Do Bond-Stretch Isomers Really Exist?

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Bond-stretch isomerism is the unusual phenomenon whereby molecules differ only in the *length* of one or more bonds. As such, bond-stretch isomers differ significantly from structural, geometrical, and optical isomers, whose interconversion requires more than the simple stretch of a bond. The chemist's traditional view of a bond between two atoms consists of a *single* minimum on a potential energy surface at a point that corresponds to the bond length (Figure 1a). In contrast, the existence of bond-stretch isomers requires both (i) a *double* minimum on a potential energy surface and (ii) a *significant* barrier between the two minima (Figure 1b). This notion of bond-stretch isomerism, in which isomers are related only by the stretching of a bond, is as counterintuitive as it is fascinating. In this Account, we provide a historical perspective of the phenomenon, followed by a review of our recent work that questions the entire existence of bond-stretch isomerism.[1]

The Concept and the Discovery

The concept of bond-stretch isomerism was introduced by Hoffmann in a 1972 theoretical study on a series of hypothetical molecules of the type $(CH)_5{}^+$ and $(CH)_4CO$.[2] Significantly, Hoffmann's work demonstrated that, for these hypothetical species, a double minimum may be obtained on the potential energy surface as a result of the crossing of energy levels, and thereby laid the foundation for bond-stretch isomerism. However, could it actually be possible for the barrier between the two minima to be sufficiently large so that individual bond-stretch isomers may be *isolated*?[3] In fact, as we shall see, experimental evidence in support of bond-stretch isomerism had already been discovered about a year prior to Hoffmann's proposal.

In 1970, Chatt reported that the complex *mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ could be isolated in both blue and green isomeric forms.[4] The blue and green isomers had very similar melting points (blue mp 155–157 °C; green mp 153–156 °C), but different ν(Mo=O) stretching frequencies (blue, 954 cm^{-1}; green, 943 cm^{-1}), and were originally proposed to be geometric isomers, namely, *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ and *trans-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$, differing only in whether the two chloride ligands were cis or trans. Single-crystal X-ray diffraction established a cis configuration of chloride

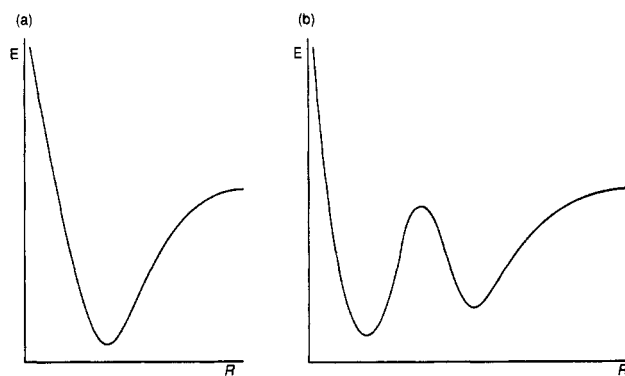Gerard Parkin received his B.A., M.A., and D. Phil degrees from the Queen's College, Oxford University. Both his undergraduate and graduate research was carried out under the guidance of Professor Malcolm L. H. Green. In 1985 he moved to the California Institute of Technology as a NATO postdoctoral fellow to work with Professor John E. Bercaw. He joined the faculty of Columbia University in 1988 and was promoted to Associate Professor in 1991. He is the recipient of an A. P. Sloan Research Fellowship (1991–1993), a Camille and Henry Dreyfus Teacher–Scholar Award (1991–1996), and a Presidential Faculty Fellowship Award (1992–1997). His principal research interests are in the areas of synthetic, structural, and mechanistic inorganic chemistry.

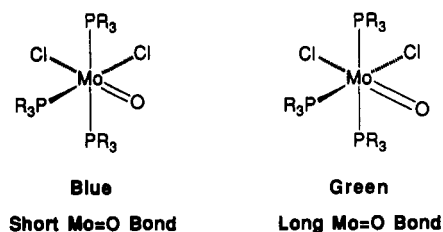**Figure 1.** Potential energy surfaces for a normal bond (a) and a pair of bond-stretch isomers (b).

Figure 2. Bond-stretch or distortional isomerism in *cis-mer*-MoOCl$_2$(PR$_3$)$_3$.

ligands for the blue isomer, i.e., *cis-mer*-MoOCl$_2$(PMe$_2$-Ph)$_3$, from which it was assumed that the green isomer possessed a trans configuration.[4,5] However, X-ray diffraction studies on the green analogue *mer*-MoOCl$_2$(PEt$_2$Ph)$_3$ in 1971 revealed that the chloride ligands were cis and not trans.[6] The coordination environments around the molybdenum centers of blue *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ and green *cis-mer*-MoOCl$_2$(PEt$_2$Ph)$_3$ were similar, with the most notable exception being that the Mo=O bond length in green *cis-mer*-MoOCl$_2$(PEt$_2$Ph)$_3$ [1.803 (11) Å] was *significantly* longer than that observed in blue *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ [1.676 (7) Å]. This result prompted Chatt to suggest that the green isomer of *mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ also possessed a coordination geometry identical to that of blue *cis-mer*-MoOCl$_2$(PMe$_2$-Ph)$_3$, but with the exception that the Mo=O bond lengths for the two isomers were different. Chatt termed the blue and green *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ complexes "distortional isomers" (Figure 2).[6a] The green isomer of *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ was structurally characterized at a later date and, consistent with the above proposal, was also found to possess a long Mo=O bond length of 1.80 (2) Å.[7] At this point it needs to be emphasized that terminal Mo=O bond

(1) (a) Yoon, K.; Parkin G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 1437–1438. (b) Yoon, K.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 2210–2218.

lengths for monooxo molybdenum complexes are normally in the range ca. 1.65–1.70 Å,[8] so that it is the long Mo=O bond lengths of the green isomers that are unprecedented.

Following Chatt's early work, Wieghardt was the next to report examples of distortional isomerism.[9] Of particular interest, the blue [d(W=O), 1.72 (2) Å] and green [d(W=O), 1.89 (2) Å] isomers of the cationic tungsten oxo derivative of the N,N',N''-trimethyl-1,4,7-triazacyclononane ligand [(Me₃tacn)W(O)Cl₂]⁺ were reported to be remarkably robust: in solution, the blue and green isomers were stable for several days and in the solid state did not interconvert at temperatures up to 177 °C![9a] A complete understanding of this unusual phenomenon was essential, and in 1988, Jean, Lledos, Burdett, and Hoffmann provided a theoretical analysis which rationalized the presence of a double minimum in the potential energy surfaces of the distortional isomers that were known at the time and thereby reclassified the complexes as bond-stretch isomers.[10]

By 1990 a number of examples of bond-stretch or distortional isomerism had been reported.[11-14] At that time, perhaps the most striking and best characterized examples were isomers of the niobium oxo and sulfido complexes Nb(O)Cl₃(PMe₃)₃ and Nb(S)Cl₃(PMe₃)₃, described by Gibson at the Boston ACS Meeting in April 1990.[12a] In particular, the orange-yellow [d(Nd=S), 2.196 (2) Å] and green [d(Nd=S), 2.296 (1) Å] isomers of Nb(S)Cl₃(PMe₃)₃[12] were cited as appearing to prove beyond a doubt that bond-stretch isomerism was a real phenomenon.[12b]

However, despite both the increasing number of examples of bond-stretch isomerism and the theoretical rationalization, it appeared that many chemists remained skeptical, even though alternative explanations were not forthcoming. In this regard, the subject bears considerable similarity to the recent issue of "molecular dihydrogen complexes" of transition metals. The notion

that complexes could be isolated in which dihydrogen was coordinated to a metal *without* fragmentation of the H–H bond was also alien to many chemists. Such a species had only previously been considered to represent a high-energy transition state or intermediate along the reaction profile for oxidative addition of dihydrogen. However, pioneering work by Kubas and others demonstrated molecular dihydrogen complexes to be a reality and thereby established a new paradigm.[15]

A Reinvestigation of the Molecular Structures of *cis-mer*-MoOCl₂(PR₃)₃

We were intrigued by the notion of bond-stretch isomerism. What factors influenced whether a complex would exhibit bond-stretch isomerism? What factors influenced which isomer would be the most stable? How did the reactivities of the two bond-stretch isomers differ? Moreover, was it indeed a real phenomenon? However, it was not clear how to answer these questions since, in 1990, it was still not apparent which systems would exhibit bond-stretch isomerism. Therefore, we turned our attention to a complex that was closely related to the original Chatt system, the trimethylphosphine analogue *cis-mer*-MoOCl₂(PMe₃)₃, a complex previously reported by Carmona and Wilkinson.[16]

Our initial interest in this complex derived from the observation that it did not appear to behave analogously to the dimethylphenylphosphine derivative reported by Chatt. Thus, whereas the green isomer (long Mo=O bond length) irreversibly converted to the blue isomer (short Mo=O bond length) for the original dimethylphenylphosphine *cis-mer*-MoOCl₂(PMe₂Ph)₃ system, the trimethylphosphine analogues appeared to exhibit the opposite behavior, and the green isomer seemed to be the more stable of the two forms.[16] If the color of the isomer was an indication of the Mo=O bond length (i.e., blue, short; green, long), then the above observation, which suggests a reversal of the thermodynamic stabilities of the long and short bond-stretch isomers, was very surprising. However, work by Cotton had demonstrated that the related green complex *cis-mer*-MoOCl₂(PMePh₂)₃ (for which the blue form was not known) possessed a short Mo=O bond length of 1.667 (4) Å, thereby providing a precedent that the green complex *cis-mer*-MoOCl₂(PMe₃)₃ *could* also exhibit a short Mo=O bond length.[17]

The question of whether green *cis-mer*-MoOCl₂(PMe₃)₃ would exhibit a short or a long Mo=O bond length had to be answered. Hence, we determined the molecular structure of *cis-mer*-MoOCl₂(PMe₃)₃ by X-ray diffraction methods. We were astonished to find that the asymmetric unit contained two crystallographically independent molecules of *cis-mer*-MoOCl₂(PMe₃)₃, which exhibited significantly different Mo=O bond lengths. One of the molecules possessed a Mo=O bond length of 1.698 (8) Å, whereas the other molecule possessed a substantially longer Mo=O bond length of 1.866 (7) Å. We were very excited about this

(2) (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.

(3) Isolation of stable isomers at room temperature would typically require a minimum activation barrier of ca. 30 kcal mol⁻¹.

(4) Butcher, A. V.; Chatt, J. *J. Chem. Soc. A* 1970, 2652–2656.

(5) (a) Manojlovic-Muir, L. *Chem. Commun.* 1971, 147. (b) Manojlovic-Muir, L. *J. Chem. Soc. A* 1971, 2796–2800.

(6) (a) Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. *Chem. Commun.* 1971, 655–656. (b) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* 1972, 686–690.

(7) Haymore, B. L.; Goddard, W. A., III; Allison, J. N. *Proc. Int. Conf. Coord. Chem., 23rd* 1984, 535.

(8) Mayer, J. M. *Inorg. Chem.* 1988, 27, 3899–3903.

(9) (a) Wieghardt, K.; Backes-Dahmann, G.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 777–778. (b) Wieghardt, K.; Backes-Dahmann, G.; Holzbach, W.; Swiridoff, W. J.; Weiss, J. *Z. Anorg. Allg. Chem.* 1983, 499, 44–58.

(10) (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.

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

(12) (a) Gibson, V. C.; Kee, T. P.; Shaw, A.; Williams, D. N. *Abstracts of Papers*, 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. In *Acta Crystallographica*, IUC 15th International Conference of Crystallography, Bordeaux, France, 1990, *A46* (Suppl), C-221–C-222. (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.

(13) Lu, J.; Clarke, M. J. 199th National Meeting, of the American Chemical Society, Boston, MA, April 22–27, 1990; American Chemical Society: Washington, DC, 1990; INOR 583.

(14) Nugent, W. M.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; pp 152–154.

(15) (a) Kubas, G. J. *Acc. Chem. Res.* 1988, *21*, 120–128. (b) Kubas, G. J. *Comments Inorg. Chem.* 1988, *7*, 17–40. (c) Crabtree, R. H. *Acc. Chem. Res.* 1990, 23, 95–101. (d) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* 1988, 28, 299–338.

(16) Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* 1984, *3*, 347–352.

(17) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* 1987, *26*, 2848–2852.

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result since it appeared that we had trapped *both* bond-stretch isomers of *cis-mer*-MoOCl₂(PMe₃)₃ in the same crystal, thereby offering a unique opportunity to study the phenomenon of bond-stretch isomerism. Specifically, we anticipated that the presence of two bond-stretch isomers with short and long Mo=O bond lengths would be manifested by the observation of two significantly different ν(Mo=O) absorptions in the solid-state IR spectrum. However, we could only observe a single absorption assignable to ν(Mo=O) at 950 cm⁻¹, which is clearly inconsistent with the presence of two molecules which differ substantially in their Mo=O bond lengths.[18]

At this point we had to question our X-ray diffraction data. Therefore, we performed an X-ray diffraction study on a second crystal of *cis-mer*-MoOCl₂(PMe₃)₃ obtained from a different batch. The results of the second structure determination were similar to the first, in that two different Mo=O bond lengths were observed. However, the Mo=O bond lengths obtained [1.772 (12) and 2.154 (8) Å] were substantially different from the first determination, leading now to the extremely surprising observation of four bond-stretch isomers of *cis-mer*-MoOCl₂(PMe₃)₃. One can only imagine how many more bond-stretch isomers we could observe by performing further X-ray structure determinations!

The discrepancy between the two structure determinations strongly suggested that these differences were not a manifestation of bond-stretch isomerism, in which a *quadruple* minimum on the potential energy surface corresponding to bond stretching would now be required. However, the important question remained: what was actually causing these changes in bond lengths?

The first insight into the solution was provided by difference electron density plots. These plots revealed that there was an excess of electron density close to the oxo positions of the molecules that possessed long Mo=O bonds. An excess of electron density at these oxo positions could only be accounted for by a disorder in which some of the oxo sites in the crystal were occupied by an atom with greater electron density than that of oxygen, which has eight electrons. The most likely candidate for this system was chlorine, which has 17 electrons. In addition to rationalizing the increased electron density at the oxo sites, the incorporation of chloride at the oxo site was attractive because it could also offer an explanation for the observed bond lengths. An artificial increase of the Mo=O bond length would be anticipated if the oxo site was disordered with chloride, which is 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), because the X-ray diffraction experiment gives the average structure of all molecules in the crystal. Partial occupancy by chlorine could be achieved by several possible mechanisms, as illustrated in Figure 3: (i) disorder between the oxo ligand and the *trans*-chloride ligand due to packing identical molecules in different orientations at the same crystallographic site; (ii) disorder due to cocrystallization with the isostructural geometric isomer *trans-mer*-MoOCl₂(PMe₃)₃; and (iii)
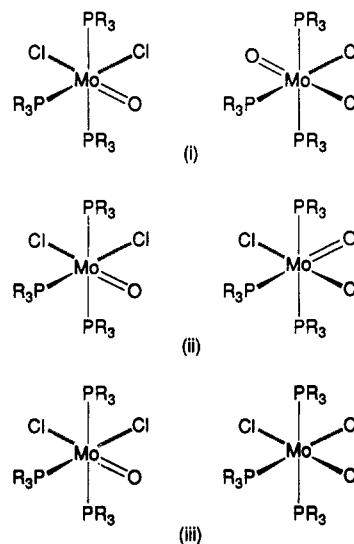

Figure 3. Possible disorder models to account for increased electron density at the oxo site of *cis-mer*-MoOCl₂(PR₃)₃.

disorder between the oxo ligand and a chloride ligand due to cocrystallization with the isostructural trichloride complex *mer*-MoCl₃(PMe₃)₃, a known compound.[16,19]

Evidence for the exact nature of the disorder was provided by ¹H NMR spectroscopy (Figure 4). The oxo complex *cis-mer*-MoOCl₂(PMe₃)₃ is diamagnetic and is observed as a triplet and doublet at δ 1.38 and 1.26. In contrast, the trichloride *mer*-MoCl₃(PMe₃)₃ is paramagnetic, so that its resonances escape the normal ¹H NMR range (δ 0–10 ppm). However, the presence of *mer*-MoCl₃(PMe₃)₃ is readily revealed by the observation of two broad resonances at δ −16 and −33 ppm (Figure 4). It was, therefore, evident that the bulk sample of *cis-mer*-MoOCl₂(PMe₃)₃ was contaminated with the trichloride impurity, *mer*-MoCl₃(PMe₃)₃. In view of the isostructural relationship between *cis-mer*-MoOCl₂(PMe₃)₃ and *mer*-MoCl₃(PMe₃)₃, cocrystallization resulting in compositional disorder seemed very likely. Thus, the observation of four apparently unique Mo=O bond lengths in *cis-mer*-MoOCl₂(PMe₃)₃, and yet only one ν(Mo=O) IR absorption, could be readily explained as a result of compositional disorder (to varying degrees) with isostructural *mer*-MoCl₃(PMe₃)₃.

In light of the above evidence for compositional disorder within crystals of *cis-mer*-MoOCl₂(PMe₃)₃ resulting in the observation of anomalous bond lengths, we were prompted to reinvestigate the original complexes for which distortional isomerism was first proposed, namely, blue and green *cis-mer*-MoOCl₂(PMe₂Ph)₃. Anticipating that the green isomer of *cis-mer*-MoOCl₂(PMe₂Ph)₃ was contaminated with the yellow paramagnetic trichloride *mer*-MoCl₃(PMe₂Ph)₃,[20] we examined the ¹H NMR spectrum, paying particular attention to the presence of broad paramagnetically shifted resonances. Such resonances were indeed observed and corresponded exactly to those of *mer*-MoCl₃(PMe₂Ph)₃. There was no doubt that the bulk sample of the *green* "isomer" of *cis-mer*-MoOCl₂(PMe₂Ph)₃ was in fact a mixture of *blue cis-mer*-MoOCl₂(PMe₂Ph)₃ and *yellow mer*-MoCl₃(PMe₂Ph)₃! UV–visible spectroscopy confirmed this proposal.

(18) (a) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* 1965, *4*, 867–873. (b) Hardcastle, F. D.; Wachs, I. E. *J. Raman Spectrosc.* 1990, *21*, 683–691.
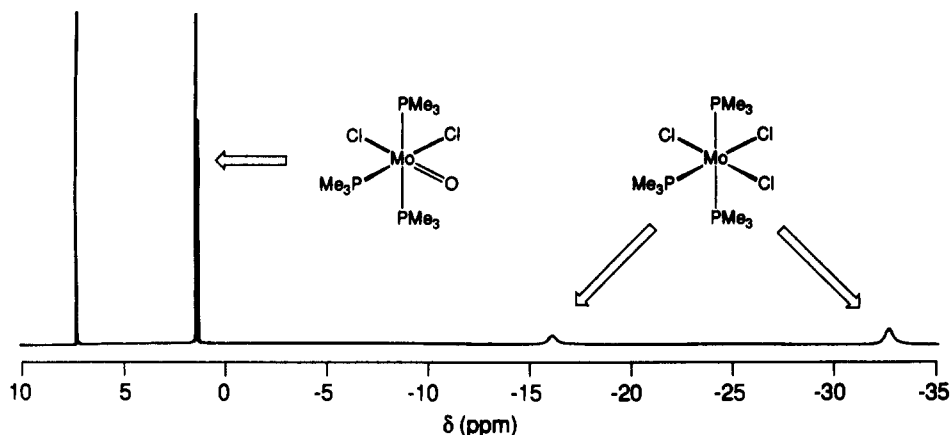
(19) Atwood, J. L.; Hunter, W. E.; Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1980, 467–470.

(20) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* 1975, 2639–2645.

Figure 4. ¹H NMR spectroscopic evidence for the contamination of bulk samples of *cis-mer*-MoOCl₂(PMe₃)₃ by the impurity *mer*-MoCl₃(PMe₃)₃.

The same conclusion has been obtained independently by Enemark and co-workers, who have used an extensive series of spectroscopic techniques to analyze the problem.[21] Moreover, Enemark reported that the observation of two different ν(Mo=O) stretching frequencies (blue, 954 cm⁻¹; green, 943 cm⁻¹) was not reproduced and that the correct ν(Mo=O) stretching frequency for blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ was 943 cm⁻¹,[21] identical to that of the green isomer. We also confirmed that this absorption in the blue complex is due to ν-(Mo=O) by the observation of the isotopic shift for the ¹⁸O-labeled derivative *cis-mer*-Mo(¹⁸O)Cl₂(PMe₂Ph)₃. It is possible that the small differences in IR stretching frequencies originally reported for green and blue *cis-mer*-MoOCl₂(PMe₂Ph)₃ may reflect solid-state packing effects, since pure *cis-mer*-MoOCl₂(PMe₂Ph)₃ is known to crystallize with more than one morphology.[1,5]

The evidence that the bulk sample of the green isomer of the oxo compound *cis-mer*-MoOCl₂(PMe₂Ph)₃ was contaminated with the trichloride *mer*-MoCl₃(PMe₂Ph)₃ was overwhelming. However, it remained to be proved that it was the presence of the trichloride impurity that was responsible for the observation of a long Mo=O bond length for the green isomer of this system. Hence, it was critical to demonstrate that the mixture was homogeneous in the solid state, so that single crystals composed of both *cis-mer*-MoOCl₂(PMe₂Ph)₃ and *mer*-MoCl₃(PMe₂Ph)₃ could be obtained. Therefore, we determined the X-ray structures of a number of crystals that differed in their extent of contamination by the trichloride complex *mer*-MoCl₃(PMe₂Ph)₃. The key results of the X-ray diffraction studies for the *mer*-MoOₓCl₃₋ₓ(PMe₂Ph)₃ series are summarized in Figure 5.

The correlation between the apparent Mo=O bond length and the degree of contamination by the trichloride *mer*-MoCl₃(PMe₂Ph)₃ impurity provided excellent evidence that this impurity was the origin of the observation of a long Mo=O bond length for the green isomer. Consistent with this suggestion that the green isomer is contaminated with the trichloride *mer*-MoCl₃(PMe₂Ph)₃, it is interesting to note that the elemental analyses reported by Chatt for the blue and green isomers were different, with the green isomer
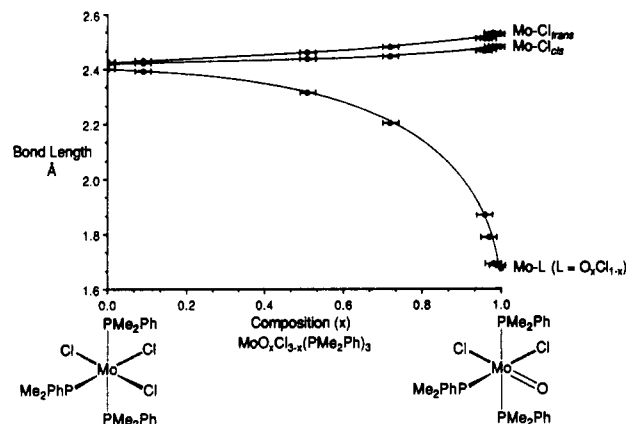

Figure 5. Apparent bond lengths as a function of composition.

having a higher chloride content.[22] As it had been shown that the long Mo=O bond length was an artifact due to crystallographic disorder, there now remained no evidence to support the existence of bond-stretch isomers for *cis-mer*-MoOCl₂(PMe₂Ph)₃, the first proposed example of the phenomenon.

At this point it is important for us to understand why the above disorder explanation for the observation of both short and long Mo=O bond lengths had not been previously considered, especially since disorder is often manifested by the observation of abnormal thermal parameters. The partial ORTEP drawings shown in Figure 6 shed some light on this issue, since it can be seen that surprisingly successful refinement could be obtained by refining the disordered site as only oxygen.[23] Although a hint of a disordered site may be gleaned by examination of the thermal ellipsoid of the oxygen atom for the structure with an Mo=O bond length of 1.871 (3) Å, it is not clear that this would be sufficient to signal an erroneous structure. Indeed, thermal parameters that are significantly worse than those in Figure 6 are frequently reported in the chemical literature without comment.

Similarly, electron-density plots for the series *mer*-MoOₓCl₃₋ₓ(PMe₂Ph)₃ shown in Figure 7 do not readily indicate the presence of disorder, in which only

(21) Desrochers, P. J.; Nebesny, K. W.; LaBarre, M. J.; Lincoln, S. E.; Loehr, T. M.; Enemark, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 9193–9200.

(22) MoOCl₂(PMe₂Ph)₃ requires: C (48.3), H (5.6), Cl (11.9). Observed for blue isomer: C (48.5), H (5.9), Cl (12.1). Observed for green isomer: C (48.0), H (5.5), Cl (12.7). See refs 4 and 21.

(23) However, for Mo=O bond lengths greater than 1.871 (3) Å, the oxygen atom refined nonpositive definite.
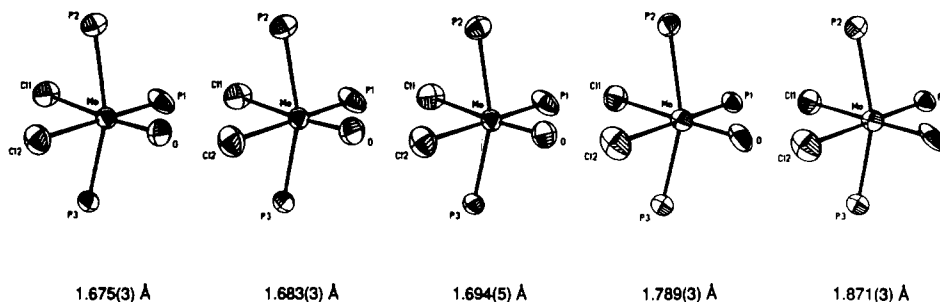
Figure 6. Variation of thermal parameters at the disordered site as a function of composition. Apparent Mo=O bond lengths are given below each structure.
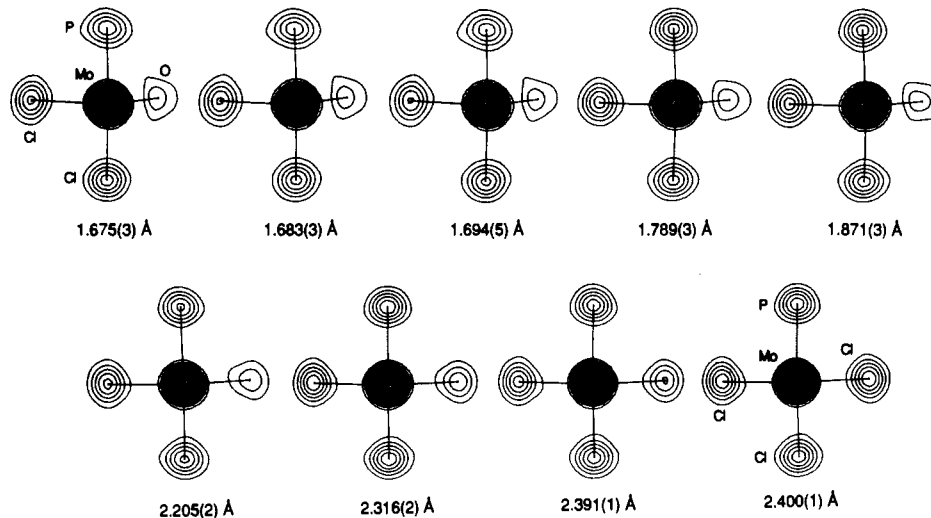
Figure 7. Variation of electron density at the disordered site as a function of composition. Apparent Mo=O bond lengths are given below each structure.

a single electron-density maximum is observed at the disordered site. Although the electron-density distribution associated with the Mo—O bond is observed to distort upon increasing the chloride occupancy, the expected increase in electron density at the disordered site is not readily apparent. Even at a distance of 2.205 (2) Å, the disordered site is still characterized by two contours of electron density, i.e., that of oxygen. Thus, the apparent Mo—O bond length itself is more sensitive to the presence of the chloride impurity than either the thermal parameters or the electron-density distribution at the disordered site. This marked sensitivity of the apparent bond length is undoubtedly due 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.

In addition to the sensitivity of the apparent Mo=O bond length to disorder, a second reason why disorder was not considered as a possibility in the early work is most probably due to the common belief that single crystals are invariably pure. Although it is indeed recognized that cocrystallization may occur,[24] it appears to be only invoked once it becomes crystallographically obvious that a site is disordered. The results described here demonstrate that the level of impurities in the earlier work was insufficient to signal an error in the

X-ray structure determination, but was more than sufficient to produce a significant change in the apparent Mo=O bond length.

Other Compositionally Disordered Structures

The interpretation of X-ray diffraction data providing examples of bond-stretch isomers for the complex *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ represents an extreme case of both the subtlety of the disorder problem and chemists' often unquestioned belief in X-ray structure determinations. It is very likely that there are many other reported structures, in which there are no obvious crystallographic anomalies, that exhibit incorrect bond lengths due to disorder. Occasionally, such problem structures may be signalled by the observation of inequivalent bond lengths for chemically inequivalent bonds. For example, the two significantly distinct Hf–CH$_3$ bond lengths [2.318 (8) and 2.382 (7) Å][25] in the otherwise symmetric molecule (η^5-C$_5$H$_5$)$_2$Hf(CH$_3$)$_2$ have been reinterpreted as arising from cocrystallization with the chloride derivative (η^5-C$_5$H$_5$)$_2$Hf(CH$_3$)Cl.[26] A related problem is also associated with the molecular structure of the tungsten(III) complex *mer*-WCl$_3$(PMe$_2$-Ph)$_3$, in which the two chemically equivalent W–Cl$_{trans}$ bonds were reported to exhibit significantly different

(24) Indeed, such a method of doping paramagnetic complexes into crystals of isostructural diamagnetic complexes is used extensively in single-crystal EPR studies. See, for example: (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.

(25) Fronczek, F. R.; Baker, E. C.; Sharp, P. R.; Raymond, K. N.; Alt, H. G.; Rausch, M. D. *Inorg. Chem.* **1976**, *15*, 2284–2289.

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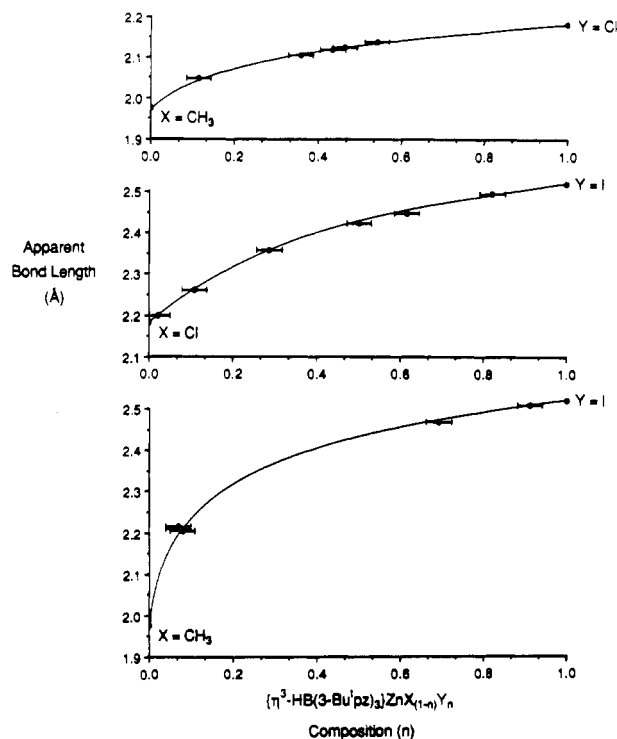
Figure 8. Variation in apparent bond lengths as a function of composition.

bond lengths of 2.437 (1) and 2.295 (2) Å.[27] We reinvestigated this structure and determined that the short 2.295 (2) Å W–Cl bond length is an artifact due to cocrystallization with the oxo impurity *cis-mer*-WOCl$_2$(PMe$_2$Ph)$_3$.[28] It is intriguing that, 20 years after an unsuspected chloride impurity resulted in an artificially long metal–oxo bond length, we now observe an oxo impurity resulting in an artificially short metal–chloride bond length!

In order to demonstrate further that cocrystallization may result in the determination of incorrect bond lengths, and also to quantify the effect, we investigated the *apparent* structural effects of doping a series of tris(3-*tert*-butylpyrazolyl)hydroboratozinc complexes, {η³-HB(3-Bu^{t}pz)$_3$}ZnX (3-Bu^{t}pz = 3-C$_3$N$_2$H$_2$Bu^t; X = Cl, Br, I, or CH$_3$), with molecules that have similar structures.[29] In each case, 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 (Figure 8). As expected, the relationship between the apparent bond length and composition is not linear, but is weighted by the relative scattering powers of the disordered groups. The most significant deviation from linearity occurs when there is considerable disparity between the scattering powers of the disordered groups, with the group with higher scattering power contributing the most to the apparent bond length. Hence, small quantities of iodide impurity have a dramatic effect on the apparent length of the Zn–CH$_3$ bond.

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Concluding Remarks

The research described in this Account has revealed that the long Mo≡O bond length for the green isomer of *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ is an artifact due to cocrystallization with the impurity *mer*-MoCl$_3$(PMe$_2$-Ph)$_3$. There is, therefore, no evidence for bond-stretch or distortional isomerism for the first system that was proposed to exhibit the phenomenon. Furthermore, recent ab initio calculations by Hall support this conclusion, in that the two stable bond-length minima obtained by extended Hückel calculations could not be reproduced at a higher level of calculation.[30] It is most likely that the present explanation was not considered in the early work due to the common belief that single crystals are invariably pure compounds, a situation that is compounded by the observation that disordered sites may also refine with apparent success.

Some comment is required for other examples of bond-stretch isomerism that have appeared in the literature since, by inference, all previous examples may be suspect. Indeed, Enemark and Wieghardt now believe that the blue and green isomers of [(Me$_3$tacn)W-(O)Cl$_2$]$^+$ are also a manifestation of contamination.[31] In this regard, it is interesting to note that, although the blue and green isomers were reported to be stable in solution for several days, addition of small amounts of water resulted in the immediate conversion of the green isomer to the blue isomer![9a] Gibson and Mc-Partlin also now recognize that the green isomer of the sulfido complex Nb(S)Cl$_3$(PMe$_3$)$_3$, which was specifically reported *not* to be disordered,[12c] is actually contaminated with the tetrachloride NbCl$_4$(PMe$_3$)$_3$.[32] However, contamination by only the tetrachloride NbCl$_4$(PMe$_3$)$_3$ cannot explain the two different ν-(Nb–S) IR stretching frequencies that are observed for the orange-yellow and green isomers in solution. The origin of the second ν(Nb≡S) IR stretching frequency remains to be determined.

Although it is now clear that the original illustration of bond-stretch isomerism is an artifact, the concept itself still exists. In view of the importance of the phenomenon and the subtlety of compositional disorder, the experimental verification of bond-stretch isomerism will require a demanding series of experiments. Central to such an endeavor will naturally be the accurate determination of bond lengths. It will, therefore, be critical to confirm the reproducibility of the X-ray diffraction analyses by repeating the structural determinations on many crystals from different batches. Once the accuracy of the X-ray diffraction results has been ascertained, it will then also be essential to verify that the single crystals studied are pure. This will be a particularly difficult task to undertake and will require the application of rigorous analytical techniques to probe for the presence of unknown impurities in each single crystal. However, until that time comes, the question will remain: Do bond-stretch isomers really exist?