Crystallographic disorder of the Re_2 unit in complexes of the type $A_2Re_2X_8$ (A = HP-n-Pr_3, $PMePh_3$; X = Cl or Br)

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Abstract

The preparation and structural characterization of three complexes containing the $[Re_2X_8]^{2-}$ (X = Cl or Br) anion are described. Crystallographic parameters are as follows: for $[HP\text{-}n\text{-}Pr_3]_2Re_2Cl_8$ (**1**) $a = 33.831(9)$, $b = 11.274(6)$, $c = 18.286(5)$ Å, $\beta = 91.11(1)°$, $V = 6955(7)$ Å^3, $Z = 8$, space group $C2/c$; for $[PMePh_3]_2Re_2Cl_8$ (**2**) $a = 10.861(2)$, $b = 11.964(3)$, $c = 16.235(4)$ Å, $\beta = 93.40(2)°$, $V = 2106(1)$, $Z = 2$, space group $P2_1/n$; for $[PMePh_3]_2Re_2Br_8$ (**3**) $a = 10.964(2)$, $b = 12.198(2)$, $c = 16.421(2)$ Å, $\beta = 93.83(1)°$, $V = 2191(1)$ Å^3, $Z = 2$, space group $P2_1/n$. These complexes exhibit an unusual form of crystallographic disorder which has been previously observed in other derivatives that contain the $[Re_2X_8]^{2-}$ anion. It is suggested that while this type of disorder must correlate with the positions of the cations relative to the anions in the crystal packing, and other factors, no simple analysis is likely to be adequate.

Introduction

Compounds containing, and which are derived from, the $[Re_2X_8]^{2-}$ anion have been the subject of numerous publications [1]. In 1963, the pyridinium salt $[pyH]_2Re_2Cl_8$ was the first of these complexes to be reported and structurally characterized [2a] but a more accurate determination followed several years later [2b]. Structural characterization of $K_2Re_2X_8\cdot 2H_2O$ [3] in 1964 led to the recognition that a quadruple bond exists between the two rhenium atoms. The structure of this potassium salt not only revealed the short Re–Re bond distance of 2.24 Å but also another important structural feature, namely that "..the eight chlorine atoms lie approximately at the corners of a cube with edge c. 3.2 Å in length", as was stated in the original paper [3b].

This surprising result did not warrant any further investigation even though it was realized that the Re_2 unit could theoretically adopt three orientations within the cube of halide atoms (Fig. 1) resulting in a unique form of crystallographic disorder. This phenomenon did not manifest itself in any of the earlier structures mentioned above (i.e. all the Re_2 units are oriented in one direction along the same axis). Careful analysis of the crystallographic data for $K_2Mo_2Cl_8\cdot 2H_2O$ [4], a compound reported in 1969 and having the same molecular structure as that of the rhenium derivative, revealed that 93% of the Mo pairs were found to lie parallel to the crystallographic z axis whilst 7% lay along a four-fold axis of their own Cl_8 cube perpendicular to the z axis, namely the x (or y) axis as shown in Fig. 1.

The first rhenium complex to exhibit this type of disorder was not reported until 1976; $[n\text{-}Bu_4N]_2Re_2Cl_8$ [5] has 74% of the Re_2 units lying in one orientation and the other 26% in a second. Recently we reported the structure of the analogous iodide derivative, $[n\text{-}Bu_4N]_2Re_2I_8$ [6] in which all three orientations are equally occupied (33%) by Re_2 units. Table 1 lists all the compounds containing $[Re_2X_8]^{2-}$ ions (X = Cl, Br or I) that have been crystallographically characterized to date with their respective percentage occupancies of the Re_2 units along the x, y and z axes.

In this paper we report the synthesis and crystallographic characterization of three new derivatives that contain a $[Re_2X_8]^{2-}$ anion; $[HP\text{-}n\text{-}Pr_3]_2Re_2Cl_8$ (**1**), $[PMePh_3]_2Re_2Cl_8$ (**2**) and $[PMePh_3]_2Re_2Br_8$ (**3**).

Experimental

Reagents

The starting material $[n\text{-}Bu_4N]_2Re_2Cl_8$ was prepared using a well-established procedure [16]. P-n-

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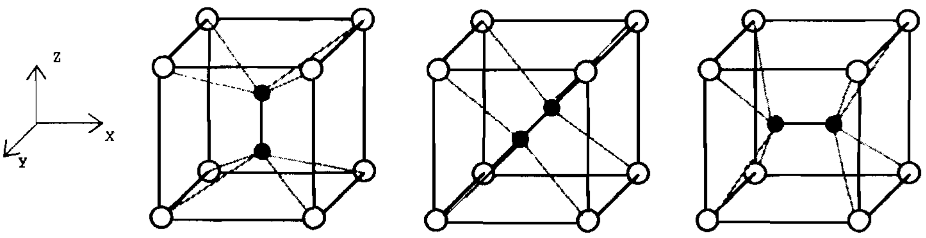

Fig. 1. A diagram showing the three orientations of a Re_2 unit within a cube of halide atoms.

TABLE 1. Percentage occupancies of the Re_2 unit along the x, y and z axes in complexes containing the $[Re_2X_8]^{2-}$ cation

Complex	Percent occupancy			Reference
	z	y	x	
$K_2Re_2Cl_8\cdot 2H_2O$	100			3
$Cs_2Re_2Cl_8\cdot H_2O$	100			7
$[NH_4]_2Re_2Cl_8$	100			8
$[pyH]_2Re_2Cl_8$	100			2
$[Me_3\text{-}pyH]_2Re_2Cl_8$	100			9
$[DMFA_2H]_2Re_2Cl_8$	100			10
$[Me_2NH_2]_2Re_2Cl_8$	100			10
$[PPh_4]_2Re_2Cl_8\cdot 2CH_2Cl_2$	100			11
$[HP\text{-}n\text{-}Pr_3]_2Re_2Cl_8$	76	24		this work
$[n\text{-}Bu_4N]_2Re_2Cl_8$	74	26		5
$[ReCl_2(depe)_2]_2Re_2Cl_8$	74	26		12
$[PMePh_3]_2Re_2Cl_8$	61	39		this work
$Cs_2Re_2Br_8$	100			13
$[pyH]_2Re_2Br_8$	100			15
$[PMePh_3]_2Re_2Br_8$	82	18		this work
$[n\text{-}Bu_4N]_2Re_2Br_8$	62	38		14
$[DMAA_2H]_2Re_2Br_8$	57	36	7	15
$[n\text{-}Bu_4N]_2Re_2I_8$	33⅓	33⅓	33⅓	6

Pr_3 was purchased from Strem Chemicals, Inc. while $n\text{-}Bu_4NBr$ was purchased from Aldrich Chemicals.

Preparation

$[HP\text{-}n\text{-}Pr_3]_2Re_2Cl_8$ (1)

Crystals suitable for X-ray crystallographic analysis were prepared by the addition of 0.5 ml of $P\text{-}n\text{-}Pr_3$ to an ethanol solution (10 ml) of $[n\text{-}Bu_4N]_2Re_2Cl_8$ (0.1 g, 8.8×10^{-5} mol). A pine boiling stick was also placed in the reaction flask. This mixture was refluxed for 3 days whereupon small blue crystals of **1** (approximately 5% yield) together with large black crystals of $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ [17] (approximately 80% yield) appeared on the boiling stick. These two types of crystals were separated manually.

$[PMePh_3]_2Re_2Cl_8$ (2)

This compound was prepared in a similar fashion to that of $[n\text{-}Bu_4N]_2Re_2Cl_8$ except that $PMePh_3Br$ was used in placed of $n\text{-}Bu_4NBr$. Suitable crystals were obtained by layering an acetone solution of **2** with diethylether.

$[PMePh_3]_2Re_2Br_8$ (3)

A methanol solution (40 ml) of **2** (0.3 g, 2.6×10^{-4} mol) was treated with 10 ml of a 40% solution of HBr. The mixture was heated to boiling in a beaker placed over a steam bath so that evaporation of the methanol occurred. Filtration of the olive-green product followed by washing with diethylether gave **3** in almost quantitative yield. Suitable crystals were obtained in a similar manner to those of **2**.

X-ray crystallography

The structures of all three compounds were determined by general procedures that have been fully described elsewhere [18]. The diffraction data were collected on Enraf-Nonius CAD-4S and Nicolet P3/F equivalent diffractometers equipped with graphite monochromated Mo Kα ($\lambda_\alpha = 0.71073$ Å) radiation. Data reduction and refinements were carried out by standard methods with the use of well-established computational procedures [19], on a Local Area VAX Cluster, employing the VAX/VMS V4.6 computer. See also 'Supplementary material'.

Results and discussion

Compound **1** was prepared serendipitously by refluxing an ethanol solution of $[\text{n-Bu}_4\text{N}]_2\text{Re}_2\text{Cl}_8$ [16] with an excess of P-n-Pr_3 for 3 days. The most likely source of the proton is from water associated with the ethanol. Compound **2** was obtained in a similar fashion to $[\text{n-Bu}_4\text{N}]_2\text{Re}_2\text{Cl}_8$ [16] but with the use of PMePh_3Br in place of $\text{n-Bu}_4\text{NBr}$, while **3** was prepared by anion exchange of **2** using a methanol solution of HBr. Table 2 lists important crystal data for **1**, **2** and **3** while Tables 3, 4 and 5 list atomic coordinates and isotropic thermal parameters for compounds **1**, **2** and **3**, respectively. An ORTEP diagram of the anion in **3**, which is representative of all three complexes, is shown in Fig. 2. See also 'Supplementary material'. Bond distances and angles are very similar to those reported for other derivatives (Table 1) and so we have chosen to omit them from this paper.

While these new derivatives are of no special chemical significance (the chemical properties of the $\text{Re}_2\text{X}_8{}^{2-}$ anion have been thoroughly investigated over the last 25 years [1]) their solid state structures display the interesting form of crystallographic disorder discussed in the introductory remarks. In compound **1** both the cation and the anion reside on general positions. The phosphorus atoms of the $\text{HP-n-Pr}_3{}^+$ cation that are closest to the center of the Re–Re bond (a distance of ≈5.9 Å) are positioned so that they lie along an axis that does not contain any of the Re_2 units. The same arrangement is present in compounds **2** and **3**. Figure 3, for **2**, shows how the phosphorus atoms are positioned relative to the $\text{Re}_2\text{Cl}_8{}^{2-}$ anion. The two orientations of the Re_2 units in **1** have occupancies of 76 and 24% which are close to the values of 74 and 26% for $[\text{n-Bu}_4\text{N}]_2\text{Re}_2\text{Cl}_8$ (see Table 1). This result was not surprising to us at first in view of the fact that the

TABLE 2. Crystal data for compounds **1**, **2** and **3**

Compound	$[\text{HP-n-Pr}_3]_2\text{Re}_2\text{Cl}_8$	$[\text{PMePh}_3]_2\text{Re}_2\text{Cl}_8$	$[\text{PMePh}_3]_2\text{Re}_2\text{Br}_8$
Formula	$\text{Re}_2\text{Cl}_8\text{P}_2\text{C}_{18}\text{H}_{44}$	$\text{Re}_2\text{Cl}_8\text{P}_2\text{C}_{38}\text{H}_{36}$	$\text{Re}_2\text{Br}_8\text{P}_2\text{C}_{38}\text{H}_{36}$
Formula weight	978.53	1210.68	1566.33
Space group	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
Systematic absences	$h0l$, $l \neq 2n$	$h0l$, $h+l \neq 2n$	$h0l$, $h+l \neq 2n$
	hkl, $h+k \neq 2n$	$0k0$, $k \neq 2n$	$0k0$, $k \neq 2n$
a (Å)	33.831(9)	10.861(2)	10.964(2)
b (Å)	11.274(6)	11.964(3)	12.198(2)
c (Å)	18.286(5)	16.235(4)	16.421(2)
β (°)	91.11(1)	93.40(2)	93.83(1)
V (Å^3)	6955(7)	2106(1)	2191(1)
Z	8	2	2
D_{calc} (g/cm$_3$)	1.869	1.909	2.374
Crystal size (mm)	0.30×0.20×0.10	0.20×0.20×0.05	0.2×0.2×0.15
μ(Mo Kα) (cm^{-1})	77.723	64.372	129.23
Data collection instrument	Enraf-Nonius CAD-4S	Nicolet P3/F Equivalent	
Radiation monochromated in incident beam (λ, Å)	Mo Kα ($\lambda_\alpha = 0.71073$ Å)		
Orientation reflections no., range (2θ) (°)	25, $4 < 2\theta < 16$	25, $21 < 2\theta < 29$	25, $25 < 2\theta < 34$
Temperature (°C)	-80 ± 2	21 ± 1	21 ± 1
Scan method	ω–2θ	ω–2θ	ω–2θ
Data collection range, 2θ (°)	$4 \leqslant 2\theta \leqslant 45$	$4 \leqslant 2\theta \leqslant 50$	$4 \leqslant 2\theta \leqslant 50$
No. unique data with $F_o{}^2 > 3\sigma(F_o{}^2)$	4496, 2617	3525, 2205	3556, 1978
No. parameters refined	181	236	236
Transmission factors, max., min. (%)	99.73, 83.95	99.81, 39.93	99.99, 77.53
R^a	0.070	0.061	0.046
$R_w{}^b$	0.090	0.062	0.047
Quality-of-fit indicator^c	1.112	1.633	1.117
Largest shift/e.s.d., final cycle	0.10	0.01	0.04
Largest peak (e/Å^3)	1.291	1.64	1.18

[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 $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

TABLE 3. Positional parameters and equivalent isotropic thermal parameters (Å^2) and their e.s.d.s for $(HP\text{-}n\text{-}Pr_3)_2[Re_2Cl_8]$ (**1**)

Atom	*x*	*y*	*z*	*B* (Å^2)[a]
Re(1)[b]	0.35996(4)	0.1536(1)	0.87542(7)	3.72(3)
Re(2)[b]	0.39016(4)	0.3283(1)	0.88116(6)	3.60(3)
Re(3)[c]	0.4017(1)	0.1942(4)	0.8814(2)	3.9(1)
Re(4)[c]	0.3443(1)	0.2871(3)	0.8721(2)	2.85(8)
Cl(1)	0.3984(2)	0.0460(6)	0.7943(5)	7.5(2)
Cl(2)	0.3064(2)	0.1777(7)	0.9516(3)	5.7(2)
Cl(3)	0.3575(2)	0.4361(6)	0.7889(4)	6.5(2)
Cl(4)	0.4365(2)	0.3031(7)	0.9748(4)	5.6(2)
Cl(5)	0.3143(2)	0.1770(6)	0.7777(3)	5.0(1)
Cl(6)	0.3891(2)	0.0479(6)	0.9703(4)	7.5(2)
Cl(7)	0.4417(2)	0.3078(7)	0.8008(4)	6.6(2)
Cl(8)	0.3522(2)	0.4346(6)	0.9632(4)	5.6(2)
P(1)	0.0653(3)	0.2418(8)	0.4236(5)	7.2(2)
P(2)	0.3181(4)	0.7684(8)	0.6828(6)	8.9(3)
C(1)	0.035(1)	0.111(4)	0.388(2)	11.8*
C(2)	0.060(1)	0.031(4)	0.373(2)	11.8*
C(3)	0.039(1)	−0.094(4)	0.335(2)	11.8*
C(4)	0.077(1)	0.231(4)	0.520(2)	11.8*
C(5)	0.053(1)	0.162(4)	0.560(2)	11.8*
C(6)	0.068(1)	0.186(4)	0.647(2)	11.8*
C(7)	0.037(1)	0.408(4)	0.418(2)	11.8*
C(8)	0.027(1)	0.433(4)	0.364(2)	11.8*
C(9)	0.002(1)	0.548(4)	0.360(2)	11.8*
C(10)	0.293(1)	0.651(4)	0.630(2)	11.8*
C(11)	0.305(1)	0.548(4)	0.642(2)	11.8*
C(12)	0.287(1)	0.434(4)	0.608(2)	11.8*
C(13)	0.306(1)	0.910(4)	0.642(2)	11.8*
C(14)	0.264(1)	0.929(4)	0.639(2)	11.8*
C(15)	0.258(1)	1.050(4)	0.595(2)	11.8*
C(16)	0.306(1)	0.754(4)	0.778(2)	11.8*
C(17)	0.324(1)	0.822(4)	0.827(2)	11.8*
C(18)	0.313(1)	0.810(4)	0.909(2)	11.8*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter define as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$. [b] Sites modeled as 0.76Re. [c] Sites modeled as 0.24 Re.

$HP\text{-}n\text{-}Pr_3^+$ cation is somewhat similar in shape to the $n\text{-}Bu_4N^+$ cation. However, $[ReCl_2(depe)_2]_2Re_2Cl_8$ [12] also has a 74/26% disorder, yet the cation is octahedral in shape, while $[n\text{-}Bu_4N]_2Re_2Br_8$ [14], although isomorphous with the chloride derivative, has very different values of 62/38%. Thus we must conclude that there are other factors apart from the shape of the cation and the size of the halide that dictate the extent to which the Re_2 units undergo this type of disorder.

Table 1 also lists several derivatives that do not exhibit any disorder. It is interesting to note that in these particular structures, the cations tend to be relatively small such as the alkali metal, ammonium and pyridinium cations.

Compounds **2** and **3** are isomorphous but the Re_2 units have different relative occupancies: 61/39% in **2** and 82/18% in **3**. This latter result is surprising since we expected the occupancies to be closer to 50%, following the trend displayed by the $n\text{-}Bu_4N^+$ derivatives. The anions of both derivatives lie on inversion centers while the $PMePh_3^+$ cations are at a distance of ≈6.2 Å from the center of the Re–Re bond and lie along an axis that is not occupied by any of the Re_2 units, just as in the case of compound **1**. This same arrangement is present in $[n\text{-}Bu_4N]_2Re_2Cl_8$ [5], which also has the two-fold disorder, but in the case of $Cs_2Re_2Cl_8$ [7], in which there is no disorder, two pairs of cesium cations lie along two different axes that are mutually perpendicular to one another and to the Re–Re axis. Hence, the packing arrangement of both the cation and anion in the crystal must govern the extent to which the Re_2 units undergo this type of disorder.

However, there are warning signs that no simple analysis based solely on electrostatic forces between the partially positive Re_2 units and the closest cations outside the quasicube will give more than a rough

TABLE 4. Positional parameters and their e.s.d.s for $[PMePh_3]_2[Re_2Cl_8]$ (**2**)

Atom	*x*	*y*	*z*	*B* (Å^2)[a]
Re(1)[b]	0.41910(8)	0.05186(8)	0.01367(6)	2.87(2)
Re(2)[c]	0.5435(1)	0.0177(1)	0.0621(1)	3.16(4)
Cl(1)	0.2493(3)	−0.0581(3)	−0.0334(2)	3.79(9)
Cl(2)	0.3744(3)	0.1555(3)	−0.1087(2)	2.92(8)
Cl(3)	0.5062(3)	0.2179(3)	0.0753(2)	2.59(7)
Cl(4)	0.3811(3)	−0.0074(3)	0.1499(2)	3.59(9)
P	0.0285(4)	−0.2730(4)	0.0861(3)	4.0(1)
C(1)	0.006(1)	−0.259(1)	−0.0235(9)	3.5(4)
C(2)	0.081(1)	−0.314(1)	−0.077(1)	4.3(4)
C(3)	0.064(2)	−0.301(2)	−0.161(1)	5.4(5)
C(4)	−0.029(2)	−0.230(2)	−0.192(1)	5.7(5)
C(5)	−0.105(2)	−0.178(2)	−0.139(1)	5.6(5)
C(6)	−0.090(1)	−0.191(1)	−0.058(1)	4.9(5)
C(7)	0.164(1)	−0.356(1)	0.109(1)	4.1(4)
C(8)	0.150(1)	−0.465(1)	0.140(1)	4.0(4)
C(9)	0.250(1)	−0.536(2)	0.149(1)	5.4(5)
C(10)	0.369(2)	−0.495(1)	0.131(1)	5.0(5)
C(11)	0.382(1)	−0.386(2)	0.102(1)	5.1(5)
C(12)	0.277(1)	−0.314(1)	0.089(1)	4.7(5)
C(13)	−0.104(1)	−0.343(1)	0.126(1)	3.7(4)
C(14)	−0.113(1)	−0.342(2)	0.210(1)	5.6(5)
C(15)	−0.210(2)	−0.398(2)	0.245(1)	6.9(6)
C(16)	−0.296(2)	−0.456(2)	0.191(1)	6.7(6)
C(17)	−0.288(1)	−0.457(2)	0.103(1)	5.4(5)
C(18)	−0.187(1)	−0.399(1)	0.071(1)	4.3(4)
C(19)	0.048(2)	−0.136(1)	0.135(1)	5.7(5)

[a] All atoms were refined anisotropically. They are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$. [b] Site modeled as 0.61 Re. [c] Site modeled as 0.39 Re.

explanation of the disorders observed. For two pairs of isomorphous compounds, namely, the $[n\text{-}Bu_4N]^+$ and $[PMePh_3]^+$ salts of $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$, not only do we find appreciable differences between the population ratios for the corresponding chloro and bromo compounds, but the two pairs diverge in opposite directions. Thus, with the $[n\text{-}Bu_4N]^+$ compounds it changes from 74/26% to 62/38%, whereas for the pair of $[PMePh_3]^+$ compounds it changes from 61/39% to 82/18%. While it is true that electrostatic considerations rationalize the absence of a third orientation, they give no insight into the changing ratios of the two orientations that do occur in each case.

It is likely that even to the extent that electrostatic forces may be the major factor influencing the qualitative nature of the disorder, it would require consideration of many other contributions from cations further away than the closest pair to arrive at a satisfactory answer. However, there is little doubt that the polarizability and deformability of the quasicubic set of halide ions, and the influence of the arrangement of counterions on these will also play a role. We are, after all, presumably not seeing simply different orientations of Re_2 units in otherwise identical quasicubes but rather a differently shaped cube for each of the two Re orientations. While we cannot resolve these shape differences by X-ray crystallography, they must surely exist.

It is also important to remember how very little energy is required to change the ratio of occupancies by a factor of ten (say from 10/1 to 1/1). At room temperature this change in ratio corresponds to a free energy change, $\Delta G = -RT\ln 10 \approx 1.4$ kcal mol^{-1}. Thus we must not expect a crude model to give any more than qualitative guidance. Nevertheless, studies are underway to see if we can choose cations that will give packing arrangements that will predispose the disorder to take certain forms. For instance, there is no case among the ionic compounds in which an exact 1/1 disorder occurs, although this has recently been reported for $W_2Cl_4(NH\text{-}t\text{-}Bu)_2(Pr_3)_2$ (R = Me or Et) [20]. Cations that stack with the $[Re_2X_8]^{2-}$ ions along a four-fold axis should lead to this result.

Supplementary material

For all three crystal structures, full tables of crystal parameters and details of data collection and refi-

TABLE 5. Positional parameters and their e.s.d.s for $[PMePh_3]_2[Re_2Br_8]$ (**3**)

Atom	x	y	z	B (Å^2)[a]
Re(1)[b]	0.41916(8)	0.05063(7)	0.01309(5)	2.41(2)
Re(2)[c]	0.5441(4)	0.0190(3)	0.0611(2)	2.21(9)
Br(1)	0.2415(2)	−0.0616(2)	−0.0336(1)	4.73(5)
Br(2)	0.3707(2)	0.1567(2)	−0.1122(1)	4.15(5)
Br(3)	0.5059(2)	0.2219(2)	0.0744(1)	4.60(5)
Br(4)	0.3775(2)	−0.0059(2)	0.1532(1)	4.54(5)
P	0.0272(5)	−0.2792(4)	0.0878(3)	3.3(1)
C(1)	0.008(2)	−0.260(1)	−0.0205(9)	2.9(4)
C(2)	0.087(2)	−0.316(1)	−0.070(1)	3.3(4)
C(3)	0.074(2)	−0.303(2)	−0.156(1)	4.1(5)
C(4)	−0.022(2)	−0.230(2)	−0.188(1)	5.1(6)
C(5)	−0.098(2)	−0.175(2)	−0.137(1)	4.8(6)
C(6)	−0.086(2)	−0.188(2)	−0.053(1)	4.8(6)
C(7)	0.158(2)	−0.363(1)	0.113(1)	3.0(4)
C(8)	0.148(2)	−0.471(1)	0.138(1)	3.2(4)
C(9)	0.249(2)	−0.535(2)	0.149(1)	4.1(5)
C(10)	0.366(2)	−0.495(2)	0.133(1)	3.8(5)
C(11)	0.379(2)	−0.386(2)	0.110(1)	4.5(5)
C(12)	0.275(2)	−0.322(1)	0.100(1)	3.3(4)
C(13)	−0.104(2)	−0.346(2)	0.124(1)	3.3(4)
C(14)	−0.112(2)	−0.351(2)	0.210(1)	4.4(5)
C(15)	−0.214(2)	−0.409(2)	0.238(1)	6.1(7)
C(16)	−0.295(1)	−0.463(2)	0.186(1)	3.8(5)
C(17)	−0.286(2)	−0.458(2)	0.104(1)	4.4(5)
C(18)	−0.186(2)	−0.401(2)	0.071(1)	4.2(5)
C(19)	0.043(2)	−0.146(1)	0.138(1)	4.6(5)

[a] All atoms were refined anisotropically. They are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$. [b] Site modeled as 0.82 Re. [c] Site modeled as 0.18 Re.

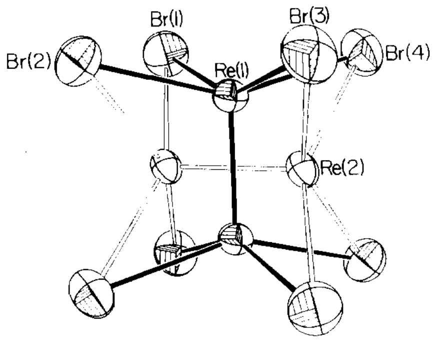

Fig. 2. An ORTEP diagram of the $Re_2Br_8^{2-}$ anion in compound **3** showing the two-fold disorder.

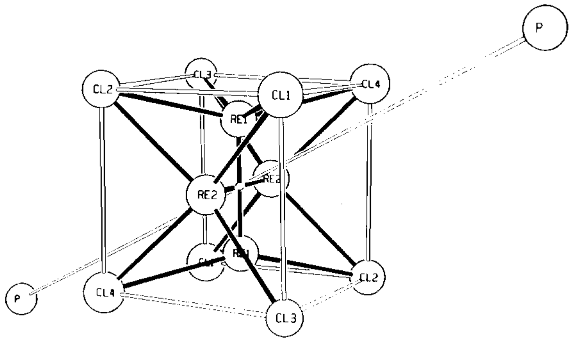

Fig. 3. An ORTEP diagram showing the positions of the phosphorus atoms in compound **2** relative to the Re_2 units.

nement, bond distances, bond angles, anisotropic parameters and tables of observed and calculated structure factors (77 pages) are available from author F.A.C.

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