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Note

Preparation and structure of the face-sharing bioctahedral ion $[Mo_2Cl_8(PEt_3)]^{2-}$ ☆

K. Vidyasagar [1]

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843-3255, USA

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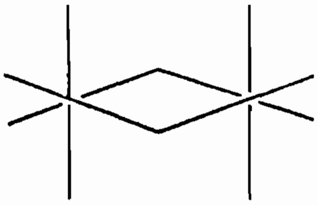
Abstract

The reaction of $[PPh_4][MoCl_4(THF)_2]$ with PEt_3 affords $[PPh_4]_2[Mo_2Cl_8(PEt_3)]$ as a dark red solid with two molecules of CH_2Cl_2 of crystallization. The crystals are triclinic ($P\bar{1}$) with $Z=2$ for a unit cell of the following dimensions: $a=13.168(5)$, $b=21.436(6)$, $c=11.852(4)$ Å, $\alpha=91.16(3)$, $\beta=100.07(3)$, $\gamma=107.22(3)$°, $V=3137$ Å^3. In the face-sharing bioctahedral (FSBO) anion, the Mo–Mo distance is 2.767(2) Å. The structure is compared to a number of other FSBO structures of general formula $Mo_2Cl_{9-n}(PR_3)_n$.

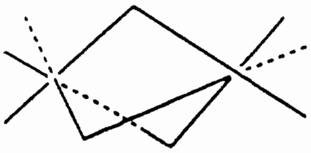
Keywords: Crystal structures; Molybdenum complexes; Chloride complexes; Phosphine complexes; Bioctahedral complexes

1. Introduction

There are two principal types of octahedral structures in which direct metal–metal bonding can be studied, the edge-sharing bioctahedron (ESBO) and the face-sharing bioctahedron (FSBO), shown as I and II.



I



II

Innumerable examples have been prepared and many structurally characterized for most of the transition metals and with a great variety of anionic (e.g., Cl^-, Br^-, I^-) and neutral (e.g., PR_3, SR_2) ligands, usually in mixed sets. $M_2X_6L_3$ species, in either of their isomeric forms, have been very commonly encountered, with the anionic species, $[M_2X_7L_2]^-$, being much rarer. The $[M_2X_8L]^{2-}$ type of anion has seldom been seen and for M = Mo has not heretofore been described. In this note, a structurally characterized example of such a species is reported.

2. Experimental

2.1. Preparation

To a solution of $[PPh_4][MoCl_4(THF)_2]$ (0.15 g, 0.21 mmol) [1] in 10 ml of dichloromethane was added PEt_3 (0.06 ml, 0.41 mmol). The mixture was refluxed with continuous stirring for 3 h to give a mixture of dark red solution and a pink solid. The dark solution was filtered, and the pink solid was washed with 2 × 10 ml of ether. When the washings and the red solution were combined and the solution concentrated, a dark red powder was obtained. This was washed several times with ether and vacuum-dried. Recrystallization was done from CH_2Cl_2/hexane. Yield: 0.1 g, 66%. The recrys-

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☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

[1] Present address: Department of Chemistry, Indian Institute of Technology, Madras 600 036, India.

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tallized material was very homogeneous in appearance and thus it is safe to assume that the crystal examined is representative of the bulk sample. The pink solid was insoluble in all common solvents and hence not characterized.

2.2. X-ray crystallography

A crystal was mounted in a glass capillary filled with a mixture of mineral oil and mother liquor. Pertinent crystallographic data are given in Table 1. Geometric and intensity data were collected with an automated diffractometer by following conventional procedures. Lattice dimensions and Laue symmetry were verified by axial photography. Intensity data, collected by the 2θ–ω method, were reduced by routine procedures. Absorption corrections were applied, based on azimuthal scans of several reflections with the diffractometer angle χ near 90°. The Mo atoms were located by use of a three-dimensional Patterson function. Following this an alternating sequence of least-squares

Table 1
Crystal data for $[PPh_4]_2[Mo_2Cl_8PEt_3]\cdot 2CH_2Cl_2$

Formula	$Mo_2Cl_{12}P_3C_{56}H_{59}$
Formula weight	1442.33
Space group	$P\bar{1}$
a (Å)	13.168(5)
b (Å)	21.436(6)
c (Å)	11.852(4)
α (°)	91.16(3)
β (°)	100.07(3)
γ (°)	107.22(3)
V (Å^3)	3137(4)
Z	2
D_{calc} (g cm^{-3})	1.527
Crystal size (mm)	0.35×0.25×0.20
μ(Mo Kα) (cm^{-1})	10.166
Data collection instrument	Rigaku AFC5R
Radiation monochromated in incident beam (λ, Å)	Mo Kα (0.71073)
Orientation reflections: number, range (2θ) (°)	25, $18.82 \leq 2\theta \leq 28.92$
Temperature (°C)	20±1
Scan method	2θ–ω
Data collection range, 2θ (°)	$4 \leq 2\theta \leq 50$
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	8282, 4528
No. parameters refined	658
Transmission factors (%): maximum, minimum	99.9, 87.8
R[a]	0.056
R_w[b]	0.072
Quality of fit indicator[c]	1.564
Largest shift/e.s.d., final cycle	0.05
Largest peak (e Å^{-3})	0.66

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

Table 2
Positional parameters and their estimated standard deviations for $[PPh_4]_2[Mo_2Cl_8PEt_3]\cdot 2CH_2Cl_2$ [a]

Atom	x	y	z	B (Å^2)
Mo(1)	0.28187(7)	0.18147(5)	0.40431(9)	2.47(2)
Mo(2)	0.11075(8)	0.20594(5)	0.48363(9)	2.59(2)
Cl(1)	0.4693(2)	0.2231(2)	0.5005(3)	3.72(8)
Cl(2)	0.3237(2)	0.2173(1)	0.2213(3)	3.06(7)
Cl(3)	0.3039(2)	0.0753(1)	0.3653(3)	3.15(7)
Cl(4)	0.0900(2)	0.1335(2)	0.3136(3)	3.55(7)
Cl(5)	0.2277(2)	0.1468(2)	0.5899(3)	3.48(7)
Cl(6)	0.2719(2)	0.2923(1)	0.4476(3)	3.69(7)
Cl(7)	0.1160(2)	0.2686(2)	0.6569(3)	3.79(7)
Cl(8)	−0.0008(2)	0.2620(2)	0.3705(3)	3.93(7)
P(3)	−0.0563(3)	0.1267(2)	0.5410(3)	3.81(8)
C(49)	−0.162(1)	0.1681(7)	0.540(1)	5.3(4)
C(50)	−0.271(1)	0.1243(8)	0.568(1)	6.8(5)
C(51)	−0.120(1)	0.0484(7)	0.463(1)	6.3(5)
C(52)	−0.180(1)	0.0558(8)	0.346(1)	6.9(5)
C(53)	−0.036(1)	0.1059(7)	0.697(1)	7.3(5)
C(54)	0.008(1)	0.0520(8)	0.721(1)	7.4(5)
P(1)	0.7271(2)	0.1044(2)	0.9827(3)	2.57(7)
C(1)	0.7500(8)	0.0278(5)	1.0080(9)	3.0(3)
C(2)	0.8149(9)	0.0072(6)	0.940(1)	4.0(3)
C(3)	0.828(1)	−0.0556(6)	0.950(1)	4.8(3)
C(4)	0.775(1)	−0.0972(6)	1.022(1)	4.8(4)
C(5)	0.710(1)	−0.0767(6)	1.091(1)	4.0(3)
C(6)	0.6956(9)	−0.0147(6)	1.082(1)	3.4(3)
C(7)	0.6251(8)	0.0937(6)	0.8553(9)	2.9(3)
C(8)	0.5761(8)	0.1453(6)	0.833(1)	3.7(3)
C(9)	0.4974(9)	0.1377(6)	0.734(1)	4.3(3)
C(10)	0.469(1)	0.0823(7)	0.659(1)	5.0(4)
C(11)	0.514(1)	0.0321(7)	0.681(1)	4.5(4)
C(12)	0.5981(9)	0.0384(6)	0.782(1)	3.6(3)
C(13)	0.6783(8)	0.1348(5)	1.0976(9)	2.7(3)
C(14)	0.5671(8)	0.1063(6)	1.104(1)	3.4(3)
C(15)	0.5260(9)	0.1349(6)	1.187(1)	4.4(3)
C(16)	0.591(1)	0.1868(6)	1.261(1)	4.6(3)
C(17)	0.700(1)	0.2137(6)	1.254(1)	4.8(4)
C(18)	0.7447(9)	0.1871(6)	1.171(1)	3.8(3)
C(19)	0.8537(8)	0.1616(5)	0.966(1)	2.9(3)
C(20)	0.8584(9)	0.2046(5)	0.877(1)	3.2(3)
C(21)	0.958(1)	0.2497(6)	0.868(1)	4.3(3)
C(22)	1.0483(9)	0.2523(7)	0.949(1)	4.8(4)
C(23)	1.043(1)	0.2103(7)	1.038(1)	5.0(4)
C(24)	0.9445(9)	0.1648(6)	1.047(1)	3.7(3)
P(2)	0.7203(2)	0.4079(2)	0.8841(3)	3.18(8)
C(25)	0.8061(8)	0.4043(6)	1.015(1)	3.0(3)
C(26)	0.860(1)	0.3564(6)	1.023(1)	5.0(4)
C(27)	0.923(1)	0.3519(6)	1.131(1)	4.9(4)
C(28)	0.932(1)	0.3928(6)	1.228(1)	4.9(4)
C(29)	0.879(1)	0.4375(7)	1.219(1)	5.1(4)
C(30)	0.815(1)	0.4451(6)	1.111(1)	4.5(3)
C(31)	0.7777(9)	0.3832(6)	0.770(1)	3.4(3)
C(32)	0.713(1)	0.3351(7)	0.685(1)	4.4(3)
C(33)	0.759(1)	0.3151(7)	0.596(1)	5.8(4)
C(34)	0.871(1)	0.3447(7)	0.597(1)	5.1(4)
C(35)	0.931(1)	0.3919(7)	0.681(1)	5.1(4)
C(36)	0.8885(9)	0.4128(7)	0.772(1)	4.4(3)
C(37)	0.7118(9)	0.4910(6)	0.868(1)	3.9(3)
C(38)	0.772(1)	0.5318(6)	0.797(1)	5.0(4)
C(39)	0.764(1)	0.5964(7)	0.793(1)	7.1(5)
C(40)	0.704(1)	0.6177(6)	0.859(2)	6.6(5)
C(41)	0.643(1)	0.5779(8)	0.928(2)	7.6(5)
C(42)	0.645(1)	0.5116(7)	0.932(1)	5.8(4)
C(43)	0.5854(9)	0.3542(6)	0.882(1)	3.8(3)
C(44)	0.569(1)	0.3135(6)	0.974(1)	4.7(4)
C(45)	0.460(1)	0.2727(6)	0.967(1)	5.2(4)
C(46)	0.378(1)	0.2694(7)	0.875(1)	5.0(4)
C(47)	0.400(1)	0.3099(7)	0.785(1)	5.7(4)

(continued)

Table 2 (*continued*)

Atom	x	y	z	B (Å^2)
C(48)	0.5036(9)	0.3537(7)	0.789(1)	4.2(3)
C(55)	0.223(1)	0.4250(8)	0.556(2)	8.8(5)
Cl(9)	0.1435(4)	0.4745(3)	0.5002(4)	9.1(2)
Cl(10)	0.2661(5)	0.4438(2)	0.7051(6)	11.0(2)
C(56)	0.520(1)	0.3704(9)	0.371(2)	9.2(6)
Cl(11)	0.6189(5)	0.3759(3)	0.2962(6)	13.9(2)
Cl(12)	0.5391(5)	0.4318(3)	0.4687(7)	17.9(2)

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

refinement cycles and difference Fourier maps was used to find the remaining non-hydrogen atoms. Refinement was carried out with the SHELX-76 program package. The final atomic positional parameters are listed in Table 2. Hydrogen atoms were omitted from the refined model.

3. Results and discussion

The cations, the anion and the CH_2Cl_2 molecules all reside on general positions in the triclinic, centered unit cell. Refinement of the structure was straightforward; it revealed $P(C_6H_5)_4^+$ ions and CCl_2 units of the expected dimensions and a dinuclear anion with the structure shown in Fig. 1 and the dimensions listed in Table 3.

It is not clear why the monophosphine anion was the only isolated product (in 66% yield) of the reaction, since the mole ratio of the reactants was such (P:Mo = 2:1) as to favor a product containing more phosphine. Indeed it had been intended that a mononuclear diphosphine-substituted complex, $[MoCl_4(PEt_3)_2]^-$ would result. In fact, the $[MoCl_4(PEt_3)_2]^-$ ion has been characterized in solution by NMR [2a] and the present author has isolated it as its PPh_4^+ salt and characterized it crystallographically [2b].

Turning now to the structural details of the $[Mo_2Cl_8(PEt_3)]^{2-}$ anion, it shows evidence of a direct attraction between the metal atoms, although not a

Table 3

Selected bond distances (Å) and angles (°) for $[PPh_4]_2[Mo_2Cl_8PEt_3]\cdot 2CH_2Cl_2$ [a]

(a) Bond distances

Atom1	Atom2	Distance	Atom1	Atom2	Distance	Atom1	Atom2	Distance
Mo(1)	Cl(1)	2.420(3)	Mo(2)	Cl(8)	2.414(4)	P(1)	C(13)	1.793(12)
Mo(1)	Cl(2)	2.415(3)	Mo(2)	P(3)	2.557(3)	P(1)	C(19)	1.800(10)
Mo(1)	Cl(3)	2.422(3)	P(3)	C(49)	1.85(2)	P(2)	C(25)	1.775(11)
Mo(1)	Cl(4)	2.463(3)	P(3)	C(51)	1.792(14)	P(2)	C(31)	1.804(14)
Mo(1)	Cl(5)	2.490(3)	P(3)	C(53)	1.904(15)	P(2)	C(37)	1.828(13)
Mo(1)	Cl(6)	2.466(3)	C(49)	C(50)	1.56(2)	P(2)	C(43)	1.803(11)
Mo(2)	Cl(4)	2.445(3)	C(51)	C(52)	1.50(2)	C(55)	Cl(9)	1.76(2)
Mo(2)	Cl(5)	2.470(3)	C(53)	C(54)	1.45(3)	C(55)	Cl(10)	1.76(2)
Mo(2)	Cl(6)	2.477(3)	P(1)	C(1)	1.776(13)	C(56)	Cl(11)	1.68(2)
Mo(2)	Cl(7)	2.410(3)	P(1)	C(7)	1.798(10)	C(56)	Cl(12)	1.67(2)

(b) Bond angles

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Cl(1)	Mo(1)	Cl(2)	92.8(1)	Cl(4)	Mo(2)	P(3)	90.6(1)	C(51)	P(3)	C(53)	103.5(7)
Cl(1)	Mo(1)	Cl(3)	90.5(1)	Cl(5)	Mo(2)	Cl(6)	90.7(1)	P(3)	C(49)	C(50)	115.(1)
Cl(1)	Mo(1)	Cl(4)	176.6(1)	Cl(5)	Mo(2)	Cl(7)	91.4(1)	P(3)	C(51)	C(52)	111.(1)
Cl(1)	Mo(1)	Cl(5)	90.1(1)	Cl(5)	Mo(2)	Cl(8)	176.9(1)	P(3)	C(53)	C(54)	116.(1)
Cl(1)	Mo(1)	Cl(6)	86.0(1)	Cl(5)	Mo(2)	P(3)	90.6(1)	C(1)	P(1)	C(7)	108.5(5)
Cl(2)	Mo(1)	Cl(3)	92.1(1)	Cl(6)	Mo(2)	Cl(7)	89.5(1)	C(1)	P(1)	C(13)	112.6(6)
Cl(2)	Mo(1)	Cl(4)	89.9(1)	Cl(6)	Mo(2)	Cl(8)	88.3(1)	C(1)	P(1)	C(19)	107.4(5)
Cl(2)	Mo(1)	Cl(5)	176.2(1)	Cl(6)	Mo(2)	P(3)	172.8(1)	C(7)	P(1)	C(13)	107.2(5)
Cl(2)	Mo(1)	Cl(6)	87.3(1)	Cl(7)	Mo(2)	Cl(8)	91.5(1)	C(7)	P(1)	C(19)	111.5(5)
Cl(3)	Mo(1)	Cl(4)	87.3(1)	Cl(7)	Mo(2)	P(3)	83.4(1)	C(13)	P(1)	C(19)	109.7(5)
Cl(3)	Mo(1)	Cl(5)	90.3(1)	Cl(8)	Mo(2)	P(3)	90.8(1)	C(25)	P(2)	C(31)	107.1(6)
Cl(3)	Mo(1)	Cl(6)	176.4(1)	Mo(1)	Cl(4)	Mo(2)	68.65(8)	C(25)	P(2)	C(37)	110.7(6)
Cl(4)	Mo(1)	Cl(5)	87.2(1)	Mo(1)	Cl(5)	Mo(2)	67.82(9)	C(25)	P(2)	C(43)	110.0(6)
Cl(4)	Mo(1)	Cl(6)	96.2(1)	Mo(1)	Cl(6)	Mo(2)	68.10(8)	C(31)	P(2)	C(37)	110.3(6)
Cl(5)	Mo(1)	Cl(6)	90.5(1)	Mo(2)	P(3)	C(49)	109.2(4)	C(31)	P(2)	C(43)	110.9(6)
Cl(4)	Mo(2)	Cl(5)	88.1(1)	Mo(2)	P(3)	C(51)	119.9(6)	C(37)	P(2)	C(43)	107.9(6)
Cl(4)	Mo(2)	Cl(6)	96.4(1)	Mo(2)	P(3)	C(53)	114.7(5)	Cl(9)	C(55)	Cl(10)	109.(1)
Cl(4)	Mo(2)	Cl(7)	174.0(1)	C(49)	P(3)	C(51)	107.4(7)	Cl(11)	C(56)	Cl(12)	117.(1)
Cl(4)	Mo(2)	Cl(8)	89.2(1)	C(49)	P(3)	C(53)	100.2(8)				

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

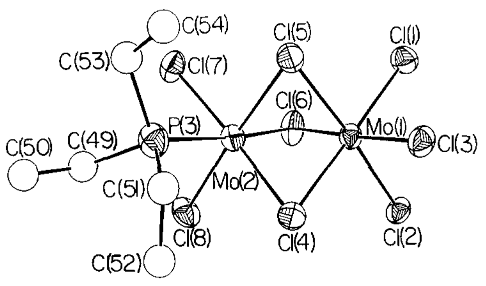

Fig. 1. $[Mo_2Cl_8(PEt_3)]^{2-}$ anion. The ORTEP drawing shows all atoms of the Mo_2Cl_8P core at the 50% probability level and the carbon atoms as spheres of arbitrary radius.

Table 4
Species of the type $Mo_2Cl_{9-n}L_n$ with three μ-Cl groups

Anion or molecule	Mo–Mo (Å)	Ref.	Notes
$[Mo_2Cl_8(PEt_3)]^{2-}$	2.767(2)	this work	
syn-$[Mo_2Cl_7(PMe_3)_2]^{2-}$	2.694(3)	[3]	a
	2.713(2)	[3]	a
	2.763(2)	[3]	a
gauche-$[Mo_2Cl_7(PMe_3)_2]^-$	2.7171(3)	[3]	
gauche-$[Mo_2Cl_7(SMe_3)_2]^-$	2.746(9)	[4]	
1,2,6-$Mo_2Cl_6(PMe_2Ph)_3$	2.6582(5)	[5]	
1,2,6-$Mo_2Cl_6(PEt_3)_3$	2.753(2)	[5]	b
	2.815(4)	[6]	b
1,2,6-$Mo_2Cl_6(C_4H_8S)_3$	2.690(1)	[7]	c

[a] There are two isomorphs, one of which has two crystallographically independent molecules.

[b] There are two isomorphs.

[c] C_4H_8S = tetrahydrothiophene.

powerful one. The Mo–Mo distance is 2.767(2) Å, the mean value of the Mo–(μ-Cl)–Mo angles is 68.2(2)° and the (μ-Cl)–Mo–(μ-Cl) angles have a mean value of 91.5°. There is no marked evidence of a *trans* influence or other electronic effect from the PEt_3 substituent. The *trans* Mo(2)–Cl(6) bridge bond is not significantly longer than the average of the other five bridge bonds, nor are the two Mo(2)–Cl distances significantly longer than the three Mo(1)–Cl distances.

Finally, it is pertinent to compare the present compound to previously reported FSBO dimolybdenum compounds containing as ligands Cl^- ions and one or more R_3P or R_2S neutral ligands. The pertinent data are given in Table 4. It is clear that there is moderate variability in the Mo–Mo bond length, the range being 2.658–2.815 Å, with the present value lying slightly above the midpoint of the range. There is no trend as a function of n in the general formula $Mo_2Cl_{9-n}L_n$.

4. Supplementary material

Full tables of bond distances and angles, a table of anisotropic thermal displacement parameters, as well as observed and calculated structure factors are available from F.A. Cotton at Texas A&M University.

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