False Minima and the Perils of a Polar Axis in X-ray Structure Solutions: Molecular Structures of $W(PMe_3)_4H_2X_2$ (X = F, Cl, Br) and $W(PMe_3)_4H_2F_2(H_2O)$

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Single-crystal X-ray diffraction is undoubtedly the most common and powerful method for the determination of molecular structures in the solid state.[1] However, it must be recognized that interpretation of the data is not always straightforward.[2] Problems in data interpretation are commonly attributed to a number of factors, including (i) incorrect space group assignment,[3] (ii) incorrect atom assignment,[4,5] (iii) disorder,[2d,6,7] and (iv) incorrect site symmetry.[8] In this paper, we describe how, in specific circumstances, models may refine into extremely deceptive false minima, characterized by well-behaved refinement and displacement parameters, but are grossly distorted from the true structures. The existence of such a phenomenon has serious implications with respect to the interpretation of certain molecular structures as determined by X-ray diffraction.

We have recently reported the structure of the eight-coordinate complex $W(PMe_3)_4H_2I_2$ as part of our investigations of the equilibrium deuterium isotope effect for the oxidative addition of H_2 to $W(PMe_3)_4I_2$.[9] Subsequently, we have determined the structures of the fluoro, chloro, and bromo derivatives $W(PMe_3)_4H_2X_2$ (X = F,[10] Cl,[11] Br[12]).[13] Unexpectedly, the structure determined for $W(PMe_3)_4H_2Cl_2$ proved to be unique compared to the other derivatives $W(PMe_3)_4H_2X_2$ (X = F, Br, I). Specifically, whereas $W(PMe_3)_4H_2X_2$ (X = F, Br, I) exhibit structures based on a trigonal dodecahedron,[14] with a distorted tetrahedral array of PMe_3 ligands (see Figure 1), all four PMe_3 ligands of $W(PMe_3)_4H_2Cl_2$ were found to be located in one hemisphere of the molecule. In view of the unprecedented nature of this ligand arrangement, due attention was naturally given to the correctness of the structure solution. However, the respectability of (i) the *R* values ($R = 0.0459$, $R_w = 0.0649$), (ii) the goodness-of-fit (GOF = 1.70), (iii) the displacement parameters, and (iv) the bond lengths about W provided no indication as to a potential error in the structure determination. Nevertheless, after much deliberation, it was determined that the structure had actually refined into an extremely deceptive false minimum. Upon recognizing the nature of the problem, it was possible to adjust the structure and so refine it in the true minimum, characterized by lower *R* values ($R = 0.0229$, $R_w = 0.0261$) and a better goodness-of-fit (GOF = 1.04). The result of this refinement is a structure analogous to those of the other halide derivatives $W(PMe_3)_4H_2X_2$ (X = F, Br, I), with a distorted tetrahedral array of PMe_3 ligands (Figure 2).[15]

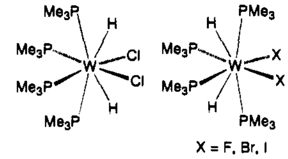

Figure 1. Structures of $W(PMe_3)_4H_2X_2$.

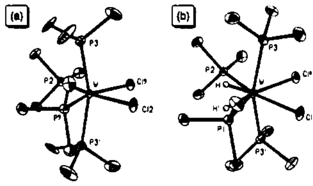

Figure 2. Structures of $W(PMe_3)_4H_2Cl_2$ corresponding to (a) the false minimum ($R = 0.0459$, $R_w = 0.0649$, GOF = 1.70) and (b) the true minimum ($R = 0.0229$, $R_w = 0.0261$, GOF = 1.04).

The occurrence of the false minimum is associated with the fact that $W(PMe_3)_4H_2Cl_2$ adopts a polar space group, namely $Cmc2_1$ (No. 36). For a space group with a polar axis, it is well known that two minima exist in a least-squares refinement procedure, corresponding to chemically identical structures which are related by reflection perpendicular to the polar axis.[16,17] Since the space group $Cmc2_1$ contains a polar *z* axis, two such minima also exist for $W(PMe_3)_4H_2Cl_2$. However, the structure corresponding to the false minimum (see Figure 2) is neither one of these minima. Rather, the incorrect structure of the false minimum corresponds to the very unusual situation in

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[1] (a) Bürgi, H.-B.; Dunitz, J. D. *Helv. Chim. Acta* **1993**, *76*, 1115−1166. (b) Hope, H. *Prog. Inorg. Chem.* **1994**, *41*, 1−19. (c) *Accurate Molecular Structures: Their Determination and Importance*; Domenicano, A., Hargittai, I., Eds.; IUCr Monographs on Crystallography; Oxford University Press: New York, 1992.

[2] (a) Ibers, J. A. In *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. (b) Donohue, J. In *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. (c) Jones, P. G. *Chem. Soc. Rev.* **1984**, *13*, 157−172. (d) Parkin, G. *Chem. Rev.* **1993**, *93*, 887−911. (e) Watkin, D. *Acta Crystallogr.* **1994**, *A50*, 411−437.

[3] For some leading references, see: (a) Marsh, R. E.; Bernal, I. *Acta. Crystallogr.* **1995**, *B51*, 300−307. (b) Marsh, R. E. *Acta. Crystallogr.* **1994**, *A50*, 450−455. (c) Marsh, R. E.; Herbstein, F. H. *Acta. Crystallogr.* **1988**, *B44*, 77−78. (d) Marsh, R. E.; Herbstein, F. H. *Acta. Crystallogr.* **1983**, *B39*, 280−287. (e) Marsh, R. E.; Schomaker, V. *Inorg. Chem.* **1979**, *18*, 2331−2336. (f) Baur, W. H.; Tillmanns, E. *Acta. Crystallogr.* **1986**, *B42*, 95−111.

[4] As a recent example, the structures of *both* (2,4,6-$Ph_3C_6H_2$)Cu and (2,4,6-$Ph_3C_6H_2$)Ag have been reinterpreted as that of partly, or entirely, (2,4,6-$Ph_3C_6H_2$)Br. See: Haaland, A.; Rypdal, K.; Verne, H. P.; Scherer, W.; Thiel, W. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2443−2445.

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[12] $W(PMe_3)_4H_2Br_2$ was prepared by metathesis of $W(PMe_3)_4H_2Cl_2$ with excess LiBr in benzene.

[13] $W(PMe_3)_4H_2F_2$ is monoclinic $P2_1/n$ (No. 14), $a = 9.952(2)$ Å, $b = 13.967(3)$ Å, $c = 16.561(2)$ Å, $\beta = 103.09(1)$°, $V = 2242(1)$ Å^3, $Z = 4$. $W(PMe_3)_4H_2F_2(H_2O)$ is orthorhombic $Cmc2_1$ (No. 36), $a = 14.246(3)$ Å, $b = 12.358(2)$ Å, $c = 12.917(2)$ Å, $V = 2274(1)$ Å^3, $Z = 4$. $W(PMe_3)_4H_2Cl_2$ is orthorhombic $Cmc2_1$ (No. 36), $a = 13.577(2)$ Å, $b = 13.395(2)$ Å, $c = 12.598(3)$ Å, $V = 2292(1)$ Å^3, $Z = 4$. $W(PMe_3)_4H_2Br_2$ is orthorhombic $Cmc2_1$ (No. 36), $a = 13.273(2)$ Å, $b = 13.656(2)$ Å, $c = 12.935(3)$ Å, $V = 2346(1)$ Å^3, $Z = 4$.

[14] Keppert, D. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 1, Chapter 2, pp 31−107.

[15] In the structure of $W(PMe_3)_4H_2Cl_2$ corresponding to the false minimum, the two transoid PMe_3 ligands are displaced substantially by *ca.* ~15° from their true positions.

[16] However, as a consequence of the polar dispersion error,[16a−f] the two structures will differ slightly in bond lengths, so it is essential to establish that the correct polarity has been determined.[g,h] (a) Cruickshank, D. W. J.; McDonald, W. S. *Acta. Crystallogr.* **1967**, *23*, 9−11. (b) Ueki, T.; Zalkin, A.; Templeton, D. H. *Acta. Crystallogr.* **1966**, *20*, 836−841. (c) Ibers, J. A.; Hamilton, W. C. *Acta. Crystallogr.* **1964**, *17*, 781−782. (d) Messmer, G. G.; Amma, E. L.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 725−730. (e) Cotton, F. A.; Foxman, B. M. *Inorg. Chem.* **1968**, *7*, 1784−1792. (f) *Anomalous Scattering*; Ramaseshan, S., Abrahams, S. C., Eds.; International Union of Crystallography, Munksgaard International Publishers: Copenhagen, 1975. (g) Flack, H. D. *Acta. Crystallogr.* **1983**, *A39*, 876−881. (h) Rogers, D. *Acta. Crystallogr.* **1981**, *A37*, 734−741.

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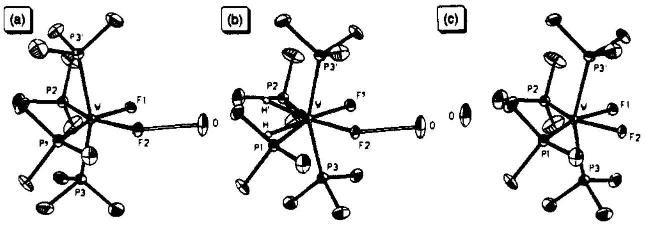

Figure 3. Structures of $W(PMe_3)_4H_2F_2(H_2O)$ corresponding to (a) the false minimum with transoid PMe_3 ligands displaced from their true positions (R = 0.0494, R_w = 0.0615, GOF = 1.57), (b) the true minimum (R = 0.0357, R_w = 0.0395, GOF = 1.01), and (c) the false minimum with H_2O displaced from its true position (R = 0.0382, R_w = 0.0429, GOF = 1.09).

which only the transoid PMe_3 ligands of the true structure are inverted along the z axis (with W located at $z = 0$).[18]

Having identified the relationship between the structures in the false and true minima, it is necessary to rationalize (i) why one of the PMe_3 ligands was initially located in the incorrect position and (ii) why the incorrect structure refined so successfully. Both of these phenomena are presumably consequences of the facts that (i) the X-ray scattering is dominated by the tungsten atom and (ii) the relationship between the tungsten atoms in this structure is appropriately described by the centrosymmetric space group *Cmcm*, even though the space group adopted by the molecule is *Cmc*2_1. In view of such pseudosymmetry, an electron density difference map based only on the position of the tungsten atom would be expected to exhibit mirror symmetry perpendicular to the polar z axis, as is indeed observed. Therefore, at this stage, the difference map represents a composite of both possible polar configurations. As more atoms are included in the model, the pseudosymmetry is removed, and the electron density difference map would consequently be expected to depart from mirror symmetry. *However, at all stages of the refinement procedure, effective mirror symmetry is observed in the electron density difference maps* (see supporting information). As a result, even in the final stages of refinement, it is possible to select the incorrect locations for a set of atoms, especially if such positions are not chemically unreasonable.[19] Perhaps even more surprising is the fact that the subsequent model refines so well (again, presumably since the scattering is dominated by the tungsten atom),[20] with the least-squares refinement calculations showing no tendency to converge to the true minimum.[21]

It is important to emphasize the latter point, *i.e.*, that the incorrect structure has all the appearances of a perfectly good solution in terms of both its refinement and displacement parameters.[22] Hence, it is plausible that other structures may also suffer from related problems of refinement into unrecognized false minima. One such example that we have discovered is that of the aqua derivative, $W(PMe_3)_4H_2F_2(H_2O)$,[23,24] a compound in which the PMe_3 ligands were also originally described as occupying positions in one hemisphere, rather than a distorted tetrahedral array about the metal center. We have re-collected data on $W(PMe_3)_4H_2F_2(H_2O)$ and have confirmed that it does indeed refine well (R = 0.0494, R_w = 0.0615, GOF = 1.57) with such a structure (Figure 3a). However, adjusting the positions of the transoid PMe_3 ligands by inversion of the z coordinates (with W at $z = 0$) allows refinement to the true structure illustrated in Figure 3b (in which the PMe_3 ligands are displaced by ~21° from their incorrect positions), with improved refinement parameters (R = 0.0357, R_w = 0.0395, GOF = 1.01). Moreover, it is also possible to refine the water molecule, which in the true structure is hydrogen-bonded to the fluoride ligands, in a position on the other side of the molecule, where it is devoid of such interactions (Figure 3c).[25] Importantly, although the change in R values (R = 0.0382, R_w = 0.0429, GOF = 1.09) from the true structure is minimal, the impact of such a structural change is quite significant, especially if one is interested in the phenomenon of hydrogen-bonding.

In summary, we have demonstrated that molecules which crystallize in polar space groups may suffer from structure solutions that refine into deceptive false minima. Although the existence of false minima is not without precedence,[18,26] the examples described here are remarkable in the sense that the false structures are dramatically different from their true structures but are nevertheless characterized by low R values and well-behaved displacement parameters. It is likely that this effect will be most pronounced when the X-ray scattering is dominated by a single atom. Thus, in addition to the well-known requirement of ensuring that the correct sense of a polar axis has been selected,[16] it is critical to establish that all of the atoms in the asymmetric unit of a polar space group belong to a single true polar configuration and that the correct molecular geometry is established.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-93ER14339) for support of this research, Dr. R. L. Harlow for communicating the information of refs 21 and 22, and the reviewers for helpful comments. G.P. is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Award (1991–1996) and a Presidential Faculty Fellowship Award (1992–1997).

Supporting Information Available: Tables of crystal structure data and electron density different maps for $W(PMe_3)_4H_2X_2$ (X = F, Cl, Br) and $W(PMe_3)_4H_2F_2(H_2O)$ (68 pages); observed and calculated structure factors (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[18] A false minimum of the type described here has been observed for $[(Ph_2MeP)_3Ir(Cl)(N_2Ph)][PF_6]$, although the incorrect structure, when compared to that for $W(PMe_3)_4H_2Cl_2$ or $W(PMe_3)_4H_2F_2(H_2O)$, was perturbed to a much less dramatic degree as far as the geometry about the metal center is concerned. Specifically, the false minimum of $[(Ph_2MeP)_3Ir(Cl)(N_2Ph)][PF_6]$ was associated with misplaced phenyl substituents of two of the Ph_2MeP ligands which consequently exhibited unreasonable geometries, such as a P–C–C angle of 136.5° rather than ~120°. Indeed, it was these unreasonable geometries that signaled the occurrence of the false minimum. Furthermore, for this example, least-squares refinement was able to shift an incorrectly placed phenyldiazo (PhN_2) group across the pseudomirror plane to its true position. See: Cowie, M.; Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7608–7617.

[19] Such a phenomenon is related to the concept of homometric structures, *i.e.*, different structures with the same Patterson map. See: *Patterson and Pattersons*; Glusker J. P., Patterson, B. K., Rossi, M., Eds.; Oxford University Press: New York, 1987.

[20] In this regard, it is worth noting that problems associated with a false minimum in the structure solution of $W(PMe_3)_4H_2Br_2$ were not as pronounced, presumably due to the fact that bromine provides a greater contribution than chlorine to the total X-ray scattering. False minima would not be observed for $W(PMe_3)_4H_2F_2$, since this complex did not adopt a polar space group.

[21] A series of structure factor calculations correlating R with the position of the transoid PMe_3 groups supports the notion that the least-squares refinement procedure would be incapable of converging from the false minimum to the true minimum for these complexes. Harlow, R., personal communication.

[22] It has, however, been pointed out that the existence of short calculated nonbonded H···H distances may be used to identify a false structure. Harlow, R., personal communication.

[23] Minqin, C.; Prout, K. *J. Struct. Chem.* **1986**, *5*, 23–27.

[24] The X-ray structure of $W(PMe_3)_4H_2F_2(H_2O)$ was originally formulated as $[W(PMe_3)_4H_2F(H_2O)][F]$ (ref 10 and 23). However, in view of the difficulty of distinguishing between O and F by X-ray diffraction, such an assignment cannot be considered definitive. Nevertheless, in view of (*i*) the observed W–F bond lengths and (*ii*) the effect on the observed displacement parameters of sequentially refining each of the possible atom sites as oxygen, we feel that a better representation is $W(PMe_3)_4H_2F_2(H_2O)$; however, X-ray diffraction cannot eliminate the possibility that the structure is in fact $W(PMe_3)_4H_2F_2(HF)$. Nevertheless, regardless of such problems in atom assignment, false minima are still observed.

[25] The closest interaction of the oxygen atom in the incorrect location is with a hydrogen atom of a PMe_3 ligand (~2.83 Å).

[26] For example, false minima have been observed in the structure refinements of $Cr_2(OAc)_4(H_2O)_2$,[26a] adamantane,[26b] and 4-(1-pyrrolidino)-pyridinium propynoate.[26c] (a) Cotton, F. A.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 688–692. (b) Donohue, J.; Goodman, S. H. *Acta Crystallogr.* **1967**, *22*, 352–354. (c) Wheeler, K. A.; Foxman, B. M. *Mol. Cryst. Liq. Crystallogr.* **1992**, *211*, 347–360.