

Bond-Stretch Isomerism in Transition Metal Complexes: A Reevaluation of Crystallographic Data

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Received July 27, 1992 (Revised Manuscript Received November 20, 1992)

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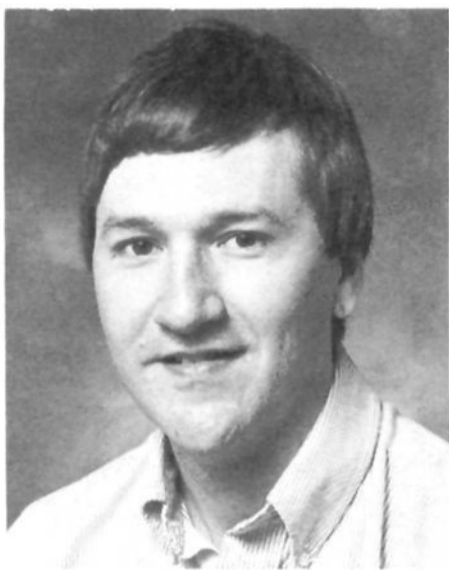
I. Introduction

The notion of isomerism, in which two (or more) molecules may differ only in the arrangement of their constituent atoms in space, has played a pivotal role in the development of chemistry. Indeed, it was the existence of optical isomers which first led van't Hoff and Le Bel to propose independently the three-dimensional tetrahedral nature of carbon in simple organic molecules. In turn, van't Hoff also predicted the existence of geometrical isomers of olefins, long before their discovery.¹ Over the years the concept of isomerism has been refined quite considerably, so that a variety of different types is presently recognized, including structural, geometrical, optical, and conformational isomerism. Today, the identification of molecular structure, and thereby the isomeric relationship between molecules, may be established by using a number of advanced techniques. In particular, X-ray crystallography, which determines the precise three-dimensional arrangement of atoms, is the most powerful method available. Indeed, as described by a recent textbook: "There can be no doubt that when a compound has to be identified there is nothing to beat a crystal structure determination. After all, the final outcome—a drawing of the molecule, with all the atoms nicely shaded and labeled—is convincing and will silence all but the most stubborn critics."² X-ray crystallography and its ability to measure accurate bond lengths within molecules are central to the new type of isomerism that forms the subject of this review—bond-stretch isomerism—the unusual phenomenon whereby molecules differ only in the *length* of one or more bonds.

II. Historical Development

A. Early Theoretical Studies

The interaction between two atoms as a function of their separation is generally represented by an energy surface of the type shown in Figure 1a. A single minimum is present at a separation that corresponds to the bond length. In contrast, the existence of isomers



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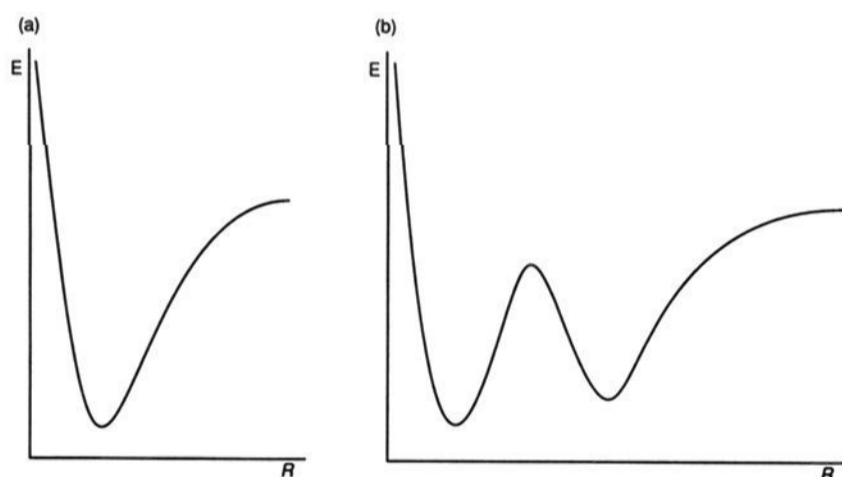


Figure 1. Potential energy surfaces for (a) a normal bond and (b) a pair of bond-stretch isomers.

which differ only in the length of one or more bonds requires the presence of a *double* minimum on the energy surface, as shown in Figure 1b.

The possibility of such a form of isomerism was first addressed theoretically by Hoffmann in a 1972 study on a series of organic molecules of the type $(\text{CH})_5^+$ and $(\text{CH})_4\text{CO}$ (Figure 2).³ Significantly, Hoffmann's work demonstrated that, for these hypothetical species, a double minimum of the type illustrated in Figure 1b could be obtained and thereby named the phenomenon *bond-stretch isomerism*. The existence of a double minimum on the energy surface of these species is due to a crossing of symmetric (S) and antisymmetric (A) levels as a function of the bond distance (R). For a normal bond, these levels do not cross, but only approach each other as the interatomic separation increases (Figure 3). However, if the S and A levels cross as a function of R , a double minimum is obtained on the energy surface, as illustrated in Figure 4. Using $(\text{CH})_5^+$ (Figure 2) as an example, Hoffmann showed that the A combination of p orbitals on C_1 and C_5 could be stabilized at large C_1 – C_5 separations (R) by favorable interaction with the p orbital on C_3 (Figure 5). Thus, as the C_1 – C_5 bond is stretched, the A component mixes

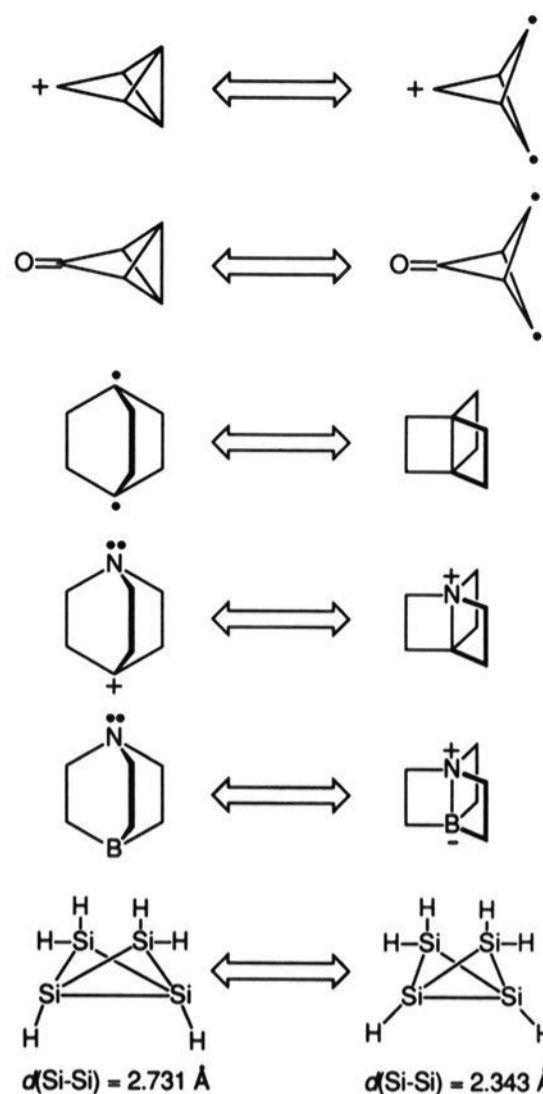


Figure 2. Some hypothetical bond-stretch isomers that have been studied theoretically.

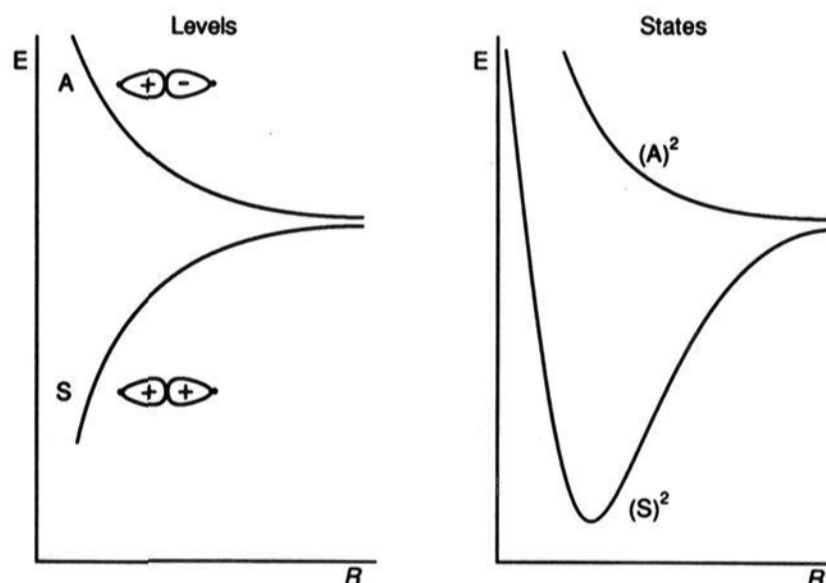


Figure 3. Energy diagram for a normal bond. Adapted from ref 3b.

substantially with the p orbital on C_3 , so that the A component sinks significantly below S, as shown in Figure 6. The overall result is the development of two minima on the energy surface. Hoffmann's theoretical analysis thereby laid the foundation for bond-stretch isomerism and was shortly followed by other theoretical analyses of heteroatom systems, e.g. $\text{B}(\text{CH}_2\text{CH}_2)_3\text{N}$ (Figure 2),⁴ Si_4H_6 (Figure 2), CSi_3H_6 , $\text{C}_2\text{Si}_2\text{H}_6$,⁵ $\text{Li}_2\text{B}_2\text{H}_4$,⁶ C_2Si_2 ,⁷ B_2Be_2 ,⁸ and C_3X ($\text{X} = \text{Be}, \text{BH}, \text{Si}$).⁹

B. Experimental Evidence: Chatt's Distortional Isomers

Experimental evidence in support of bond-stretch isomerism was to be found first for transition metal complexes and had actually been briefly reported about a year prior to Hoffmann's proposal. In 1970 Chatt

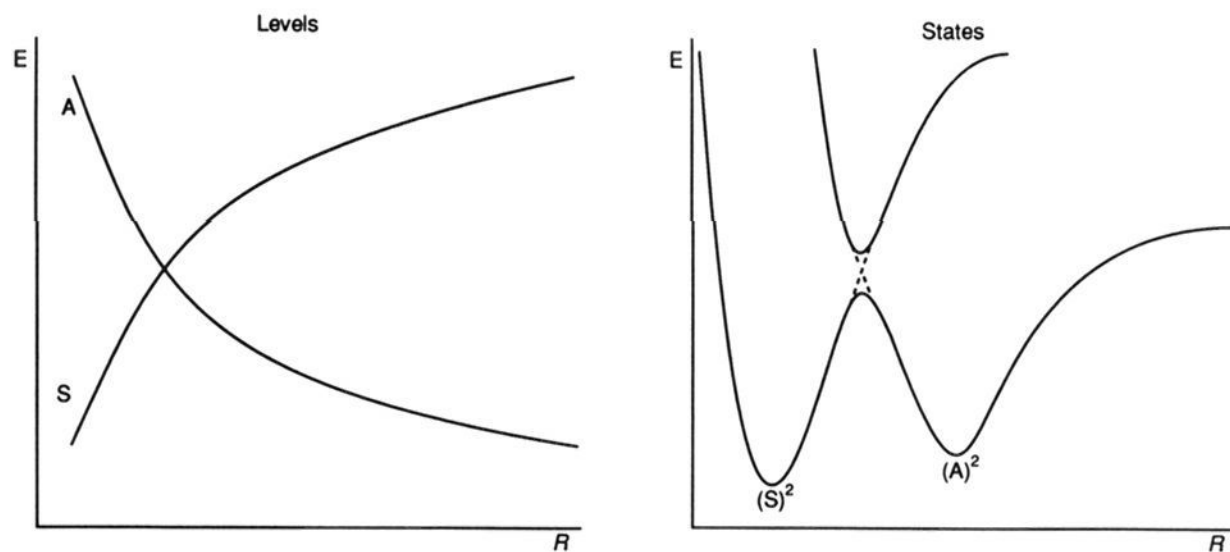


Figure 4. Energy diagram for a pair of bond-stretch isomers. Adapted from ref 3b.

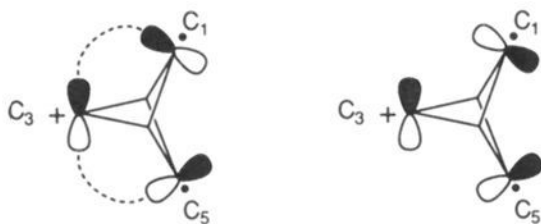


Figure 5. Stabilization of the antisymmetric (A) combination of p orbitals on C₁ and C₅ by an acceptor orbital at C₃.

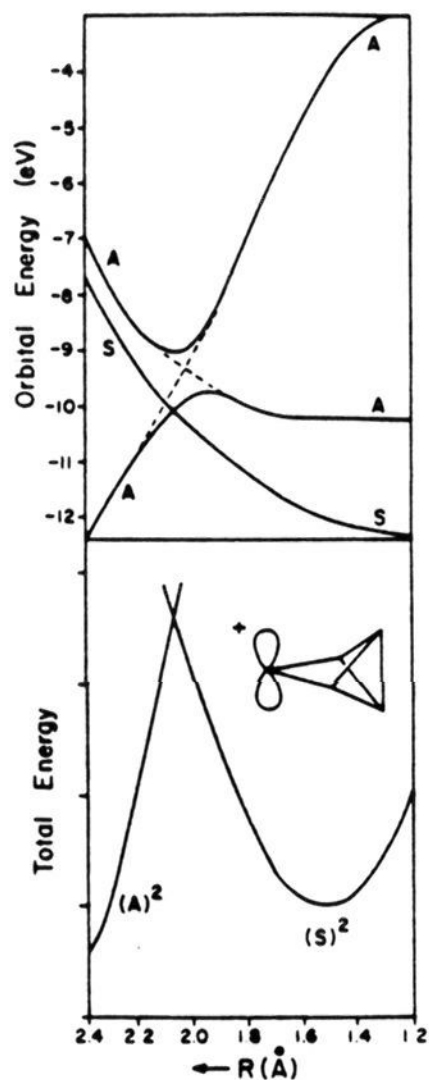


Figure 6. Highest occupied and two lower unoccupied MO's (top) and configuration energies (bottom) for stretching the C₁-C₅ bond in (CH)₅⁺. *R* is the C₁-C₅ bond distance. The total energy scale is 1.0 eV. Reprinted from ref 3b. Copyright 1972 American Chemical Society.

reported a series of octahedral molybdenum oxo complexes with a meridional arrangement of phosphine ligands, *mer*-MoOX₂(PR₃)₃ (X = Cl, Br, I, NCO, NCS; PR₃ = PMe₂Ph, PEt₂Ph, PPrⁿ₂Ph, PBuⁿ₂Ph, PMePh₂, PEtPh₂, PPrⁿPh₂).¹⁰ Although the complexes *mer*-MoOX₂(PR₃)₃ were either blue or green, depending upon the nature of both X and PR₃, one of these complexes, namely *mer*-MoOCl₂(PMe₂Ph)₃ could be

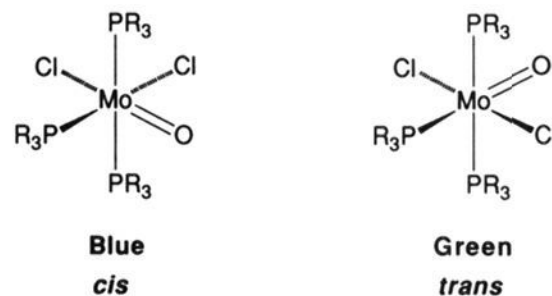


Figure 7. Original (incorrect) proposal for the structures of blue and green *mer*-MoOCl₂(PR₃)₃ complexes. Reprinted from ref 32. Copyright 1992 American Chemical Society.

Table I. Selected Bond Lengths (Å) for Mo(O)Cl₂(PMe₂Ph)₃ and Mo(O)Cl₂(PEt₂Ph)₃^a

	blue Mo(O)Cl ₂ (PMe ₂ Ph) ₃	green Mo(O)Cl ₂ (PEt ₂ Ph) ₃
Mo-O	1.676(7)	1.803(11)
Mo-Cl(1) ^b	2.551(3)	2.426(6)
Mo-Cl(2) ^b	2.464(3)	2.479(5)
Mo-P(1)	2.500(3)	2.521(5)
Mo-P(2)	2.541(3)	2.582(6)
Mo-P(3)	2.558(3)	2.556(6)

^a Taken from ref 12a. ^b Cl(1) and Cl(2) are trans and cis to O, respectively.

isolated in both blue and green isomeric forms. The blue isomer of *mer*-MoOCl₂(PMe₂Ph)₃ was reported to be the more stable, with solutions of the green isomer irreversibly converting to the blue isomer upon gentle heating. The blue and green complexes, with slightly different $\nu(\text{Mo}=\text{O})$ stretching frequencies (blue, 954 cm⁻¹; green 943 cm⁻¹), were originally proposed to be *geometric* isomers, namely *cis-mer*-MoOCl₂(PMe₂Ph)₃ and *trans-mer*-MoOCl₂(PMe₂Ph)₃, differing only in whether the two chloride ligands were cis or trans. A cis configuration of chloride ligands was established for the blue isomer by X-ray diffraction, from which it was concluded that the green isomer, and hence *all* the green complexes, possessed a trans configuration (Figure 7).^{10,11}

However, in 1971, the green oxo complex *mer*-MoOCl₂(PEt₂Ph)₃ was also shown by X-ray diffraction to possess cis, and not trans, chloride ligands.¹² Although the overall coordination environments around the molybdenum centers of blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ and green *cis-mer*-MoOCl₂(PEt₂Ph)₃ were similar, as summarized by the bond lengths listed in Table I, a substantial difference was observed for the lengths of the Mo=O bonds for the two complexes: the Mo=O bond length in green *cis-mer*-MoOCl₂(PEt₂Ph)₃ [1.803(11) Å] was *significantly* longer than that observed in

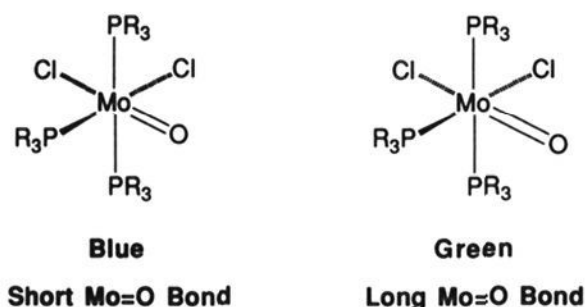


Figure 8. Proposed distortional isomerism for blue and green *cis-mer*-MoOCl₂(PR₃)₃ complexes. Reprinted from ref 32. Copyright 1992 American Chemical Society.

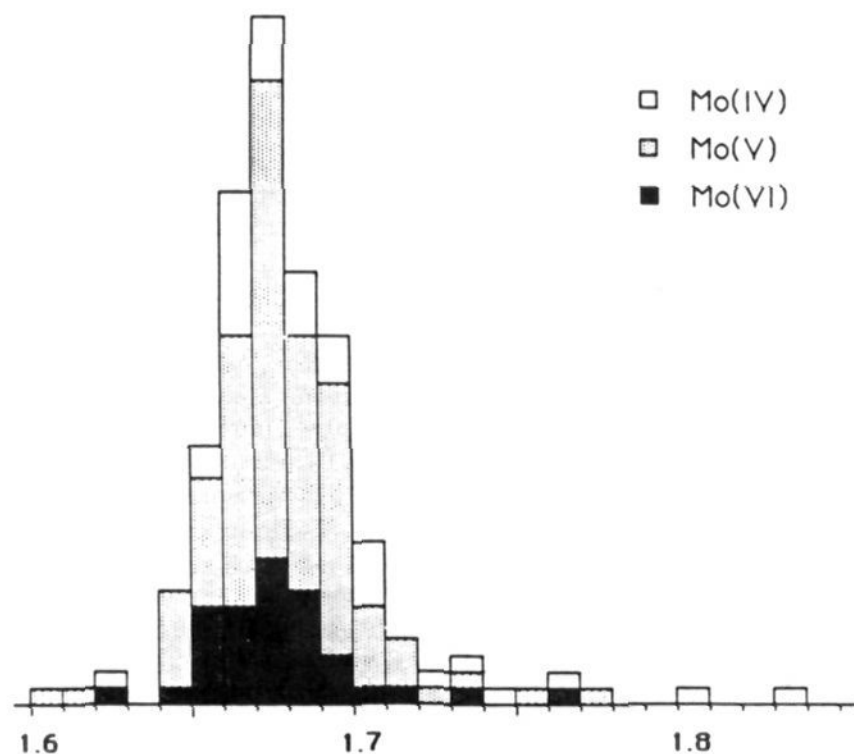


Figure 9. Distribution of molybdenum-oxygen distances (Å) for monooxo complexes in the oxidation states +4, +5, and +6. Only bond lengths with standard deviations less than 0.015 Å are included. Reprinted from ref 14a. Copyright 1988 Wiley.

blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ [1.676(7) Å]. The only other significant change in bond length was that for the trans chloride ligand (but to a much smaller degree). This result prompted Chatt to suggest that the difference between the blue and green isomers of *mer*-MoOCl₂(PMe₂Ph)₃ centered not on a *cis* versus *trans* disposition of chloride ligands, as originally proposed,^{10,11} but rather on *inequivalent* Mo=O bond lengths. Chatt proposed the term “distortional isomers” to describe these complexes (Figure 8) involving “two equilibrium arrangements of ligands, which differ in the distortions of the highly strained co-ordination polyhedron of the metal”.^{12a}

The green isomer of *cis-mer*-MoOCl₂(PMe₂Ph)₃ was structurally characterized at a later date by Haymore and, consistent with the above proposal, was also found to possess a long Mo=O bond length of 1.80(2) Å.¹³ It is important to emphasize the significance of the magnitude of the above changes in bond length. In this regard, Nugent and Mayer have recently reported a statistical survey of metal-oxo bond lengths, and the results for monooxo complexes of molybdenum are summarized in Figure 9.¹⁴ Significantly, a relatively narrow distribution is observed, with a mean Mo=O bond length of 1.678 Å for 122 different structures. Hence, it is apparent that, of the pair of blue and green bond-stretch isomers, it is the unstable green isomer with a long Mo=O bond length of 1.80(4) Å that is unusual.

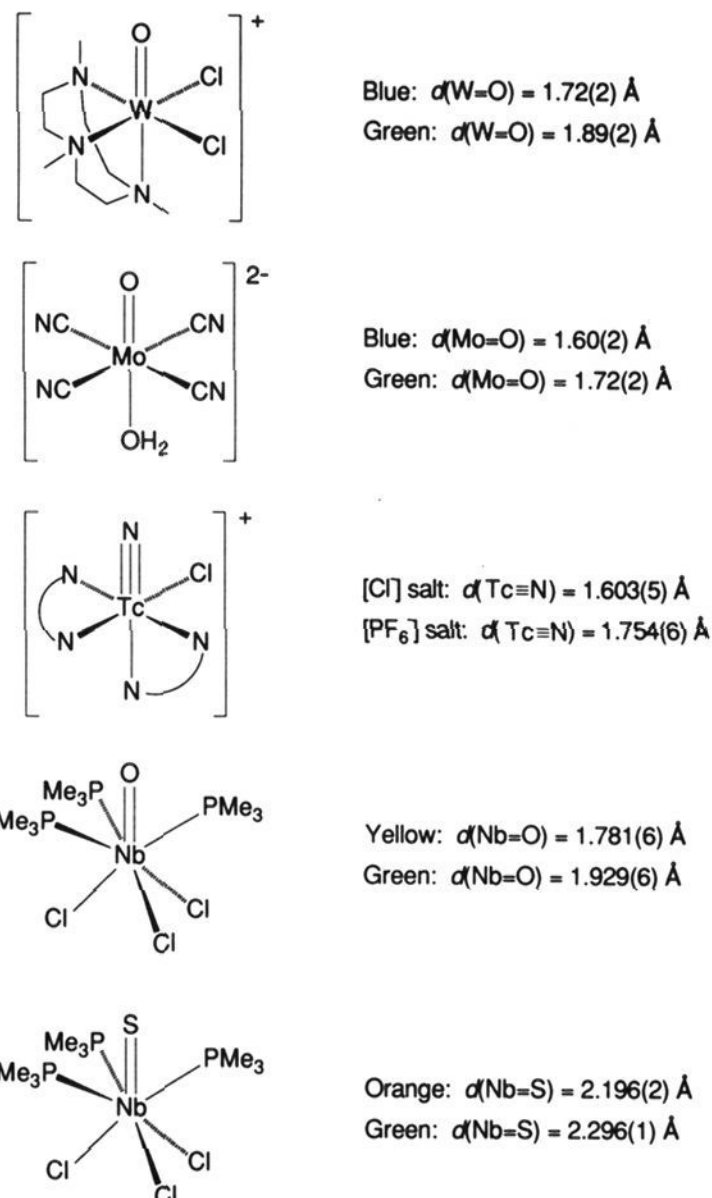


Figure 10. Structurally characterized bond-stretch isomers.

C. Other Examples of Bond-Stretch Isomerism

A number of other transition metal complexes have been proposed to exhibit bond-stretch isomerism (or distortional isomerism) since the original report. Examples of bond-stretch isomers that have been structurally characterized include [(Me₃tacn)W(O)Cl₂]⁺ (Me₃tacn = *N,N',N''*-trimethyl-1,4,7-triazacyclononane),¹⁵ [Mo(CN)₄(O)(OH₂)]²⁻,¹⁶ [*cis*-Tc(N)Cl(phen)₂]⁺,¹⁷ Nb(O)Cl₃(PMe₃)₃,¹⁸ and Nb(S)Cl₃(PMe₃)₃,¹⁸ as shown in Figure 10. In addition, two geometric isomers of the oxo-bridged complex [[η³-HB(pz)₃]Mo(O)Cl₂(μ-O)] have been reported, one with a center of symmetry (*C_i*) through the bridging oxo ligand and one with an approximate *C₂* axis through the bridging oxo ligand.¹⁹ Further to the geometrical difference, a striking structural difference was also observed in the lengths of the terminal Mo=O bonds: the *C₂* isomer exhibited a bond length of 1.671(4) Å, whereas the *C_i* isomer exhibited a substantially longer bond length of 1.779(6) Å. Although the *C_i* and *C₂* complexes are not strictly bond-stretch isomers since they also have different geometrical structures, the origin of the long bond length for the *C_i* isomer was linked to the phenomenon of bond-stretch isomerism.

Examples of bond-stretch isomerism are not restricted to metal-oxo complexes, with examples having also been reported for metal-nitrido and metal-sulfido complexes.^{18,20} Furthermore, bond-stretch isomerism has also been postulated for the complexes [η³-HB(pz)₃]ReOCl₂,²¹ [(Me₃tacn)Mo(NO)Cl(OEt)]⁺,²² and [(Me₃tacn)W(NO)Br(OEt)]⁺²² without the aid of structure determination by X-ray diffraction (Figure 11).

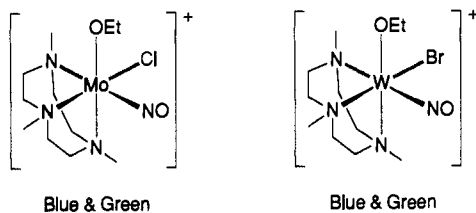
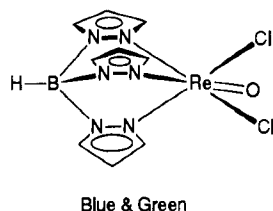


Figure 11. Proposed bond-stretch isomers without X-ray structure determinations.

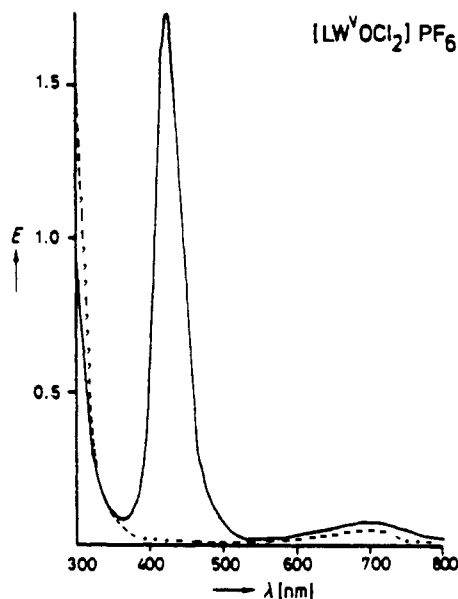


Figure 12. Electronic absorption spectra of blue [(Me₃tacn)W(O)Cl₂][PF₆] (---) (3.5×10^{-3} M) and green [(Me₃tacn)W(O)Cl₂][PF₆] (—) (2.0×10^{-3} M) in dry acetonitrile (1-cm cuvette). Reprinted from ref 15. Copyright 1985 VCH.

The blue [$d(W=O)$ 1.72(2) Å] and green [$d(W=O)$ 1.89(2) Å] cationic tungsten oxo derivatives [(Me₃tacn)W(O)Cl₂]⁺¹⁵ represent important examples since these were the first set of bond-stretch isomers that were reported to be stable in solution for several days, as demonstrated by the UV-visible spectra shown in Figure 12. In the solid state, the isomers were remarkably robust and did not interconvert at temperatures up to ca. 180 °C. The blue and green isomers also exhibited different $\nu(W=O)$ stretching frequencies of 980 and 960 cm⁻¹, respectively, with the higher energy vibration corresponding to the shorter W=O bond. The orange-yellow [$d(Nb=S)$ 2.196(2) Å] and green [$d(Nb=S)$ 2.296(1) Å] isomers of Nb(S)Cl₃(PMe₃)₃¹⁸ are also particularly interesting, since they provided the first example of bond-stretch isomerism for sulfido derivatives, and were also cited by McPartlin as appearing to prove beyond doubt that bond-stretch isomerism was a real phenomenon.^{18b} However, the $\nu(Nb=S)$ stretching frequencies of the isomers of Nb(S)Cl₃(PMe₃)₃ did not correlate with Nb=S bond lengths in the same manner observed for the oxo

complexes described above, in that the complex with the longer Nb—S bond exhibited the unprecedented higher $\nu(Nb=S)$ stretching frequency (489 cm⁻¹ versus 455 cm⁻¹).

D. Theoretical Rationalization for Bond-Stretch Isomerism in Transition Metal Complexes

In 1988 Jean, Lledos, Burdett, and Hoffmann extended the earlier calculations on hypothetical species in order to rationalize the presence of double minima on the potential energy surfaces of the complexes actually reported to exhibit the phenomenon.²³ Two electronic mechanisms were proposed in order to rationalize the existence of bond-stretch isomers for the aforementioned transition metal complexes.

1. An Electronic Crossing of Filled and Empty Orbitals (a First-Order Jahn-Teller Effect)

The energy diagram shown in Figure 13 illustrates the effect of stretching the W—O bond for the d¹ species [W(O)H₅]²⁻, a model for the complex [(Me₃tacn)W(O)Cl₂]⁺. The left-hand side of Figure 13 illustrates the splitting of the t_{2g} block for an octahedral complex that is induced by π -bonding with oxygen. The d_{xy} orbital is purely nonbonding, while the d_{xz} and d_{yz} orbitals are destabilized by interaction with the filled p orbitals on oxygen. As the W—O bond is stretched, the d_{xz} and d_{yz} orbitals are stabilized and would become degenerate with the d_{xy} orbital at infinite separation. As such, no crossing in the d block would be expected. Incorporation of a π -donor chloride substituent cis to the oxo ligand has the effect of destabilizing d_{xy} and d_{xz} orbitals, but would leave d_{yz} unaffected (compare the left-hand sides of Figures 13 and 14). Therefore, the possibility arises that a crossing may occur in the d block as the W—O bond is lengthened, as shown in Figure 14. As the W—O bond is lengthened the HOMO transforms from an orbital that is originally W—O nonbonding (d_{xy}) to one that is W—O antibonding after the crossing (d_{yz}). This change also corresponds to depopulation of the originally occupied antibonding W—Cl orbital, so that stretching of the W—O bond should be compensated by a stronger cis W—Cl interaction. However, a similar treatment revealed that an orbital crossing in the d block would not be expected for the situation in which π -donor ligands are located trans to the oxo ligand. Indeed, since both the d_{yz} and d_{xz} orbitals are destabilized by interaction with the chloride substituent, while the d_{xy} orbital remains nonbonding, such an interaction actually mitigates against an orbital crossing (Figure 15). Application of these considerations suggested that [(Me₃tacn)W(O)Cl₂]⁺, with two cis chloride ligands, would be a good candidate for this electronic mechanism, which was supported further by extended Hückel calculations on the model complex [(NH₃)₃W(O)Cl₂]⁺.

2. Reorganization of d- π Bonding (a Second-Order Jahn-Teller Effect)

Although the mechanism described above provided an explanation for bond-stretch isomerism in [(Me₃tacn)W(O)Cl₂]⁺, it did not provide a satisfactory answer for complexes of the type *cis-mer*-MoOCl₂(PR₃)₃ in

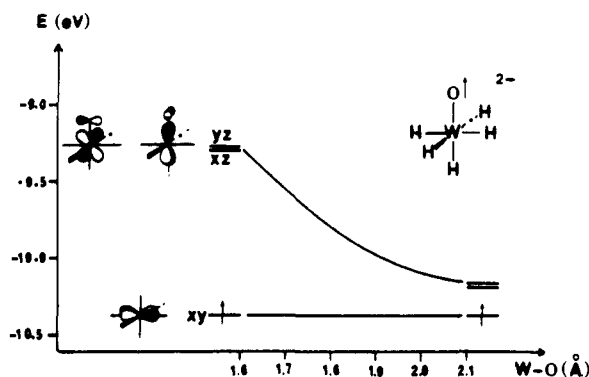


Figure 13. Energy of the low-lying d orbitals in the model d^1 complex $[\text{WOH}_5]^{2-}$ as a function of W-O stretching. Reprinted from ref 23a. Copyright 1988 American Chemical Society.

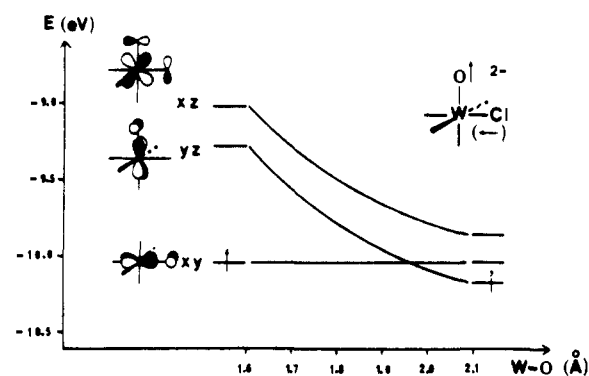


Figure 14. Energy of the low-lying d orbitals in the model d^1 complex $[\text{WOCIH}_4]^{2-}$, with chlorine atom cis to oxygen, as a function of W-O stretching alone. Adapted from ref 23a.

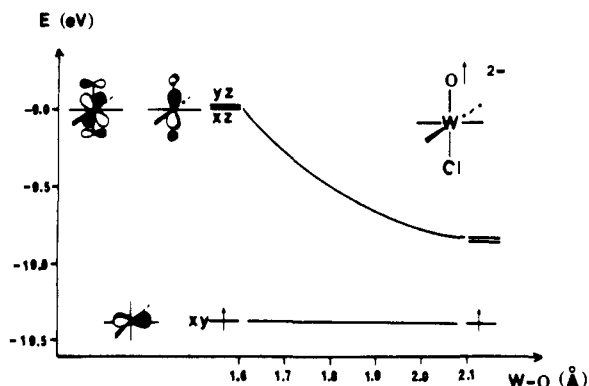


Figure 15. Energy of the low-lying d orbitals in the model d^1 complex $[\text{WOCIH}_4]^{2-}$, with chlorine atom trans to oxygen, as a function of W-O stretching alone. Adapted from ref 23a.

which the presence of a trans chloride substituent would inhibit an orbital crossing. An alternative mechanism for these complexes was suggested by recognizing that the stretching of the Mo-O bond was accompanied by a shortening of the trans Mo-Cl bond. This observation suggested that a double minimum could result from a reorganization of the $d-\pi$ bonding: in one isomer the $d-\pi$ bond would be developed mainly within the Mo-O interaction, and in the other isomer the $d-\pi$ bond would be developed mainly within the Mo-Cl_{trans} interaction. In order to test the role that such an interaction may play, the symmetric d^2 species [*trans*-MoCl₂H₄]²⁻ was first studied. Examination of Figure 16 indicates that as asymmetry is induced in the Mo-Cl bond lengths the $1e_u$ orbital is strongly stabilized by mixing with the

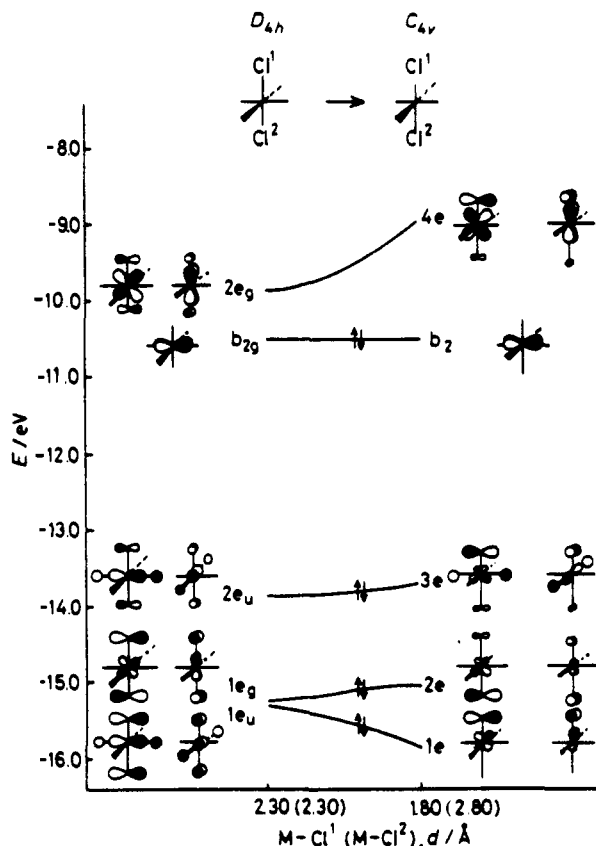


Figure 16. Orbital diagram for the asymmetric distortion of the two Mo-Cl bonds in the model complex *trans*- $[\text{MoCl}_2\text{H}_4]^{2-}$. Reprinted from ref 23b. Copyright 1988 American Chemical Society.

$2e_g$, thereby promoting a distortion on π -grounds. If this π -component dominates over the σ -component (which has a minimum at the symmetric geometry), then two minima would result (Figure 17), but if the σ -component dominates only a single minimum would be observed. This mechanism could therefore provide an explanation for bond-stretch isomerism in *cis-mer*- $\text{MoOCl}_2(\text{PR}_3)_3$.

E. Structural Changes in Isomers with Different Spin States

The above examples of bond-stretch isomerism in transition metal complexes are all characterized by a principal change in a single bond length, with the remainder of the molecule being relatively unperturbed. There are, however, other examples of isomerism that may be related to bond-stretch isomerism, but which are also accompanied by significant additional changes within the molecule. Indeed, it is well known that there are many transition metal complexes that exhibit different spin states (high spin/low spin equilibria) for which significant structural changes are also observed.²⁴ The principal structural changes between the different spin states may center on either (i) differences in their bond lengths or (ii) differences in their geometrical shapes with, for example, $\text{Ni}[\text{PPh}_2(\text{CH}_2\text{Ph})]_2\text{Br}_2$ existing as both square-planar and tetrahedral isomers.²⁵ Similarly, the isomers hexamethylbenzene and hexamethyl(Dewar benzene) are related by changes in several bonds, and not just a single-bond length.

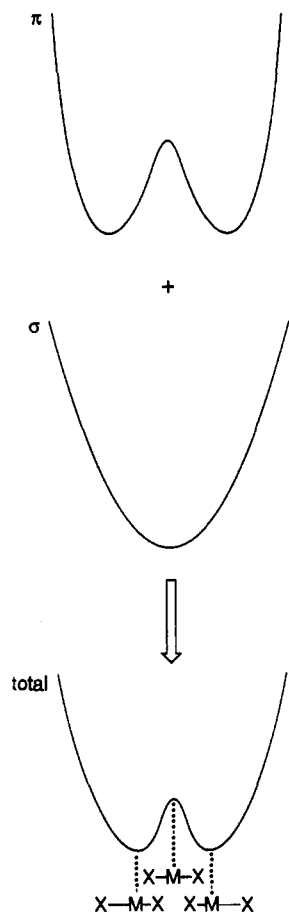


Figure 17. The total energy as a function of distance is a result of opposite trends for E_σ (single minimum) and E_π (double minimum). For this example the double minimum dominates.

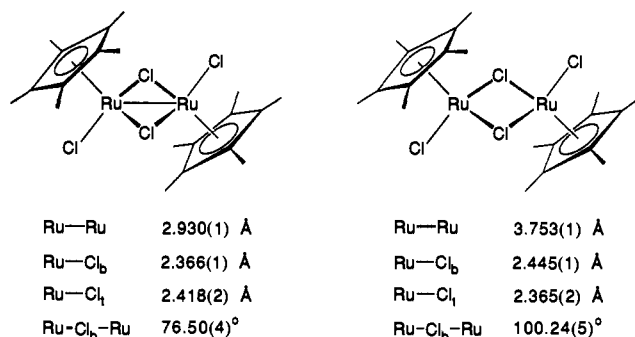


Figure 18. Deformational isomers of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2]_2$.

More recently, Kölle using X-ray diffraction has established the presence of two structurally different isomers within a single crystalline sample of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2]_2$.²⁶ The two isomers differ substantially in both their Ru—Ru separations [2.930(1) Å versus 3.753(1) Å] and Ru—Cl—Ru bond angles [76.50(4)° versus 100.24(5)°], and also in their Ru—Cl bond lengths (Figure 18). Magnetic susceptibility and solution NMR studies suggested that the isomers differ in their magnetic properties such that one isomer is a singlet with a Ru—Ru bond [2.930(1) Å], whereas the other isomer is a triplet without a significant Ru—Ru bonding interaction [Ru...Ru = 3.753(1) Å]. Extended Hückel calculations have provided a qualitative explanation for the observed geometries and spin states of the two isomers.²⁷ Since the isomers of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2]_2$ are related by changes of several bond lengths and angles,

Table II. Selected Bond Lengths (Å) for $\text{Mo}(\text{O})\text{Cl}_2(\text{PMePh}_2)_3$ and $\text{Mo}(\text{O})(\text{NCO})_2(\text{PEt}_2\text{Ph})_3$ ^a

	$\text{Mo}(\text{O})\text{Cl}_2(\text{PMePh}_2)_3$	$\text{Mo}(\text{O})(\text{NCO})_2(\text{PEt}_2\text{Ph})_3$ ^b	
Mo—O	1.667(4)	1.678(8)	1.690(8)
Mo—X(1) ^c	2.509(2)	2.18(1)	2.18(1)
Mo—X(2) ^c	2.466(2)	2.10(1)	2.09(1)
Mo—P(1)	2.555(2)	2.542(4)	2.524(4)
Mo—P(2)	2.570(2)	2.548(4)	2.555(4)
Mo—P(3)	2.577(2)	2.575(4)	2.577(4)

^a Taken from ref 29. ^b Two molecules of $\text{Mo}(\text{O})(\text{NCO})_2(\text{PEt}_2\text{Ph})_3$ in asymmetric unit. ^c X(1) and X(2) are trans and cis to O, respectively.

the term “bond-stretch isomers” is not particularly appropriate for this system so that Kölle has introduced the term “deformational isomers” to describe them. A related example is provided by the complex $[\text{Rh}_2(\mu\text{-Cl})_2(\mu\text{-AuPPh}_3)(\text{CNC}_8\text{H}_9)_4]_2[\text{PF}_6]_2$ which exists as red and green isomers with different conformations and different Rh—Rh bond lengths.²⁸

III. Recent Studies on Bond-Stretch Isomerism in *cis-mer-MoOX₂(PR₃)₃* Complexes

A. *cis-mer-MoOCl₂(PMePh₂)₃* and *cis-mer-MoO(NCO)₂(PEt₂Ph)₃*

Cotton has recently reported the structures of two complexes that are closely related to Chatt's early work, namely green *cis-mer-MoOCl₂(PMePh₂)₃* and blue *cis-mer-MoO(NCO)₂(PEt₂Ph)₃*.²⁹ Important bond lengths for these complexes are summarized in Table II. Significantly, the blue complex *cis-mer-MoO(NCO)₂(PEt₂Ph)₃* crystallized with two independent molecules in the asymmetric unit, as illustrated in Figure 19. Although the coordination environment about the metal is similar for both molecules, the orientation of the alkyl and aryl groups on the phosphine ligands differ considerably. However, the variation in orientation of the phosphine substituents has little effect on the Mo=O bond lengths for the two independent molecules, which are very similar [1.678(8) and 1.690(8) Å] and close to the short Mo=O bond length observed for blue *cis-mer-MoOCl₂(PMe₂Ph)₃* [1.676(7) Å].¹¹

Unexpectedly, Cotton did not observe the anticipated long (ca. 1.80 Å) Mo=O bond length for the green complex *cis-mer-MoOCl₂(PMePh₂)₃*. Surprisingly, a short Mo=O bond length of 1.667(4) Å was determined for green *cis-mer-MoOCl₂(PMePh₂)₃*, close to the value for blue *cis-mer-MoOCl₂(PMe₂Ph)₃* [1.676(7) Å].¹¹ Thus, the green complex *cis-mer-MoOCl₂(PMePh₂)₃* more closely resembled the blue isomer of *cis-mer-MoOCl₂(PMe₂Ph)₃* rather than green *cis-mer-MoOCl₂(PEt₂Ph)₃*. Since a hypothetical distortional isomer of *cis-mer-MoOCl₂(PMePh₂)₃* would presumably have a longer Mo=O bond (ca. 1.80 Å), the possibility existed that it could also be green, and therefore difficult to identify if it was present.

B. *cis-mer-MoOCl₂(PMe₃)₃*

The trimethylphosphine analogue *cis-mer-MoOCl₂(PMe₃)₃* was first prepared by Carmona and Wilkinson in 1984, by the reaction of $\text{MoCl}_4(\text{THF})_2$ with PMe_3 and H_2O in THF.³⁰ This reaction generally produced green crystals of *cis-mer-MoOCl₂(PMe₃)₃*, but occa-

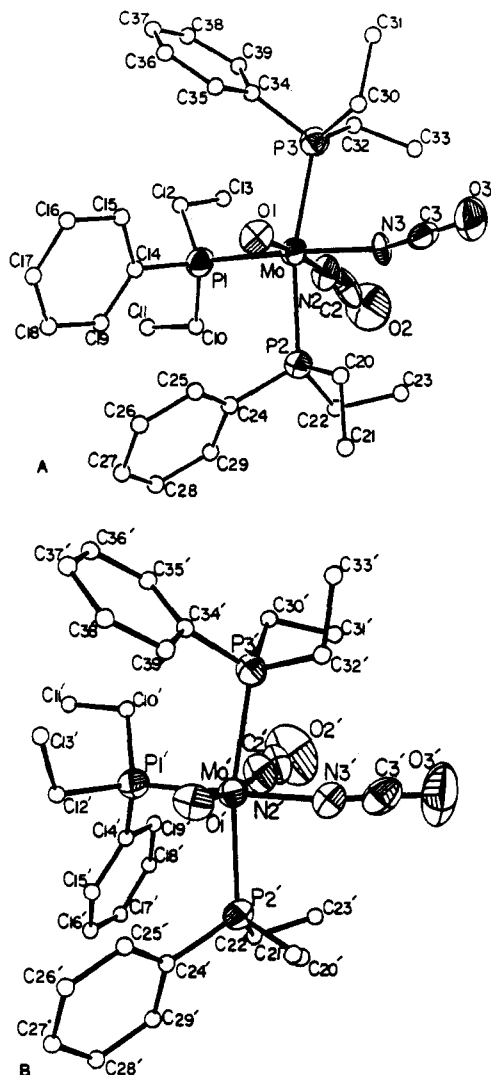


Figure 19. ORTEP views of two independent molecules of $\text{Mo}(\text{O})(\text{NCO})_2(\text{PEt}_2\text{Ph})_3$. Reprinted from ref 29. Copyright 1987 American Chemical Society.

sionally, under apparently the same conditions, blue crystals of $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3$ could be obtained, which possessed identical IR and ^1H NMR spectra to those of the green isomer. The conditions for formation of the blue isomer could not be ascertained, which seemed to suggest that the green isomer of $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3$ was the more stable of the two forms. Although the molecular structure of neither blue or green isomers had been determined by X-ray crystallography, the observations were in contrast to Chatt's dimethylphenylphosphine $\text{cis-mer-MoOCl}_2(\text{PMe}_2\text{Ph})_3$ system, where the green isomer (long $\text{Mo}=\text{O}$ bond length) irreversibly converted to the blue isomer (short $\text{Mo}=\text{O}$ bond length).

The molecular structure of green $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3$ was determined by X-ray diffraction methods in 1991.³¹⁻³³ The asymmetric unit contained two crystallographically independent molecules of $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3$, as shown in Figure 20. Significantly, the two molecules differed substantially in the lengths of the $\text{Mo}=\text{O}$ bonds, 1.698(8) versus 1.866(7) Å. The observation of pairs of crystallographically inequivalent, but chemically equivalent, molecules in a crystal is not uncommon (see for example the structure of $\text{cis-mer-MoO}(\text{NCO})_2(\text{PEt}_2\text{Ph})_3$ described in section III.A).

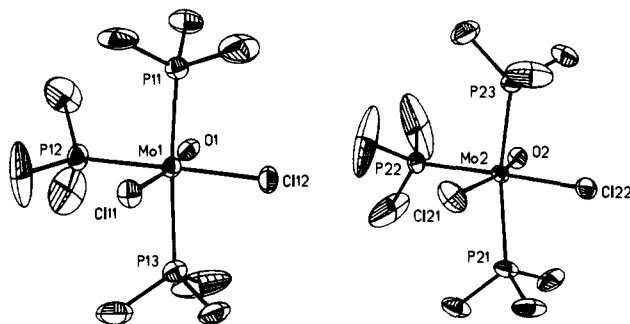


Figure 20. ORTEP drawings for the two crystallographically independent molecules of $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3$. Reprinted from ref 32. Copyright 1992 American Chemical Society.

Table III. Bond Lengths (Å) around Mo in $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3^a$

	crystal no. 1		crystal no. 2	
	molecule no. 1	molecule no. 2	molecule no. 1	molecule no. 2
Mo-O	1.698(8)	1.866(7)	1.772(12)	2.154(8)
Mo-Cl(1)	2.509(4)	2.513(2)	2.496(7)	2.476(4)
Mo-Cl(2)	2.469(2)	2.470(3)	2.462(4)	2.448(4)
Mo-P(1)	2.538(3)	2.524(3)	2.540(5)	2.530(6)
Mo-P(2)	2.497(2)	2.497(3)	2.493(5)	2.512(5)
Mo-P(3)	2.520(3)	2.567(4)	2.510(5)	2.560(6)

^a Taken from ref 32.

However, chemically equivalent bond lengths are expected to differ only slightly (<0.05 Å) between the molecules due to crystal packing forces.³⁴ Therefore, the X-ray structure determination suggested that *both* bond-stretch isomers of $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3$ were present in the same crystal. However, only one $\nu(\text{Mo}=\text{O})$ stretching frequency could be observed in the solid-state IR spectrum, rather than the expected two absorptions corresponding to $\nu(\text{Mo}=\text{O})$ of the long and short isomers. The observation of only one $\nu(\text{Mo}=\text{O})$ stretching frequency in the solid-state IR spectrum of $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3$ was inconsistent with the presence of two molecules which differ substantially in their $\text{Mo}=\text{O}$ bond lengths.³⁵ Therefore, a second X-ray structure determination, on a crystal of $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3$ obtained from a different batch, was undertaken. The results of the two X-ray diffraction studies are summarized in Table III. Surprisingly, *two new* $\text{Mo}=\text{O}$ bond lengths of 1.772(12) and 2.154(8) Å were observed for the second structure determination, with other Mo-Cl and Mo-P bond lengths being similar to those of the first structure determination. The discrepancy between the two structure determinations strongly suggested that the differences in $\text{Mo}=\text{O}$ bond lengths were not a manifestation of the phenomenon of bond-stretch isomerism, in which a *quadruple* minimum on the energy surface would now be required.

The origin of the variation in $\text{Mo}=\text{O}$ bond lengths for $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3$ was attributed to crystallographic disorder due to cocrystallization with the isostructural trichloride complex $\text{mer-MoCl}_3(\text{PMe}_3)_3$, an impurity.³⁶ The presence of the contaminant $\text{mer-MoCl}_3(\text{PMe}_3)_3$ was verified by examination of the ^1H NMR spectrum of the sample over the range δ -35 to 10 ppm (Figure 21). In addition to the sharp resonances of $\text{cis-mer-MoOCl}_2(\text{PMe}_3)_3$ in the normal diamagnetic range, two broad resonances were also observed at δ -16 and -33 ppm, corresponding to paramagnetic *mer-*

Table IV. Apparent Bond Lengths in *mer*-MoO_xCl_{3-x}(PMe₂Ph)₃ as a Function of Composition^a

composition	color	<i>d</i> (Mo-L), Å	<i>d</i> (Mo-Cl _{trans}), Å	<i>d</i> (Mo-Cl _{cis}), Å
Mo(PMe ₂ Ph) ₃ OCl ₂	blue	1.675(3)	2.528(1)	2.481(1)
Mo(PMe ₂ Ph) ₃ O _{0.99} Cl _{2.01}	blue	1.683(3)	2.528(1)	2.479(1)
Mo(PMe ₂ Ph) ₃ O _{0.98} Cl _{2.02}	green-blue	1.694(5)	2.529(1)	2.481(2)
Mo(PMe ₂ Ph) ₃ O _{0.97} Cl _{2.03}	green	1.789(3)	2.510(1)	2.471(2)
Mo(PMe ₂ Ph) ₃ O _{0.96} Cl _{2.04}	green	1.871(3)	2.510(1)	2.465(2)
Mo(PMe ₂ Ph) ₃ O _{0.72} Cl _{2.28}	green	2.205(2)	2.481(1)	2.447(2)
Mo(PMe ₂ Ph) ₃ O _{0.51} Cl _{2.49}	green	2.316(2)	2.460(1)	2.437(2)
Mo(PMe ₂ Ph) ₃ O _{0.09} Cl _{2.91}	yellow-green	2.391(1)	2.430(1)	2.422(2)
Mo(PMe ₂ Ph) ₃ Cl ₃	yellow	2.400(1)	2.427(1)	2.420(1)

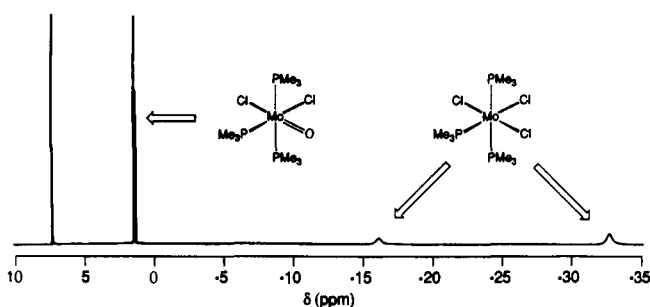
^a Taken from ref 32.

Figure 21. ¹H NMR spectrum of *cis-mer*-MoOCl₂(PMe₂Ph)₃ in C₆D₆ (δ 7.15 ppm) over the range δ -35 to +10 ppm. Reprinted from ref 32. Copyright 1992 American Chemical Society.

MoCl₃(PMe₂Ph)₃. Cocrystallization of *cis-mer*-MoOCl₂(PMe₂Ph)₃ with *mer*-MoCl₃(PMe₂Ph)₃ would result in incorporation of small quantities of chloride into the oxo site and thereby result in an artificial increase of the "Mo=O" bond length, since the chloride ligand would be located at a much greater distance from the molybdenum center (ca. 2.45 Å for Mo-Cl versus ca. 1.68 Å for Mo=O). Different degrees of contamination at the crystallographic sites would give rise to a variation in apparent "Mo=O" bond lengths. Thus, the observation of four apparently unique Mo=O bond lengths for *cis-mer*-MoOCl₂(PMe₂Ph)₃, and yet only one ν (Mo=O) absorption, was explained as a result of compositional disorder with isostructural *mer*-MoCl₃(PMe₂Ph)₃.

C. A Reinvestigation of Bond-Stretch Isomerism in *cis-mer*-MoOCl₂(PMe₂Ph)₃

1. X-ray Crystallographic Studies

The evidence described above (section III.B), that compositional disorder was responsible for the observation of anomalous "Mo=O" bond lengths for *cis-mer*-MoOCl₂(PMe₂Ph)₃, suggested that a similar explanation may also hold for the blue and green isomers of *cis-mer*-MoOCl₂(PMe₂Ph)₃, the original complexes for which distortional isomerism was first proposed.³¹⁻³³ Indeed, examination of solutions of the green isomer of *cis-mer*-MoOCl₂(PMe₂Ph)₃ by ¹H NMR spectroscopy revealed that the samples were contaminated with paramagnetic *mer*-MoCl₃(PMe₂Ph)₃,³⁷ a yellow complex. The bulk sample of the green "isomer" of *cis-mer*-MoOCl₂(PMe₂Ph)₃ was therefore proposed to consist of a mixture of blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ and yellow *mer*-MoCl₃(PMe₂Ph)₃. It was suggested that the difficulty of observing small amounts of paramagnetic *mer*-MoCl₃(PMe₂Ph)₃ under normal ¹H NMR

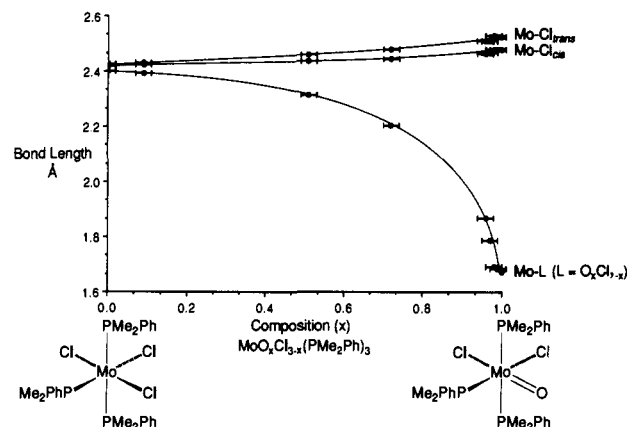


Figure 22. Apparent bond lengths as a function of composition. Reprinted from ref 32. Copyright 1992 American Chemical Society.

conditions prevented earlier workers from reaching this conclusion.

In addition to demonstrating that the bulk sample of the green "isomer" was contaminated with *mer*-MoCl₃(PMe₂Ph)₃, it was necessary to prove that the mixture was *homogeneous* in the solid state (i.e. a solid solution), so that *single crystals* composed of both *cis-mer*-MoOCl₂(PMe₂Ph)₃ and *mer*-MoCl₃(PMe₂Ph)₃ may be obtained, and that these crystals give rise to long Mo=O bond lengths. Therefore, X-ray diffraction studies were performed on a series of crystals of composition *mer*-MoO_xCl_{3-x}(PMe₂Ph)₃ (0 ≤ *x* ≤ 1), in which the extremes varied from pure blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ to yellow *mer*-MoCl₃(PMe₂Ph)₃. The results of this investigation are summarized in Table IV and Figure 22. The data clearly illustrate how the apparent "Mo=O" bond length varied as a function of the composition, thereby resulting in a potential continuum of bond lengths. The blue "isomer" of *cis-mer*-MoOCl₂(PMe₂Ph)₃ was pure and showed the shortest Mo=O bond length. However, the green "isomer" was a variable mixture of blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ and yellow *mer*-MoCl₃(PMe₂Ph)₃, thus resulting in apparently long Mo=O bond lengths. These results strongly indicated that there was no structural evidence for bond-stretch isomerism for the complexes that were originally proposed to exhibit the phenomenon.

Oxygen and chlorine atoms have substantially different X-ray scattering powers, so that it may have been anticipated that the disorder described above would have been readily revealed by the presence of abnormal temperature factors. Therefore, it is important to address the issue of why crystallographic disorder

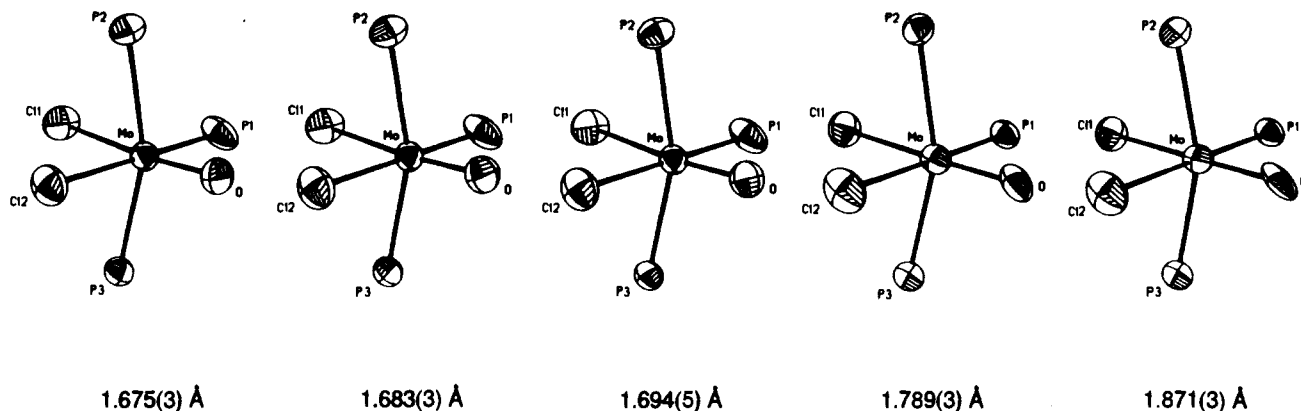


Figure 23. Variation of thermal parameters at the disordered site as a function of composition. Reprinted from ref 32. Copyright 1992 American Chemical Society.

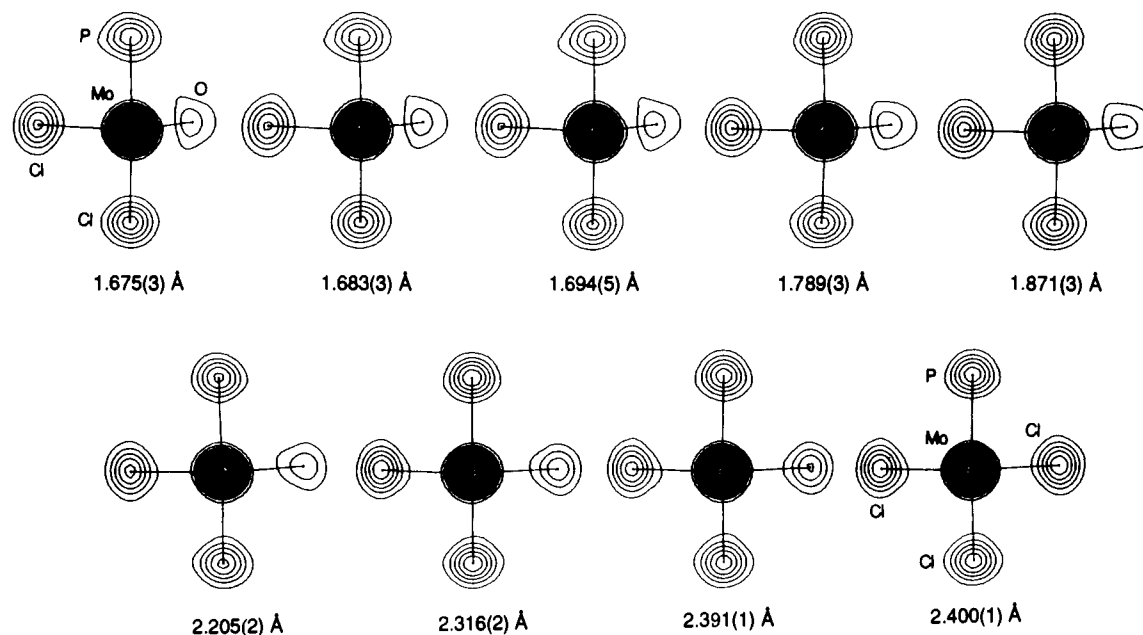


Figure 24. Variation of electron density at the disordered site as a function of composition. Reprinted from ref 32. Copyright 1992 American Chemical Society.

was not considered in the original work, especially since the green "isomer" *cis-mer*- $\text{MoOCl}_2(\text{PET}_2\text{Ph})_3$ was reported to exhibit normal temperature factors for molybdenum, chlorine, phosphorus, and oxygen atoms.^{12b} In this regard, surprisingly successful refinement was also obtained by refining the disordered site as only oxygen for many of the structures of the series *mer*- $\text{MoO}_x\text{Cl}_{3-x}(\text{PMe}_2\text{Ph})_3$ ($0 < x < 1$) (Figure 23). However, although the thermal ellipsoids of the oxygen atoms were observed to deform as the degree of disorder increased, it should be noted that significantly worse thermal parameters appear regularly in the literature, so that it is not clear that this observation alone would be sufficient to signal an erroneous structure.

Similarly, the presence of disorder was not readily discerned by examination of electron density plots for the series *mer*- $\text{MoO}_x\text{Cl}_{3-x}(\text{PMe}_2\text{Ph})_3$ (Figure 24), in which only a *single* electron density maximum was observed at the disordered site. Moreover, the anticipated increase in electron density at the disordered site was also not readily apparent. Therefore, it was proposed that it was likely that disorder was not considered in the earlier studies because it is the apparent bond length itself that is more sensitive to

the chloride impurity, than either the thermal parameters or electron density distribution at the disordered site. The extreme sensitivity of the apparent "Mo=O" bond length to the chloride impurity is due principally to two factors: (i) the much longer bond length of Mo-Cl (ca. 2.45 Å) versus Mo=O (ca. 1.68 Å) and (ii) the much greater X-ray scattering power of Cl versus O.

At this point it is worthwhile to comment upon the interpretation of the estimated standard deviations (esd or σ), that are commonly associated with crystal structure determinations and are frequently used to indicate whether the differences in two measurements, such as bond lengths, are significant. The basic assumption in the derivation of estimated standard deviations is that differences in observed quantities from the true values are only due to *random* errors.³⁸ For such a scenario, if two measurements differ from one another by 2.7σ , there is 99% probability that the measurements represent two distinct values.^{38a} More commonly, chemists use a 3σ criterion to determine whether measured bond lengths are, or are not, significantly different. However, such interpretation is only valid if there is no *systematic* error in the data, such as disorder or absorption problems. If there is

any systematic error in the data, the esd's that are calculated on the assumption that there is only random error are naturally an underestimate of the true error. Indeed, to quote from a recent text concerning systematic errors:^{38b} "Systematic errors that do not alter the precision are those that do not change the distribution representing the random errors but only displace it. Such errors are especially insidious because there is no evidence in the data themselves to betray their presence." A simple example that illustrates how quoted esd's need not necessarily be a good indication of possible deviation from a true bond length is provided by the apparent Mo-L (L = O_{0.72}Cl_{0.28}) "bond length" of 2.205(2) Å in the disordered crystal *mer*-MoO_{0.72}Cl_{0.28}(PMe₂Ph)₃.^{31,32} Although the "bond length" is precise, with an esd of 0.002 Å, the value is highly inaccurate in that it deviates 265σ from the true Mo-O bond length [1.675(3) Å] and 97σ from the true Mo-Cl bond length [2.400(1) Å]! Hence, the 3σ criterion, often cited to indicate significant differences in true bond lengths, is not necessarily always appropriate.

Furthermore, the accuracy of esd's has been recently evaluated by a statistical analysis of 100 crystal structures in which each structure had been determined independently by two different research groups.³⁹ The results of this survey concluded that (i) esd's of non-hydrogen atoms are underestimated, (ii) esd's of heavy-atom positions are less reliable than those of light-atom positions, and (iii) the esd's of cell parameters are grossly underestimated by a factor of 5 for cell lengths and 2.5 for cell angles.

2. Spectroscopic Studies

The suggestion that the green "isomer" of *cis-mer*-MoOCl₂(PMe₂Ph)₃ was an intimate mixture of blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ and yellow *mer*-MoCl₃(PMe₂Ph)₃, while providing a good explanation for the differences in bond lengths, did not rationalize the observation of two different ν(Mo=O) stretching frequencies (blue, 954 cm⁻¹; green 943 cm⁻¹). However, solid-state Raman studies (Figure 25) by Enemark have shown that blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ also exhibits a ν(Mo=O) stretching frequency of 943 cm⁻¹, identical to that of the green "isomer",⁴⁰ in accord with the notion that the blue and green forms are not bond-stretch isomers.

Even though Enemark had demonstrated that blue and green forms of *cis-mer*-MoOCl₂(PMe₂Ph)₃ exhibited identical ν(Mo=O) stretching frequencies, it was important to determine the reason for the discrepancy with the original value (954 cm⁻¹) reported by Butcher and Chatt for ν(Mo=O) of the blue isomer.¹⁰ In this regard, Gibson et al. have identified that the discrepancy in ν(Mo=O) stretching frequencies is due to the fact that the blue isomer may be obtained in two different crystalline modifications.⁴¹ Although it was known previously that two different blue crystalline modifications exist [(i) "blue I" orthorhombic *Pbca*, *a* = 17.009(6) Å, *b* = 16.528(5) Å, *c* = 19.311(8) Å,¹¹ and (ii) "blue II" orthorhombic *Pbca*, *a* = 11.294(1) Å, *b* = 17.627(3) Å, *c* = 28.280(5) Å³²], Gibson et al. have successfully determined the conditions required to crystallize each form. Thus, modification blue I (i.e. the original Chatt form) is obtained by crystallization from ethanol in the presence of added water, whereas in dry solvent the

modification blue II is obtained. The two different crystalline modifications exhibit slightly different ν-(Mo=O) stretching frequencies in the solid state (blue I 955 cm⁻¹ and blue II 943 cm⁻¹),⁴¹ possibly due to crystal packing forces, since only one value is observed in solution.

The molecular structure of the blue I modification has been redetermined, and the Mo=O bond length [1.663(2) Å]⁴¹ reported to be significantly shorter than that of 1.675(3) Å³² in the lower frequency blue II form. Gibson et al. have therefore proposed a distinction between the terms "distortional isomerism" and "bond-stretch isomerism", suggesting that the two blue forms of *cis-mer*-MoOCl₂(PMe₂Ph)₃ be described as "distortional isomers", but not "bond-stretch isomers".⁴¹

However, it should also be pointed out that the original Mo=O bond length reported by Chatt for the blue I modification [1.676(7) Å]¹¹ is different to the value [1.663(2) Å]⁴¹ redetermined by Gibson et al., and in fact, is actually slightly longer than the Mo=O bond length in the blue II form [1.675(3) Å].³² Furthermore, Gibson et al. have also redetermined the Mo=O bond length in the blue II form to be 1.682(7) Å.⁴¹ To summarize, there are now two sets of reported Mo=O bond lengths for each of the blue forms of *cis-mer*-MoOCl₂(PMe₂Ph)₃: blue I [1.663(2) Å⁴¹ and 1.676(7) Å¹¹] and blue II [1.675(3) Å³² and 1.682(7) Å⁴¹]. In light of the discussion on the interpretation of esd's in section III.C.1, it would appear that such differences in Mo=O bond lengths in the two blue crystalline forms may not be as significant as proposed above.⁴¹

Enemark has also used a series of other techniques to confirm that the green "isomer" of *cis-mer*-MoOCl₂(PMe₂Ph)₃ is a mixture of blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ and yellow *mer*-MoCl₃(PMe₂Ph)₃.⁴⁰ Thin-layer chromatography of green *cis-mer*-MoOCl₂(PMe₂Ph)₃ indicated the presence of a yellow mobile component that corresponded to *mer*-MoCl₃(PMe₂Ph)₃. UV-visible electronic spectra, shown in Figure 26, indicated that the color of the green isomer of *cis-mer*-MoOCl₂(PMe₂Ph)₃ is due in part to an absorption at 410 nm, which corresponds to that of yellow *mer*-MoCl₃(PMe₂Ph)₃. Indeed, the spectrum of green *cis-mer*-MoOCl₂(PMe₂Ph)₃ could be reproduced independently by mixing blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ and yellow *mer*-MoCl₃(PMe₂Ph)₃ in the correct proportions. X-ray photoelectron spectroscopy also provided supporting evidence that green *cis-mer*-MoOCl₂(PMe₂Ph)₃ was a mixture.

3. Theoretical Reevaluation of Bond-Stretch Isomerism in [(Me₃tacn)W(O)Cl₂]⁺ and *cis-mer*-MoOCl₂(PR₃)₃

Hall has recently carried out ab initio MO calculations on the model complexes [*fac*-W(O)Cl₂(NH₃)₃]⁺ and [*cis-mer*-Mo(O)Cl₂(PH₃)₃] in order to explore the bond-stretch isomerism phenomenon at a higher level of theory.⁴² It was concluded that the second-order Jahn-Teller effect, the magnitude of which is overemphasized by the extended Hückel method, was in fact too weak to produce the bond-length changes observed for *cis-mer*-Mo(O)Cl₂(PR₃)₃, so that only one isomer should exist. Similarly, only one stable bond-stretch isomer was predicted to exist for [*fac*-W(O)Cl₂(NH₃)₃]⁺.

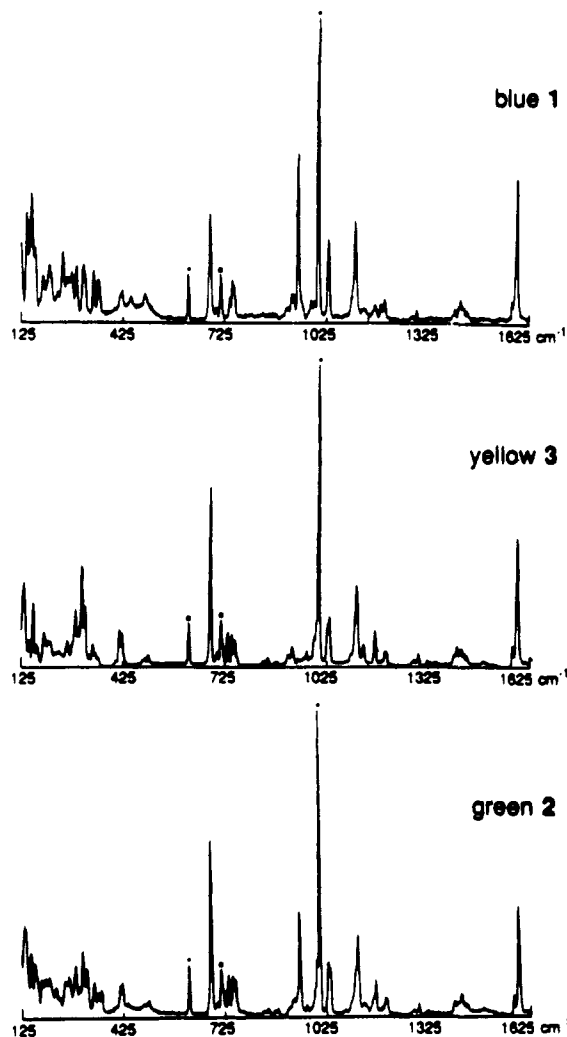


Figure 25. Raman spectra (125–1625 cm^{-1}) of blue *cis-mer*- $\text{MoOCl}_2(\text{PMe}_2\text{Ph})_3$ (1), green *cis-mer*- $\text{MoOCl}_2(\text{PMe}_2\text{Ph})_3$ (2), and yellow *cis-mer*- $\text{MoCl}_3(\text{PMe}_2\text{Ph})_3$ (3). Unshifted $\text{PMe}_2\text{-Ph}$ bands are marked with a dot (●). Adapted from ref 40.

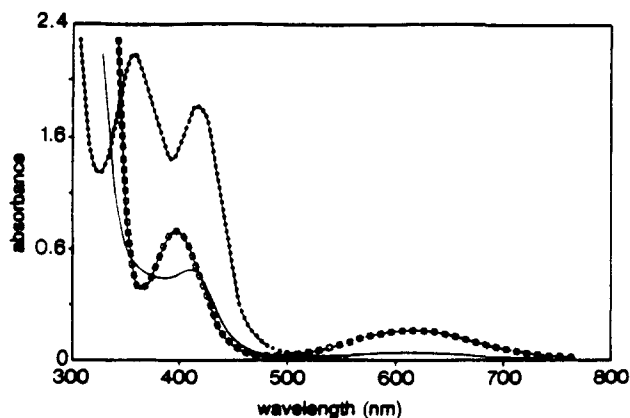


Figure 26. Visible spectra of blue *cis-mer*- $\text{MoOCl}_2(\text{PMe}_2\text{Ph})_3$ (1) (□), green *cis-mer*- $\text{MoOCl}_2(\text{PMe}_2\text{Ph})_3$ (2) (—), and yellow *cis-mer*- $\text{MoCl}_3(\text{PMe}_2\text{Ph})_3$ (3) (●) in dry acetonitrile. Concentrations: blue 1, 3.80 mM; green 2, 18.5 mg in 25.0 mL; yellow 3, 1.17 mM. Reprinted from ref 40. Copyright 1991 American Chemical Society.

IV. Controlled Crystallographic Disorder in $[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{ZnX}$ Complexes

Although crystallographic disorder is well known, the presence of a disorder is normally only discerned at the stage of refinement when an anomaly, e.g. unusual

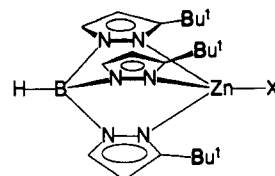


Figure 27. Molecular structure of $[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{ZnX}$. Reprinted from ref 43. Copyright 1991 American Chemical Society.

thermal parameters or residual electron density, is detected. Indeed, such examples normally represent crystallographic problem structures and have been solved with different degrees of success. The interpretation of X-ray diffraction data providing examples of bond-stretch isomers for the blue and green forms of *cis-mer*- $\text{Mo}(\text{O})\text{Cl}_2(\text{PMe}_2\text{Ph})_3$ represents an extreme example of the subtlety of crystallographic disorder. The ability of crystallographic disorder to influence strongly a determined bond length, for a structure in which there is no *obvious* crystallographic anomaly, has significant ramifications. However, until recently, crystallographic disorder in single crystals had not previously been studied in a systematic manner. This section describes some recent studies designed to investigate the effects of crystallographic disorder in a controlled manner.

A. Disorder between Structurally Similar Groups

The most common source of crystallographic disorder is derived from packing equivalent molecules in different orientations; however, it is difficult (if not impossible) to control such disorder in a defined manner. A simpler method for controlling disorder at a crystallographic site involves doping a crystal with structurally similar molecules. Importantly, this method allows the composition of the disordered site to be determined by a method that is independent of the disorder model used for refinement. For this reason, further studies to quantify the sensitivity of the apparent bond length to the composition of a disordered site have centered on cocrystallization of a series of structurally related tris(pyrazolyl)hydroborato zinc complexes, $[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{ZnX}$ (3-Bu^tpz = 3-C₃N₂H₂-Bu^t; X = Cl, Br, I, CH₃, CN) in which the tripod ligand confers considerable stability and crystallinity to the complexes (Figure 27).⁴³

The results of X-ray diffraction studies on single crystals composed of pairs of the complexes $[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{ZnCl}$, $[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{ZnI}$, and $[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{ZnCH}_3$, over a range of compositions, are summarized in Table V and Figure 28. The compositions of the disordered sites were determined by both ¹H NMR analysis of the specific crystal used in the diffraction study, and also by refining site occupancies. The good agreement that is obtained for the series $[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{ZnCl}_{1-n}\text{I}_n$ is illustrated by Figure 29.

Significantly, for each structure, only a single "atom" was observed at the disordered site, corresponding to an *apparent* Zn–X bond length that was a composite for the pair of complexes concerned. Furthermore, electron density maps for the series of complexes $[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{ZnCl}_{1-n}\text{I}_n$ (Figure 30) indicate how only a single electron density maximum was observed at the disordered site. As expected, the relationship

Table V. Apparent Bond Lengths as a Function of Composition^a

composition ^b	$d(\text{Zn-L}),^c \text{ \AA}$	composition ^b	$d(\text{Zn-L}),^c \text{ \AA}$	composition ^b	$d(\text{Zn-L}),^c \text{ \AA}$
[Zn]Cl	2.183(2)	[Zn]CH ₃	1.971(4)	[Zn]CH ₃	1.971(4)
[Zn]Cl _{0.98} I _{0.02}	2.198(1)	[Zn](CH ₃) _{0.88} Cl _{0.12}	2.049(4)	[Zn](CH ₃) _{0.93} I _{0.07}	2.209(3)
[Zn]Cl _{0.89} I _{0.11}	2.261(1)	[Zn](CH ₃) _{0.64} Cl _{0.36}	2.105(2)	[Zn](CH ₃) _{0.93} I _{0.07}	2.216(3)
[Zn]Cl _{0.71} I _{0.29}	2.358(1)	[Zn](CH ₃) _{0.56} Cl _{0.44}	2.118(3)	[Zn](CH ₃) _{0.92} I _{0.08}	2.203(3)
[Zn]Cl _{0.50} I _{0.50}	2.241(1)	[Zn](CH ₃) _{0.54} Cl _{0.46}	2.123(2)	[Zn](CH ₃) _{0.31} I _{0.69}	2.467(1)
[Zn]Cl _{0.38} I _{0.62}	2.446(1)	[Zn](CH ₃) _{0.46} Cl _{0.54}	2.136(3)	[Zn](CH ₃) _{0.09} I _{0.91}	2.508(1)
[Zn]Cl _{0.18} I _{0.82}	2.494(1)	[Zn]Cl	2.183(2)	[Zn]I	2.518(1)
[Zn]I	2.518(1)				

^a Taken from ref 43. ^b [Zn] = [η^3 -HB(3-Bu^tp_z)₃]Zn. Compositions were determined by ¹H NMR analysis of the crystal. In most cases similar compositions were also measured for the bulk sample. ^c The Zn-L (L = X_{1-n}Y_n) bond lengths listed are those for a model in which the coordinates of a single composite atom (L) are refined at the disordered site.

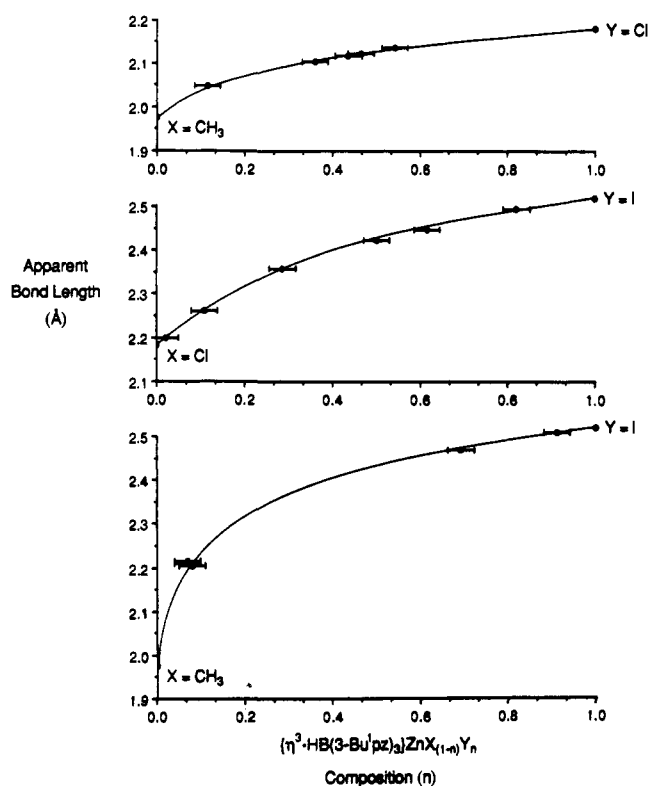


Figure 28. Variation in apparent bond length as a function of composition. Reprinted from ref 43. Copyright 1991 American Chemical Society.

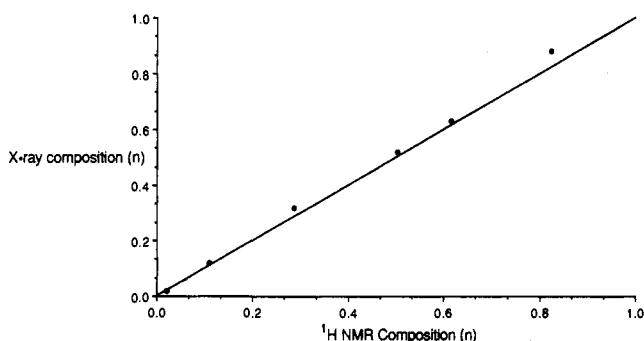


Figure 29. Comparison of the composition of [η^3 -HB(3-Bu^tp_z)₃]ZnCl_{1-n}I_n as determined by ¹H NMR analysis and by refining occupancies. For reference, the line drawn with a slope of unity represents perfect agreement. Reprinted from ref 43. Copyright 1991 American Chemical Society.

between the apparent bond length and composition was not linear, but was weighted by the relative scattering powers of the disordered groups. The most significant deviation from linearity occurred when there was considerable disparity between the scattering

powers of the disordered groups, with the group of the higher scattering power contributing most to the apparent bond length. Thus, small quantities of iodide impurities exhibited a pronounced effect on observed apparent bond lengths.

It was also noted that for the series [η^3 -HB(3-Bu^tp_z)₃]ZnCl_{1-n}I_n reasonable thermal parameters could still be obtained at impurity levels that were sufficient to result in a significant apparent change in the true bond length. The effect on the thermal parameters of refining the disordered site as (i) Cl only, (ii) I only, and (iii) a composite atom (L = Cl_{1-n}I_n) are summarized in Figure 31. Refining the disordered site as Cl resulted in the expected shrinking of the thermal ellipsoid as the iodide content (and hence increased electron density) at the disordered site increased. Conversely, refining the disordered site as I resulted in the expected expansion of the thermal ellipsoid as the iodide content decreased. Furthermore, the result of refining the disordered site as a composite atom (L = Cl_{1-n}I_n) demonstrated that expansion of the thermal ellipsoid along the bond vector, which may have been anticipated because the disordered atoms are located at different positions along this vector, was *not* observed for the [η^3 -HB(3-Bu^tp_z)₃]ZnCl_{1-n}I_n system. Indeed, the disordered site of the crystal of composition [η^3 -HB(3-Bu^tp_z)₃]ZnCl_{0.5}I_{0.5} refined very well as *bromine*, as shown in Figure 32, even though the crystal studied contained *no bromine*! For comparison, the ORTEP drawing for authentic [η^3 -HB(3-Bu^tp_z)₃]ZnBr, also shown in Figure 32, indicates the very close similarity with the "artificial" bromide [η^3 -HB(3-Bu^tp_z)₃]ZnCl_{0.5}I_{0.5}. This observation not only reiterates the suggestion that the observation of "normal" thermal parameters is not necessarily a good indicator that an observed bond length is correct, but also indicates that the assignment of the *atom* may not even be correct.

B. Disorder between Structurally Inequivalent Groups

Controlled disorder between structurally inequivalent groups has been investigated by determining the effect that partial occupancy of a halide ligand (X = Cl, Br, I) may exert upon the apparent structure of the cyanide derivative [η^3 -HB(3-Bu^tp_z)₃]ZnCN.⁴⁴ By varying the halide ligand from chloride to iodide, the location of the disordered atom with respect to the C≡N group could be varied. Single crystals of [η^3 -HB(3-Bu^tp_z)₃]ZnCN doped with [η^3 -HB(3-Bu^tp_z)₃]ZnX (X = Cl, Br, I) were readily prepared by cocrystallization from dichloromethane or THF solutions and were analyzed by X-ray diffraction. After data collection, the com-

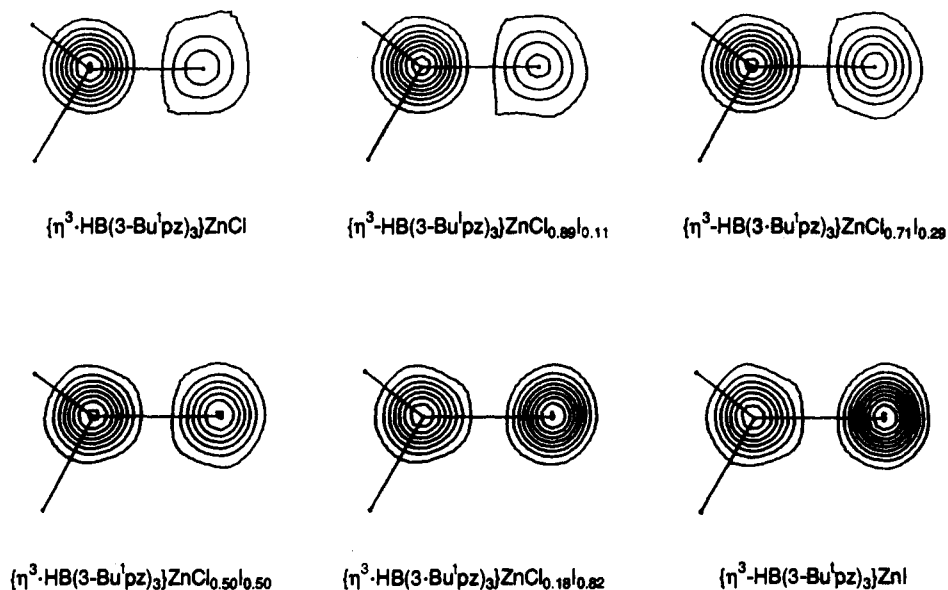


Figure 30. Electron density contours in the plane N(12)–Zn–Cl_{1–n}I_n illustrating the change in electron density at the disordered site for a selection of the series [η^3 -HB(3-Bu^tpz)₃]ZnCl_{1–n}I_n. The solid lines indicate bonds to zinc. Reprinted from ref 43. Copyright 1991 American Chemical Society.

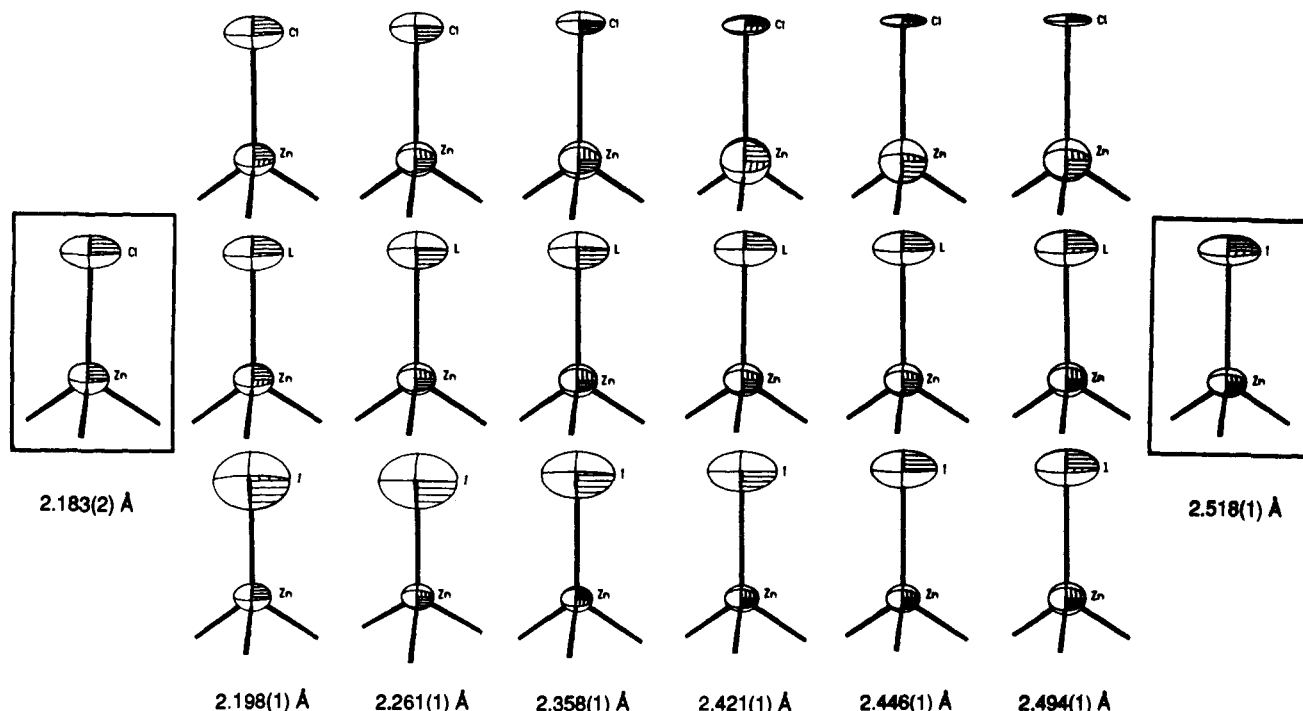


Figure 31. Thermal ellipsoids for the series [η^3 -HB(3-Bu^tpz)₃]ZnCl_{1–n}I_n as the result of refining as (i) Cl (upper row), (ii) I (lower row), and (iii) a composite atom (middle row). Reprinted from ref 43. Copyright 1991 American Chemical Society.

position of each crystal was determined by ¹H NMR spectroscopy.

For chloride- and bromide-doped crystals of composition [η^3 -HB(3-Bu^tpz)₃]Zn(CN)_{0.8}Cl_{0.2} and [η^3 -HB(3-Bu^tpz)₃]Zn(CN)_{0.95}Br_{0.05}, the disorder between the halide and the carbon of the cyanide ligand was not resolved. The partial ORTEP drawings for [η^3 -HB(3-Bu^tpz)₃]Zn(CN)_{0.8}Cl_{0.2} in Figure 33 illustrate the results of two different refinement procedures. The drawing on the left-hand side of Figure 33 represents a refinement in which the disorder was neglected (i.e. one in which the crystal was considered to be pure [η^3 -HB(3-Bu^tpz)₃]ZnCN), while the drawing on the right-hand side represents a refinement in which the disordered

site was modeled by refining the carbon site as a composite of chlorine and carbon. Similar refinement procedures were carried out for [η^3 -HB(3-Bu^tpz)₃]Zn(CN)_{0.95}Br_{0.05}, as shown in Figure 34. Comparison of the thermal ellipsoids associated with the cyanide ligand of [η^3 -HB(3-Bu^tpz)₃]Zn(CN)_{0.8}Cl_{0.2} (left hand side of Figure 33) and pure [η^3 -HB(3-Bu^tpz)₃]ZnCN (Figure 35) reveals an unsatisfactory solution in that the thermal ellipsoid of the nitrogen atom is enlarged compared with that for the pure complex, whereas the thermal ellipsoid of the carbon atom is reduced. Such behavior is anticipated: the chloride dopant would be located much closer to carbon than the nitrogen of the cyanide ligand, thus resulting in an increase in electron density

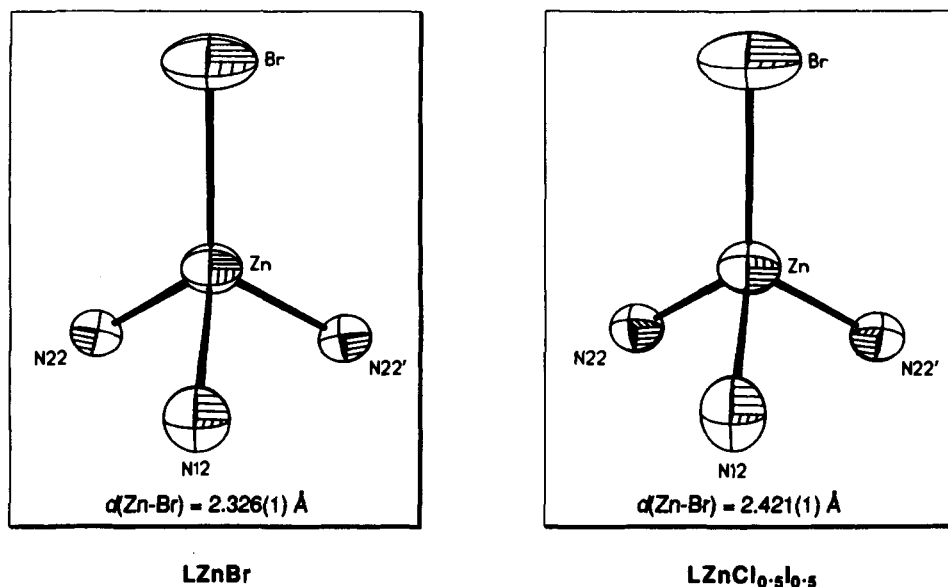


Figure 32. Comparison of thermal parameters of the disordered structure $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{ZnCl}_{0.5}\text{I}_{0.5}$ when refined as $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{ZnBr}$, with that of authentic $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{ZnBr}$. Reprinted from ref 43. Copyright 1991 American Chemical Society.

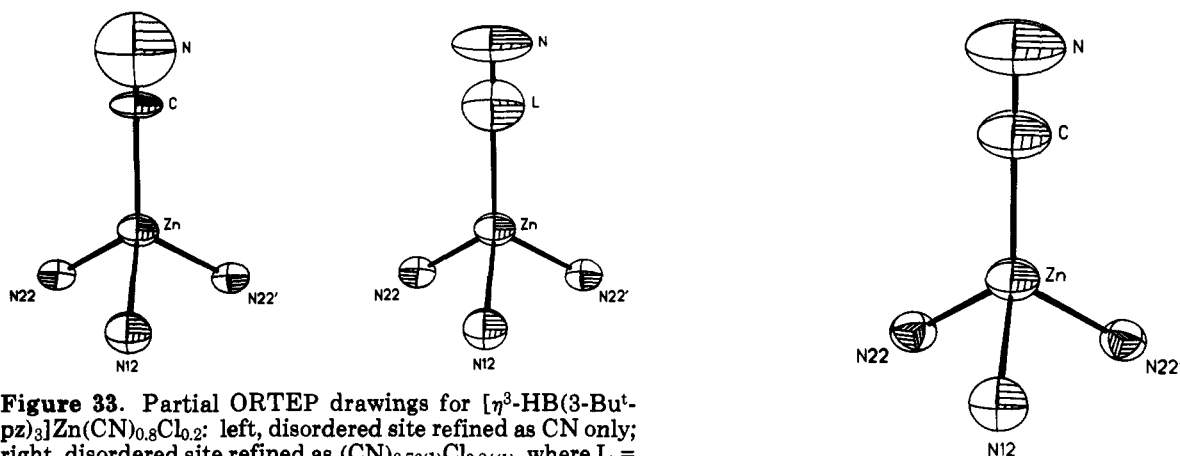


Figure 33. Partial ORTEP drawings for $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{Zn(CN)}_{0.8}\text{Cl}_{0.2}$: left, disordered site refined as CN only; right, disordered site refined as $(\text{CN})_{0.76(1)}\text{Cl}_{0.24(1)}$, where $\text{L} = \text{C}_{0.76(1)}\text{Cl}_{0.24(1)}$ and $\text{N} = \text{N}_{0.76(1)}$. Reprinted from ref 44. Copyright 1992 American Chemical Society.

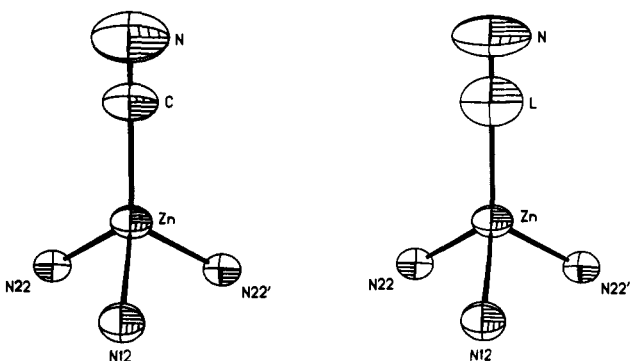


Figure 34. Partial ORTEP drawings for $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{Zn(CN)}_{0.96}\text{Br}_{0.04}$: left, disordered site refined as CN only; right, disordered site refined as $(\text{CN})_{0.96(1)}\text{Br}_{0.04(1)}$, where $\text{L} = \text{C}_{0.96(1)}\text{Br}_{0.04(1)}$ and $\text{N} = \text{N}_{0.96(1)}$. Reprinted from ref 44. Copyright 1992 American Chemical Society.

at the carbon site, and a reduction of electron density at the nitrogen site, which is now only partially occupied. Significantly, the *apparent* Zn-C bond length [2.094(4) Å] was observed to be longer than for the pure complex [1.962(6) Å], and the C≡N bond length [0.996(9) Å] is correspondingly shorter than for the pure

Figure 35. Partial ORTEP drawing for $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{ZnCN}$. Reprinted from ref 44. Copyright 1992 American Chemical Society.

complex [1.117(9) Å]. The overall distance between zinc and the nitrogen of the cyanide ligand [3.09(1) Å] was similar to that observed in pure $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{ZnCN}$ [3.08(1) Å]. Thus, the role of the chloride impurity serves mainly to shift the apparent position of the carbon atom away from zinc and toward nitrogen, thereby apparently shortening the C≡N bond length. Although the ORTEP drawing for $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{Zn(CN)}_{0.8}\text{Cl}_{0.2}$ was not a good representation of pure $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{ZnCN}$, the bromide-doped crystal of composition $[\eta^3\text{-HB(3-Bu}^t\text{pz)}_3]\text{Zn(CN)}_{0.96}\text{Br}_{0.04}$ refined well in the absence of a disorder model (left-hand side of Figure 34). However, the bond lengths associated with the CN ligand were observed to be incorrect, with a long Zn-C bond length [2.018(5) Å] and a short C≡N bond length [1.040(8) Å]. Modeling the disorder by refining the carbon site as a composite of bromine and carbon resulted in only minor changes in bond lengths associated with the CN group [$d(\text{Zn-C}) = 2.035(6) \text{ \AA}$; $d(\text{C}\equiv\text{N}) = 1.058(9) \text{ \AA}$].

Although the disorder between (i) CN and Cl and (ii) CN and Br was not resolved, disorder between cyanide and iodide in a crystal of composition $[\eta^3\text{-HB(3-Bu}^t\text{-}$

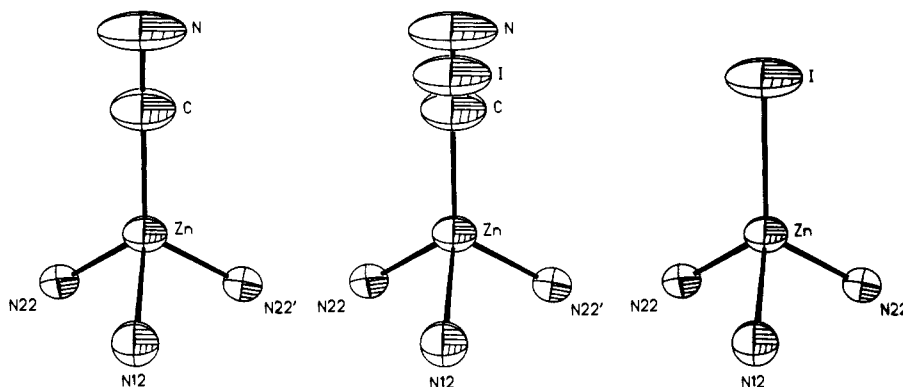


Figure 36. Partial ORTEP drawings for $[\eta^3\text{-HB}(3\text{-Bu}'\text{pz})_3]\text{Zn}(\text{CN})_{0.9}\text{I}_{0.1}$ with disordered site refined as $(\text{CN})_{0.906(4)}\text{I}_{0.094(4)}$: center, superposition of CN and I groups at the disordered site; left and right, disordered site separated into composite molecules. Reprinted from ref 44. Copyright 1992 American Chemical Society.

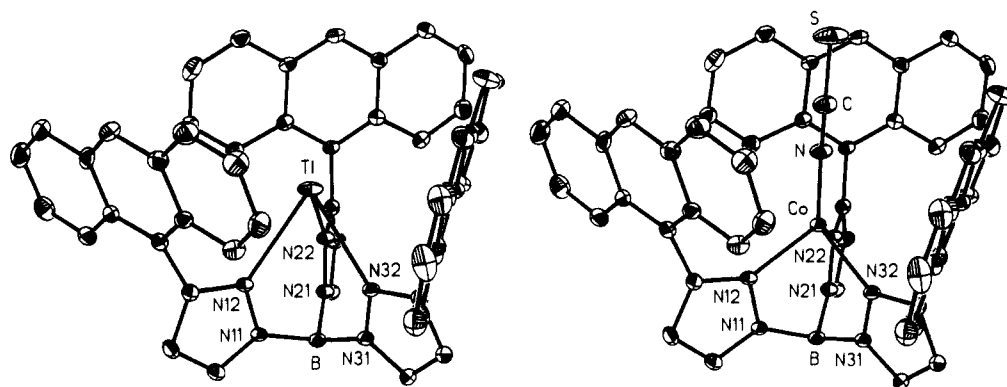


Figure 37. Two molecules that differ by a chain of three atoms but which still cocrystallize.

$\text{pz})_3]\text{Zn}(\text{CN})_{0.9}\text{I}_{0.1}$ was readily resolved, in that three peaks were observed in the electron density difference map. The result of refining the cyanide and iodide groups with partial occupancies is shown in Figure 36, and comparison with the ORTEP drawings of the pure complexes may suggest that the refinement procedure used was successful. However, although the bond lengths associated with the Zn–CN and Zn–I groups compared reasonably well with those of the pure compounds, the observed bond lengths were *not* identical with the true values. Therefore, it was suggested that although resolved structures obtained by such a refinement procedure may be taken as good evidence for the nature of the disorder, bond lengths derived from disordered structures should be treated with caution, especially when accurate structural details are required.

More extreme examples of disorder may also occur. For example, the complex $[\eta^3\text{-HB}(3\text{-anthracenylpz})_3]\text{-Tl}$ cocrystallizes with $[\eta^3\text{-HB}(3\text{-anthracenylpz})_3]\text{CoNCS}$, so that in effect a site that is disordered between a vacancy and a chain of *three* atoms results (Figure 37).⁴⁵

V. Crystallographic Disorder in Other Systems

The key results (sections III.B, III.C, and IV) of the investigation of controlled disorder at crystallographic sites have not only highlighted the extreme sensitivity of apparent bond lengths to the composition of the disordered site, but have also indicated the subtlety of disorder. Crystallographic disorder may often go undetected, even though apparent bond lengths may be influenced. Thus, derived bond lengths may be

incorrect even when there is no *obvious* crystallographic anomaly. Hence, it is very likely that many other structures, not just those proposing bond-stretch isomerism, may suffer from undetected problems. Indeed, Ibers,⁴⁶ Donohue,⁴⁷ and Jones⁴⁸ have provided excellent critical reviews on the evaluation of X-ray diffraction data to which the interested reader is referred. Moreover, Marsh has also highlighted the pitfalls of incorrect space group determinations.⁴⁹ In this section we attempt to summarize examples of erroneous structures that are a result of crystallographic disorder. The errors associated with these structures range from the incorrect determination of a bond length to the complete misformulation of a compound. However, by virtue of the nature of the problem, the discussion is by no means intended to be comprehensive and is only intended to highlight the types of problems that may be encountered.

A. Some Other Metal–Oxo Bond Length Determinations

An early X-ray structure determination of $[\text{Ph}_4\text{As}][\text{Mo}(\text{O})\text{Br}_4(\text{OH}_2)]$ reported a value of 1.78(7) Å for the Mo=O bond length.⁵⁰ In view of Mo=O bond lengths associated with other molybdenum–oxo complexes, Cotton viewed that the observed bond length was too long and inaccurate, and therefore determined the X-ray structures of some other derivatives of $[\text{Mo}(\text{O})\text{Br}_4(\text{OH}_2)]^-$.⁵¹ The structure of $[\text{pyH}]_5[\text{Mo}(\text{O})\text{Br}_4(\text{OH}_2)]_3\text{-Br}_2$ contained two crystallographically independent molecules of $[\text{Mo}(\text{O})\text{Br}_4(\text{OH}_2)]^-$ with almost identical Mo=O bond lengths of 1.61(2) and 1.62(2) Å. Moreover, the Mo=O bond length in the corresponding

Table VI. Bond Lengths (Å) around Mo in *cis-mer*-WOC_l₂(PMe₃)₃^a

	molecule no. 1	molecule no. 2
W—O		1.67(1)
W—Cl(X1)	2.492(3)	2.483(6)
W—Cl(X2)	2.473(4)	2.475(3)
W—P(X1)	2.504(4)	2.499(4)
W—P(X2)	2.468(3)	2.473(3)
W—P(X3)	2.510(5)	2.517(4)

^a Taken from ref 52.

complex [Et₄N][Mo(O)Br₄(OH₂)] was determined to be 1.65(1) Å. Thus, these three independent measurements of the Mo=O bond length for [Mo(O)Br₄(OH₂)]⁻ are all in the range 1.61–1.65 Å, substantially less than the earlier reported value of 1.78(7) Å, which is, therefore, presumably incorrect. Indeed, the X-ray diffraction study of [Mo(O)Br₄(OH₂)]⁻ that yielded a Mo=O bond length of 1.78(7) Å was performed on a crystal that was supposed to contain the [Mo₂Br₃]²⁻ anion, and it was only in the final stages of refinement that its (true?) identity as an oxo derivative was revealed.

The molecular structure of the tungsten complex *cis-mer*-WOC_l₂(PMe₃)₃ was reported by Wilkinson, Hursthouse, and co-workers.⁵² *cis-mer*-WOC_l₂(PMe₃)₃ is isomorphous with the molybdenum analogue (section III.B)^{31,32} and contains two crystallographically independent molecules in the asymmetric unit. The bond lengths reported for the two molecules of *cis-mer*-WOC_l₂(PMe₃)₃ are presented in Table VI, from which it is observed that a W=O bond length [1.67(1) Å] was only reported for one of the two molecules. No comment was given regarding the missing entry for the W=O bond length for the other molecule. Retrieval of the atomic coordinates from the Cambridge Crystallographic Data Base revealed that the other molecule is characterized by a long W=O bond length [1.77 Å]. By analogy with the molybdenum system (section III.B),^{31–33} the presence of the trichloride *mer*-WCl₃(PMe₃)₃ contaminant seems likely.

Cotton has also recently reported the molecular structures of the tungsten-oxo complexes *cis-mer*-W(O)Br₂(PMe₂Ph)₃ and *cis-mer*-W(O)Br₂(PMePh₂)₃.⁵³ The blue-green complex *cis-mer*-W(O)Br₂(PMePh₂)₃ exhibited a W=O bond length of 1.701(4) Å. However, the purple oxo complex *cis-mer*-W(O)Br₂(PMe₂Ph)₃ was obtained as two different crystalline modifications which exhibited different W=O bond lengths. A monoclinic version with composition *cis-mer*-W(O)Br₂(PMe₂Ph)₃·(PhCH₃)_{0.5} possessed a W=O bond length of 1.70(1) Å, similar to that for *cis-mer*-W(O)Br₂(PMePh₂)₃, whereas an orthorhombic modification of composition *cis-mer*-W(O)Br₂(PMe₂Ph)₃ possessed a substantially longer W=O bond length of 1.784(6) Å. Therefore, Cotton has questioned the reliability of the latter bond length determination, raising the possibility that the observed bond length is an artifact due to disorder with *mer*-WBr₃(PMe₂Ph)₃. Since examination of the thermal ellipsoids provided no evidence to support the occurrence of disorder, it was considered that the amount of impurity required to influence the bond length would have been insufficient to have a detectable effect on the thermal parameters. The presence of an impurity seems very likely for this system,

especially since each crystal was obtained unintentionally and the sources of the oxo ligands are unknown.

The effect of crystal decomposition on derived bond lengths has been demonstrated for the dioxygen complex [Ir(dppe)(η²-O₂)] [PF₆] (dppe = Ph₂PCH₂CH₂-PPh₂), in which the first structure determination revealed an O—O bond length of 1.625(23) Å, substantially longer than that expected for two oxygen atoms linked by a σ bond (ca. 1.49 Å).⁵⁴ Subsequent work has revealed that the unusually long O—O bond length is an artifact due to crystal decomposition, and redetermination of the structure revealed a significantly shorter O—O bond length of 1.52(1) Å.^{55,56} In addition to affecting the O—O bond length, decomposition of the crystal also resulted in a substantial apparent inequivalence of the two chemically equivalent Ir—P bonds [2.283(7) and 2.452(9) Å],⁵⁴ compared with the redetermined structure [2.308 and 2.342 Å].⁵⁵

B. Compositional Disorder and Incorrect Metal–Ligand Bond Lengths

A recent X-ray diffraction study on the complex *mer*-WCl₃(PMe₂Ph)₃ reported that even though the three W—P bond lengths [2.514(1), 2.536(1), and 2.555(1) Å] were similar, the three W—Cl bond lengths [2.295(2), 2.437(1), and 2.441(1) Å] were different, with one exceptionally short W—Cl bond.⁵⁷ The most surprising observation was that the short W—Cl bond length did not correspond to the unique chloro substituent that was located trans to PMe₂Ph, but rather corresponded to one of the chloro substituents that are mutually trans to each other. Since the complex *mer*-WCl₃(PMe₂Ph)₃ has a molecular plane of symmetry, the unexpected result that two chemically equivalent W—Cl bonds may have substantially different bond lengths of 2.437(1) and 2.295(2) Å was obtained. The origin of the inequivalence of the two trans W—Cl bond lengths was determined to be cocrystallization of *mer*-WCl₃(PMe₂Ph)₃ with the isostructural oxo complex *cis-mer*-WOC_l₂(PMe₂Ph)₃.⁵⁸ Thus, in an analogous fashion to that in which the incorporation of chloride into the oxo site of *cis-mer*-MoOC_l₂(PMe₂Ph)₃ resulted in an apparent lengthening of the Mo=O bond,^{31–33} the incorporation of an oxo ligand into one of the chloride sites of *mer*-WCl₃(PMe₂Ph)₃ would be expected to result in an apparent shortening of the W—Cl bond. Evidence for the presence of the oxo impurity *cis-mer*-WOC_l₂(PMe₂Ph)₃ was readily provided by examination of the ³¹P{¹H} NMR spectrum. The ³¹P{¹H} NMR spectrum of the oxo complex *cis-mer*-WOC_l₂(PMe₂Ph)₃⁵⁹ matched exactly with that reported for *mer*-WCl₃(PMe₂Ph)₃. Since *mer*-WCl₃(PMe₂Ph)₃ is paramagnetic and not readily observed by ³¹P NMR spectroscopy, only the diamagnetic *cis-mer*-WOC_l₂(PMe₂Ph)₃ impurity was detected. Contamination by the diamagnetic oxo complex *cis-mer*-WOC_l₂(PMe₂Ph)₃ in this sample was also verified by ¹H NMR spectroscopy.

The X-ray structure of *mer*-WCl₃(PMe₂Ph)₃ was redetermined on a crystal that was shown by ¹H NMR spectroscopic analysis to come from a sample that was contaminated with ca. 20 molar % *cis-mer*-WOC_l₂(PMe₂Ph)₃. Although many of the bond lengths for the redetermined structure of *mer*-WCl₃(PMe₂Ph)₃ corresponded closely to the original report,⁵⁷ a noticeable difference was observed for the two trans W—Cl

bonds. Significantly, the very short W–Cl bond length of 2.295(2) Å reported for the original structure was not reproduced, and instead a longer W–Cl bond length of 2.342(4) Å was observed. It should be noted that although the two *trans* W–Cl bond lengths are still not identical, the difference between the two structures provides good evidence that the *apparently* short W–Cl bond length is due to cocrystallization with the *oxo cis-mer*-WOC₂(PMe₂Ph)₃ impurity, in which the two structures differ due to different levels of contamination. Indeed, the structure of *pure mer*-WCl₃(PMe₂Ph)₃ still remains to be determined. The phenomenon has thus come full circle: 20 years ago a chloride impurity resulted in the observation of an artificially long metal–oxo bond length, whereas today an oxo impurity is observed to result in an artificially short metal–chloride bond length.

A related effect has been observed for (η⁵-C₅H₅)₂-Hf(CH₃)₂. The molecular structure of (η⁵-C₅H₅)₂Hf(CH₃)₂ was originally reported to exhibit two significantly distinct Hf–CH₃ bond lengths [2.318(8) and 2.382(7) Å], in an otherwise symmetric molecule.⁶⁰ The origin of the inequivalence has subsequently been reinterpreted as arising from cocrystallization with the chloride derivative (η⁵-C₅H₅)₂Hf(CH₃)Cl.⁶¹ Similarly, a long Mo–C bond length [2.439(5) Å] was originally reported for Mo₂(CH₃)₄(PMe₃)₄.⁶² However, further work has revealed that the true Mo–C bond length in Mo₂(CH₃)₄(PMe₃)₄ is substantially shorter [2.1489(4) Å] and that the previous structure was most probably performed on a sample that was contaminated with Mo₂Cl₄(PMe₃)₄.⁶³

Compositional disorder is not restricted to changes in the ligand environment. Indeed, the metal itself may experience compositional disorder. An interesting example is provided by the X-ray structure of the dinicotinate complex *trans*-[Cr(nic-N)₂(H₂O)₄], which was also reported to possess a low-spin electronic configuration for the Cr(II) center.⁶⁴ Subsequent studies revealed that the sample of low-spin “*trans*-[Cr(nic-N)₂(H₂O)₄]” was in fact a solid solution of high-spin *trans*-[Cr(nic-N)₂(H₂O)₄] diluted by the isostructural zinc complex *trans*-[Zn(nic-N)₂(H₂O)₄].⁶⁵ X-ray diffraction studies on a pure sample of *trans*-[Cr(nic-N)₂(H₂O)₄] demonstrated that the coordination environment about Cr [Cr–N = 2.128(2) Å, Cr–O = 2.039(2) and 2.471(3) Å]⁶⁵ was substantially different to that in the original structure [Cr–N = 2.136(8) Å, Cr–O = 2.10(2) and 2.16(2) Å].⁶⁴ In particular, the elongated Cr–O bond [2.471(3) Å], characteristic of a Jahn–Teller distortion, was not observed for the original structure in which the Cr–O bond lengths were more similar [Cr–O = 2.10(2) and 2.16(2) Å].

C. Exceptionally Short N–N and C–O Bond Lengths in Transition Metal Dinitrogen and Carbonyl Complexes

An X-ray diffraction study on the bis(dinitrogen) complex *trans*-Cr(dmpe)₂(N₂)₂ (dmpe = Me₂PCH₂CH₂PMe₂) revealed an unusually short N–N bond length of 0.985(4) Å.⁶⁶ However, subsequent work has suggested that the origin of the exceptionally short N–N bond length in this molecule is compositional disorder with the *chloride impurity*, *trans*-Cr(dmpe)₂Cl₂.⁶⁷ Disorder between the N atom coordinated to Cr and the

Cl impurity was neither resolved, nor detected, with the result that a N–N bond length shorter than in N₂ [1.0976(1) Å]⁶⁸ was originally reported.⁶⁶

A further example of unresolved disorder between chloride and a diatomic group has also been suggested⁶⁹ for *trans*-Rh(PBu^t)₂(CO)Cl, for which a C–O bond length of 0.987(11) Å,⁷⁰ shorter than that in free CO (1.128 Å), was observed.

Although for the aforementioned examples, the crystallographic disorder was not originally indicated by the X-ray structure determination itself, but was rather suggested by the observation of unusual N–N and C–O bond lengths, there are many documented examples of disorder between monoatomic and diatomic groups that have been successfully identified. One such example is *trans* disorder between N₂ and Cl in the complex *trans*-ReCl(N₂)(PMe₂Ph)₄,⁷¹ for which an apparent N–N bond length of [0.94 Å] was originally observed. After modeling the disorder, a substantially longer N–N bond length of 1.06(3) Å was derived.

Disorder was also observed between the chloride and dinitrogen ligands of the complex *trans*-RhCl(N₂)-(PPrⁱ)₂,⁷² but in spite of the acknowledged disorder, the complex was claimed to provide the first example of a dinitrogen ligand that was coordinated in a “side-on” (η²) fashion. However, Ibers and co-workers have redetermined the structure of this complex and have concluded that the dinitrogen ligand is, in fact, coordinated in an end-on (η¹) fashion.⁷³

Other complexes that are known to exhibit disorder between groups that are not isostructural include *trans*-IrCl(CO)(PPh₃)₂,⁷⁴ *trans*-RhCl(CO)(PPh₃)₂,^{75–78} *trans*-IrCl(CO)[P(C₆H₄-*o*-CH₃)₃]₂,⁷⁹ *trans*-Ir(CH₃)(CO)-(PPh₃)₂,⁸⁰ *trans*-Ir(OCH₃)(CO)(PPh₃)₂,⁸¹ IrI(CO)(O₂)(PPh₃)₂,⁸² IrCl(CO)(O₂)(PPh₃)₂,⁸³ and [M-(PMe₃)₄(N₂)₂]/[M(PMe₃)₄Cl₂] (M = Mo, W).⁸⁴ The structures of these complexes have been solved with varying degrees of success, as illustrated by Table VII.

D. Incorrect Formulation of Compounds due to Crystallographic Disorder

In addition to affecting observed bond lengths, compositional disorder has also resulted in the incorrect formulation of a compound. A good example is provided by the complex *trans*-Re(O)Cl₃(PEt₂Ph)₂. In 1962 Chatt and Rowe reported the synthesis of a violet complex, tentatively proposed to be the hydroxide complex *trans*-Re(OH)Cl₃(PEt₂Ph)₂ on the basis of a preliminary X-ray structure determination.⁸⁵ In a subsequent publication, Chatt and co-workers reformulated the “violet complex” as a 10–22% solid-solution of intensely violet *trans*-ReCl₄(PEt₂Ph)₂ in the green oxo complex *trans*-Re(O)Cl₃(PEt₂Ph)₂, and *not* the hydroxide derivative *trans*-Re(OH)Cl₃(PEt₂Ph)₂.⁸⁶ However, following Chatt’s reformulation that the “violet complex” was a mixture, in 1982 other workers redetermined the structure by X-ray diffraction and concluded, on the basis of a long Re–O bond length [1.795(4) Å], that the “violet complex” was, in fact, the hydroxide derivative *trans*-Re(OH)Cl₃(PEt₂Ph)₂ and not a mixture!⁸⁷ Recent work by Mayer and Conry using NMR, IR, and CV studies have confirmed Chatt’s reformulation that the “violet complex” is indeed a mixture of *trans*-Re(O)Cl₃(PEt₂Ph)₂ and *trans*-ReCl₄(PEt₂Ph)₂.⁸⁸ It is intriguing that the formulation of

Table VII. A Selection of Structures in Which Disorder between Diatomic and Monoatomic Groups Occurs^a

disordered system	$d(M-X)$, Å	$d(M-YZ)$, Å	$d(X...Y)$, Å	d_{min} , Å	$d(X...Y)/d_{min}$	resolved	ref
$[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{Zn}(\text{CN})_x\text{Cl}_{1-x}$	2.183(2) ^b	1.962(6) ^b	0.22	0.77	0.29	no	<i>g</i>
$[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{Zn}(\text{CN})_x\text{Br}_{1-x}$	2.325(1) ^b	1.962(6) ^b	0.36	0.77	0.47	no	<i>g</i>
$[\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3]\text{Zn}(\text{CN})_x\text{I}_{1-x}$	2.518(1) ^b	1.962(6) ^b	0.56	0.77	0.73	yes	<i>g</i>
$[\text{Mo}(\text{PMe}_3)_4(\text{N}_2)_2]/[\text{Mo}(\text{PMe}_3)_4\text{Cl}_2]$	2.420(6) ^b	2.08(1) ^c	0.34	0.84	0.40	yes	<i>h</i>
$[\text{W}(\text{PMe}_3)_4(\text{N}_2)_2]/[\text{W}(\text{PMe}_3)_4\text{Cl}_2]$	2.46(1) ^c	2.04(2) ^c	0.42	0.84	0.50	yes	<i>h</i>
$[\text{Cr}(\text{dmpe})_2(\text{N}_2)_2]/[\text{Cr}(\text{dmpe})_2\text{Cl}_2]$	2.35(1) ^d	1.874(3) ^c	0.48	0.84	0.57	no	<i>i</i>
$\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4$	2.521(4) ^c	1.97(2) ^c	0.55	1.18	0.47	no	<i>j</i>
<i>trans</i> - $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	2.382(3) ^c	1.791(13) ^c	0.59	0.84	0.70	yes	<i>k</i>
<i>trans</i> - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	2.395(1) ^e	1.821(5) ^e	0.57	0.84	0.68	no	<i>l</i>
<i>trans</i> - $\text{IrCl}(\text{CO})[\text{P}(o\text{-MeC}_6\text{H}_4)_3]_2$	2.43(1) ^c	1.67(4) ^c	0.76	1.04	0.73	yes	<i>m</i>
<i>trans</i> - $\text{IrCl}(\text{CO})[\text{P}(p\text{-MeC}_6\text{H}_4)_3]_2$	2.364(2) ^c	1.817(8) ^c	0.55	0.93	0.59	yes	<i>n</i>
<i>trans</i> - $\text{Ir}(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$	2.17 ^f	1.84 ^f	0.33	0.84	0.39	no	<i>o</i>

^a $d_{min} = \lambda/2\sin\theta$; taken from ref 44. ^b Bond lengths obtained independently for a pure crystal. ^c Bond lengths obtained from the disordered structure. ^d Average Cr-Cl bond length in $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ [2.351(3) and 2.345(3) Å] (ref *ic*). ^e Bond lengths for an ordered polymorph (reference *la*). ^f Estimated values determined from a disordered structure. ^g Yoon, K.; Parkin, G. *Inorg. Chem.* 1992, 31, 1656-1662. ^h Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *Polyhedron* 1983, 2, 185-193. ⁱ (a) Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* 1983, 105, 5954-5956. (b) Salt, J. E.; Girolami, G. S.; Wilkinson, G.; Motevalli, M.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* 1985, 685-692. (c) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* 1985, 1339-1348. ^j Davis, B. R.; Ibers, J. A. *Inorg. Chem.* 1971, 10, 578-585. ^k Churchill, M. R.; Fettingner, J. C.; Buttrey, L. A.; Barkan, M. D.; Thompson, J. S. *J. Organomet. Chem.* 1988, 340, 257-266. ^l (a) Rheingold, A. L.; Gelb, S. J. *Acta Crystallogr.* 1987, C43, 785-786. (b) Del Pra, A.; Zanotti, G.; Segula, P. *Cryst. Struct. Commun.* 1979, 8, 959-964. ^m Brady, R.; De Camp, W. H.; Flynn, B. R.; Schneider, M. L.; Scott, J. D.; Vaska, L.; Werneke, M. F. *Inorg. Chem.* 1975, 14, 2669-2675. ⁿ Churchill, M. R.; Fettingner, J. C.; Rappoli, B. J.; Atwood, J. D. *Acta Crystallogr.* 1987, C43, 1697-1699. ^o Rees, W. M.; Churchill, M. R.; Li, Y.-J.; Atwood, J. D. *Organometallics* 1985, 4, 1162-1167.

Chatt's "violet complex" oscillated from a hydroxide derivative, to a mixture, to a hydroxide complex, before finally being recognized as a mixture.

The incorrect determination of bond lengths and misformulation of a compound do not require a crystal to be impure, since disorder between inequivalent groups can also be achieved as a result of packing identical molecules in different orientations in the crystal. An early example of this type of disorder was observed for a molecule originally believed to be a dicarbonyl derivative of a ruthenium porphyrin complex, $\text{Ru}(\text{TPP})(\text{CO})_2$ [TPP = *meso*-tetraphenylporphyrin dianion].⁸⁹ Surprisingly, both carbonyl ligands were reported to exhibit an unprecedented *bent* coordination mode to the ruthenium center, with a Ru-C-O bond angle of 153.3(9)°. The structure that was reported was also unexpected since previous studies on the complex had suggested that it was only a *monocarbonyl*, and not *dicarbonyl*, complex. Therefore, Ibers, Holm, and co-workers reinvestigated the structure of " $\text{Ru}(\text{TPP})(\text{CO})_2$ " and determined that the proposed dicarbonyl was, in fact, a monocarbonyl-ethanol complex $\text{Ru}(\text{TPP})(\text{CO})(\text{EtOH})$.⁹⁰ Since the molecule resided on a crystallographic center of symmetry, the CO and EtOH ligands were statistically disordered, so that a superposition was observed. The earlier study failed to locate the methyl group of the disordered ethanol ligand, and therefore presumed the molecule to be " $\text{Ru}(\text{TPP})(\text{CO})_2$ ", in which the "carbonyl" ligands appeared to be bent since they corresponded to a composite of a linear carbonyl and bent ethanol fragment. Indeed, the observed "Ru-C-O" bond angle of 153.3(9)° for the bent carbonyl ligand corresponds closely to the average (154°) of the true Ru-C-O angle of 176° and of the Ru-O-C(α -Et) angle of 133°.

A closely related example is provided by a complex that was originally proposed to be the six-coordinate aquahydroxy iron(III) porphyrin derivative (TPP)Fe(OH)(OH₂).⁹¹ However, at a later date it was realized that the complex was in fact the *five*-coordinate *chloride* derivative. The new crystallographic model required

the single chloride ligand to be statistically distributed on both sides of the plane of the porphyrin ring in the solid state.^{92,93} Since a statistically disordered chlorine atom (with 8.5 electrons) has a very similar electron density to that of an ordered oxygen atom (with 8 electrons), it is not surprising that a crystallographic model involving two ordered oxygen atoms may be interpreted as a successful solution for a structure that really consists of a single disordered chlorine atom.⁹⁴

In the above example of "(TPP)Fe(OH)(OH₂)", the occurrence of crystallographic disorder resulted in the proposal of a molecular structure that exhibited a *higher* coordination number than really present. The reverse situation may also occur, in which crystallographic disorder results in the incorrect proposal of a *lower* coordination number. For example, the complex $\text{TaBr}_3(\text{PPhMe}_2)_2$ has recently been claimed to provide the first example of the unprecedented five-coordinate MX_3L_2 stoichiometry for tantalum.⁹⁵ The structure of $\text{TaBr}_3(\text{PPhMe}_2)_2$ was described as a square pyramid, with an apical bromine atom that was statistically disordered above and below the plane of the square base. However, Cotton has noted several peculiarities with the reported structure.⁹⁶ First of all, unlike typical square pyramidal geometries, the tantalum atom was *not* displaced significantly from the plane of the square basal ligands toward the apical bromine atom. Secondly, there was a substantial difference in the Ta-Br bond lengths (ca. 2.52 versus 2.38 Å), and in particular, a short Ta-Br bond length of 2.38 Å was unacceptable. Recognizing that the interatomic dimensions of the disordered five-coordinate " $\text{TaBr}_3(\text{PMe}_2\text{Ph})_2$ " molecule closely resembled those in the *six*-coordinate *octahedral* complex $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$,⁹⁷ Cotton rationalized that both molecules were of the same type, i.e. $\text{TaX}_4(\text{PMe}_2\text{Ph})_2$, and suggested that the two *disordered* bromine atoms (with 17.5 electrons each) in the structure of " $\text{TaBr}_3(\text{PMe}_2\text{Ph})_2$ " were in fact two *ordered* chlorine atoms (with 17 electrons each). Since the overall electron density is similar, there would be no appreciable effect on the quality of the refinement. However, the

identity of the atom as chlorine would explain the short (ca. 2.38 Å) Ta–X bond length. It was, therefore, proposed that the five-coordinate complex “TaBr₃–(PMe₂Ph)₂” was in reality a six-coordinate octahedral complex of composition TaCl_xBr_{4–x}(PMe₂Ph)₂, with $x \approx 2$. The chloride contamination was suggested to derive from the CH₂Cl₂ solvent used for the preparation which involved the reduction of TaBr₅ by Mg in the presence of PMe₂Ph. It is also intriguing, and ironic, that this example represents the unusual situation whereby an incorrect disordered structure was imposed on a structure which was, in fact, ordered.

The molecular structure of the square-planar rhodium(II) complex *trans*-Rh(PPh₃)₂Cl₂, proposed to be the paramagnetic impurity in Wilkinson’s catalyst, has been reported.⁹⁸ More recently, the molecular structure of the closely related triisopropylphosphine derivative *trans*-Rh(PPr₃)₂Cl₂ has been determined by Harlow and co-workers.⁹⁹ However, the Rh–Cl bond lengths for the two complexes were significantly different, with *trans*-Rh(PPh₃)₂Cl₂ exhibiting a substantially longer bond length of 2.428(4) Å, compared with 2.298(1) Å for *trans*-Rh(PPr₃)₂Cl₂. Furthermore, Harlow et al. noted that the red-purple color of *trans*-Rh(PPr₃)₂Cl₂ contrasted worryingly with the yellow color reported for *trans*-Rh(PPh₃)₂Cl₂, and therefore suggested that the latter may be contaminated with significant amounts of the carbonyl derivative *trans*-Rh(PPh₃)₂(CO)Cl, with which it is isostructural.¹⁰⁰ Indeed, Dunbar has reexamined the molecular structure of *trans*-Rh(PPh₃)₂(CO)Cl in detail.¹⁰¹ Although the rhodium atom lies on a crystallographic center of symmetry, so that the CO and Cl ligands are necessarily disordered, the structure was readily modeled by assigning half-occupancies to the three closely spaced peaks assigned to the CO and Cl ligands, resulting in the residuals $R = 0.030$ and $R_w = 0.025$. However, Dunbar also demonstrated that successful refinement ($R = 0.038$ and $R_w = 0.033$) could also be achieved by refining the molecule as the *dichloride trans*-Rh(PPh₃)₂Cl₂, by assigning the Cl atom full occupancy and excluding the C and O atoms. The metric parameters of this refinement procedure for *trans*-Rh(PPh₃)₂(CO)Cl compared very well with that of the original report of the alleged *trans*-Rh(PPh₃)₂Cl₂. Taken together with the essentially identical spectral properties, the data strongly support the suggestion that the compound proposed to be *trans*-Rh(PPh₃)₂Cl₂ is, or contains significant amounts of, *trans*-Rh(PPh₃)₂(CO)Cl.

A related example of undetected disorder between the methyl (CH₃) and ethylidyne (C≡CH₃) ligands of W(PMe₃)₄(CH₃)(CCH₃) resulted in the terminal carbon atom of the disordered ethylidyne ligand not being located, so that the molecule was originally formulated as the *dimethyl* derivative W(PMe₃)₄(CH₃)₂.¹⁰² However, X-ray diffraction studies on a better quality crystal successfully revealed the presence of the disordered methyl group of the ethylidyne ligand, thereby reformulating “W(PMe₃)₄(CH₃)₂” as W(PMe₃)₄(CH₃)(C–CH₃).¹⁰³

Hopkins has also observed a similar example of disorder for the related methylidyne–fluoride complex W(dmpe)₂(F)(CH) (dmpe = Me₂PCH₂CH₂PMe₂), in which the fluoride and methylidyne ligands are disordered.¹⁰⁴ Furthermore, an interesting progression in

the degree of disorder is observed for the series of complexes W(dmpe)₂(X)(CH) (X = F, Cl, Br, I). Thus, whereas the fluoride and methylidyne ligands in W(dmpe)₂(F)(CH) are completely disordered, the chloride analogue W(dmpe)₂(Cl)(CH) crystallizes with two molecules in the asymmetric unit, such that one of the molecules exhibits disordered chloride and methylidyne ligands, but ordered dmpe ligands, and the other molecule exhibits ordered chloride and methylidyne ligands but disordered dmpe ligands. In contrast, the larger bromide and iodide derivatives are completely ordered.

E. Incorrect Formulation of Compounds in the Absence of Crystallographic Disorder

Since atoms of similar atomic number, for example oxygen and fluorine, have similar X-ray scattering powers, it is often very difficult to distinguish definitively between such pairs by using X-ray diffraction techniques. Therefore, as the result of the incorrect assignment of an atom, the incorrect formulation of a compound can also occur even when the crystal is pure and there is no crystallographic disorder. An example of the difficulty of distinguishing between oxygen and fluorine by X-ray diffraction is illustrated by the fact that a molecule which was originally proposed to be a fluorine-substituted ferracyclopentadiene, with an unprecedented fluorine bridge between carbon and boron atoms,¹⁰⁵ is now recognized to contain a *hydroxy* bridge. The molecule has therefore been reformulated as a Lewis acid–base adduct between BF₃ and a hydroxy-substituted ferracyclopentadiene.¹⁰⁶

Carbon and oxygen may also be difficult to distinguish. For example, the complex that was originally considered to be tetrameric tetramethylplatinum [Me₃Pt(μ-Me)]₄^{107a} is now recognized to be the hydroxy-bridged complex [Me₃Pt(μ-OH)]₄.^{107b} Furthermore, the bridging ethoxy ligand in the trinuclear complex [Mo₃(OCH₂CH₃)₂(O₂CCH₃)₃(H₂O)]₃[CF₃SO₃]₂^{108a} was later reformulated as an *ethylidyne* ligand, i.e. [Mo₃(CCH₃)₂(O₂CCH₃)₃(H₂O)]₃[CF₃SO₃]₂.^{108b} It should also be noted that the β-carbon atom of the proposed ethoxy ligand was not located in the original structure determination, an observation that was suggested to be a result of disorder.

It is also difficult to distinguish between sulfur and chlorine by X-ray diffraction, and Cotton has reported that the bridging chloride complexes Nb₂(μ-Cl)₂Cl₄(SMe₂)₄, Ta₂(μ-Cl)₂Cl₄(SMe₂)₄, and Nb₂(μ-Cl)₂Cl₄(EtS–CH₂CH₂SEt)₂ should be reformulated as having two μ-S groups, rather than two μ-Cl groups.¹⁰⁹

Similar problems may also be observed for pairs of transition metals, as illustrated by the original report of the molecular structure of the complex Co(η²-S₂-CSEt)₃.¹¹⁰ An unusual feature of this structure centered on the mean Co–S bond length of 2.398(1) Å, which was substantially longer than had been observed previously [ca. 2.26–2.27 Å] for other complexes of the type Co(η²-S₂CX)₃. Therefore, Lippard reinvestigated the structure of Co(η²-S₂CSEt)₃ and found that the mean Co–S bond length was in fact 2.266(7) Å,¹¹¹ substantially shorter than the previously reported value [2.398(1) Å], and also in excellent agreement with the values for related molecules [2.26–2.27 Å]. Lippard recognized that the original structure was not that of the cobalt

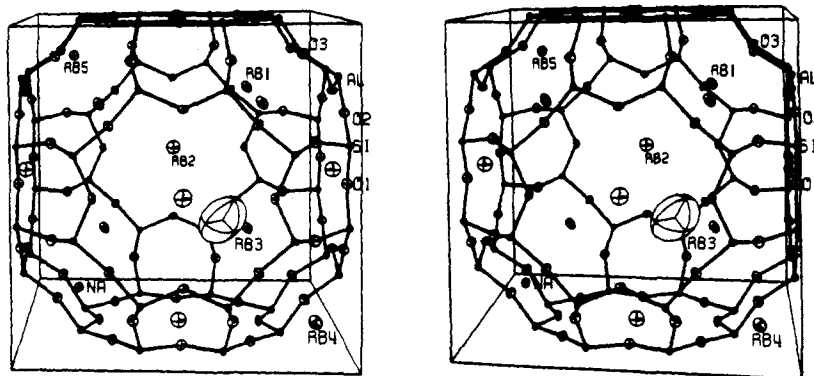


Figure 38. Stereoview of dehydrated $\text{Rb}_{11}\text{Na}_1\text{-A}$ illustrating the zero-coordinate Rb^+ cation (labeled RB3). Reprinted from ref 121c. Copyright 1977 American Chemical Society.

complex $\text{Co}(\eta^2\text{-S}_2\text{CSEt})_3$, but was actually that of the chromium derivative $\text{Cr}(\eta^2\text{-S}_2\text{CSEt})_3$, for which a Cr-S bond length of 2.398(1) Å was in close agreement with the corresponding values for related molecules. For example, the mean Cr-S bond length in $\text{Cr}(\eta^2\text{-S}_2\text{COEt})_3$ is 2.393(8) Å. The suggestion that the original structure of " $\text{Co}(\eta^2\text{-S}_2\text{CSEt})_3$ " was actually $\text{Cr}(\eta^2\text{-S}_2\text{CSEt})_3$ was also supported by the essentially identical unit cell dimensions of the two crystals.

Finally, an extreme example in which X-ray diffraction has incorrectly identified atom-types is provided by the structure of the unusual compound $[\text{ClF}_6]^-[\text{CuF}_4]^+$, which has been proposed to be, in fact, that of $[\text{SiF}_6]^-[\text{Cu}(\text{OH}_2)_4]^+$.¹¹²

A further problem in using X-ray diffraction to determine the structures of molecules is associated with the frequent difficulty of locating hydrogen atoms. Although in most circumstances the correct structures of molecules can be determined without locating hydrogen atoms, the misformulation of complexes may also arise by the incorrect identification of a group that may or may not carry a hydrogen atom. For example, Koch has proposed the reformulation of some compounds that have been claimed to contain terminal alkoxide ligands. On the basis that the terminal Mo-OR bond distances in the complexes $[\text{Mo}_4\text{O}_6\text{Cl}_4(\text{OPr}^n)_6]^{113}$ and $[\text{Mo}_4\text{O}_8\text{Cl}_4(\text{OEt})_4]^{2-}$ ¹¹⁴ were outside the range for terminal alkoxides in other molybdenum complexes,¹¹⁵ Koch has identified that the terminal ligands are *alcohols* and not alkoxides. The molecules have therefore been reformulated as the alcohol solvates $[\text{Mo}_4\text{O}_6\text{Cl}_4(\text{OPr}^n)_4(\text{HOPr}^n)_2]$ and $[\text{Mo}_4\text{O}_8\text{Cl}_4(\text{OEt})_2(\text{HOEt})_2]^{2-}$.^{19,116} In a similar vein, Theopold has demonstrated that the complex $\text{Cp}^*\text{Co}=\text{CoCp}^*$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), which was originally cited as the first example of an unbridged metal-metal double bond,¹¹⁷ is in fact bridged by *three hydride ligands*, $\text{Cp}^*\text{Co}(\mu\text{-H})_3\text{CoCp}^*$.¹¹⁸⁻¹²⁰

F. "Zero-Coordinate" Ions

Several zeolite structures have been claimed to contain "zero-coordinate" and "near-zero-coordinate" cations.^{121,122} "Zero-coordinate" ions have been defined as ions whose separation exceeds the sum of their corresponding radii by more than 1.0 Å.¹²¹ For example, the closest approach of one of the Rb^+ ions (labeled RB3 in Figure 38) in dehydrated crystals of Rb^+ -exchanged zeolite 4A was reported to exceed the sum of the appropriate ionic radii by more than 1.5 Å.¹²¹

However, more recent studies have revealed that these originally formulated examples of "zero-coordinate" and "near-zero-coordinate" cations in zeolites are artifacts.¹²³

VI. Some Comments on Bond-Stretch Isomerism in Other Transition Metal Complexes

The accumulated evidence documented above serves to emphasize the subtlety of crystallographic disorder, in that bond lengths may be incorrectly determined even when there is no obvious crystallographic anomaly. In light of the fact that there is now no evidence to support bond-stretch isomerism in *cis-mer-MoOCl}_2(\text{PMe}_2\text{Ph})_3, the original complex proposed to exhibit the phenomenon, all other proposed examples are now suspect. This section describes additional studies on some previously reported examples of bond-stretch isomerism in order to provide a current perspective of the phenomenon.*

A. Isomers of $[(\text{Me}_3\text{tacz})\text{W}(\text{O})\text{Cl}_2]^+$

The blue [$d(\text{W}=\text{O})$ 1.72(2) Å] and green [$d(\text{W}=\text{O})$ 1.89(2) Å] isomers of the cation $[(\text{Me}_3\text{tacz})\text{W}(\text{O})\text{Cl}_2]^+$ have been reinvestigated by Enemark and Wieghardt, who have shown that the system is considerably more complex than that for *cis-mer-MoOCl}_2(\text{PMe}_2\text{Ph})_3. In particular, the system is proposed to be composed of *three* components with different oxidation states: $[(\text{Me}_3\text{tacz})\text{W}(\text{O})\text{Cl}_2]^+$, $[(\text{Me}_3\text{tacz})\text{W}(\text{O})_2\text{Cl}]^+$, and $[(\text{Me}_3\text{tacz})\text{W}(\text{O})\text{Cl}(\text{solv})]^+$.¹²⁴ Such a result also provides an explanation for the observation that, although the blue and green forms are stable in solution for several days, addition of small amounts of water to a solution of the green isomer resulted in the immediate conversion to the blue isomer.¹⁵*

In some related work, Wieghardt has prepared and structurally characterized blue and green forms of $(\text{Me}_3\text{tacz})\text{TiCl}_3$.¹²⁵ IR spectroscopy revealed that there is a band at 938 cm^{-1} in the green form that is very weak in the blue form. Furthermore, the intensity of the band varies with each preparation. It was concluded that the green form of $(\text{Me}_3\text{tacz})\text{TiCl}_3$ is contaminated with the oxo complex $(\text{Me}_3\text{tacz})\text{Ti}(\text{O})\text{Cl}_2$, an analogue of which, $(\text{Me}_3\text{tacz})\text{Ti}(\text{O})(\text{NCS})_2$, has been fully characterized.

B. Isomers of $[\text{cis-Tc}(\text{N})\text{Cl}(\text{phen})_2]^+$

The cation $[\text{cis-Tc}(\text{N})\text{Cl}(\text{phen})_2]^+$ has been isolated as two different salts: $[\text{cis-Tc}(\text{N})\text{Cl}(\text{phen})_2][\text{Cl}]\cdot\text{H}_2\text{O}$

Table VIII. Some Properties of the Oxo and Sulfido Complexes Nb(E)Cl₃(PMe₃)₃

Nb(X)Cl ₃ (PMe ₃) ₃	<i>d</i> (Nb=X), Å	<i>ν</i> (Nb=X), cm ⁻¹
yellow-Nb(O)Cl ₃ (PMe ₃) ₃	1.781(6)	882
green-Nb(O)Cl ₃ (PMe ₃) ₃	1.929(6)	871
orange-Nb(S)Cl ₃ (PMe ₃) ₃	2.196(2)	455
green-Nb(S)Cl ₃ (PMe ₃) ₃	2.296(1)	489

and [*cis*-Tc(N)Cl(phen)₂][PF₆]. The original X-ray structure determinations revealed substantially different Tc≡N bond lengths of 1.603(5) and 1.754(6) Å, respectively.¹⁷ However, Clarke has now established that the 1.754(6) Å bond length observed for [*cis*-Tc(N)Cl(phen)₂][PF₆] is an artifact due to an 85:15 enantiomeric disorder.¹²⁶ Implementation of a suitable disorder model resulted in the Tc≡N bond length being reduced substantially by more than 0.15 Å to 1.593(5) Å, in close agreement with that for [*cis*-Tc(N)Cl(phen)₂][Cl]·H₂O [1.603(5) Å] and also other technetium nitrido complexes.

C. Isomers of Nb(O)Cl₃(PMe₃)₃ and Nb(S)Cl₃(PMe₃)₃

Bond-stretch isomers of the oxo and sulfido complexes Nb(O)Cl₃(PMe₃)₃ and Nb(S)Cl₃(PMe₃)₃ have been cited as providing the best evidence so far for the reality of the phenomenon of bond-stretch isomerism.^{18b,c} Some properties of these complexes are summarized in Table VIII.

The original refinement of the structure of green-Nb(O)Cl₃(PMe₃)₃ showed marked elongation of the oxygen atom thermal ellipsoid along the Nb—O bond vector, which has been interpreted as due to disorder with the isostructural tetrachloride NbCl₄(PMe₃)₃, which is green. Implementation of a disorder model resulted in the Nb=O bond length being reduced from 2.087(5)^{18b} to 1.929(6) Å,^{18c} which is still substantially longer than that in the yellow form, 1.781(6) Å. In view of the disorder problem, some caution in interpretation of the 1.929(6) Å bond length for green-Nb(O)Cl₃(PMe₃)₃ was recommended.

Although contamination of the green oxo complex Nb(O)Cl₃(PMe₃)₃ by NbCl₄(PMe₃)₃ was recognized early on, the sulfido analogues were originally reported to be free from a disorder problem.^{18c} However, Gibson and McPartlin have more recently reported evidence which indicates that the green sulfido complex Nb(S)Cl₃(PMe₃)₃ is also contaminated with the green tetrachloride NbCl₄(PMe₃)₃.¹²⁷ Furthermore, X-ray structure determinations on green Nb(S)Cl₃(PMe₃)₃ obtained from different batches have given rise to different Nb=S bond lengths (2.219 and 2.225 Å).¹²⁸ Since sulfur and chlorine have very similar X-ray scattering powers, it is not unanticipated that the disorder for the green sulfido complex was more difficult to detect than for the green oxo complex. Indeed, Cotton (*vide supra*) has recently highlighted the inability of X-ray crystallography to distinguish between sulfur and chlorine.¹⁰⁹

Although disorder between (i) oxygen and chlorine and (ii) sulfur and chlorine may explain the variation in Nb=O and Nb—S bond lengths observed for Nb(X)Cl₃(PMe₃)₃, Gibson and McPartlin emphasize that it does not explain the observation of different *ν*(Nb=X) stretching frequencies, which remain the sole pieces of

evidence that are still in support of bond-stretch isomerism for this system.¹²⁷ An alternative explanation may be that the additional *ν*(Nb=X) stretching frequencies are due to the presence of a presently undetected and unidentified impurity.^{129,130}

VII. Summary and Conclusions

The emphasis of the research that has been reviewed in this article has been to highlight the subtle effects that undetected crystallographic disorder may play in the determination of molecular structures by single crystal X-ray diffraction. Such effects of disorder can range from the incorrect determination of bond lengths, to the incorrect formulation of compounds. These examples serve to emphasize that the observation of low *R* values, low esd's, and well-behaved thermal parameters are not always sufficient indications of a *true* structure. Many of the topics described in this article have centered on disorder due to the presence of impurities in single crystals. It is very likely that one of the principal reasons for neglecting to consider compositional disorder when performing X-ray structure determinations is undoubtedly due to the common belief that single crystals are inherently pure, even though it is recognized that such a method of doping paramagnetic complexes into crystals of isostructural diamagnetic complexes is used extensively in single crystal EPR studies.¹³¹ It is this general belief that single crystals are pure, compounded by the subtlety of the disorder problem, that results in many of the misinterpretations described in this review.

The interpretation of X-ray diffraction data in providing apparent experimental verification for bond-stretch isomerism in *cis-mer*-MoOCl₂(PMe₂Ph)₃ represents an extreme example of the subtlety of the disorder problem. Moreover, it is also a reflection of the influential power and the exactness that is often *believed* to be inherent in a X-ray structure determination. Indeed, as cited in the introduction: "There can be no doubt that when a compound has to be identified there is nothing to beat a crystal structure determination. After all, the final outcome—a drawing of the molecule, with all the atoms nicely shaded and labeled—is convincing and will silence all but the most stubborn critics."² While this statement may be correct for the majority of structures, it is important to recognize the limitations of the technique so that results are not overinterpreted.⁴⁸

In summary, the following points should be highlighted:

(i) Crystallographic disorder may be difficult to detect, and unsuspected crystallographic disorder can result in both (a) the incorrect determination of bond lengths and (b) the incorrect formulation of compounds.

(ii) Cocrystallization of structurally related molecules, resulting in the formation of single-crystal solid solutions, may be more common than presently appreciated. Hence, the possibility of compositional disorder should be considered when performing X-ray structure determinations, especially if there are any unusual measured bond lengths. In this regard, spectroscopic analysis of the *same* crystal used in the diffraction study may prove informative, as would repeating the structure determination on a crystal obtained from a different batch.

(iii) The observation of a long Mo=O bond length in the green "isomer" of *cis-mer*-MoOCl₂(PMe₂Ph)₃ is an artifact due to compositional disorder with isostructural *mer*-MoCl₃(PMe₂Ph)₃. There is no evidence for bond-stretch isomerism in the first system that was proposed to exhibit the phenomenon.

(iv) The 3 σ criterion for establishing whether or not two bond lengths are significantly different is only valid if there is no systematic error in the data. Systematic errors may be difficult to detect, but, as in ii above, repeating the structure determination on a crystal obtained from a different batch may provide a more accurate estimate of the error, especially if compositional disorder is the source of the systematic error.

Finally, although the original example of bond-stretch isomerism has been shown to be the result of an artifact and that there is presently no definitive evidence of bond-stretch isomerism in other complexes, the concept itself still remains. Only a combination of time and a demanding series of analytical experiments will reveal whether or not it is actually possible for bond-stretch isomers to exist under normal conditions.

Addendum

1. Anomalous atomic distances in semibullvalene derivatives have been attributed to disorder with nonequivalent valence tautomers,¹³² and a review of atomic motions in molecular crystals has been published.¹³³

2. The X-ray structure of the perchlorate salt [Co(en)₂Cl(benzimidazole)][ClO₄]₂¹³⁴ has been shown to be incorrect.¹³⁵ In particular, the composition determined by the X-ray analysis was incorrect in that the complex was actually a chloride salt of approximate composition [Co(en)₂Cl(benzimidazole)]Cl₂·1.3-H₂O, rather than a perchlorate salt. Other corrections included a revised calculated density of 1.56 g cm⁻³, rather than 2.94 g cm⁻³, and also a change in space group to monoclinic C2/c rather than triclinic P1.

VIII. Acknowledgment

I sincerely wish to thank Keum Yoon the graduate student who carried out portions of the research described in this article. I also thank Professors V. C. Gibson, J. Enemark, K. Wieghardt, M. Hopkins, J. Burdett, and K. Dunbar for providing information prior to publication. Professors A. L. Rheingold, B. Foxman, F. A. Cotton, S. J. Lippard, S. A. Koch, A. Bino, K. Seff, H. D. Kaesz, W. E. Broderick, M. H. Chisholm, J. M. Mayer, H. Quast, and R. E. Marsh are all thanked for very helpful discussions. The reviewers of this manuscript are also thanked for their helpful comments. This work was supported in part by the National Science Foundation (CHE-9007512).

IX. References and Notes

- (1) Ihde, A. J. *The Development of Modern Chemistry*; Harper and Row: New York, 1970.
- (2) Ebsworth, E. A. V.; Rankin, D. W. H.; Craddock, S. *Structural Methods in Inorganic Chemistry*, 2nd ed.; CRC Press: Boca Raton, 1991.
- (3) (a) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779-786. (b) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 1661-1668.
- (4) Paddon-Row, M. N.; Radom, L.; Gregory, A. R. *J. Chem. Soc., Chem. Commun.* **1976**, 427-429.
- (5) (a) Schleyer, P. v. R.; Sax, A. F.; Kalcher, J.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 364-366. (b) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 2888-2891. (c) Nagase, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1988**, 54-56. (d) Collins, S.; Dutler, R.; Rauk, A. *J. Am. Chem. Soc.* **1987**, *109*, 2564-2569. (e) Schoeller, W. W.; Dabisch, T.; Busch, T. *Inorg. Chem.* **1987**, *26*, 4383-4389.
- (6) Kaufmann, E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3987-3992.
- (7) (a) Sudhakar, P. V.; Güner, O. F.; Lammertsma, K. *J. Phys. Chem.* **1989**, *93*, 7289-7292. (b) Lammertsma, K.; Güner, O. F. *J. Am. Chem. Soc.* **1988**, *110*, 5239-5245.
- (8) Güner, O. F.; Lammertsma, K. *J. Am. Chem. Soc.* **1990**, *112*, 508-516.
- (9) Sudhakar, P. V.; Lammertsma, K. *J. Phys. Chem.* **1992**, *96*, 4830-4834.
- (10) Butcher, A. V.; Chatt, J. *J. Chem. Soc. (A)* **1970**, 2652-2656.
- (11) (a) Manojlovic-Muir, L. *J. Chem. Soc. (D)* **1971**, 147. (b) Manojlovic-Muir, L. *J. Chem. Soc. (A)* **1971**, 2796-2800.
- (12) (a) Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc. (D)* **1971**, 655-656. (b) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1972**, 686-690.
- (13) Haymore, B. L.; Goddard, W. A., III; Allison, J. N. *Proc. Int. Conf. Coord. Chem.* **1984**, *23*, 535.
- (14) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (b) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899-3903.
- (15) Wieghardt, K.; Backes-Dahmann, G.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 777-778.
- (16) Wieghardt, K.; Backes-Dahmann, G.; Holzbach, W.; Swiridoff, W. J.; Weiss, J. *Z. Anorg. Allg. Chem.* **1983**, *499*, 44-58.
- (17) (a) Lu, J.; Clarke, M. *Book of Abstracts*, J. 199th National Meeting of the American Chemical Society, Boston, MA, April 22-27, 1990; American Chemical Society: Washington, DC, 1990; INOR 583. (b) Clarke, M. J. Personal communication.
- (18) (a) Gibson, V. C.; Kee, T. P.; Shaw, A.; Williams, D. N. *Book of Abstracts*, 199th National Meeting of the American Chemical Society, Boston, MA, April 22-27, 1990; American Chemical Society: Washington, DC, 1990; INOR 134. (b) Bashall, A.; McPartlin, M. *Acta Crystallogr.* **1990**, *A46* (Suppl.), C-221-C-222 (IUC 15th International Conference of Crystallography, Bordeaux, France). (c) Bashall, A.; Gibson, V. C.; Kee, T. P.; McPartlin, M.; Robinson, O. B.; Shaw, A. *Angew. Chem.* **1991**, *103*, 1021-1023; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 980-982.
- (19) Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594-1602.
- (20) For some other examples related to bond-stretch isomerism see ref 14a, p 153.
- (21) Degman, I. A.; Behm, J.; Cook, M. R.; Herrmann, W. A. *Inorg. Chem.* **1991**, *30*, 2165-2170.
- (22) Backes-Dahmann, G.; Wieghardt, K. *Inorg. Chem.* **1985**, *24*, 4044-4049.
- (23) (a) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 4506-4516. (b) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1988**, 140-142.
- (24) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527-622.
- (25) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.
- (26) Kölle, U.; Kossakowski, J.; Klaff, N.; Wesemann, L.; Englert, U.; Herlich, G. E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 690-691.
- (27) Kölle, U.; Lueken, H.; Handrick, K.; Burdett, J. K.; Balleza, S. *Inorg. Chem.*, in press.
- (28) Bray, K. L.; Drickamer, H. G.; Mingos, D. M. P.; Watson, M. J.; Shapley, J. R. *Inorg. Chem.* **1991**, *30*, 864-866.
- (29) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 2848-2852.
- (30) Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347-352.
- (31) Yoon, K.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 1437-1438.
- (32) Yoon, K.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 2210-2218.
- (33) Parkin, G. *Acc. Chem. Res.* **1992**, *25*, 455-460.
- (34) Indeed, the similarity of such bond lengths often provides a good indication of the accuracy of the structure determination: Rheingold, A. L.; Harper, J. R. *J. Organomet. Chem.* **1991**, *403*, 335-344.
- (35) (a) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 867-873. (b) Hardcastle, F. D.; Wachs, I. E. *J. Raman Spec.* **1990**, *21*, 683-691.
- (36) The complex *mer*-MoCl₃(PMe₂Ph)₃ has been previously reported. See ref 30 and also: Atwood, J. L.; Hunter, W. E.; Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 467-470.
- (37) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639-2645.
- (38) (a) Glusker, J. P.; Trueblood, K. N. *Crystal Structure Analysis*, 2nd ed.; Oxford University Press: New York, 1985. (b) Stout, G. H.; Jensen, L. H. *X-Ray Structure Determination: A Practical Guide*, 2nd ed.; Wiley: New York, 1989.
- (39) Taylor, R.; Kennard, O. *Acta Crystallogr.* **1986**, *B42*, 112-120.
- (40) Desrochers, P. J.; Nebesny, K. W.; LaBarre, M. J.; Lincoln, S. E.; Loeher, T. M.; Enemark, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 9193-9200.

- (41) Bashall, A.; Bligh, S. W. A.; Edwards, A. J.; Gibson, V. C.; McPartlin, M.; Robinson, O. B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1607-1609.
- (42) Song, J.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 4433-4437.
- (43) Yoon, K.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 8414-8418.
- (44) Yoon, K.; Parkin, G. *Inorg. Chem.* **1992**, *31*, 1656-1662.
- (45) Han, R.; Trofimenko, S.; Parkin, G. Unpublished results.
- (46) Ibers, J. A. *Critical Evaluation of Chemical and Physical Structural Information*; Lide, D. R., Paul, M. A., Eds.; National Academy of Sciences: Washington, DC, 1974; pp 186-198.
- (47) Donohue, J. *Critical Evaluation of Chemical and Physical Structural Information*; Lide, D. R., Paul, M. A., Eds.; National Academy of Sciences: Washington, DC, 1974; pp 199-218.
- (48) Jones, P. G. *Chem. Soc. Rev.* **1984**, *13*, 157-172.
- (49) (a) Marsh, R. E. *Inorg. Chem.* **1988**, *27*, 2902-2903. (b) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr.* **1988**, *B44*, 77-88. (c) Marsh, R. E. *Inorg. Chim. Acta* **1989**, *157*, 1-2. (d) Marsh, R. E. *Inorg. Chem.* **1990**, *29*, 573-574. (e) Marsh, R. E. *Inorg. Chem.* **1990**, *29*, 1449-1450.
- (50) Scane, J. G. *Acta Crystallogr.* **1967**, *23*, 85-89.
- (51) Cotton, F. A.; Bino, A. *Inorg. Chem.* **1979**, *18*, 2710-2713.
- (52) Chiu, K. W.; Lyons, D.; Wilkinson, Thornton-Pett, M.; Hursthouse, M. B. *Polyhedron* **1983**, *2*, 803-810.
- (53) Cotton, F. A.; Mandal, S. K. *Inorg. Chim. Acta* **1992**, *194*, 179-187.
- (54) McGinney, J. A.; Payne, N. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 6301-6310.
- (55) Nolte, M. J.; Singleton, E.; Laing, M. *J. Am. Chem. Soc.* **1975**, *97*, 6396-6400.
- (56) In addition to a decrease in intensities of check reflections, the decomposition of the crystal was accompanied by a substantial change in the β angle of the monoclinic cell, from 95.18° to 95.83° over 62.5 h of irradiation. (See ref 55.)
- (57) Hills, A.; Hughes, D. L.; Leigh, G. J.; Prieto-Alcón, R. *J. Chem. Soc., Dalton Trans.* **1991**, 1515-1517.
- (58) Yoon, K.; Parkin, G.; Hughes, D. L.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1992**, 769-773.
- (59) Butcher, A. V.; Chatt, J.; Leigh, G. J.; Richards, P. L. *J. Chem. Soc., Dalton Trans.* **1972**, 1064-1069.
- (60) Fronczek, F. R.; Baker, E. C.; Sharp, P. R.; Raymond, K. N.; Alt, H. G.; Rausch, M. D. *Inorg. Chem.* **1976**, *15*, 2284-2289.
- (61) Hunter, W. E.; Hrcir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750-755.
- (62) Girolami, G. S.; Mainz, V. V.; Andersen, R. A.; Vollmer, S. H.; Day, V. W. *Inorg. Chem.* **1981**, *103*, 3953-3955.
- (63) Cotton, F. A.; Wiesinger, K. J. *Inorg. Chem.* **1990**, *29*, 2594-2599.
- (64) Cooper, J. A.; Anderson, B. F.; Buckley, P. D.; Blackwell, L. F. *Inorg. Chim. Acta* **1984**, *91*, 1-9.
- (65) Broderick, W. E.; Pressprich, M. R.; Geiser, U.; Willett, R. D.; Legg, J. I. *Inorg. Chem.* **1986**, *25*, 3372-3377.
- (66) Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954-5956.
- (67) Salt, J. E.; Girolami, G. S.; Wilkinson, G.; Motevalli, M.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 685-692.
- (68) *CRC Handbook of Chemistry and Physics*, 69th ed.; Weast, R. C., Ed.; CRC Press Inc.: Boca Raton, FL, 1988; p F-166.
- (69) Sherwood, D. E., Jr.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 93-100.
- (70) Schumann, H.; Heisler, M.; Pickardt, J. *Chem. Ber.* **1977**, *110*, 1020-1026.
- (71) Davis, B. R.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 578-585.
- (72) Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazzetta, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1828-1834.
- (73) Thorn, D. L.; Tulip, T. H.; Ibers, J. A. *J. Chem. Soc., Dalton Trans.* **1979**, 2022-2025.
- (74) Churchill, M. R.; Fetting, J. C.; Buttrey, L. A.; Barkan, M. D.; Thompson, J. S. *J. Organomet. Chem.* **1988**, *340*, 257-266.
- (75) Del Pra, A.; Zanotti, G.; Segula, P. *Cryst. Struct. Commun.* **1979**, *8*, 959-964.
- (76) Rheingold, A. L.; Geib, S. J. *Acta Crystallogr.* **1987**, *C43*, 784-786.
- (77) Ceriotti, A.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1983**, *247*, 345-350.
- (78) Chen, Y.-J.; Wang, J.-C.; Wang, Y. *Acta Crystallogr.* **1991**, *C47*, 2441-2442.
- (79) Brady, R.; De Camp, W. H.; Flynn, B. R.; Schneider, M. L.; Scott, J. D.; Vaska, L.; Werneke, M. F. *Inorg. Chem.* **1975**, *14*, 2669-2675.
- (80) Rees, W. M.; Churchill, M. R.; Li, Y.-J.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162-1167.
- (81) Fetting, J. C.; Churchill, M. R.; Bernard, K. A.; Atwood, J. D. *J. Organomet. Chem.* **1988**, *340*, 377-388.
- (82) McGinney, J. A.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 2243-2250.
- (83) La Placa, S. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1965**, *87*, 2581-2586.
- (84) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *Polyhedron* **1983**, *2*, 185-193.
- (85) Chatt, J.; Rowe, G. A. *J. Chem. Soc.* **1962**, 4019-4033.
- (86) Chatt, J.; Garforth, J. D.; Johnson, N. P.; Rowe, G. A. *J. Chem. Soc. (A)* **1964**, 601-606.
- (87) Sacerdoti, M.; Bertolasi, V.; Gilli, G.; Duatti, A. *Acta Crystallogr.* **1982**, *B38*, 96-100.
- (88) (a) Mayer, J. M. *Chemtracts: Inorg. Chem.* **1991**, *3*, 115-117. (b) Conry, R. R.; Mayer, J. M. Personal communication.
- (89) Cullen, D.; Meyer, E., Jr.; Srivastava, T. S.; Tsutsui, M. *J. Chem. Soc., Chem. Commun.* **1972**, 584-585.
- (90) Bonnet, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2141-2149.
- (91) Fleischer, E. B.; Miller, C. K.; Webb, L. E. *J. Am. Chem. Soc.* **1964**, *86*, 2342-2347.
- (92) (a) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992-1996. (b) Hoard, J. L.; Hamor, M. J.; Hamor, T. A.; Caughey, W. S. *J. Am. Chem. Soc.* **1965**, *87*, 2312-2319.
- (93) It should be noted that the iron atoms, as well as the chlorine atoms, are randomly distributed about the porphyrin plane. (See ref 92.)
- (94) It has also been suggested that the bis(aqua) complex (TPP)Zn(OH₂)₂ is really the disordered mono(aqua) complex (TPP)Zn(OH₂); Glick, M. D.; Cohen, G. H.; Hoard, J. L. *J. Am. Chem. Soc.* **1967**, *89*, 1996-1998.
- (95) Hovnanian, N.; Hubert-Pfalzgraf, L. G.; Le Borgne, G. *Inorg. Chem.* **1985**, *24*, 4647-4651.
- (96) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1986**, *25*, 1728-1729.
- (97) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *24*, 4046-4050.
- (98) Ogle, C. A.; Masterman, T. C.; Hubbard, J. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1733-1734.
- (99) Harlow, R. L.; Thorn, D. L.; Baker, R. T.; Jones, N. L. *Inorg. Chem.* **1992**, *31*, 993-997.
- (100) Chaloner, P. A.; Claver, C.; Hitchcock, P. B.; Masdeu, A. M.; Ruiz, A. *Acta Crystallogr.* **1991**, *C47*, 1307-1308.
- (101) Dunbar, K. R.; Haefner, S. C. *Inorg. Chem.* **1992**, *31*, 3676-3679.
- (102) Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1979**, 926-927.
- (103) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204-1211.
- (104) Hopkins, M. D. Personal communication.
- (105) Mirkin, C. A.; Lu, K.-L.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 461-462.
- (106) Mirkin, C. A.; Lu, K.-L.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6155.
- (107) (a) Rundle, R. E.; Sturdivant, J. H. *J. Am. Chem. Soc.* **1947**, *69*, 1561-1567. (b) Cowan, D. O.; Kriehoff, N. G.; Donnay, G. *Acta Crystallogr.* **1968**, *B24*, 287-288.
- (108) (a) Bino, A.; Ardon, M.; Maor, I.; Kaftory, M.; Dori, Z. *J. Am. Chem. Soc.* **1976**, *98*, 7093-7095. (b) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1981**, *103*, 243-244.
- (109) Babaian-Kibala, E.; Cotton, F. A.; Kibala, P. A. *Inorg. Chem.* **1990**, *29*, 4002-4005.
- (110) Villa, A. C.; Manfredotti, A. G.; Guastini, C.; Nardelli, M. *Acta Crystallogr.* **1972**, *B24*, 2231-2236.
- (111) Li, T.-I.; Lippard, S. J. *Inorg. Chem.* **1973**, *13*, 1791-1792.
- (112) von Schnering, H. G.; Vu, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 408.
- (113) Beaver, J. A.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1973**, 1376-1380.
- (114) Belicchi, M. F.; Fava, G. G.; Pelizzi, C. *J. Chem. Soc., Dalton Trans.* **1983**, 65-69.
- (115) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681-722.
- (116) Koch, S. A.; Lincoln, S. *Inorg. Chem.* **1982**, *21*, 2904-2905.
- (117) Schneider, J. J.; Goddard, R.; Werner, S.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1124-1126.
- (118) Kersten, J. L.; Rheingold, A. L.; Theopold, K. H.; Casey, C. P.; Widenhofer, R. A.; Hop, C. E. C. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1341-1343; *Angew. Chem.* **1992**, *104*, 1364-1366.
- (119) For the corrigendum see: Schneider, J. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1392; *Angew. Chem.* **1992**, *104*, 1422.
- (120) For a theoretical argument against the proposed formulation of unbridged Cp*Co=CoCp*, see: Abrahamson, H. B.; Nicolai, G. P.; Heinekey, D. M.; Casey, C. P.; Bursten, B. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 471-473; *Angew. Chem.* **1992**, *104*, 464-466.
- (121) (a) Leung, P. C. W.; Kunz, K. B.; Seff, K.; Maxwell, I. E. *J. Phys. Chem.* **1975**, *79*, 2157-2162. (b) Firor, R. L.; Seff, K. *J. Am. Chem. Soc.* **1976**, *98*, 5031-5033. (c) Firor, R. L.; Seff, K. *J. Am. Chem. Soc.* **1977**, *99*, 1112-1117.
- (122) (a) Subramanian, V.; Seff, K. *J. Phys. Chem.* **1977**, *81*, 2249-2251. (b) Firor, R. L.; Seff, K. *J. Am. Chem. Soc.* **1977**, *99*, 7059-7061. (c) Firor, R. L.; Seff, K. *J. Am. Chem. Soc.* **1978**, *100*, 978-980. (d) Firor, R. L.; Seff, K. *J. Am. Chem. Soc.* **1978**, *100*, 3091-3096. (e) McCusker, L. B.; Seff, K. *J. Am. Chem. Soc.* **1978**, *100*, 5052-5057.
- (123) (a) Pluth, J. J.; Smith, J. V. *J. Phys. Chem.* **1979**, *83*, 741-749. (b) Pluth, J. J.; Smith, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 4704-4708. (c) Pluth, J. J.; Smith, J. V. *J. Am. Chem. Soc.* **1982**, *104*, 6977-6982. (d) Pluth, J. J.; Smith, J. V. *J. Am. Chem. Soc.* **1983**, *105*, 1192-1195.
- (124) Desrochers, P. J.; Enemark, J. H.; Wiegardt, K. Personal communication.
- (125) Bodner, A.; Jeske, P.; Weyhermüller, W.; Wiegardt, K.; Dubler, E.; Schmale, H.; Nuber, B. *Inorg. Chem.* **1992**, *31*, 3737-3748.

- (126) Clarke, M. J.; Lu, J. *Inorg. Chem.* **1992**, *31*, 2476-2480.
- (127) Gibson, V. C.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1992**, 947-956.
- (128) It has been described (ref 127) that the bond lengthening which appeared to be present in the green form of $\text{Nb(S)Cl}_3(\text{PMe}_3)_3$ was originally an embarrassment to the case of bond-stretch isomerism because, on the basis of the IR data, the orange-yellow form would have been expected to have the longer Nb=S bond. Since it is now recognized that the green form is contaminated with green $\text{NbCl}_4 \cdot (\text{PMe}_2)_3$, the true Nb=S bond length is not known, and it has been proposed that it could be shorter than the orange-yellow isomer.
- (129) For other comments regarding this system, see: Mayer, J. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 286-287.
- (130) For a discussion of possible impurities, see: ref 127.
- (131) (a) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6416-6422. (b) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422-6433. (c) Baker, R. T.; Morton, J. R.; Preston, K. F.; Williams, A. J.; Le Page, Y. *Inorg. Chem.* **1991**, *30*, 113-116.
- (132) (a) Quast, H.; Carlsen, J.; Janiak, R.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1992**, *125*, 955-968. (b) Jackman, L. M.; Benesi, A.; Mayer, A.; Quast, H.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *J. Am. Chem. Soc.* **1989**, *111*, 1512-1513.
- (133) Dunitz, J. D.; Maverick, E. F.; Trueblood, K. N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 880-895.
- (134) Rowan-Gordon, N.; Nguyenpho, A. A.; Mondon-Konan, E.; Turner, A. H.; Butcher, R. J.; Okonkwo, A. S.; Hayden, H. H.; Storm, C. B. *Inorg. Chem.* **1991**, *30*, 4374-4380.
- (135) Marsh, R. E. *Inorg. Chem.* **1992**, *31*, 4890.