Inorganica Chimica Acta, 215 (1994) 103–107

The unusual crystallographic disorder of M_2 units in $M_2Cl_4(PEt_3)_4$ (M = Re, Mo)

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(Received July 30, 1993)

Abstract

The crystal structures of $Re_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(PEt_3)_4$ have been reinvestigated. Both compounds crystallize in the space group $I\bar{4}3m$ (No. 217) and have the metal–metal vectors disordered equally in each Cartesian direction. In the non-centrosymmetric space group ($I\bar{4}3m$, No. 217), there are two possible orientations for the whole molecule which are related by an inversion center. For $Re_2Cl_4(PEt_3)_4$, one orientation gave $R = 0.0309$, $R_w = 0.0370$, quality-of-fit = 0.84; while the other one gave $R = 0.0361$, $R_w = 0.0434$, quality-of-fit = 0.99. The Hamilton significance test indicates that the first one can be accepted at the 99.99% confidence level. For $Mo_2Cl_4(PEt_3)_4$, one orientation gave $R = 0.0369$, $R_w = 0.0457$, quality-of-fit = 1.20, while the other one gave $R = 0.0385$, $R_w = 0.0508$, quality-of-fit = 1.33. The first orientation can be accepted at the 99.99% confidence level based on the Hamilton significance test. The closest distance between H atoms on the terminal C of PEt_3 in one $Re_2Cl_4(PEt_3)_4$ molecule and H atoms on the terminal C of a misoriented PEt_3 in its closest neighbors is 1.38 Å, well below the sum of the van der Waals radii of two H atoms. The corresponding value in $Mo_2Cl_4(PEt_3)_4$ is 1.67 Å, also well below the sum of the van der Waals radii of two H atoms. This requires Cl and P be ordered. The published structure of $Re_2Cl_4(PEt_3)_4$ with space group $Im\bar{3}m$ (No. 229) was incorrect. The Re–Re bond distance of 2.250(4) Å, resulting from the present work, is consistent with an Re–Re triple bond between two Re atoms. The newly determined dimensions of the $Mo_2Cl_4(PEt_3)_4$ molecules are essentially the same as those previously published. The absolute structure of $Mo_2Cl_4(PEt_3)_4$ was confirmed by measuring Bijvoet pairs in a separate data collection using Cu radiation

Key words. Crystal structures; Rhenium complexes, Molybdenum complexes, Halide complexes, Tertiary phosphine complexes

Introduction

It is well known that compounds containing the $[M_2X_8]^{n-}$ ions, as well as many of their substituted derivatives, such as the $M_2X_4(PR_3)_4$ and $M_2X_4(R_2PCH_2CH_2PR_2)_2$ compounds, display a special type of crystallographic disorder [1]. The shapes of these molecules are such that very often the ion or molecule can occupy some of the lattice sites oriented in one or both of the directions perpendicular to the major orientation. A further consequence of the shapes of these species is that the positions of the ligand atoms in the misoriented ones are so close to those of the correctly oriented ones that they cannot be seen to be different. Hence, one observes what appears to be only a misorientation of the M_2 unit within the ligand cage

A special case of this kind of disorder occurs when the center of the $[M_2X_8]^{n-}$ or $M_2X_4(PR_3)_4$ molecules resides on a position of such high crystallographic symmetry ($\bar{3}$ or $\bar{4}3m$) that there are equal numbers of ions or molecules in each of three mutually perpendicular directions. The first reported example of this was provided by $Re_2Cl_4(PEt_3)_4$ [2] but, according to the published structure, there was a further disorder: namely, the occupancy of each coordination site by 1/2 Cl and 1/2 PEt_3.

Later, $Mo_2Cl_4(PEt_3)_4$ was found to have a three-fold disorder of the Mo_2 units but with the ligands ordered [3]. The reportedly different crystallographic comportment of these two very similar systems led us to examine

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SSDI 0020-1693(93)03685-4

both of them further and we now show that they are, in fact, the same.

Experimental

Preparation

$Re_2Cl_4(PEt_3)_4$ was synthesized according to the literature [4]. Crystallization was carried out by dissolving crystalline $Re_2Cl_4(PEt_3)_4$ in toluene, then layering methanol at room temperature. Black crystals with a regular shape were formed in a few days.

$Mo_2Cl_4(PEt_3)_4$ crystals were obtained at room temperature as a byproduct in the preparation of $Mo_4Cl_8(PEt_3)_4$ [5]. $Mo_2Cl_4(PEt_3)_4$ crystals used for the absolute structure determination were obtained by dissolving $Mo_2Cl_4(PEt_3)_4$ powder in toluene, and layering with methanol at room temperature.

Crystal structure determination

In both cases, the compounds form cubic crystals and a combination of systematic absences (only those for body centering) together with considerations having to do with the expected D_{2d} symmetry of the $M_2X_4P_4$ cores leads rather straightforwardly to the conclusion that there are three possible choices of space group, $I432$ (No. 211), $Im\bar{3}m$ (No. 229) and $I\bar{4}3m$ (No. 217). For reasons that are not evident now, $Im\bar{3}m$ (No. 229) was chosen when the structure of $Re_2Cl_4(PEt_3)_4$ was first solved and refined. In this space group the $m\bar{3}m$ site symmetry requires scrambling of the two types of ligand (as well as the three-way disorder of the Re_2 units), whereas in $I\bar{4}3m$, no scrambling of the ligands is called for.

We first collected a new set of data for $Re_2Cl_4(PEt_3)_4$ and showed that an excellent refinement in $I\bar{4}3m$ was possible. The Re atom occupies 1/3 of the 12e positions to give the three-fold equally disordered metal–metal vector. Cl and P atoms occupy 8c positions, but they were indistinguishable from each other. As in the case of chiral molecules crystallized in a non-centrosymmetric space group, both configurations can be refined, but the correct one should give better results. Structure refinements were carried out for both assignments. The one with Cl at (0.138, 0.138, −0.138) gave $R = 0.0309$, $R_w = 0.0370$, quality-of-fit = 0.84; while the other one with Cl at (0.138, 0.138, 0.138) gave $R = 0.0361$, $R_w = 0.0434$, quality-of-fit = 0.99. The Hamilton significance test [6] indicated that the first configuration is correct at the 99.99% confidence level. The C(2) atom could not be put on a mirror plane, and it was therefore refined on a general position with half occupancy. The distance between the disordered C(2) atoms is 1.0(1) Å. When the constraint on C(1) was released, the

TABLE 1 Crystallographic data for $Re_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(PEt_3)_4$

	$Re_2Cl_4(PEt_3)_4$	$Mo_2Cl_4(PEt_3)_4$[a]	$Mo_2Cl_4(PEt_3)_4$[b]
Formula	$C_{24}H_{60}Cl_4P_4Re_2$	$C_{24}H_{60}Cl_4P_4Mo_2$	$C_{24}H_{60}Cl_4P_4Mo_2$
Formula weight	986.85	806.3	806.3
Space group	$I\bar{4}3m$ (No. 217)		
a (Å)	12.335(2)	12.388(4)	12.386(3)
V (Å^3)	1877(1)	1901(1)	1900(1)
Z	2	2	2
D_{calc} (g/cm^3)	1.746	1.409	1.409
Crystal size (mm)	0.20 × 0.20 × 0.50	0.10 × 0.20 × 0.25	0.20 × 0.22 × 0.25
μ (cm^{-1})	70.03 (Mo Kα)	98.99 (Cu Kα)	98.99 (Cu Kα)
Data collection instrument	Nicolet P3/F	Rigaku AFC5R	Rigaku AFC5R
Radiation (monochromated)	Mo Kα	Cu Kα	Cu Kα
Orientation reflections no.	25	25	25
range, 2θ (°)	20–30	52–53	51–53
Temperature (°C)	20		
Scan method	ω–2θ		
Data collection range, 2θ (°)	4–46	4–116	4–120
No. unique data	159	160	328
No. data with $F_o^2 > 3\sigma(F_o^2)$	112	122	249
No. parameters refined	26	29	29
Transmission factors: max., min.	0.9999, 0.6594	1.000, 0.7304	1.000, 0.8014
R[c]	0.0309	0.0369	0.0877
R_w[d]	0.0370	0.0457	0.1115
Quality-of-fit indicator[e]	0.84	1.20	2.85
Largest shift/e.s.d., final cycle	0.2	0.2	0.1
Largest peak (e/Å^3)	1.03	0.24	0.84

[a] Unique data. [b] Bijvoet pairs measurement without averaging them. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma(|F_o|)$. [e] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$

refinement converged with the distance between the disordered C(1) atoms being 0.10 Å, suggesting that C(1) should be on the mirror plane.

We also refined the structure in $Im\bar{3}m$. Starting coordinates from the published structure were used, and the refinement converged to: $R=0.0597$, $R_w=0.0741$, quality-of-fit = 1.84. The bond distances and bond angles are similar to those published. The figures of merit are much worse than those from the structure refined in $I\bar{4}3m$.

To pursue further the question of whether or not it is possible to have some sort of disorder between Cl and PEt_3, H atoms were placed on the terminal C of PEt_3 in ideal positions for both orientations. The closest distance between H atoms on the terminal C of PEt_3 in one $Re_2Cl_4(PEt_3)_4$ molecule and H atoms on the terminal C of a misoriented PEt_3 in its closest neighbors is 1.38 Å, well below the sum of the van der Waals radii of two H atoms.

We then obtained the original data [2] and found that the model refines well in $I\bar{4}3m$ using these data also. Again both assignments for Cl and P were used to refine the structure. The one with Cl at (0 138, 0.138, −0.138) gave $R=0.0283$ (unit weights), quality-of-fit = 1.14. The other one with Cl at (0.137, 0.137, 0.137) gave $R=0.0271$ (unit weights), quality-of-fit = 1.09, largest shift/e.s.d., 0.05, largest residual peak, 0.51 e/Å^3 The corresponding figures for the refinement in $Im\bar{3}m$, in the same order, were: 0.041, 1.22, 0.05, 0.89. We now conclude that the previous use of $Im\bar{3}m$ for $Re_2Cl_4(PEt_3)_4$ was incorrect; the space group for this compound is $I\bar{4}3m$, as it is for $Mo_2Cl_4(PEt_3)_4$.

The first structural refinement for $Mo_2Cl_4(PEt_3)_4$ was straightforward. The published coordinates [3] with both C atoms on a mirror plane were used as input, and the refinement (using the SDP programs) gave $R=0.0849$, $R_w=0.1102$, quality-of-fit = 3.31. When the constraints on the C atoms were released, they moved away from the mirror plane. Refinement with C(1) and C(2) at general positions with half occupancy (using the SHELX programs) gave $R=0.0369$, $R_w=0.0457$, quality-of-fit = 1.20, for Cl at (0.139, 0.139, 0.139). The figures of merit for Cl at (0.139, 0.139, −0.139) were $R=0.0385$, $R_w=0.0508$, quality-of-fit = 1.33. The distances between the two disordered C(1) and C(2) atoms are 0.82(5) and 1.17(7) Å, respectively. The Hamilton significance test indicated that the first configuration can be accepted at the 99.99% confidence level.

To further confirm that the absolute structure of $Mo_2Cl_4(PEt_3)_4$ is indeed distinguishable in the non-centrosymmetric space group, Bijvoet pairs were collected using Cu radiation on a Rigaku AFC5R. Following every 20 measurements of h, k, l values, the corresponding 20 $\bar{h}, \bar{k}, \bar{l}$ values were measured. Pairs of $F_{O,hkl}/F_{O,\bar{h}\bar{k}\bar{l}}$ and $F_{C,hkl}/F_{C,\bar{h}\bar{k}\bar{l}}$ were compared and indicated that the correct absolute structure was, in this case, the one with Cl at (0.137, 0.137, 0.137), for which $R=0.0877$, $R_w=0.1115$, quality-of-fit = 2.85. Refinement of the inverted structure resulted in $R=0.0905$, $R_w=0.1155$, quality-of-fit = 2.95.

Results and discussions

The crystallographic data for $Re_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(PEt_3)_4$ are summarized in Table 1. Figure 1 shows the ORTEP drawing of $Re_2Cl_4(PEt_3)_4$ with three-fold metal–metal disorder and disordered C(2). Figure 2 shows the ORTEP drawing of $Mo_2Cl_4(PEt_3)_4$ with three-fold metal–metal disorder and disordered C(1) and C(2).

Table 2 lists positional and equivalent isotropic thermal parameters for $Re_2Cl_4(PEt_3)_4$ refined in $I\bar{4}3m$ for both the new and the old data. Table 3 lists positional and equivalent isotropic thermal parameters for $Mo_2Cl_4(PEt_3)_4$. The selected bond distances and angles for $Re_2Cl_4(PEt_3)_4$ using both the new and old data are listed in Table 4. The corresponding values for $Mo_2Cl_4(PEt_3)_4$ are listed in Table 5.

A comparison of Re–Re, Re–Cl and Re–P distances among $Re_2Cl_4(PR_3)_4$ complexes is given in Table 6. The Re–Re distance is quite consistent, corresponding to a Re–Re triple bond. For $Re_2Cl_4(PMe_3)_4$ [7] and $Re_2Cl_4(PMe_2Ph)_4$ [8] the two complexes without any metal–metal disorder, where the Re–Cl and Re–P dis-

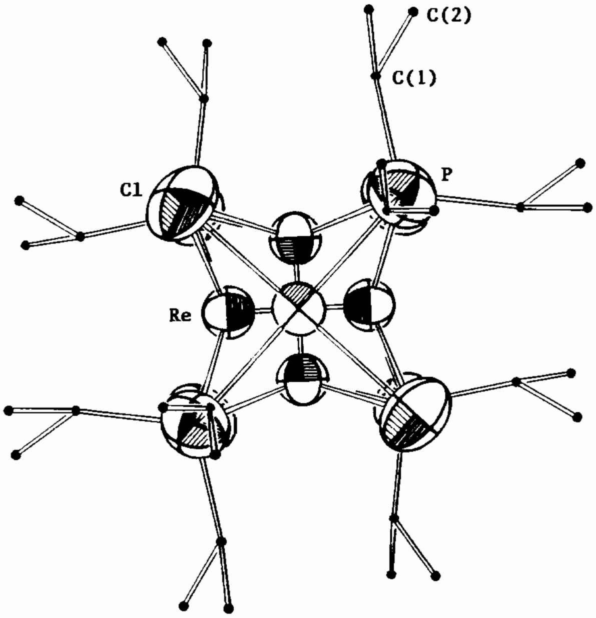

Fig 1 ORTEP diagram of $Re_2Cl_4(PEt_3)_4$ drawn with 50% probability ellipsoids indicating all of the modes of disorder. Carbon atoms are shown as spheres of arbitrary radii.

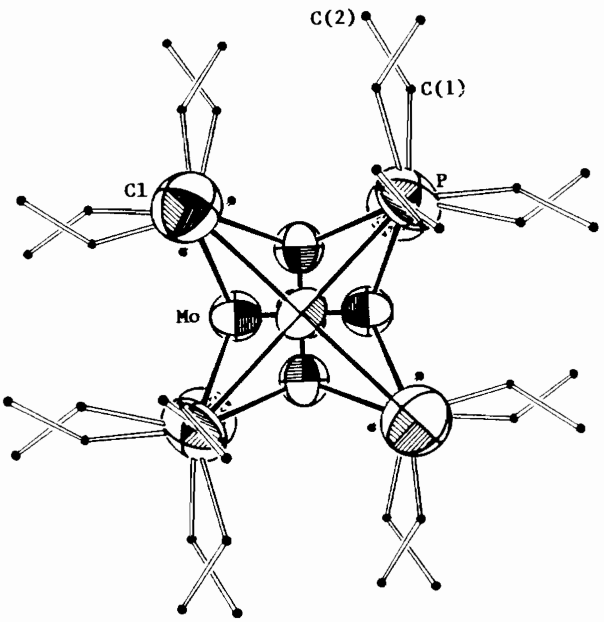

Fig. 2 ORTEP diagram of $Mo_2Cl_4(PEt_3)_4$ drawn with 50% probability ellipsoids indicating all of the modes of disorder Carbon atoms are shown as spheres of arbitrary radii

TABLE 2. Positional and equivalent isotropic thermal parameters for $Re_2Cl_4(PEt_3)_4$

Atom	x	y	z	U_{eq} (Å^2)
Data 1992 ($I\bar{4}3m$)				
Re	0.0912(2)	0.000	0.000	0.0682(6)
Cl	0.1383(8)	x	$-x$	0.121(3)
P	0.1357(9)	x	x	0.117(3)
C(1)	0.111(2)	x	0.286(2)	0.226(5)
C(2)	0.165(4)	0.107(4)	0.363(2)	0.242(5)
Data 1976 re-refined in $I\bar{4}3m$				
Re	0.0913(2)	0.000	0.000	0.0654(6)
Cl	0.1368(7)	x	x	0.119(4)
P	0.1376(8)	x	$-x$	0.109(4)
C(1)	0.110(3)	x	−0.284(2)	0.239(8)
C(2)	0.166(4)	0.104(4)	−0.362(2)	0.219(9)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as. $(4/3)[a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos\ \gamma)U(1,2) + ac(\cos\ \beta)U(1,3) + bc(\cos\ \alpha)U(2,3)]$

TABLE 3 Positional and equivalent isotropic thermal parameters for $Mo_2Cl_4(PEt_3)_4$

Atom	x	y	z	U_{eq} (Å^2)
Mo	0.0861(2)	0.000	0.000	0.0655(6)
Cl	0.1395(3)	x	x	0.115(2)
P	0.1392(3)	x	$-x$	0.106(2)
C(1)	0.104(2)	0.150(2)	−0.279(1)	0.189(5)
C(2)	0.163(3)	0.096(3)	−0.368(2)	0.222(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos\ \gamma)U(1,2) + ac(\cos\ \beta)U(1,3) + bc(\cos\ \alpha)U(2,3)]$

TABLE 4 Selected bond distances (Å) and angles (°) for $Re_2Cl_4(PEt_3)_4$

Data 1992 ($I\bar{4}3m$)			
Re–Re	2.250(4)	Re–Cl	2.48(2)
Re–P	2.431(2)	P–C(1)	1.90(3)
C(1)–C(2)	1.15(4)		
Re–Re–Cl	103.5(1)	Re–Re–P	103.1(2)
Cl–Re–Cl	152.9(3)	Cl–Re–P	87.0(3)
P–Re–P	153.9(5)	Re–P–C(1)	122(1)
Re–P–C(1)	90(1)	P–C(1)–C(2)	136(3)
C(1)–P–C(1)	106(1)		
Data 1976 re-refined in $I\bar{3}4m$			
Re–Re	2.254(4)	Re–Cl	2.453(2)
Re–P	2.47(2)	P–C(1)	1.87(3)
C(1)–C(2)	1.20(5)		
Re–Re–Cl	103.2(2)	Re–Re–P	103.4(1)
Cl–Re–Cl	153.5(4)	Cl–Re–P	87.0(3)
P–Re–P	153.2(3)	Re–P–C(1)	120(1)
Re–P–C(1)	88(1)	P–C(1)–C(2)	133(3)
C(1)–P–C(1)	109(2)		

TABLE 5 Selected bond distances (Å) and angles (°) for $Mo_2Cl_4(PEt_3)_4$

Mo–Mo	2.132(5)	Mo–Cl	2.531(1)
Mo–P	2.525(6)	P–C(1)	1.79(2)
C(1)–C(2)	1.49(3)		
Mo–Mo–Cl	105.1(1)	Mo–Mo–P	105.1(1)
Cl–Mo–Cl	149.7(2)	Cl–Mo–P	86.1(1)
P–Mo–P	149.8(2)	Mo–P–C(1)	130.5(8)
Mo–P–C(1)	97.9(8)	Mo–P–C(1)	120.9(8)
P–C(1)–C(2)	124(2)	C(1)–P–C(1)	100(1)

tances are reliable, the difference between the Re–Cl and Re–P distances is small. For $Re_2Cl_4(PEt_3)_4$ and $Re_2Cl_4(PPr_3)_4$ [7], the two complexes with significant metal–metal disorder, the Re–Cl and Re–P distances become less accurate. As there is actually more than one set of ligand orientations present in the crystal, which are indistinguishable by X-ray diffraction, we obtain only average values for the Re–Cl and Re–P distances and associated angles. Similar results have also been found in $Mo_2Cl_4(PR_3)_4$ complexes [3].

In the absolute structure determination for $Mo_2Cl_4(PEt_3)_4$, the difference between structure factors for Bijvoet pairs is small for most pairs. There are, however, two pairs displaying significant differences. The comparison of F_O and F_C for these two reflections in both configurations is given in Table 7. In the correct configuration, F_O and F_C for these two reflections are consistent. In the wrong configuration, F_C for these two reflections correspond to their Bijvoet pairs

TABLE 6. Comparison of major bond distances (Å) for some $Re_2Cl_4(PR_3)_4$ compounds

	PEt_3	n-PPr_3	PMe_3	PMe_2Ph
Disorder	1/3:1/3:1/3	0.43:0.29:0.28	1.0:0.0:0.0	1.0:0.0:0.0
Re–Re	2.250(4)	2.252(2)[a]	2.247(1)	2.241(1)
Re–Cl[b]	2.48(2)	2.44(1)	2.380(1)	2.387(3)
Re–P[b]	2.431(2)	2.452(4)	2.417(1)	2.42(2)

[a] The major orientation. [b] The Re–Cl and Re–P distances are the average of two similar values in the last three columns.

TABLE 7. Comparison of F_o and F_c for two Bijvoet pairs for $Mo_2Cl_4(PEt_3)_4$

h k l	F_o	$\sigma(F)$	F_c	
			Correction configuration	Wrong configuration
2 1 1	93.1	1.4	97.1	88.0
$\bar{2}\ \bar{1}\ \bar{1}$	84.4	1.3	88.7	96.5
4 1 1	15.5	0.3	15.5	13.0
$\bar{4}\ \bar{1}\ \bar{1}$	13.8	0.3	13.5	15.0

Acknowledgement

We thank the National Science Foundation for financial support.

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