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Three-fold Disordering of the Re_2 Unit in the $Re_2Cl_6(PEt_3)_2$ Molecule

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Abstract

When crystallized from toluene, $Re_2Cl_6(PEt_3)_2$ forms crystals that incorporate interstitial toluene molecules, and have the composition $Re_2Cl_6(PEt_3)_2\cdot C_7H_8$. Space group $R\bar{3}c$, with $a = 12.433(5)$, $c = 32.549(10)$ Å, $V = 4357(1)$ Å^3 and $Z = 6$. The two rhenium atoms are disordered over six positions that form an octahedron within a cubic rhombohedron defined by six chlorine and two phosphorus atoms, and centered at a crystallographic $\bar{3}$ position. The disorder is analogous to that previously found in $[N(C_4H_9)_4]_2Re_2I_8$.

Introduction

The first reactions of the $Re_2Cl_8^{2-}$ ion to be studied were with phosphines [1], and the first structurally characterized derivative [2] was $Re_2Cl_6(PEt_3)_2$. When recrystallized from 1-chlorobutane, this green compound formed monoclinic crystals that contain no solvent of crystallization. These crystals belong to space group $P2_1/n$ with two molecules in the unit cell, each residing on a center of inversion. The structure showed no evidence of disorder (although in 1968 there was no reason to suspect any) and it refined smoothly to $R_1 = 0.052$, $R_2 = 0.063$ and $\Sigma w[|F_o| - |F_c|]^2/(m - n) = 1.23$, with all atoms having well-behaved displacement ellipsoids.

Recently, we have, by chance, grown crystals of $Re_2Cl_6(PEt_3)_2$ from toluene and found that they are different, having a composition $Re_2Cl_6(PEt_3)_2\cdot C_7H_8$ and being rhombohedral. Moreover, they display disordering of the Re_2 unit (which occurs frequently [3]) in a special form that has been observed only once before [4]. In this special case, a body diagonal of the quasi-cube of ligand atoms coincides with a three-fold axis of the crystal and the dimetal units are equally disordered over the three equivalent off-diagonal directions.

Experimental

Synthesis of $Re_2Cl_6(PEt_3)_2$

$Re_2Cl_4(PEt_3)_4$, 0.12 g (0.12 mmol), tetraphenylbiphosphine (Ph_4P_2) 0.08 g (0.24 mmol) and 5 ml of benzene were placed in a Schlenk tube equipped with a reflux condenser and a boiling stick. The reaction mixture was refluxed under argon for 16 h. After cooling it to room temperature, the reddish-brown reaction mixture was decanted to leave behind a green crystalline substance on the boiling stick and at the bottom of the Schlenk tube. The green substance was vacuum dried, redissolved in toluene and then layered with hexane. After two days, green crystals of $Re_2Cl_6(PEt_3)_2\cdot C_7H_8$ were formed. Isomorphous crystals of this compound could be grown from benzene/hexane.

X-ray Crystallography

A block-shaped crystal of $Re_2Cl_6(PEt_3)_2\cdot C_7H_8$ was mounted at the tip of a quartz fiber with a low temperature halocarbon grease. Geometric and intensity data were gathered with an Enraf-Nonius CAD-4 diffractometer equipped with a low temperature device by following the procedures described previously [6]. Pertinent crystallographic data are given in Table 1. Lattice dimensions and Laue symmetry were verified by axial photography. From systematic absences, the choice of space group was limited to $R3c$ or $R\bar{3}c$. From our attempts to refine in both the space groups, the correct one has been found to be $R\bar{3}c$, which after smooth convergence gave a better quality of fit. Intensity data, gathered by the $2\theta-\omega$ method, were reduced by routine procedures. (Calculations were carried out using Micro-Vax II (Micro VMS V4.5) with the programmes SHELXS-86 and the commercial package SDP/V V3.0.) Absorption corrections were applied, based on azimuthal scans of several reflections with the diffractometer angle χ near 90° [7].

The rhenium, chlorine and phosphorus atoms were located via Patterson maps. The rhenium atoms were found to reside on 36 general positions that describe octahedra centered at $\bar{3}$ positions (000). From its close resemblance to the $[Re_2I_8]^{2-}$ ion in

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TABLE 1. Crystal data for $Re_2Cl_6(PEt_3)_2 \cdot C_7H_8$

Formula	$Re_2Cl_6P_2C_{19}H_{38}$
Formula weight	913.58
Space group	$R\bar{3}c$
Systematic absences	$hkl, -h+k+l \neq 3n$; $00l, l \neq 6n$
a (Å)	12.433(5)
b (Å)	12.433(5)
c (Å)	32.549(10)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	4357(1)
Z	6
D_{calc} (g/cm^3)	2.089
Crystal size (mm)	0.50 × 0.20 × 0.25
μ(Mo Kα), (cm^{-1})	91.174
Data collection instrument	Enraf-Nonius CAD4
Radiation monochromated in incident beam (λ, Å)	Mo Kα (0.71073)
Orientation reflections number, range (2θ) (°)	25, $22.74 \leq 2\theta \leq 36$
Temperature (°C)	-80 ± 1
Scan method	$2\theta-\omega$
Data collection range, 2θ (°)	$4 \leq 2\theta \leq 50$
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	857, 508
No. parameters refined	49
Transmission factors (%) maximum, minimum	99.9, 44.9
R[a]	0.036
R_w[b]	0.044
Quality-of-fit indicator[c]	1.106
Largest shift/e.s.d., final cycle	0.50
Largest peak (e/Å^3)	0.422

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2\{|F_o|\}$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

$[N(C_4H_9)_4]_2Re_2I_8$ [4], it was immediately recognized that the rhenium (general) position is indeed occupied by only 1/3 Re because of three-fold disorder. The phosphorus atom was found to be on the three-fold axis. The rest of the atoms were found by an alternating sequence of least-squares refinements and difference Fourier maps. One carbon atom, C(3), residing near a special position $(0,0,\frac{3}{4})$ accounts for the six atoms of the phenyl ring of the solvent molecule, toluene. The seventh atom is apparently disordered over all the six positions outside the phenyl ring, and attempts to include this atom in the refinement were not successful. In the final cycle, 49 parameters were refined giving a data to parameter ratio of 10.3 and residuals of $R = 0.036$ and $R_w = 0.044$. Positional parameters are presented in Table 2 and bond distances and bond angles are given in Table 3.

TABLE 2. Positional parameters and their e.s.d.s for $Re_2Cl_6(PEt_3)_2 \cdot C_7H_8$

Atom	x	y	z	B (Å^2)
Re[a]	0.08119(7)	0.00809(7)	0.01694(2)	4.04(2)
Cl	0.0175(2)	−0.2084(2)	0.02705(6)	6.60(5)
P	0.000	0.000	0.08663(9)	5.30(5)
C(1)	0.0094(9)	0.1434(9)	0.1035(4)	11.4(3)
C(2)	−0.054(1)	0.153(1)	0.1350(6)	18.8(5)
C(3)	0.070(2)	0.129(2)	0.7508(5)	30(1)

[a] Site modeled as 1/3 of Re. All atoms are refined anisotropically and they are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \text{gamma})\beta_{12} + ac(\cos \text{beta})\beta_{13} + bc(\cos \text{alpha})\beta_{23}]$.

TABLE 3. Selected bond distances (Å) and angles (°) for $Re_2Cl_6(PEt_3)_2 \cdot C_7H_8$

Atom 1	Atom 2	Distance
Bond distances		
Re	Re′	2.219(1)
Re	Cl	2.419(2)
Re	Cl′	2.380(3)
Re	Cl″	2.256(2)
Re	P	2.464(3)
P	C(1)	1.813(12)
C(1)	C(2)	1.34(2)
C(3)	C(3)′	1.27(4)
C(3)	C(3)″	1.52(3)

Atom 1	Atom 2	Atom 3	Angle
Bond angles			
Re′	Re	Cl	100.96(6)
Re′	Re	Cl′	103.22(6)
Re′	Re	Cl″	110.81(7)
Re′	Re	P	96.79(5)
Cl	Re	Cl′	155.41(7)
Cl	Re	Cl″	87.30(8)
Cl	Re	P	85.98(5)
Cl′	Re	Cl″	88.25(7)
Cl′	Re	P	86.83(5)
Cl″	Re	P	152.36(7)
Re	P	C(1)	114.6(4)
Re	P	C(1)	120.8(4)
Re	P	C(1)	84.9(4)
C(1)	P	C(1)	111.2(5)
P	C(1)	C(2)	125.0(9)
C(3)′	C(3)	C(3)″	120.(2)

Numbers in parentheses are e.s.d.s in the least significant digits.

Results and Discussion

The reaction between $Re_2Cl_4(PEt_3)_2$ and Ph_4P_2 in benzene appears to give a mixture of products, one of which is $Re_2Cl_6(PEt_3)_2$. Characterization of the other product(s) is still underway.

Although disordered structures for $M_2X_8{}^{n-}$ ions and their derivatives were well known, and documented [3] in 1982, the years since have seen the discovery of many more cases. It is fair to say that this type of disorder occurs so commonly in this class of compounds that in every structure determination one must be alert to its possible presence.

In the most common situation, the dimetal complex, be it a molecule or an ion, resides on a position in the crystal where crystallographic symmetry can be satisfied without disorder. In some of these cases, of which the previously known monoclinic form of $Re_2Cl_6(PEt_3)_2$ is an example, no detectable degree of disorder occurs. However, in many others there is a two-fold disorder, with the majority of M_2 units oriented in one direction (typically 65–95%) while all of the others lie in only one other direction. No case has yet been reported in which there are three directions unequally populated, although we shall soon describe one, nor has there yet been a case where two orientations are equally populated.

Three-fold disorders with equal populations for all three orientations have been reported only three times in the past. The first example was found in $Re_2Cl_4(PEt_3)_4$ [5], where the midpoint of the molecule resides on a position of crystallographic $m3m$ (O_h) symmetry. These symmetry requirements can be satisfied only by disordering the PEt_3 and Cl ligands over the eight cube vertices in addition to placing the Re_2 units in three orthogonal directions. A second example of this 'ultimate' form of disorder was later found for $Mo_2Cl_4(PEt_3)_4$ albeit in a different cubic space group [8]. The imposition of just one three-fold axis was found for the first (and only previous) time in the structure of $[(C_4H_9)_4N]_2[Re_2I_8]$ only recently [4].

An ORTEP drawing of the $Re_2Cl_6(PEt_3)_2$ molecule is presented as Fig. 1. Re represents the rhenium with the site occupancy of 1/3. For the sake of clarity, the carbon atoms have been arbitrarily reduced and only two of the six fractionally occupied Re positions are represented as ellipsoids. The common midpoint of three Re–Re lines is a crystallographic $\bar{3}$ center and the line joining two phosphorus atoms is a crystallographic three-fold axis. Unlabelled atoms can be derived from those labelled by applying the operations arising from the $\bar{3}$ axis.

The disorder in this structure provides a unique opportunity to see directly the effect of disorder on the apparent values of molecular dimensions. In the class of multiply-bonded dimetal complexes there is no previous example of a compound forming both ordered and disordered crystals. It has, of course, been previously recognized that a single observed ligand set cannot exactly correspond to the demands of each one of two or three differently oriented dimetal units. In cases where one M_2 orientation is heavily predominant (say 90% or more) it can probably be assumed that the observed, averaged ligand atom positions approximate closely to those appropriate to this major molecule and that the bond lengths and angles therefrom are fairly accurate. Still, the e.s.d.s on such dimensions certainly cannot be assigned their usual significance, nor is it clear what they do convey.

What we find in the present case are some very large discrepancies between the ordered and disordered structures, although some dimensions agree rather well. The quantities to be discussed are listed in Table 4. Not surprisingly perhaps, the Re–Re

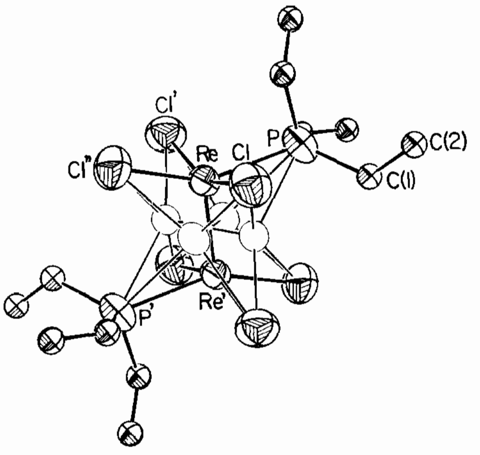

Fig. 1. A view of the $Re_2Cl_6(PEt_3)_2$ molecule in the disordered structure. One orientation of the Re_2 unit is featured, but the other two and the bonds they form are shown in lighter outline. Note that Cl'' is *trans* to P not only in the featured molecule, but in the others as well.

TABLE 4. Comparison of molecular dimensions of $Re_2Cl_6(PE_3T)_2$ in ordered and disordered structures

Dimension	Values (Å or °) in	
	Ordered structure	Disordered structure
Re–Re	2.222(3)	2.219(1)
Re–P	2.449(6)	2.464(3)
Re–Cl(*trans*)	2.352(7)	2.256(2)
Re–Cl(*cis*)	2.294(6), 2.299(6)	2.419(2), 2.380(3)
Re–Re–P	97.5(2)	96.79(5)
Re–Re–Cl(*trans*)	116.3(2)	110.81(7)
Re–Re–Cl(*cis*)	103.1(2), 104.1(2)	100.96(6), 103.22(6)

distance in the present case, 2.219(1) Å, agrees completely with that in the ordered structure. The Re–P distance also agrees fairly closely with the previous one; the difference, 0.015(7) Å, is within the 3σ level, assuming (as we probably should not) that we can treat the present e.s.d. as genuine.

Most of the Re–Re–X angles are also in fair agreement, but the two sets of Re–Cl distances show pronounced disagreement. In the ordered structure there was a small but unambiguous *trans* effect, that is, the Re–Cl bond *trans* to the Re–P bond was longer, by about 0.05 Å than the *cis* ones. In the present structure we see the reverse, with the *trans* Re–Cl bond being *c.* 0.15 Å longer. This relationship is an artifact of the disorder. We must recognize that the $\bar{3}$ symmetry does *not* make set of six Re/3 atoms an octahedron, but rather, a trigonal antiprism. In fact, it is an antiprism that is appreciably flattened, and this causes a shortening of all the Re–Cl distances *trans* to the Re–P distances and an elongation of all the other Re–Cl distances. The magnitude of the flattening can be appreciated by noting that the 'Re–Re' distances in the triangular faces perpendicular to the $\bar{3}$ axis are 1.69 Å while the other 'Re–Re' distances are only 1.46 Å.

The molecules are packed so as to preserve the Re–Re and Re–P distances and the Re–Re–P angles in each one. It is not possible simultaneously to conserve all the other dimensions of an ideal individual molecule while employing only one set of Cl positions for all three orientations. In the disordered structure, the apparent distortions (each molecule is, presumably, undistorted) accumulate in the Cl atom positions.

Supplementary Material

Tables of structure factors, anisotropic thermal displacement parameters, and non-bonded contacts, and a drawing of the molecule viewed down the $\bar{3}$ axis are available from author F.A.C. on request.

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