Inorganica Chimica Acta

LETTER

The Structure of the Face-sharing Bioctahedral Hexachloro(tris-triethylphosphino)-dimolybdenum(III) Molecule

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(Received February 19, 1990)

Recently, the synthesis [1] of the edge-sharing bioctahedral complex $Mo_2Cl_6(PEt_3)_4$ has been reported, eqn. (1). This complex was of interest to

$$2MoCl_3(THF)(PEt_3)_2 \xrightarrow[\text{toluene}]{\text{reflux, 10 min}} Mo_2Cl_6(PEt_3)_4 + 2THF \quad (1)$$

us for it was found to contain a very long Mo–Mo separation ($d_{(MoMo)} = 3.730(1)$ Å) and we were interested in measuring the magnetic susceptibility of this complex over a temperature range. At least three attempts to repeat the published preparation of this edge-sharing complex were conducted. The preliminary results of the magnetic measurements were essentially not consistent with $Mo_2Cl_6(PEt_3)_4$ being the only species present. Fortunately, one of the attempted experiments for this complex afforded two sorts of crystals, one of a brown color (presumably $Mo_2Cl_6(PEt_3)_4$) and one of a blue–green appearance. The UV spectrum in CH_2Cl_2 of the solution which yielded those crystals contained a broad peak at 580 nm. This is similar to that obtained for $Mo_2Cl_4(PEt_3)_4$ [2] and $Mo_2Cl_6(THF)_3$ [3]. We decided to investigate the structure of the blue–green crystals and a crystallographic structure determination** gives the results shown in Fig. 1 and Table 1 where some of the principal dimensions are listed. The geometry of the complex is that of a dimer of the face-sharing bioctahedral type with three bridging chloride ligands. There are two terminal chlorine atoms and one PEt_3 ligand bonded to one Mo atom and one terminal chlorine atom and two PEt_3 ligands on the other Mo atom. The two Mo atoms, one bridging, Cl(1), and terminal, Cl(21), chloride ligands and a terminal P atom, P(11), together with one of the ethyl groups attached to this P atom, C(121) and C(122), are all situated on a crystallographic mirror plane. The Mo–Mo distance of 2.815(4) Å suggests that there is a bonding interaction between the Mo atoms. The average Mo–Cl–Mo angle is 70.0(2)°. As expected the bridging chloride ligand to Mo atom distances are slightly longer than the terminal chloride to Mo atom distances, 2.404(9)–2.492(9) versus 2.36(1) Å, respectively.

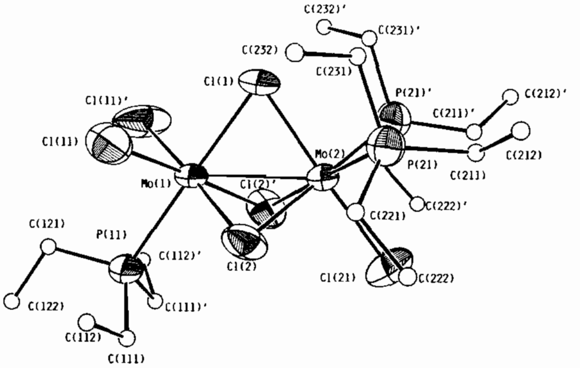

Fig. 1. An ORTEP drawing of $Mo_2Cl_6(PEt_3)_3$. Hydrogen atoms are omitted and carbon atoms are represented by spheres of arbitrary size. Mo, Cl and P atoms are represented by the ellipsoids of thermal displacement drawn at the 50% level.

The most remarkable attribute of this structure is the short Mo to Mo distance of 2.815(4) Å. This is clearly indicative of Mo–Mo bonding whereas the Mo to Mo distance in the edge-sharing bioctahedral complex $Mo_2Cl_6(PEt_3)_4$ was 3.730(1) Å [1] which is indicative of no Mo–Mo bonding. However, it should be pointed out that the distance obtained here is similar to those observed in related face-sharing bioctahedral dimolybdenum complexes which are in the range 2.52 to 2.82 Å [4].

In retrospect it should not be surprising to obtain this complex. An equilibrium involving $W_2Cl_6(PEt_3)_4$ and $W_2Cl_6(PEt_3)_3$ and free PEt_3, eqn. (2), has been previously observed and the structures of both of these tungsten dimers were also discussed [5].

$$W_2Cl_6(PEt_3)_4 \rightleftharpoons W_2Cl_6(PEt_3)_3 + PEt_3 \quad (2)$$

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**The compound crystallizes in space group $P2_1/m$, $a = 11.351(4)$, $b = 17.560(4)$, $c = 7.906(5)$ Å, $\beta = 90.29(4)°$, $V = 1576(1)$ Å^3, $Z = 2$. For 112 refined parameters and 1118 unique reflections having $F_o^2 > 3\sigma(F_o^2)$, the structure was refined to $R = 0.105$ and $R_w = 0.133$.

0020-1693/90/$3.50

TABLE 1. Bond distances and angles for complex $Mo_2Cl_6(PEt_3)_3$[a]

Bond distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance	Atom1	Atom2	Distance
Mo(1)	Mo(2)	2.815(4)	Mo(2)	Cl(21)	2.36(1)	C(111)	C(112)	1.52(6)
Mo(1)	Cl(1)	2.492(9)	Mo(2)	P(21)	2.588(8)	C(121)	C(122)	1.60(8)
Mo(1)	Cl(2)	2.444(8)	P(11)	C(111)	1.84(3)	C(211)	C(212)	1.68(8)
Mo(1)	Cl(11)	2.36(1)	P(11)	C(121)	1.76(5)	C(221)	C(222)	1.57(6)
Mo(1)	P(11)	2.54(1)	P(21)	C(211)	1.84(2)	C(231)	C(232)	1.64(5)
Mo(2)	Cl(1)	2.404(9)	P(21)	C(221)	1.84(3)			
Mo(2)	Cl(2)	2.478(8)	P(21)	C(231)	1.84(2)			

Bond angles (°)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Mo(2)	Mo(1)	Cl(1)	53.4(2)	Mo(1)	Mo(2)	Cl(21)	127.0(3)	C(111)	P(11)	C(121)	109(2)
Mo(2)	Mo(1)	Cl(2)	55.7(2)	Mo(1)	Mo(2)	P(21)	122.7(2)	Mo(2)	P(21)	C(211)	104(1)
Mo(2)	Mo(1)	Cl(11)	126.0(3)	Cl(1)	Mo(2)	Cl(2)	91.4(2)	Mo(2)	P(21)	C(221)	103(1)
Mo(2)	Mo(1)	P(11)	125.2(3)	Cl(1)	Mo(2)	Cl(21)	176.6(4)	Mo(2)	P(21)	C(231)	105(1)
Cl(1)	Mo(1)	Cl(2)	90.2(2)	Cl(1)	Mo(2)	P(21)	88.9(2)	C(211)	P(21)	C(221)	114(2)
Cl(1)	Mo(1)	Cl(11)	91.6(3)	Cl(2)	Mo(2)	Cl(21)	91.0(3)	C(211)	P(21)	C(231)	114(2)
Cl(1)	Mo(1)	P(11)	178.7(3)	Cl(2)	Mo(2)	P(21)	86.9(2)	C(221)	P(21)	C(231)	114(2)
Cl(2)	Mo(1)	Cl(11)	90.1(3)	Cl(21)	Mo(2)	P(21)	88.8(3)	P(11)	C(111)	C(112)	114(2)
Cl(2)	Mo(1)	P(11)	88.9(2)	Mo(1)	Cl(1)	Mo(2)	70.2(2)	P(11)	C(121)	C(122)	110(4)
Cl(11)	Mo(1)	P(11)	89.4(3)	Mo(1)	Cl(2)	Mo(2)	69.8(2)	P(21)	C(211)	C(212)	97(2)
Mo(1)	Mo(2)	Cl(1)	56.4(2)	Mo(1)	P(11)	C(111)	113(1)	P(21)	C(221)	C(222)	107(3)
Mo(1)	Mo(2)	Cl(2)	54.6(2)	Mo(1)	P(11)	C(121)	109(2)	P(21)	C(231)	C(232)	110(2)

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

The complex reported here is essentially a substitution product of the $Mo_2Cl_9^{3-}$ ion [6] and other related dimeric molecules so far published include $(Me_2S)Cl_2Mo(\mu\text{-}Cl)_3MoCl(SMe_2)_2$ [7] verified by ^1H NMR data and analysis, $Mo_2Cl_6(THF)_3$ [3] verified by electronic spectra and analysis and $(Ph_2EtP)Cl_2Mo(\mu\text{-}Cl)_3MoCl(PEtPh_2)_2$ [8] verified by analysis and molecular weight.

We have been informed by Professor R. Poli of the University of Maryland that he has also obtained $Mo_2Cl_6(PEt_3)_3$ in a different crystalline form.

Supplementary Material

Detailed experimental and crystallographic details, lists of structure factors, positional and anisotropic displacement parameters are available on request from author F.A.C.

Acknowledgement

These studies were supported by the National Science Foundation.

References

1. H. D. Mui and R. Poli, *Inorg. Chem.*, *28* (1989) 3609.
2. F. A. Cotton, L. M. Daniels, G. L. Powell, A. J. Kahaian, T. J. Smith and E. F. Vogel, *Inorg. Chim. Acta*, *144* (1988) 109.
3. I. W. Boyd and A. G. Wedd, *Aust. J. Chem.*, (1976) 1829.
4. F. A. Cotton and R. L. Luck, *Inorg. Chem.*, *28* (1989) 182.
5. S. T. Chacon, M. H. Chisholm, W. E. Streib and W. V. D. Sluys, *Inorg. Chem.*, *28* (1989) 6.
6. R. Saillant, R. B. Jackson, W. E. Streib, K. Folting and R. A. D. Wentworth, *Inorg. Chem.*, *10* (1971) 1453.
7. P. M. Boorman, K. J. Moynihan and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, (1982) 899.
8. M. W. Anker, J. Chatt, G. J. Leigh and A. G. Wedd, *J. Chem. Soc., Dalton Trans.*, (1975) 2639.