Crystal Structure of a Trinuclear Dinitrogen-bridged Complex: Di-μ-dinitrogen-tetrachlorobis[chlorotetrakis(dimethylphenylphosphine)-rhenio]molybdenum–Dichloromethane (1/1)

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The crystal structure of the title compound has been determined by Patterson methods from three-dimensional *X*-ray data and refined by full-matrix least squares to *R* 0.068 for 1 893 observed reflections. Crystals are monoclinic, space group $P2_1/c$, with a = 16.710(10), b = 14.164(10), c = 19.084(11) Å, β = 114.3(5)°, Z = 2. The N–N bond length is longer than those of mononuclear dinitrogen complexes. The structure contains a linear Re–N–N–Mo–N–N–Re chain.

THE terminal dinitrogen complex *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ is known to form dinitrogen-bridged binuclear complexes in the presence of a suitable molecule capable of acting as an electron acceptor.[1] While, in general, only one rhenium dinitrogen complex binds to the acceptor group, a trinuclear titanium dirhenium complex has recently been prepared [2] and the crystal structure of the title complex showed that this is also trinuclear.

EXPERIMENTAL

Crystals suitable for *X*-ray diffraction were obtained by solute diffusion of the complex in dichloromethane into n-hexane, in which the complex is insoluble.[3]

Crystal Data.—$C_{65}H_{90}Cl_8MoN_4P_8Re_2$, M = 1 927.2, Monoclinic, a = 16.710(10), b = 14.164(10), c = 19.084(11) Å, β = 114.3(5)°, U = 4 117.8 Å^3, Z = 2, D_c = 1.554 g cm^{-3}. Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 36.9 cm^{-1}. Space group $P2_1/c$ (C^5_{2h}).

Crystallographic Measurements.—Cell parameters were measured from precession photographs, and intensities were initially collected on Weissenberg multipack films for the layers $h0$—$10l$ by use of Cu-K_α radiation (μ 108.6 cm^{-1}). A rhomb-shaped platy crystal of dimensions 0.03 × 0.22 × 0.22 mm (a^* normal to the plate) was used. Intensities were measured by the S.R.C. micro-densitometer service † for a total of 1 306 observed reflections.[4] After solution of the structure by use of these data, a crystal of slightly larger dimensions (0.03 × 0.25 × 0.27 mm) was used for collection of the layers $h0$—$10l$ by use of Mo-K_α radiation on a Hilger and Watts Y 190 automatic diffractometer. By use of the collection techniques already described,[5] 1 893 observed reflections were obtained. These data were corrected for absorption but as the film data were not

TABLE 1

(*a*) Atomic parameters

Atom	x	y	z	β_{11} * or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	0.242 32(7)	0.379 96(10)	0.741 13(6)	0.002 25(6)	0.006 19(9)	0.002 08(5)	0.000 07(8)	0.000 23(3)	0.000 42(7)
Mo	0.0	0.5	0.5	0.003 2(2)	0.007 4(3)	0.002 5(1)	−0.000 2(1)	0.000 9(1)	−0.000 2(2)
Cl(1)	0.081 7(5)	0.446 2(7)	0.428 7(4)	0.005 0(4)	0.009 4(7)	0.003 6(3)	−0.000 3(4)	0.002 3(3)	−0.001 1(4)
Cl(2)	0.068 3(5)	0.653 4(6)	0.516 1(4)	0.005 8(4)	0.007 2(8)	0.003 0(3)	−0.000 9(4)	0.000 9(3)	0.000 0(3)
Cl(3)	0.360 5(5)	0.319 5(7)	0.858 2(4)	0.003 8(4)	0.011 0(8)	0.003 8(3)	0.001 5(4)	0.000 2(3)	0.002 0(4)
P(1)	0.142 7(5)	0.252 6(7)	0.743 0(4)	0.004 1(4)	0.007 3(8)	0.003 6(3)	−0.000 3(4)	0.001 6(3)	0.000 2(4)
P(2)	0.302 8(5)	0.279 1(8)	0.671 6(5)	0.004 3(4)	0.009 2(9)	0.004 2(4)	0.001 1(5)	0.001 1(3)	0.000 5(4)
P(3)	0.329 0(5)	0.518 3(7)	0.729 7(4)	0.003 6(4)	0.006 5(7)	0.003 4(3)	−0.000 5(4)	0.000 8(3)	0.000 4(3)
P(4)	0.201 0(5)	0.471 2(7)	0.832 5(4)	0.003 5(4)	0.008 4(9)	0.003 2(3)	0.000 3(4)	0.000 8(3)	0.00 02(4)
N(1)	0.095(1)	0.456(2)	0.597(1)	4.0(4)					
N(2)	0.151(1)	0.429(2)	0.653(1)	4.3(5)					
C(11)	0.193(2)	0.164(3)	0.821(2)	5.3(7)					
C(12)	0.091(2)	0.179(3)	0.655(2)	7.4(9)					
C(21)	0.226(2)	0.265(3)	0.567(2)	5.4(7)					
C(22)	0.324(3)	0.158(3)	0.706(2)	7.7(9)					
C(31)	0.432(2)	0.541(3)	0.811(2)	5.5(7)					
C(32)	0.267(2)	0.634(3)	0.710(2)	5.0(6)					
C(41)	0.094(2)	0.532(3)	0.787(2)	5.8(7)					
C(42)	0.188(2)	0.396(3)	0.906(2)	5.1(6)					

(*b*) Group parameters

Group †	x^0	y^0	z^0	θ_1	θ_2	θ_3
RB1	−0.042 3(9)	0.309 5(11)	0.750 4(8)	139.3(12)	56.1(8)	200.7(13)
RB2	0.495 6(12)	0.315 0(16)	0.676 4(11)	−66.4(36)	72.8(9)	71.0(36)
RB3	0.377 3(9)	0.532 6(13)	0.583 2(7)	96.9(24)	69.3(6)	−85.3(24)
RB4	0.324 3(9)	0.626 9(12)	0.949 1(8)	−70.1(11)	54.6(7)	−3.8(24)
Solv.	0.156 6(19)	0.569 6(25)	0.061 6(15)	165.0(42)	16.8(41)	225.8(15)

* B_{ij} is a symmetric tensor defined by the expression exp $[-(h_r h_s \beta^{rs})]$. † x^0, y^0, z^0 Are fractional co-ordinates of the local origin of the group, and angles θ_r (°) are defined in the text.

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[2] R. Robson, *Inorg. Chem.*, 1974, **13**, 475.

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[4] P. A. Machin and M. Elder, S.R.C. Microdensitometer service, Notes for Weissenberg Film processing, 1974.

[5] P. D. Cradwick and A. S. de Endredy, *J.C.S. Dalton*, 1975, 1926.

the two sets were not merged. All the results discussed were obtained from the diffractometer data, unless otherwise stated.

Structure Determination.—The structure was solved from the film data by normal heavy-atom Patterson and Fourier methods and was refined by full-matrix least squares with a local program RBLS in which the benzene rings were specified as rigid bodies with D_{6h} symmetry and C–C taken as 1.392 Å. The full structure (except for the solvent molecule) was refined with unit weights and isotropic temperature factors to R 0.08 and by assuming anisotropic temperature factors for rhenium, molybdenum, chlorine, and phosphorus to R 0.074. By use of the diffractometer data, a disordered solvent molecule was identified from a Fourier calculation and this was included in the refinement as a rigid body (C–Cl 1.767 Å, Cl–C–Cl 109°); R converged at 0.068.

TABLE 2

Derived parameters and estimated standard deviations for group atoms

Group	Atom	x	y	z	B_{iso}
RB1	C(1R1)	0.037(2)	0.283(5)	0.749(2)	4.5(6)
	C(2R1)	0.017(3)	0.253(4)	0.809(2)	5.9(8)
	C(3R1)	−0.062(3)	0.279(3)	0.811(2)	5.9(8)
	C(4R1)	−0.121(2)	0.335(5)	0.753(2)	6.5(8)
	C(5R1)	−0.101(3)	0.366(4)	0.693(2)	6.2(7)
	C(6R1)	−0.022(3)	0.339(3)	0.691(2)	6.7(9)
RB2	C(1R2)	0.412(3)	0.305(13)	0.673(3)	7.1(9)
	C(2R2)	0.483(3)	0.318(9)	0.744(2)	7.3(9)
	C(3R2)	0.567(3)	0.328(6)	0.747(2)	9.4(12)
	C(4R2)	0.580(3)	0.325(13)	0.680(3)	9.0(11)
	C(5R2)	0.510(3)	0.312(9)	0.609(2)	10.4(13)
	C(6R2)	0.425(3)	0.302(6)	0.606(2)	7.5(9)
RB3	C(1R3)	0.359(2)	0.523(5)	0.647(1)	3.9(6)
	C(2R3)	0.444(2)	0.543(6)	0.656(1)	5.0(7)
	C(3R3)	0.462(3)	0.552(9)	0.591(2)	5.8(7)
	C(4R3)	0.396(2)	0.542(5)	0.518(1)	7.7(9)
	C(5R3)	0.292(3)	0.513(9)	0.574(2)	5.5(7)
	C(6R3)	0.310(2)	0.522(6)	0.509(1)	7.2(9)
RB4	C(1R4)	0.275(3)	0.561(2)	0.897(2)	3.9(6)
	C(2R4)	0.249(2)	0.655(3)	0.893(2)	5.7(8)
	C(3R4)	0.301(3)	0.719(2)	0.948(2)	8.2(10)
	C(4R4)	0.380(3)	0.690(2)	1.006(2)	6.9(9)
	C(5R4)	0.406(2)	0.596(3)	1.010(2)	6.5(8)
	C(6R4)	0.353(3)	0.523(2)	0.955(2)	5.0(7)
Solv *	Cl(1S)	0.245(4)	0.560(14)	0.121(4)	14.6(10)
	C(SOL)	0.163(7)	0.625(5)	0.047(5)	12.0(26)
	Cl(2S)	0.066(4)	0.556(14)	0.007(5)	19.1(14)

* Solvent atoms were given weights of 0.5.

For the final least-squares cycles a weighting scheme of the type $w = a^2/[a^2 + (F - b)^2]$ with $a = 60$ and $b = 112.8$ was introduced so that $\langle w(\Delta F)^2\rangle$ was invariant with F_o. For both data sets, it was necessary to adjust individual layer scale factors to allow for instrumental setting errors. The scattering factors used included the anomalous scattering for rhenium, molybdenum, chlorine, and phosphorus and all the values were taken from ref. 6. Fourier syntheses were computed by use of a modified version of FORDAP and all the computations were made on an IBM 1130 computer.

In all the Tables, estimated standard deviations in the last figures are given in parentheses. Table 1 gives atomic and group parameters and Table 2 the atomic parameters for the group atoms derived from the equation $x_r = x_r^0 + (\alpha)(\rho)(\beta)x_r^1$ (r = 1—3) where x_r^1 are fractional co-ordinates of the group atoms referred to a local origin, x_r^0 are the fractional co-ordinates of the local origin referred to the crystallographic origin, β transforms x_r^1 to orthogonal axes, $\alpha = \beta^{-1}$, and ρ is the rotation matrix given below in

$$\begin{pmatrix} \cos\theta_1\cos\theta_3 - \sin\theta_1\sin\theta_2\sin\theta_3, & -\sin\theta_1\cos\theta_2, & \cos\theta_1\sin\theta_3 + \sin\theta_1\sin\theta_2\cos\theta_3 \\ \sin\theta_1\cos\theta_3 + \cos\theta_1\sin\theta_2\sin\theta_3, & \cos\theta_1\cos\theta_2, & \sin\theta_1\sin\theta_3 - \cos\theta_1\sin\theta_2\cos\theta_3 \\ -\cos\theta_2\sin\theta_3, & \sin\theta_2, & \cos\theta_2\cos\theta_3 \end{pmatrix}$$

which the angles θ_r (r = 1—3) represent rotations about the z axis, the new x axis, and the new y axis, respectively (xyz are orthogonal). This system of angles has previously been used by Scherringer.[7] The root-mean-square displacements and direction cosines of the principal axes of the β_{ij} tensors referred to crystallographic axes are deposited with the structure factors,* and selected interatomic distances and angles are listed in Table 3. Table 4 gives

TABLE 3

Selected bond lengths and angles

(*a*) Bond lengths (Å)			
Re–C(13)	2.449(7)	Mo–Cl(1)	2.412(8)
Re–P(1)	2.466(9)	Mo–Cl(2)	2.413(8
Re–P(2)	2.433(9)	Mo–N(1)	1.975(20)
Re–P(3)	2.498(8)		
Re–P(4)	2.484(8)	N(1)–N(2)	1.154(29)
Re–N(2)	1.888(21)		
P(1)–C(1R1)	1.86(5)	P(2)–C(1R2)	1.86(6)
P(1)–C(11)	1.86(3)	P(2)–C(21)	1.88(3)
P(1)–C(12)	1.86(4)	P(2)–C(22)	1.84(4)
P(3)–C(1R3)	1.84(4)	P(4)–C(1R4)	1.84(3)
P(3)–C(31)	1.81(3)	P(4)–C(41)	1.85(3)
P(3)–C(32)	1.90(4)	P(4)–C(42)	1.84(3)
(*b*) Angles (°)			
P(1)–Re–P(2)	90.7(3)	P(3)–Re–P(4)	89.5(3)
P(2)–Re–P(3)	91.5(3)	P(4)–Re–P(1)	89.3(3)
Cl(3)–Re–P(1)	91.6(3)	N(2)–Re–P(1)	88.9(8)
Cl(3)–Re–P(2)	86.1(3)	N(2)–Re–P(2)	95.4(7)
Cl(3)–Re–P(3)	94.3(3)	N(2)–Re–P(3)	85.2(8)
Cl(3)–Re–P(4)	83.9(3)	N(2)–Re–P(4)	94.5(7)
P(1)–Re–P(3)	173.9(3)	N(1)–Mo–Cl(1)	90.4(7)
P(2)–Re–P(4)	170.1(3)	Cl(1)–Mo–Cl(2)	90.5(3)
Cl(3)–Re–N(2)	178.4(7)	Cl(2)–Mo–N(1)	90.5(7)
Re–N(2)–N(1)	177.1(22)	Mo–N(1)–N(2)	178.6(21)
C(11)–P(1)–C(12)	103.3(17)	C(21)–P(2)–C(22)	103.1(17)
C(11)–P(1)–C(1R1)	103.9(19)	C(21)–P(2)–C(1R2)	105.9(18)
C(11)–P(1)–Re	114.7(11)	C(21)–P(2)–Re	112.6(11)
C(12)–P(1)–C(1R1)	94.8(20)	C(22)–P(2)–C(1R2)	98.1(56)
C(12)–P(1)–Re	117.8(13)	C(22)–P(2)–Re	115.0(13)
Re–P(1)–C(1R1)	119.4(21)	Re–P(2)–C(1R2)	120.0(48)
C(31)–P(3)–C(32)	105.4(15)	C(41)–P(4)–C(42)	103.2(14)
C(31)–P(3)–C(1R3)	103.5(15)	C(41)–P(4)–C(1R4)	104.2(17)
C(31)–P(3)–Re	116.5(11)	C(41)–P(4)–Re	114.0(10)
C(32)–P(3)–C(1R3)	96.7(21)	C(42)–P(4)–C(1R4)	98.7(14)
C(32)–P(3)–Re	113.8(10)	C(42)–P(4)–Re	112.7(11)
Re–P(3)–C(1R3)	118.5(19)	Re–P(4)–C(1R4)	121.5(15)

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[6] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1959.

[7] C. Scherringer, *Acta Cryst.*, 1963, **16**, 546.

various least-squares planes. The atom-numbering scheme is shown in Figure 1 and the molecular packing viewed down the *b* axis in Figure 2.

The final N–N bond length [1.154(29) Å] differs considerably from that reported previously [1.276(53) Å],[3] the discrepancy resulting from (*a*) the use of data containing absorption errors and (*b*) an unrealistic weighting scheme (unit weights). Refinement under the same conditions with the Mo-K_α data resulted in R 0.076 and N–N 1.194(40) Å, *i.e.* within 1σ of a double bond, whereas the final value [1.154(29) Å] is within 2σ of a triple bond.

TABLE 4

Equations of least-squares planes through various atoms, in the form $lX + mY + nZ = P$ where X is parallel to a, Y lies in the ab plane, and Z is parallel to c^*. Deviations (Å) of relevant atoms from a plane are given in square brackets

(1): P(1)—(4)

$$-0.4596X - 0.3418Y - 0.8196Z = -5.0538$$

[Re 0.04, P(1) 0.17, P(2) −0.17, P(3) 0.17, P(4) −0.17]

(2): Mo, Cl(1), Cl(2)

$$-0.4236X - 0.3084Y - 0.8503Z = 0.0$$

(3): RB1

$$-0.2391X + 0.8193Y - 0.5209Z = 0.5801$$

(4): RB2

$$-0.0933X - 0.9909Y - 0.0960Z = -3.5347$$

(5): RB3

$$-0.1950X - 0.9803Y - 0.0288Z = -0.6936$$

(6): RB4

$$0.7878X - 0.2148Y - 0.5772Z = -2.6279$$

Angles (°) between planes: (1)–(2) 3.2, (4)–(5) 78.8, (3)–(4) 137.7, (4)–(6) 7.0, (3)–(5) 93.7, (5)–(6) 85.8.

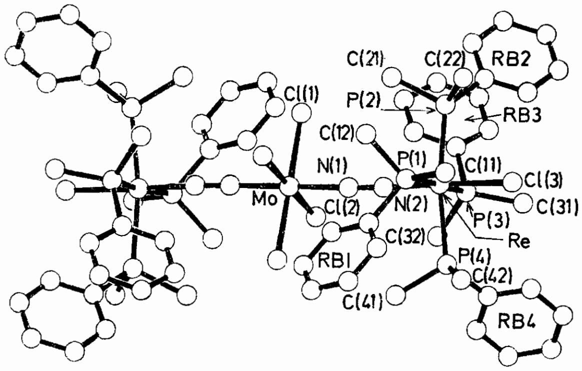

FIGURE 1 Atom-numbering scheme

DISCUSSION

The structure consists of discrete molecules of $[MoCl_4(\mu\text{-}N_2)\{ReCl(PMe_2Ph)_4\}_2]$ in which the two octahedral rhenium groups are related by a centre of symmetry at molybdenum. Comparison of the geometry (Table 3) with that of the related binuclear complex $[MoCl_4(N_2)(OMe)\{ReCl(PMePh)_4\}]$ [1] shows that the two structures are in many respects very similar. To facilitate reference to the two molecules in this discussion the terms ' binuclear ' and ' trinuclear ' are used and, in all numerical comparisons, values for the trinuclear complex appear first.

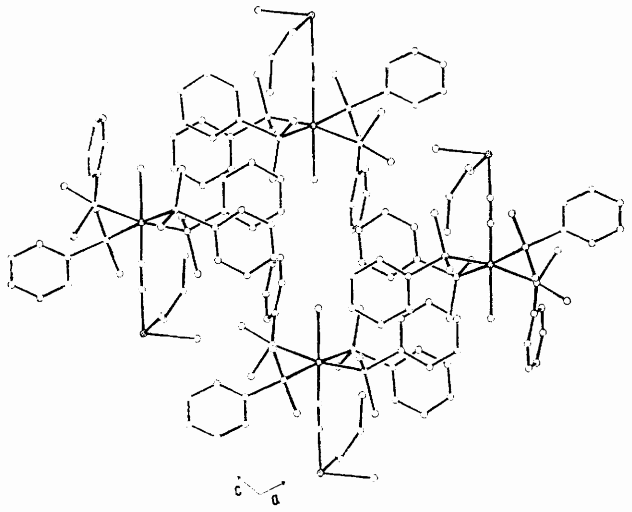

FIGURE 2 Molecular packing viewed down the *b* axis

The weighted averages of the Re–P bonds in the two structures are 2.474(4), and 2.476(3) Å, and the Re–Cl bonds [2.449(7) and 2.418(6) Å] are similar to like bonds in comparable structures (see Table IX of ref. 8). The mean Mo–Cl bonds are 2.413(6) and 2.392 5(5) Å. The molecules differ significantly, however, in the dimensions of the linear Re–N–N–Mo bridges. Although the N–N bonds are not statistically different [1.154(29) and 1.18(3) Å], the Re–N [1.888(21) and 1.815(15) Å] and Mo–N [1.975(20) and 1.900(10) Å] bonds differ by 3σ. These differences can be rationalized in terms of a molecular-orbital scheme extending over the whole bridge system.[9] The binuclear complex has a higher positive charge on the molybdenum atom (Mo^V–Mo^{IV} in the trinuclear complex) resulting in a greater withdrawal of electrons from the N_2 molecular-orbital system, a weaker N–N bond, and more N→Re electron donation. This is consistent with the dinitrogen stretching frequencies observed in the i.r. absorption spectra at 1 800 and 1 660 cm^{-1}).

The equatorial chlorine and phosphorus atoms are further from the eclipsed position in the tri- than in the bi-nuclear complex. The angle through which the phosphorus atoms must be rotated to eclipse the chlorine atoms is *ca.* 18° in the former but closer to 5° in the latter.

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