Incorrect atom connectivity in X-ray structure solutions associated with a "partial polar ambiguity": a non-macrocyclic structure for the macrocyclic lead complex, [η^4-Me_8taa]Pb

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The divalent lead complex [η^4-Me_8taa]Pb has been synthesized by metathesis of PbI_2 with Li_2[Me_8taa] in THF (Me_8taaH_2 = octamethyldibenzotetraaza[14]annulene). [η^4-Me_8taa]Pb exists as (at least) three structural modifications, namely the triclinic chloroform solvate [η^4-Me_8taa]Pb · $CHCl_3$, and the primitive and *C*-centered orthorhombic polymorphs of the dichloromethane solvate [η^4-Me_8taa]Pb · CH_2Cl_2. The structures of each of these modifications have been determined by single crystal X-ray diffraction. Of most significance, the *C*-centered orthorhombic polymorph [η^4-Me_8taa]Pb · CH_2Cl_2 is subject to the existence of a false minimum in the structure solution refinement procedure, the result of which is the generation of a non-macrocyclic structure for a compound that is actually macrocyclic. Significantly, even though it does not exhibit the true connectivity of the molecule, the errant structure is characterized by a low *R* value and well-behaved displacement parameters. The manifestation of the false minimum is a consequence of the crystal belonging to a polar space group, which results in a "partial polar ambiguity." As such, the result serves to emphasize that care must be taken to ensure that, for polar space groups, all atoms of the derived structure belong to a single true polar configuration, rather than a hybrid of the two possible true polar configurations.

Single crystal X-ray diffraction is widely recognized as the most essential technique for structure determination in the solid state.[1] Furthermore, with the advent of charge-coupled device (CCD) detectors, which allow for more rapid data collection, as well as the collection of data on weakly diffracting crystals,[2] the technique is becoming increasingly more important and popular. The increased availability of diffraction data, however, must be balanced carefully with the accuracy of the derived results, since it is almost inevitable that the number of erroneous structures will increase with the number of data sets collected. For this reason, it is becoming critical that the factors that influence X-ray structure solutions are more widely recognized by the general user, rather than just by the experienced crystallographer.[3] In this regard, factors such as (*i*) incorrect space group assignment,[4–6] (*ii*) incorrect atom assignment,[7,8] (*iii*) disorder[3d,9,10] and (*iv*) incorrect site symmetry,[11] are well-established sources of problems in solving X-ray structures.[12] Not so widely recognized, however, is the ability of an X-ray structure solution to refine into a false minimum.[13] For example, solutions for molecules in polar space groups[14] may refine into false minima such that entire groups of atoms are incorrectly located in positions that are related to their true locations by a reflection perpendicular to the polar axis.[15] An early demonstration of such an effect was provided by Ibers and co-workers for the complex [(Ph_2MeP)$_3$Ir(Cl)(N_2Ph)][PF_6];[16] however, for this particular example, the structure corresponding to the false minimum was readily recognized as incorrect by the observation of unreasonable geometries within the Ph_2MeP ligands (for example, a P—C—C angle of 136.5° rather than *ca.* 120°). More recently, we have described a rather dramatic example of a false minimum associated with the structure of $W(PMe_3)_4H_2Cl_2$.[17] Explicitly, whereas the true structure of $W(PMe_3)_4H_2Cl_2$ is based on a trigonal dodecahedron,[18] with a distorted tetrahedral array of PMe_3 ligands, the structure associated with the false minimum has all four PMe_3 ligands located in one hemisphere of the molecule (Fig. 1).[17] Despite the significant difference in structures, the *R* value and displacement parameters for the structure associated with the false minimum provided no indication of a potential error in the structure determination, clearly emphasizing the deceptive nature of the false minimum. In this paper, we reveal an interesting and more extreme example of this effect, one in which the structure corresponding to the false minimum has a significantly different atom connectivity from that of the true structure. Specifically, we report the occurrence of a false minimum that corresponds to a *non*-macrocyclic structure for the macrocyclic lead complex [η^4-Me_8taa]Pb (Me_8taaH_2 = octamethyldibenzotetraaza[14]annulene).

Results and Discussion

Synthesis and structure of [η^4-Me_8taa]Pb

The four-coordinate divalent lead complex [η^4-Me_8taa]Pb has been prepared by metathesis of PbI_2 with Li_2[Me_8taa] in THF (Scheme 1), a synthesis analogous to that used for the germanium and tin analogues [η^4-Me_8taa]Ge[19] and [η^4-Me_8taa]Sn.[20] The less substituted tetramethyldibenzotetraaza[14]annulene derivatives [η^4-Me_4taa]Ge,[21] [η^4-Me_4taa]Sn[21] and [η^4-Me_4taa]Pb[22] have also been reported by Cowley and co-workers. X-ray diffraction studies revealed that [η^4-Me_8taa]Pb crystallizes as at least three different structural modifications:[23] thus, solutions in $CHCl_3$ were observed to crystallize as the triclinic solvate [η^4-Me_8taa]Pb · $CHCl_3$, while solutions in CH_2Cl_2 crystallize as both *C*-centered and primitive polymorphs of the ortho-

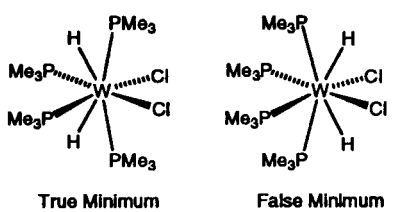
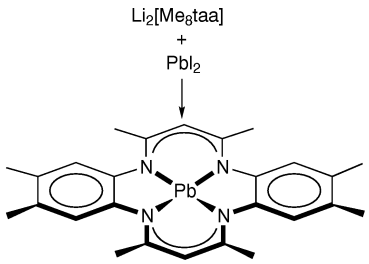


Fig. 1 Structures corresponding to the true and false minima in the refinement of $W(PMe_3)_4H_2Cl_2$

Table 1 Crystal and intensity collection data for the three structural modifications of [η⁴-Me_8taa]Pb

	[η⁴-Me_8taa]Pb · $CHCl_3$	[η⁴-Me_8taa]Pb · CH_2Cl_2	[η⁴-Me_8taa]Pb · CH_2Cl_2
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Formula	$C_{27}H_{31}Cl_3N_4Pb$	$C_{27}H_{32}Cl_2N_4Pb$	$C_{27}H_{32}Cl_2N_4Pb$
M	725.10	690.66	690.66
Space group	$P\bar{1}$ (No. 2)	*Pnma* (No. 62)	$Cmc2_1$ (No. 36)
a/Å	11.514(3)	7.656(1)	23.142(3)
b/Å	12.383(3)	23.121(3)	15.534(3)
c/Å	12.544(3)	30.948(5)	7.666(1)
α/°	64.14(2)	90	90
β/°	68.81(2)	90	90
γ/°	66.88(2)	90	90
U/Å³	1440.5(6)	5478(2)	2755.9(7)
Z	2	8	4
Radiation (λ/Å)	0.710 73	0.710 73	0.710 73
ρ (calcd)/g cm^{-3}	1.672	1.675	1.665
μ(Mo-Kα)/mm^{-1}	6.156	6.377	6.338
2θ range/°	3–50	3–45	3–50
No. of data	5056	3662	2461
No. of restraints	0	0	1
No. of parameters	317	320	162
R_1 [$I > 2\sigma(I)$][a]	0.0543	0.0560	0.0461 [0.0499][c]
wR_2 [$I > 2\sigma(I)$][b]	0.1327	0.0936	0.0954 [0.1164][c]
GOF	1.055	1.025	1.020 [1.144][c]
Flack parameter (*x*)			0.21(2) [0.55(3)][c]

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)]^2 / \sum[w(F_o^2)^2]\}^{1/2}$. [c] Values in brackets are for the structure of the false minimum.



Scheme 1

rhombic solvate [η⁴-Me_8taa]Pb · CH_2Cl_2 (Table 1). The molecular structure of each of these structural modifications has been determined by X-ray diffraction, as illustrated in Fig. 2–4; selected bond lengths and angles for each of the structures are listed in Tables 2–4. The coordination geometries about lead in each of the structures are summarized in Table 5, and indicate that there is little variation between the different modifications. For comparison, the data for the tin and germanium analogues, [η⁴-Me_8taa]Sn and [η⁴-Me_8taa]Ge, are also included in Table 3 and, as expected, the progression in M—N bond lengths corresponds closely to the variation in covalent radii of Ge (1.22 Å), Sn (1.40 Å) and Pb (1.54).[24]

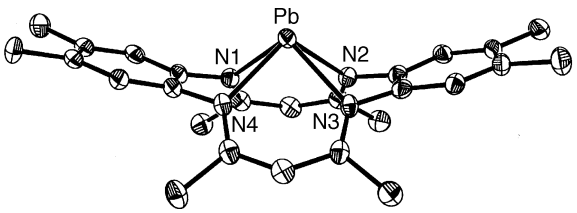


Fig. 2 Molecular structure of triclinic [η⁴-Me_8taa]Pb · $CHCl_3$ (solvent omitted for clarity)

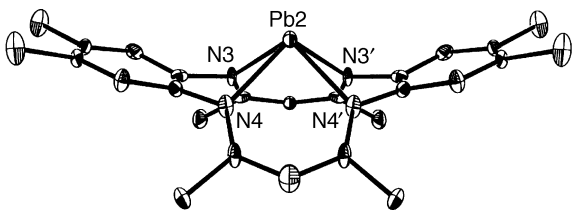


Fig. 3 Molecular structure of one of the molecules of orthorhombic-*P* [η⁴-Me_8taa]Pb · CH_2Cl_2 (solvent omitted for clarity)

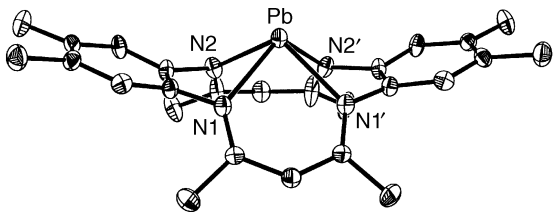


Fig. 4 Molecular structure of orthorhombic-*C* [η⁴-Me_8taa]Pb · CH_2Cl_2 (solvent omitted for clarity)

Table 2 Selected bond lengths (Å) and angles (°) for [η⁴-Me_8taa]Pb · $CHCl_3$ in $P\bar{1}$

Pb—N1	2.390(8)
Pb—N2	2.372(8)
Pb—N3	2.380(8)
Pb—N4	2.352(8)
N1—Pb—N2	78.1(3)
N3—Pb—N4	78.0(3)
N1—Pb—N4	68.0(3)
N2—Pb—N3	68.2(3)
N1—Pb—N3	114.4(3)
N2—Pb—N4	115.2(3)

Table 3 Selected bond lengths (Å) and angles (°) for [η⁴-Me_8taa]Pb · CH_2Cl_2 in $Cmc2_1$

Pb—N1	2.360(9)
Pb—N2	2.391(9)
N1—Pb—N1′	79.2(4)
N2—Pb—N2′	76.5(4)
N1—Pb—N2	70.1(5)
N1—Pb—N2′	116.6(5)

Table 4 Selected bond lengths (Å) and angles (°) for [η⁴-Me_8taa]Pb · CH_2Cl_2 in *Pnma*

Pb1—N1	2.381(13)
Pb1—N2	2.40(2)
Pb2—N3	2.35(2)
Pb2—N4	2.374(13)
N1—Pb1—N1′	77.2(6)
N2—Pb1—N2′	78.5(11)
N1—Pb1—N2	69.2(5)
N1—Pb1—N2′	115.8(5)
N3—Pb2—N3′	78.4(9)
N4—Pb2—N4′	78.6(6)
N3—Pb2—N4	68.6(5)
N3—Pb2—N4′	115.9(6)

A non-macrocyclic structure for [η⁴-Me_8taa]Pb due to a false minimum in the structure solution refinement procedure

Albeit interesting, the most important aspect of the present work is not concerned with the existence of three different crystalline modifications of [η⁴-Me_8taa]Pb, but rather focuses on the orthorhombic *C*-centered polymorph [η⁴-Me_8taa]Pb · CH_2Cl_2. In particular, the initial solution obtained for the *C*-centered polymorph [η⁴-Me_8taa]Pb · CH_2Cl_2, which was actually the first modification to be studied, corresponded to a structure in which the macrocyclic [η⁴-Me_8taa] ligand had apparently been cleaved, as illustrated in Fig. 5. Since such a structure clearly did not correspond to that expected for [η⁴-Me_8taa]Pb on the basis of its spectroscopic data, the possibility existed that the crystal studied was not representative of the bulk sample.[25] However, in view of the difficulty of X-ray diffraction distinguishing between closely related pairs of atoms (*e.g.* O and N) and locating hydrogen atoms in the presence of a heavy atom such as lead, the precise chemical nature of the single crystal studied could not be definitively ascertained on the basis of the X-ray diffraction data alone. For example, rather than the structure shown in Fig. 5, the possibility also existed that the crystal studied was a hydrolysis product, such as an acetylacetonate derivative, in which case N1 and N1′ should be regarded as oxygen.[26] Regardless of the exact nature of the crystal studied, in view of the low *R* value (0.0499) and well-behaved displacement parameters, a reasonable interpretation of the diffraction data would have been the conclusion that the crystal studied was *not* that of [η⁴-Me_8taa]Pb. Such a conclusion, however, would have been erroneous since the structure shown in Fig. 5 actually corresponds to a *false minimum* in the refinement procedure; the true *macrocyclic* structure is that discussed above and is shown in Fig. 4. Remarkably, the *R* value for the true structure (0.0461) is *not* substantially lower than that corresponding to the false minimum (Table 1).

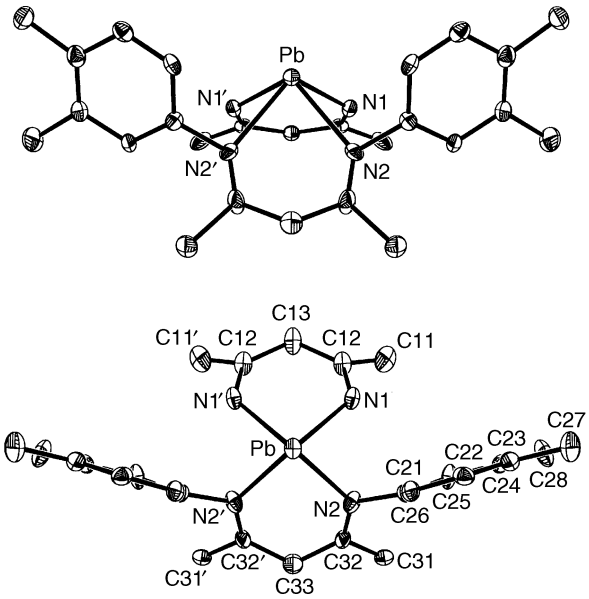


Fig. 5 Molecular structure corresponding to the false minimum of orthorhombic-*C* [η⁴-Me_8taa]Pb · CH_2Cl_2 (solvent omitted for clarity)

The initial consideration that the non-macrocyclic structure shown in Fig. 5 did not correspond to the true structure was based on the recognition that *C*-centered [η⁴-Me_8taa]Pb · CH_2Cl_2 belongs to a polar space group ($Cmc2_1$) and that, as described in the introduction, structure solutions for crystals with polar space groups may refine into false minima.[16,17] Specifically, for a molecule containing a single heavy atom, solutions corresponding to false minima of this type are associated with selected groups of atoms being incorrectly placed in positions that are related to their true locations by a reflection perpendicular to the polar axis (with the heavy atom situated at the origin of the polar axis).[27] Such an effect, which involves only a selection of atoms being misplaced, has been termed a "partial polar ambiguity"[17b] in order to distinguish it from the well-known "polar dispersion error",[28] an effect which is concerned with problems arising when *all* atoms are incorrectly located from their true positions by a reflection perpendicular to the polar axis.

The root of this problem is associated with the well-known ability of a single heavy atom to impose effective mirror symmetry perpendicular to the polar axis in the early stages of refinement. In essence, the observed electron density difference maps correspond to a superposition of the two possible true polar configurations,[29] which arises due to the fact that the heavy atoms are arranged in a centrosymmetric manner with respect to each other, even though the molecules themselves are not. Indeed, the illusion of centrosymmetry in such electron density difference maps can be so convincing that truly

Table 5 Comparison of the structures of [η⁴-Me_8taa]M (M = Ge, Sn, Pb)

	Space group	d(M—N_{av})/Å[a]	Θ_{1av}/°[b]	Θ_{2av}/°[b]	Θ_{3av}/°[b]	d(M···N_4)/Å[c]
[η⁴-Me_8taa]Pb · $CHCl_3$	$P\bar{1}$	2.37[2]	68.1[1]	78.1[1]	114.8[4]	1.28
[η⁴-Me_8taa]Pb · CH_2Cl_2	$Cmc2_1$	2.38[2]	70.1(5)	77.9[14]	116.6(5)	1.25
[η⁴-Me_8taa]Pb · CH_2Cl_2	*Pnma*	2.39[1]	69.2(5)	77.9[7]	115.8(5)	1.27
		2.36[1][d]	68.6(5)[d]	78.5[1][d]	115.9(6)[d]	1.25[d]
[η⁴-Me_8taa]Sn[e]	$P2_1/n$	2.26[2]	71.2[3]	80.4[8]	120.8[1]	1.12
[η⁴-Me_8taa]Ge[f]	$P2_1/c$	2.10[2]	75.1[5]	83.4[1]	128.9[6]	0.91

[a] d(M—N_{av}) is the average M—N bond length. Numbers in brackets indicate the range of values. [b] Θ_{1av}, Θ_{2av} and Θ_{3av} are the average values for the three sets of N—M—N bond angles. Numbers in brackets indicate the range of values; numbers in parentheses are the esd of a single value. [c] d(M···N_4) is the displacement of M from the macrocyclic N_4 plane. [d] Values for two independent 1/2 molecules in the asymmetric unit. [e] Ref. 20. [f] M. C. Kuchta and G. Parkin, unpublished results.

non-centrosymmetric structures have been incorrectly assumed to be centrosymmetric (for further discussion, see below).

Having recognized the nature of the problem because of our previous encounter with a false minimum for $W(PMe_3)_4H_2Cl_2$,[17] it was possible to determine the manner in which the aromatic substituents had been misplaced, adjust their positions accordingly, and so obtain the true structure depicted in Fig. 4. The relationship between the true and false structures is visually illustrated by Fig. 6, in which the misplaced aromatic groups (C21*–C28* and their symmetry equivalents) are superimposed upon the true structure. Examination of Fig. 6 indicates that the true (C21–C28) and false (C21*–C28*) locations are related by a non-crystallographic mirror plane that is perpendicular to the crystallographic *c* axis and is approximately coincident with the atoms Pb—N2—C31—C32—C33. The relationship between the true and false locations is further demonstrated by a comparison of their atomic coordinates, as summarized in Table 6. Thus, whereas the respective *x* and *y* coordinates of C2*X* and C2*X** are comparable, the *z* coordinates are related by reflection through the origin, *i.e.*, $z(C2X) = -z(C2X^*)$.[30] Since the false structure is a hybrid of two polar configurations, it may be expected that the Flack *x* parameter,[28i,31] which ranges from 0 for the correct absolute structure to 1 for the incorrect absolute structure, would be capable of indicating such a situation. However, since it is known that intermediate values of *x* may indicate a racemic twin,[31] it is not obvious that a value of *ca.* 0.5 would automatically provide an immediate indication that the derived connectivity was incorrect.

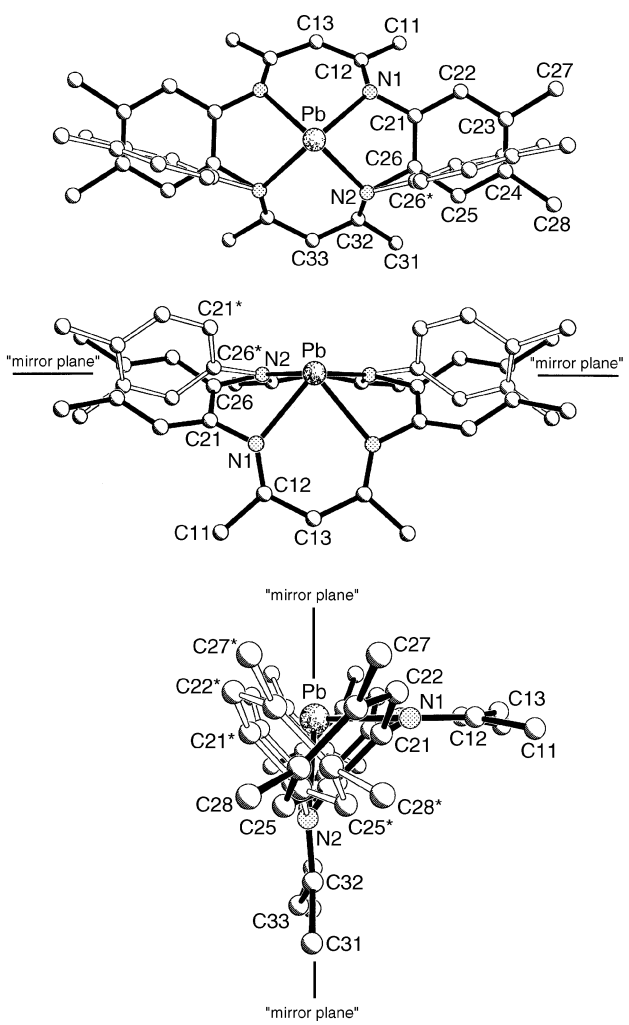


Fig. 6 Superposition of the true (bold bonds) and false (open bonds) structures for orthorhombic-*C* $[\eta^4\text{-}Me_8taa]Pb \cdot CH_2Cl_2$. The *middle* and *bottom* structures illustrate the "mirror plane" relationship between the correct (C21—C26) and incorrect (C21*—C28*) location of the aromatic groups

Table 6 Relationship between the atomic coordinates for the true [C(21)–C(28)] and misplaced [C(21*)–C(28*)] aromatic groups in orthorhombic *C*-centered $[\eta^4\text{-}Me_8taa]Pb \cdot CH_2Cl_2$

Atom	*x*	*y*	*z*
C21	1180(4)	6304(7)	1580(15)
C21*	1190(5)	6291(9)	−1544(19)
C22	1692(5)	5833(8)	1858(16)
C22*	1687(6)	5831(9)	−1847(20)
C23	2195(5)	6003(8)	885(19)
C23*	2197(6)	5995(10)	−878(23)
C24	2202(4)	6641(9)	−355(24)
C24*	2203(5)	6629(11)	353(24)
C25	1690(4)	7092(8)	−716(16)
C25*	1690(5)	7082(9)	702(19)
C26	1188(4)	6945(7)	308(31)
C26*	1190(5)	6939(8)	−339(19)
C27	2728(5)	5479(10)	1314(21)
C27*	2730(6)	5477(12)	−1353(24)
C28	2741(5)	6897(10)	−1381(22)
C28*	2740(6)	6888(12)	1387(31)

In addition to recognizing the relationship between the true and false locations of the aromatic groups, it is important to emphasize that the illusion created by the transformation $z(C2X) \rightarrow -z(C2X)$, in which a single C—N bond has apparently been cleaved, thereby allowing the aromatic substituents apparently to rotate *ca.* 90° from their true positions, is a direct consequence of the orientation of the molecule with respect to the polar axis. Specifically, since the *z* coordinate of N2 is close to zero (or, more generally, close to that of the heavy atom), N2 remains connected to C26* in the false structure. In contrast, since the *z* coordinate of N1 is far from zero, it is not possible for it to remain bonded to C21* in the false structure, thereby giving the illusion that the macrocycle has fragmented.

Interestingly, despite the dramatic difference between the true and false structures, the *R* value for the false structure is low and is certainly in the range deemed "acceptable" for publication. In this regard, it must be emphasized that, counter to the notion that may be held by some chemists, *R* values for lead and "heavy atom" structures are not always low. For example, of all lead structures listed in the Cambridge Structural Database,[32] 44% have *R* values greater than 0.05 and 5% have *R* values greater than 0.1.[33] In fact, lead structures with *R* values greater than 0.15 have also been published.[34]

The atom displacement parameters (see Fig. 5) also do not provide any obvious indication that the aromatic groups have been entirely misplaced. A quantitative analysis of the displacement parameters using PLATON,[35,36] nevertheless indicates that three atoms are characterized by unusual parameters, with U_3/U_1 greater than 5.0.[37,38] However, since two atoms for the true structure are also characterized by unusual displacement parameters,[39] this illustrates that such a criterion can not be regarded as an indication that the derived connectivity of the false minimum is incorrect.

It is, therefore, important to consider what other factors could be used to indicate that (in the absence of knowing the "true" structure) the connectivity corresponding to the false minimum is incorrect. For this reason, the bond lengths and angles for the lead molecules of the true and false structures are compared in Table 7. Inspection of Table 7 indicates that there is a very good correspondence in pairs of related bond lengths for the two structures; the only significant exception,

Table 7 Comparison of bond lengths (in Å) and angles (in °) for structures of the true and false minima of [η^4-Me_8taa]Pb

	True Minimum	False Minimum
Pb—N1	2.360(9)	2.347(12)
Pb—N2	2.391(9)	2.389(9)
C11—C12	1.52(2)	1.26(2)
C12—C13	1.43(3)	1.49(5)
C12—N1	1.293(14)	1.29(2)
C31—C32	1.509(14)	1.52(2)
C32—C33	1.455(12)	1.45(2)
C32—N2	1.25(2)	1.27(2)
C21—C22	1.41(2)	1.37(2)
C22—C23	1.41(2)	1.42(2)
C23—C24	1.37(2)	1.36(2)
C24—C25	1.40(2)	1.40(2)
C25—C26	1.42(2)	1.42(2)
C21—C26	1.39(2)	1.37(2)
C23—C27	1.51(2)	1.52(2)
C24—C28	1.53(2)	1.53(2)
N1′—Pb—N1	79.2(4)	78.2(5)
N2′—Pb—N2	76.5(4)	76.5(4)
N1—Pb—N2	70.1(5)	65.3(7)
N1—Pb—N2′	116.6(5)	111.3(6)
C26—N2—C32	122.3(12)	123.3(12)
C11—C12—C13	113(2)	127(3)
C13—C12—N1	125(2)	130(3)
C11—C12—N1	121.1(11)	103(2)
C31—C32—C33	112.3(11)	115.2(13)
C33—C32—N2	122.4(14)	124(2)
C32—N2—C26	122.3(12)	123.3(12)
N2—C26—C21	118.2(12)	118.1(13)
N2—C26—C25	120(2)	121(2)
C26—C25—C24	120.0(12)	120.1(13)
C25—C24—C23	119.2(11)	119.1(13)
C24—C23—C22	120.8(11)	120.0(14)
C23—C22—C21	121.2(11)	121.0(14)
C22—C21—C26	117.7(10)	119.8(12)
C21—C26—C25	120.8(10)	119.6(11)
C22—C23—C27	117.3(13)	117(2)
C24—C23—C27	121.9(11)	122.8(14)
C23—C24—C28	123.6(11)	123.8(13)
C25—C24—C28	117.3(13)	117(2)

however, is concerned with the location of C11. For example, the C11—C12 bond length is 1.52(2)Å in the true structure and 1.26(2) Å in the false structure. Likewise, the C11—C12—N1 bond angle is 121.1(11)° in the true structure and 103(2)° in the false structure. While these values for the false structure should certainly arouse suspicion concerning the accuracy of the structure, the issue remains as to whether the bulk connectivity of the structure would be called into question. For example, it is not uncommon for poorly refined structures, with high *R* values, unrealistic displacement parameters, and dubious bond lengths and angles to appear in the literature, with the disclaimer that the structure is sufficiently good to establish atom connectivity. The present work demonstrates that atom connectivity may not necessarily be correct, even for structure refinements that are not ill-behaved.

Unreasonable nonbonded intermolecular and intramolecular interactions may also be used as indicators of a problem with a structure solution. In this regard, the lead atom of the incorrect structure does exhibit shorter nonbonded interactions to hydrogen atoms (located in calculated positions) than does the lead atom in the true structure. For example, the four shortest interactions are in the range 2.58–3.40 Å for the false structure and 3.05–3.89 Å for the true structure. Of these interactions, the closest interaction (2.58 Å) for lead in the false structure is that with H21A, the non-existent (in reality) hydrogen atom of the errant misplaced aryl group. Such a separation is intermediate between the sum of the covalent radii (1.84 Å) and the sum of the van der Waals radii (*ca.* 3.54 Å).[40] Interactions of this type are not uncommon (especially when they may be imposed by the constraints of ligand geometry),[41] and so they alone would not necessarily be taken as evidence that the derived structure is unreasonable. Thus, for this particular example, non bonded interactions do not strongly suggest that the derived connectivity (for the false minimum) is incorrect. Finally, the structure corresponding to the false minimum passed the Hirshfeld rigid bond test[42] using PLATON at the 2.5 sigma level,[43] so that this analysis likewise does not provide a decisive means of indicating that this particular structure had refined into a false minimum.

The problem encountered with the $Cmc2_1$ structure of [η^4-Me_8taa]Pb·CH_2Cl_2 has closely related origins to situations in which non-centrosymmetric structures have been refined incorrectly in centrosymmetric space groups. It should be emphasized that such a problem is completely counter to the more common error of incorrectly refining a centrosymmetric structure in a non-centrosymmetric space group.[4] In fact, the ability to refine a non-centrosymmetric structure in a centrosymmetric space group is not intuitively obvious,[44] with Marsh having noted that: "There is little danger that a centrosymmetric description of a demonstrably non-centrosymmetric structure will find its way into the literature."[4a] Nevertheless, such situations do arise because of the deceptive ability of a heavy atom to create electron density difference maps in non-centrosymmetric space groups that have all the appearances of a centrosymmetric space group, even in the late stages of refinement.

For example, Cp*$TaCl_3$(η^2-$COSiMe_3$) was originally described as a fully mirror-plane disordered structure in the centrosymmetric orthorhombic *Pcam*;[45] however, Rheingold subsequently demonstrated that the structure is, in fact, ordered in the non-centrosymmetric $Pca2_1$.[46] Likewise, we have shown that the tris(pyrazolyl)hydroborato complex, [Tp^{But}]In, which was reported to exhibit an unusual type of twofold disorder in *Cmcm*, such that a nitrogen atom of one molecule was coincident with the boron atom of its disordered configuration,[47] is in fact perfectly ordered in the non-centrosymmetric $Cmc2_1$.[6] Watkin has also described in detail the considerable problems that were encountered due to pseudosymmetry in the solution of a mixed sandwich ruthenium complex, [Cp*(ArH)Ru]$^+$, in space group $P1$.[3e,48] These literature examples serve to emphasize that structures belonging to polar space groups can be refined (with apparent success?) in centrosymmetric space groups as disordered structures, even though atoms are forced (by virtue of the space group symmetry) to be placed in sites that are actually unoccupied. In the present example of [η^4-Me_8taa]Pb, atoms are also refined in sites that are unoccupied, but the latter is not a consequence of being forced to do so by the space group symmetry; rather, the ability to refine atoms in sites that are unoccupied is a result of the fact that the lead atoms are centrosymmetrically related to each other, and that these atoms dominate the scattering and thereby result in the generation of electron density maps which exhibit *pseudo*-centrosymmetry. Nevertheless, even with this rationale, it is still perhaps surprising how well the atoms in unoccupied sites do refine.

Summary

Orthorhombic ($Cmc2_1$) [η^4-Me_8taa]Pb·CH_2Cl_2 provides an interesting example of a complex that is subject to the occurrence of a false minimum in an X-ray structure solution refinement. Rather strikingly, the structure of the false minimum corresponds to one in which the macrocycle has apparently been cleaved. Furthermore, despite the fact that the false structure does not exhibit the true connectivity of the molecule, it is nevertheless characterized by a low *R* value and well-behaved displacement parameters. Such an observation

reinforces the notion that care must be taken to ensure that, for a molecule belonging to a polar space group, all atoms of the derived structure belong to a single true polar configuration, rather than to a hybrid of the two possible true polar configurations. Finally, the dramatically incorrect connectivity of the false structure calls into question the appropriateness of the often encountered phrase that is used for poor quality refinements: "the X-ray structure determination establishes the connectivity of the molecule."

Experimental

General

All manipulations were performed using a combination of glovebox, high-vacuum and Schlenk techniques.[49] Solvents were purified and degassed by standard procedures. ^{1}H and ^{13}C NMR spectra were measured on Varian VXR 200, 300 and 400 spectrometers. IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 spectrophotometer. Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization (CH_4) techniques. Elemental analyses were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer. $Li_2[Me_8taa]\cdot(Et_2O)_2$ was prepared by the literature method.[50]

Synthesis of [η^4-Me$_8$taa]Pb

THF (*ca.* 10 mL) was added to a stirred mixture of PbI_2 (0.93 g, 2.02 mmol) and $Li_2[Me_8taa]\cdot(Et_2O)_2$ (1.12 g, 2.00 mmol) at room temperature. The mixture was stirred for *ca.* 4 h and the resulting orange precipitate was isolated by filtration and washed with pentane (2 × 25 mL), giving [η^4-Me$_8$taa]Pb as a bright orange solid (1.0 g, 83%). Anal. calcd for [η^4-Me$_8$taa]Pb: C, 51.5; H, 5.0; N, 9.3%. Found: C, 52.0; H, 4.7; N, 8.6%. MS: m/z = 606 (M^+). ^{1}H NMR (C_6D_6): δ 2.01 [s, 12 H, 4 CH_3], 2.07 [s, 12 H, 4 CH_3], 4.63 [s, 2 H, 2 C*H*], 6.78 [s, 4 H, 4 C*H*]. ^{13}C NMR (C_6D_6): 19.6 [q, $^1J_{CH}$ = 126, 4 *C*H$_3$], 23.0 [q, $^1J_{CH}$ = 127, 4 *C*H$_3$], 100.4 [d, $^1J_{CH}$ = 155, 2 *C*H], 126.3 [d, $^1J_{CH}$ = 155, 4 *C*H], 131.1 [s, 4 *C*], 141.3 [s, 4 *C*], 158.8 [s, 4 *C*]. IR data (KBr, cm^{-1}): 2964(w), 2921(w), 2864(w), 1654(w), 1636(w), 1620(m), 1558(s), 1469(s), 1418(s), 1266(m), 1227(m), 1170(m), 1021(m), 999(m), 879(m), 751(m), 673(w), 617(w).

X-Ray structure determinations

Crystals suitable for X-ray diffraction analysis were obtained from both CH_2Cl_2 and $CHCl_3$. The factors influencing crystallization of [η^4-Me$_8$taa]Pb·CH_2Cl_2 as either primitive or *C*-centered modifications were not investigated. Crystal data, data collection and refinement parameters for [η^4-Me$_8$taa]Pb·$CHCl_3$ and [η^4-Me$_8$taa]Pb·CH_2Cl_2 are summarized in Table 1. A typical procedure is provided by the example of [η^4-Me$_8$taa]Pb·$CHCl_3$. A single crystal of [η^4-Me$_8$taa]Pb·$CHCl_3$ was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected at room temperature using graphite monochromated Mo-Kα X-radiation (λ = 0.710 73 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization and absorption effects. The structure was solved using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures on F^2 using SHELXTL 93 (Version 5.0). Of the two possible space groups, $P1$ (No. 1) and $P\bar{1}$ (No. 2), a satisfactory solution was obtained in the centrosymmetric alternative, $P\bar{1}$ (No. 2). Hydrogen atoms on carbon were included in calculated positions. The weighting scheme used was $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$, and the constants a and b were suggested by the program. Refinement data are summarized in Table 1.

Systematic absences for orthorhombic-P [η^4-Me$_8$taa]Pb·CH_2Cl_2 were consistent with *Pnma* (No. 62) and $Pn2_1a$ (No. 33), of which a satisfactory solution was obtained in the centrosymmetric alternative, *Pnma* (No. 62). Hydrogen atoms on carbon were included in calculated positions. The weighting scheme used was $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$, and the constants a and b were suggested by the program. Refinement data are summarized in Table 1.

Systematic absences for orthorhombic-C [η^4-Me$_8$taa]Pb·CH_2Cl_2 [51] were consistent with $Cmc2_1$ (No. 36), *Cmcm* (No. 63) and *C*2*cm* (No. 40), of which a successful solution was obtained in $Cmc2_1$ (No. 36).[52] Hydrogen atoms on carbon were included in calculated positions. Friedel pairs were collected and refinement of the Flack x parameter (using TWIN and BASF commands) allowed the correct polarity to be established. The weighting scheme used was $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$, and the constants a and b were suggested by the program. Refinement data are summarized in Table 1, which also includes the data associated with the false minimum. However, since the values of a (0.067) and b (0) suggested by the program were different from those suggested for the true structure [*i.e.*, a (0.045) and b (2.39)], the refinement was also carried out using the latter constants. The values of R_1 (0.0500), wR_2 (0.1086) and GOF (1.144) using this weighting scheme differed little from the values presented in Table 1.

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rate have been confused. For example, the rather unusual four-coordinate colorless molybdenum complex $Mo(PMe_3)_2Cl_2$ [7a] has been subsequently determined to be, in fact, the zinc complex $Zn(PMe_3)_2Cl_2$.[7b] Likewise, the structures of both of the mono-coordinate copper and silver aryl complexes, (2,4,6-$Ph_3C_6H_2$)Cu and (2,4,6-$Ph_3C_6H_2$)Ag,[7c] have been suggested to be that of partly, or entirely, the bromide compound (2,4,6-$Ph_3C_6H_2$)Br.[7d] (*a*) K. Fromm, M. Plaikner and E. Z. Hey-Hawkins, *Naturforsch*., 1995, **50B**, 894. (*b*) F. A. Cotton and G. Schmid, *Polyhedron*, 1996, **15**, 4053. (*c*) R. Lingnau and J. Strähle, *Angew. Chem*., *Int. Ed. Engl*., 1988, **27**, 436. (*d*) A. Haaland, K. Rypdal, H. P. Verne, W. Scherer and W. R. Thiel, *Angew Chem*., *Int. Ed. Engl*., 1994, **33**, 2443.

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11 For example, the structure of *cis*-$[Pt(C_6H_{11}NH_2)_2Cl_2]$ [11a] has been suggested to be actually that of the *trans* derivative,[11b] an error that is due to locating the platinum on a twofold axis rather than on an inversion center. (*a*) J. Iball and S. N. Scrimgeour, *Acta Crystallogr*., *Sect. B*, 1977, **33**, 1194. (*b*) C. J. L. Lock, R. A. Speranzini and M. Zvagulis, *Acta Crystallogr*., *Sect. B*, 1980, **36**, 1789.

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15 It should also be noted that the existence of false minima has also been observed for situations that are unrelated to problems associated with a polar axis. For example, false minima were detected in the structure refinements of $Cr_2(OAc)_4(H_2O)_2$,[15a] adamantane[15b] and 4-(1-pyrrolidino)pyridinium propynoate.[15c] (*a*) F. A. Cotton and G. W. Rice, *Inorg. Chem*., 1978, **17**, 688; (*b*) J. Donohue and S. H. Goodman, *Acta Crystallogr*., 1967, **22**, 352; (*c*) K. A. Wheeler and B. M. Foxman, *Mol. Cryst. Liq. Cryst*., 1992, **211**, 347.

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23 Since the compositions of the three structural modifications are not the same, it is inappropriate to consider them as polymorphs. See: J. P. Glusker, M. Lewis and M. Rossi, *Crystal Structure Analysis for Chemists and Biologists*, VCH, New York, 1994.

24 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 3rd edn., 1960, pp. 224 and 256.

25 Indeed, it was because of this notion that the additional structural modifications (as described in the text) were discovered due to further attempts to crystallize [η^4-Me_8taa]Pb.

26 The most likely "chemical interpretation" of the structure as illustrated in Fig. 5 would be to incorporate hydrogen atoms on N1 and N1′.

27 The ability to locate atoms in incorrect positions is also related to the concept of homometric structures, *i.e.* different structures with the same Patterson map. See: *Patterson and Pattersons*, eds. J. P. Glusker, B. K. Patterson and M. Rossi, Oxford University Press, New York, 1987.

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30 It should be noted that the relationship between the z coordinates of the true and false locations $z(C2X) = -z(C2X^*)$ is only true because Pb is arbitrarily situated at $z = 0$. More generally, the relationship would be $z(C2X) = z(Pb) - z(C2X^*)$, if Pb were not to be located at $z = 0$.

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37 U_1, U_2 and U_3 are the three main axes components of the thermal ellipsoid.

38 Specifically, the ratios of U_3/U_1 for C1, C11 and C32 are 15.58, 5.22 and 5.08, respectively.

39 The ratios of U_3/U_1 for C1 and C32 are 8.40 and 15.15, respectively.

40 The covalent radii of H and Pb are 0.30 and 1.54 Å, respectively; the van der Waals radius of H is 1.20 Å, while that of lead can be estimated as 0.8 Å greater than its covalent radius. See ref. 24.

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52 The combined figures of merit (CFOM) generated by the program XPREP of SHELXTL™ (version 5.0) for the space groups $Cmc2_1$ (No. 36), *Cmcm* (No. 63) and *C2cm* (No. 40) are 3.71, 14.88 and 7.28, respectively.

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