asymmetric distortion from  $\text{Mo-Cl}_1 = \text{Mo-Cl}_2 = 2.3 \text{ \AA}$  to  $\text{Mo-Cl}_1 = 1.8 \text{ \AA}$  and  $\text{Mo-Cl}_2 = 2.8 \text{ \AA}$ .

uation. In the perovskites and also one-dimensional systems of the general formula  $\text{MXL}_n$  ( $\text{X} = \text{O}, \text{N}$ ;  $\text{L} = \text{Cl}, t\text{-C}_4\text{H}_9\text{O}$ ;  $n = 3, 4$ ), less electronegative bridging atoms  $\text{X}$  give rise to a smaller HOMO-LUMO gap and the distorting effect is accentuated. In contrast to these chain systems where there are probably no known symmetrical oxide or nitride bridged examples, the species  $\text{Mo}(\text{CN})_4\text{O}_4^{4-}$  and  $\text{Mo}(\text{CO})_4\text{O}_2$  are both experimentally characterized as symmetrical molecules.<sup>22</sup>

These comments highlight the problem with our approach (and indeed the earlier one on the perovskites). It is difficult with these one-electron models to accurately portray these distortions in *numerical* terms and to make reliable predictions as to those systems (in terms of the identity of the metal and ligands) which will be distorted and which will not. Our calculations, for example, suggest that both  $\text{trans-MoO}_2\text{H}_4^{4-}$  and  $\text{MoCl}_2\text{H}_4^{2-}$  should be distorted. Although there is an example of a distorted trans chloride,<sup>23</sup> all of the dioxo complexes are symmetrical.<sup>22</sup> The problem is clearly that we compute the wrong balance between the functional behavior of  $E_\pi$  and  $E_\sigma$ .

It is interesting to inquire why the  $\sigma$  manifold has a single minimum and resists asymmetric distortion. The reason is quite simple. The  $\sigma$  set arises via population of orbitals involving ligand  $s$  and  $p\sigma$  orbitals. During asymmetrization their interaction with the metal increases since the loss in overlap on stretching is more than compensated on compression. A two-orbital, four-electron destabilization results as shown in Figure 13.

**Complex 3.** The greatest geometrical change in going from **3a** to **3b** (**3** =  $\text{Mo}(\text{OH}_2)(\text{CN})_4^{2-}$ ) is the lengthening of  $\text{Mo-O}$  and  $\text{Mo-OH}_2$  bonds by 0.12 and 0.48  $\text{\AA}$ , respectively.<sup>12</sup> (This latter change is certainly much too large. Large thermal parameters are associated with this oxygen in the structure refinement and the real  $\text{Mo}(\text{OH}_2)$  distance could well be different. The location of the water molecule in both isomers is in fact open to question.



**Figure 14.** Energy of some molecular orbitals (those in which  $xy$ ,  $xz$ , and  $yz$  participate the most) in complex **3** upon simultaneous stretching of  $\text{W-O}$  and  $\text{W-(OH}_2\text{)}$  (from 1.5 to 1.9  $\text{\AA}$  and from 2.2 to 2.6  $\text{\AA}$ , respectively) and shortening of  $\text{W-CN}$  (from 2.2 to 2.0  $\text{\AA}$ ).

There are two structure determinations of **3a**, one with a  $\text{Mo-(OH}_2\text{)}$  distance of 2.48  $\text{\AA}$  and the other 2.27  $\text{\AA}$ .<sup>24</sup> Simultaneously, a slight shortening of the mean value of  $\text{Mo-CN}$  bonds takes place ( $2.19 \rightarrow 2.13 \text{ \AA}$ ).<sup>12</sup> In this distortion, two bonds trans to each other are thus weakened, while those cis to them are strengthened (**3**), suggesting a reorganization of the  $d-\pi$  bonding in the complex. At first sight, the problem is reminiscent of the varieties of colors observed for  $d^7$  molecules  $\text{Co}^{\text{II}}\text{L}_5$  (where  $\text{L} = \text{CN}^-, \text{CNC}_6\text{H}_5$ ).<sup>25</sup> Here though the explanation lies with the details of the local  $\text{CoC}_5$  coordination. The presence of a close counterion is sufficient to change the axial-basal angle by  $5^\circ$  or so and leads to significant spectral changes. In complexes **3**, however, the  $\text{O-Mo-C}$  angles remain invariant in blue and green isomers.

In Figure 14 (left-hand side) are drawn the molecular orbitals in which  $xy$ ,  $xz$ , and  $yz$  participate the most. The two lowest orbitals are the bonding combination of  $xz$  or  $yz$  with oxygen lone pairs and  $\pi_{\text{CN}}$  orbitals. They are almost degenerate because the  $\text{Mo-OH}_2$  bond is so long that the orbitals on water interact very little with the metal. Above is the highest occupied MO,  $xy$  stabilized by four  $\pi_{\text{CN}}^*$  orbitals on the ligands. Finally, the highest MOs shown are  $(xz, yz)$  which are stabilized by only two  $\pi_{\text{CN}}^*$  orbitals and destabilized by oxygen lone pairs and the out-of-phase combination of  $xy$  with  $\pi_{\text{CN}}^*$  orbitals. These are the lowest unoccupied MOs of the complex. The energy gap between the frontier MOs is large (1.16 eV for  $\text{Mo-O} = 1.60 \text{ \AA}$  and  $\text{Mo-(OH}_2\text{)} = 2.48 \text{ \AA}$ ) because  $xy$  and  $(xz, yz)$  are differentiated not only by the interaction with oxygen lone pairs but also by the

(22) (a) Day, V. W.; Hoard, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 3374-3379. (b) Crayston, J. A.; Almond, M. J.; Downs, A. J.; Poliakov, M.; Turner, J. J. *Inorg. Chem.* **1984**, *23*, 3051-3056.

(23) Diebold, T.; Chevrier, B.; Weiss, R. *Inorg. Chem.* **1979**, *18*, 1193-1200. This complex is paramagnetic with one electron in  $b_{2g}$  and one in the  $2e_g$  block, the latter working against the distortion. Therefore, the computed total energy curve is almost flat for a small distortion, while there is a stabilization for a hypothetical diamagnetic complex.

(24) Robinson, R. R.; Schlemper, E. O.; Murmann, R. K. *Inorg. Chem.* **1975**, *14*, 2035-2041.

(25) See: (a) Jurnak, F. A.; Greig, D. R.; Raymond, K. R. *Inorg. Chem.* **1975**, *14*, 2585-2589. (b) Brown, L. D.; Raymond, K. R. *Ibid.* **1975**, *14*, 2590-2594. (c) Brown, L. D.; Greig, D. R.; Raymond, K. R. *Ibid.* **1975**, *14*, 645-649 and references therein. (d) Color changes also occur with  $\text{Cr}(\text{CO})_5$  in various matrices: Turner, J. J.; Perutz, R. N. *J. Am. Chem. Soc.* **1975**, *97*, 4791-4800.

Table II. Parameters Used in Extended Hückel Calculations

orbital	$H_{ii}$ , eV	$\zeta_1$	$\zeta_2$	$C_1^a$	$C_2^a$
H 1s	-13.60	1.300			
C 2s	-21.40	1.625			
2p	-11.40	1.625			
N 2s	-26.00	1.950			
2p	-13.40	1.950			
O 2s	-32.30	2.275			
2p	-14.80	2.275			
P 3s	-18.60	1.600			
3p	-14.00	1.600			
Cl 3s	-30.00	2.033			
3p	-15.00	2.033			
Mo 4d	-10.50	4.540	1.900	0.5899	0.5899
5s	-8.34	1.960			
5p	-5.24	1.920			
W 5d	-10.37	4.982	2.068	0.6685	0.5424
6s	-8.26	2.341			
6p	-5.17	2.309			

<sup>a</sup> These are the coefficients in the double- $\zeta$  expansion.

stabilization arising from  $\pi^*_{CN}$  orbitals, larger for  $xy$  than for ( $xz$ ,  $yz$ ). As we have noticed above, this substitution pattern is unfavorable for a crossing in the d block, whatever the type of distortion.

In a first series of calculations, the simultaneous lengthening of Mo–O and Mo–OH<sub>2</sub> bonds was studied, keeping fixed the lengths of the Mo–CN bonds to 2.15 Å. This distortion reduces the overlap between oxygen lone pairs and  $xz$  or  $yz$  on the metal, so that the coefficient of the oxygen lone pairs in the bonding MOs of lowest energy (Figure 14) decreases. As a result the participation of  $\pi_{CN}$  in these orbitals increases, as well as the overlap population associated with the Mo–CN bonds. Therefore, lengthening of both Mo–O and Mo–OH<sub>2</sub> bonds will tend to shorten the Mo–CN ones. This is what is found experimentally. Let us now allow this shortening along with the stretchings of Mo–O and Mo–OH<sub>2</sub> bonds. The evolution of the energy of the MOs mostly affected by this distortion is shown in Figure 14. Shortening the Mo–CN bonds stabilizes the HOMO ( $xy + \pi^*_{CN}$ ) since the bonding interactions with  $\pi^*_{CN}$  orbitals is increased and destabilizes the antibonding counterpart  $xy - \pi^*_{CN}$ . This factor favors a structure with short Mo–CN bonds. The electron transfer from the metal to the  $\pi$ -acceptor ligands is increased and the C≡N bonds weakened. On the other hand, the participation of the oxygen lone pairs in the orbitals of lowest energy decreases while that of the  $\pi_{CN}$  orbitals increases. Since oxygen is a better  $\pi$  donor than CN, these two orbitals are destabilized along the distortion which lengthens Mo–O and Mo–OH<sub>2</sub> bonds and shortens Mo–CN ones. Conversely, the vacant orbitals ( $xz$ ,  $yz$ ) –  $p_0 + \pi^*_{CN}$  are stabilized since the antibonding interactions are reduced and the bonding ones increased. Note that in one of the potential bond-stretch isomers (Mo–O “long”, Mo–CN “short”), the metal atom should be more positive than in the other (smaller  $\pi$ -donor → metal and larger metal →  $\pi$ -acceptor electron transfer). One situation is thus best for bonding to oxygen and the other best for bonding to cyanide. A double minimum could then result if the functional form of the energetic dependence on Mo–C and Mo–O distance is favorable, a comment difficult to substantiate by calculation. Such a distortion can, of course, occur in any molecule, but it is perhaps more likely to be found in systems where the bonding characteristics of the ligands are quite different ( $\pi$ -donor and  $\pi$ -acceptor in the present case).

In the light of our earlier discussion of the antisymmetric motion encouraged by a SOJT effect, it is perhaps surprising at first sight that this molecule (well set up with four  $\pi$ -acceptor ligands) does not distort in this way. Perhaps the single  $\pi$ -faced and rather poor  $\pi$ -donor qualities of the water ligand are to blame here. Our results in this section should be interpreted with more care than those for earlier ones. This is simply because the crystallographic determination here is not as good as in other systems.

**The Special Case of Cu<sup>II</sup>.** The structural chemistry of copper is perhaps the most diverse of any of the elements. The geometries of Cu<sup>II</sup> complexes are very strongly controlled by the demands

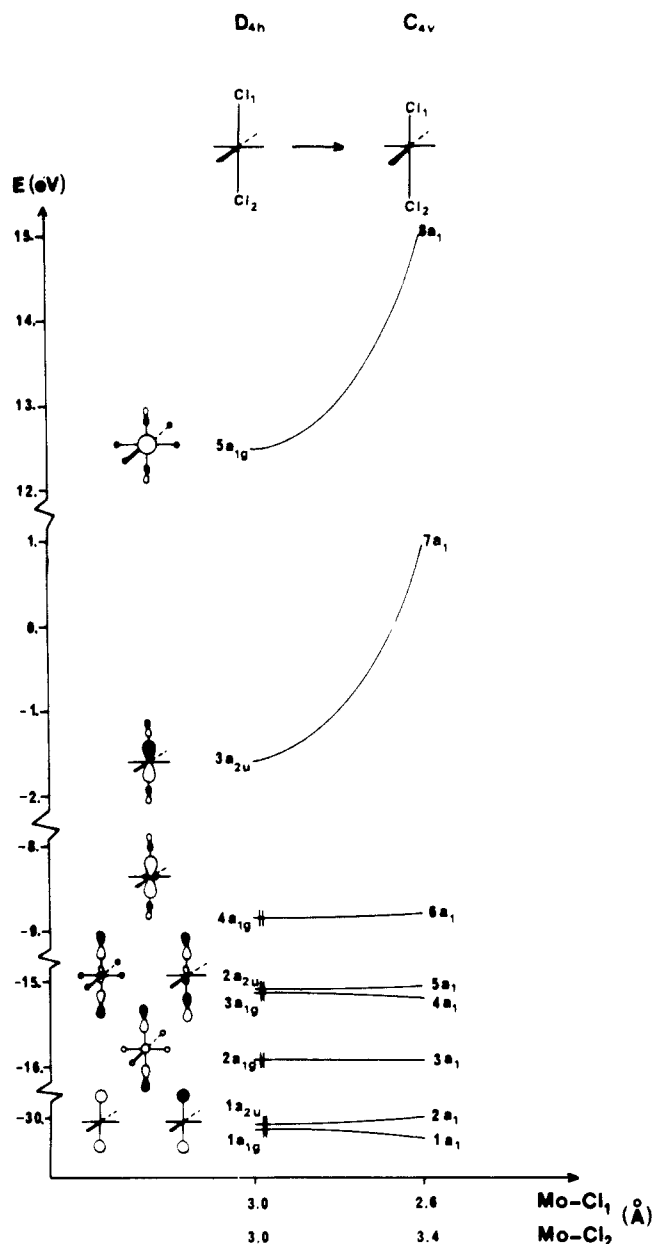
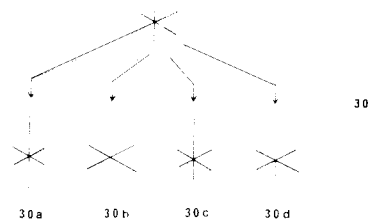


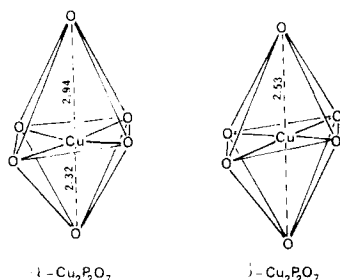
Figure 15. Energy of some of the  $\sigma$  orbitals in  $trans$ -MoCl<sub>2</sub>H<sub>4</sub><sup>9+</sup> upon an asymmetric distortion from Mo–Cl<sub>1</sub> = Mo–Cl<sub>2</sub> = 3.0 Å to Mo–Cl<sub>1</sub> = 2.6 Å and Mo–Cl<sub>2</sub> = 3.4 Å.

of Jahn–Teller mechanisms of both first and second order. “Octahedral” complexes of copper are virtually always distorted to give two long and four short M–ligand distances (30a) although



sometimes the long distances are so long that the complex is effectively square planar (30b). Sometimes the distortion is asymmetric (30c) with an extreme form (30d) that is a five-coordinate, square-pyramidal molecule. The distortions shown in 30a,b are controlled by (a) the stabilization of the three-quarters full ( $x^2 - y^2$ ,  $z^2$ ) pair of orbitals on the metal and (b) a second-order Jahn–Teller effect involving the  $(n + 1)s$  orbital. The contribution from (a) is strictly only a first-order one if all the ligands are equivalent and an exactly octahedral geometry results. Here we

are interested in the process that takes a symmetric complex with long metal-ligand bonds (**30a**) to its asymmetric analogue **30c**. Complexes of both types are known for systems of the same stoichiometry. **31**, for example, shows the  $\alpha$  and  $\beta$  isomers of  $\text{Cu}_2\text{P}_2\text{O}_7$ ,<sup>26</sup> as an example. From calculations on  $\text{MoCl}_2\text{H}_4^{9-}$  we see the opposite behavior to what we have seen before. Here the  $\pi$  manifold resists asymmetrization but  $\sigma$  favors it. It is easy to see where the  $\pi$  effect comes from. It is exactly the same argument we used before for the single minimum in the  $\sigma$  manifold for  $d^{1,2}$  compounds. All the  $\pi$  levels are full at  $d^9$  (see Figure 12) and the asymmetric motion leads to a two-level, four-electron destabilization.



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Figure 15 shows the levels of the  $\sigma$  system and the origin of the energetically favorable asymmetric stretch for the case of a long M-Cl bond (a similar effect is found in Figure 10). As the two metal trans ligand bonds are lengthened a dramatic drop is found in the energies of the orbitals largely  $(n+1)s$ ,  $(n+1)p$ . At long distance, this p orbital is effectively  $\sigma$  nonbonding. These low-lying orbitals may effectively mix with occupied  $\sigma$  orbitals during an asymmetric distortion via a second-order Jahn-Teller process to give a double minimum in the  $\sigma$  manifold. A word of caution, however. This has to be a very qualitative picture since our one-electron model is expected to be an even poorer approximation at these long distances than before. Thus the details of the coordination polyhedron around  $\text{Cu}^{\text{II}}$  will be even more difficult to mimic computationally than that for the low count complexes earlier. There is good evidence that the size of the distortion is controlled to a large extent by the local crystal environment, and certainly these long, weak bonds should be readily manipulable by such weak forces.

### Conclusions

We have suggested that the observed cases of bond-stretch isomerism are either the result of a real level crossing or as a

second-order Jahn-Teller distortion. The latter is typical of three-center four-electron  $\pi$  systems. In the process we have also come across some systems or distortions that have not been observed as yet, for instance **22**. These are worth looking for. We also feel that the observed structures may underestimate the extent of asymmetry, especially M-Cl distances. We do suggest that some of these structure be reinvestigated, and others in the series studied too, so that we can be more certain of the trends observed. Finally, we think that our calculations reopen the question of metal-halogen multiple bonding. We have clearly defined  $\text{MO}$ ,  $\text{MN}(\text{R})_n$ ,  $\text{MC}(\text{R})_n$  multiple bonding, why not  $\text{MX}$ , especially for  $\text{X} = \text{Cl}, \text{Br}$ ? Such bonding is formally here in these bond-stretch isomers.

**Note Added in Proof:** Dr. D. M. P. Mingos (private communication) has enquired as to how these results are changed if the real bond angles, present in these molecules, are used in the computations. These angle variations lead to quantitative changes of course, but the overall picture described in the paper is maintained.

**Acknowledgment.** J.K.B. and R.H. thank the National Science Foundation for support (DMR 8414175 and CHE 8406119). A.L. thanks the Ministerio de Education y Ciencia (Spain) for a postdoctoral fellowship and the CIRIT of Generalitat de Catalunya for a grant. We acknowledge the help of Prof. K. Wieghardt in communicating results prior to publication and for helpful comments and Prof. B. Haymore and Prof. S. Shaik for useful discussions.

### Appendix

The calculations are of the extended Hückel type<sup>27</sup> with the parameters given in Table II. Idealized octahedral geometries have been assumed. The bond lengths used for the model complexes are  $\text{M}-\text{Cl} = 2.35 \text{ \AA}$ ,  $\text{M}-\text{H} = 1.70 \text{ \AA}$ ,  $\text{M}-\text{O} = 1.70 \text{ \AA}$ ,  $\text{M}-\text{CN} = 2.15 \text{ \AA}$ ,  $\text{C}\equiv\text{N} = 1.15 \text{ \AA}$ . The experimental bond lengths were used for calculations on actual molecules.

(27) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397-1412. (b) Ammeter, J. H.; Bürgi, H.-B.; Thibault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686-3692.

(28) **Note Added in Proof:** In  $d^1 \text{ MoO}(\text{X})_4(\text{H}_2\text{O})^-$  complexes, with four  $\pi$ -donors cis to oxygen ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), an orbital crossing is likely to occur on Mo-O stretching (Figure 3) and these complexes are nice candidates for bond-stretch isomerism. The X-ray structure of  $\text{MoO}(\text{Br})_4(\text{H}_2\text{O})^-$  gives a short Mo-O distance of  $1.62 \text{ \AA}$  (Bino, A.; Cotton, F. A. *Inorg. Chem.* **1979**, *18*, 2710), while a previous investigation gave  $1.78 \text{ \AA}$  (Scane, J. G. *Acta Crystallogr.* **1967**, *23*, 85). A reinvestigation of the structure of this complex is therefore suggested to see whether one of the two reported structures is wrong or whether two bond-stretch isomers have been actually characterized.

(26) Robertson, B. E.; Clavo, C. *Acta Crystallogr.* **1967**, *22*, 665-672; *Can. J. Chem.* **1968**, *46*, 605-612.