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The Structure of an Iodide Complex of the Type $Mo_2X_4(LL)_2$ Exhibiting Two Different Rotational Geometries in the Solid State

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Abstract

The compound which we have prepared by reacting $Mo_2(\mu\text{-dppm})_2Cl_4$ with NaI in acetone and which has a stoichiometry close to that for $Mo_2(dppm)_2I_4$, forms thin plates when crystals are grown from $CH_2Cl_2-CH_3OH$. It crystallizes in the triclinic space group $P\bar{1}$ with the following unit cell dimensions: $a = 14.931(6)$, $b = 22.960(7)$, $c = 12.794(4)$ Å, $\alpha = 100.30(2)$, $\beta = 114.76(3)$, $\gamma = 93.90(3)°$, $V = 3868(6)$ Å^3, and $Z = 3$. The structure was refined to $R = 0.088$ ($R_w = 0.125$) for 6430 data with $F^2 > 3.0\sigma(F^2)$. There are two independent sets of molecules in the unit cell both of which possess a structure in which the dppm ligands are present in an intramolecular bridging mode with a transoid disposition to one another. One molecule, which resides on a crystallographic inversion center, has an apparent Mo–Mo distance of 2.178(3) Å and an eclipsed rotational geometry, while the two symmetry related molecules in general positions have a Mo–Mo distance of 2.152(2) Å and a twist angle (*i.e.* average torsional angle, χ) of 17[2] Å. This is one of the first instances where two quite different rotational geometries are present in the solid state for a molecule of this general type, a result which indicates that crystal packing forces can play an important role in determining the exact rotational geometry. There is crystallographic and chemical evidence that these crystals contain small amounts of chloride and that the true composition may actually be $Mo_2(dppm)_2I_{4-x}Cl_x$, with $x \sim 0.2$.

Introduction

We have recently carried out a detailed study of the reactions of the quadruply bonded dimolybdenum(II) complexes $Mo_2(\mu\text{-dppm})_2X_4$ (X = Cl, Br, or I) with isocyanide ligands [1]. In the course of this work, we prepared the iodo derivative $Mo_2(\mu\text{-dppm})_2I_4$ which we proposed bore a close structural relationship to the analogous chloride and bromide complexes (at least on the basis of its spectroscopic properties). In view of previous structure determinations on $Mo_2(\mu\text{-dppm})_2Cl_4$ [2] and $Mo_2(\mu\text{-dppm})_2Br_4$ [3] and the current interest in understanding the factors which influence the rotational geometry in molecules of the type $M_2X_4(LL)_2$ (X = halogen; LL = an intramolecular bridging phosphine (or arsine) ligand) [4, 5], we have determined the crystal structure of this compound. This is one of the first reports on the structure of a multiply bonded iodo derivative of the type $Mo_2I_4L_4$, although single crystal X-ray structure determinations have been carried out on the salts $(LH)_2Mo_2I_6(H_2O)_2$ (L = pyridine or picoline) [6, 7].†

Experimental

A sample of the material formulated as the acetone solvate $Mo_2(\mu\text{-dppm})_2I_4\cdot1.5C_3H_6O$ was available from an earlier study [1]. Crystals suitable for an X-ray diffraction study were grown by carefully layering methanol over a dichloromethane solution of the complex. Slow diffusion afforded crystals of the complex as thin plates.

X-ray Structure Determination and Solution

The structure solution, which was carried out on the assumption that the crystals were of stoichiometry $Mo_2(\mu\text{-dppm})_2I_4$, was determined by following the procedures described below. The crystal parameters and information relating to data collection and structure refinement are listed in Table I.

A single crystal of dimensions 0.25 × 0.24 × 0.01 mm was mounted on a glass fiber with epoxy resin. The crystal was indexed, and data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and a standard-focus

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†Structure determinations have now been completed on another crystalline form of $Mo_2(\mu\text{-dppm})_2I_4$ and on β-$Mo_2(dppe)_2I_4$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (see refs. 9 and 12).

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TABLE I. Crystallographic Data and Data Collection Parameters

Formula	$I_4Mo_2P_4C_{50}H_{44}$
Formula weight	1468.30
Space group	$P\bar{1}$
a (Å)	14.931(6)
b (Å)	22.960(7)
c (Å)	12.794(4)
α (deg)	100.30(2)
β (deg)	114.76(3)
γ (deg)	93.90(3)
V (Å^3)	3868(6)
Z	3
D_c (g cm^{-3})	1.891
Crystal dimensions (mm)	0.25 × 0.24 × 0.01
Temperature (°C)	24.0
Radiation (wavelength)	Mo Kα (0.71073 Å)
Monochromator	graphite
Linear absorption coefficient (cm^{-1})	29.99
Absorption correction applied	empirical[a]
Diffractometer	Enraf-Nonius CAD4
Scan method	θ-2θ
h, k, l limits	0 to 15, −21 to 21, −13 to 13
2θ Range (deg)	4.00–45.00
Scan width (deg)	1.00 + 0.35 tan(θ)
Take-off angle (deg)	5.00
Programs used	Enraf-Nonius SDP
F(000)	2100.0
Unique data	10165
Data with $I > 3.0\sigma(I)$	6430
Number of variables	811
Largest shift/e.s.d. in final cycle	3.26
R[b]	0.088
R_w[c]	0.125
Goodness of fit[d]	2.683

[a] See ref. 8. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [d] Goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

molybdenum X-ray tube. The takeoff angle was 5.0°. The centered settings of 25 reflections with $22° < 2\theta < 28°$ were used to determine the cell constants (Table I). The structure was refined in the space group $P\bar{1}$. Four octants, *viz.*, (h, k, l), $(h, \bar{k}, l)$, $(h, k, \bar{l})$, and $(h, \bar{k}, \bar{l})$ were collected at 24.0 °C with use of the θ–2θ scan technique to a maximum value for 2θ of 45°. The vertical aperture was 4.0 mm, and the horizontal aperture was determined by (1.50 + 1.00 tan θ) mm. The scan width was calculated from (0.60 + 0.35 tan θ)°. After a pre-scan of the peak the final scan rate chosen was that required to give an intensity 50 times greater than $\sigma(I)$ with the restriction that the peak be scanned in no more than 60 s. Of the 10 165 unique reflections collected only the 6430 reflections with $F^2 > 3.0\sigma(F^2)$ were used during refinement. The value of the p factor used in the weighting scheme to calculate $\sigma(F)$ was 0.07. Three standard reflections were monitored after every hour of beam exposure during data collection and displayed no systematic variation in intensity.

The crystals were poorly shaped irregular plates with faces that were not of high quality. The absorption coefficient was 29.99 cm^{-1}. An analytical absorption correction was applied, but did not prove satisfactory. Consequently, an empirical absorption correction was used [8].

All calculations were performed on a PDP 11/34 computer using the Enraf-Nonius structure determination package. Corrections for anomalous dispersion were applied to all atoms. The least-squares program minimized the function $w(|F_o| - |F_c|)^2$, where the weighting factor $w = 1/\sigma^2(F_o)$.

From the volume of the cell it was determined that $Z = 3$. Since in the space group $P\bar{1}$ there are two general positions, at least one molecule was required to be located in a special position. The location of the molybdenum atoms was found using direct methods and led to a solution with two molecules in symmetry related general positions and a third molecule in a special position. All other atoms were located in a difference Fourier map after refinement of the scale factor and the molybdenums. Further refinements of atomic positions and anisotropic thermal parameters resulted in final residuals of $R = 0.088$ and $R_w = 0.125$. In spite of these rather high residuals the final difference Fourier map displayed no peaks of chemical significance. Hydrogen atoms were not included in the final least-squares refinement. Table II lists the atomic positional parameters and their errors, excluding the phenyl carbon atoms. Tables III and IV list the intramolecular bond distances and angles (excluding the phenyl rings). Tables listing thermal parameters (S1), and bond distances (S2) and bond angles (S3) associated with the phenyl rings are available as supplementary material, as well as figures (Figures S1 and S2) which show the full atomic numbering scheme.

Results and Discussion

The indications from a previous study detailing the preparation and characterization of $Mo_2(\mu\text{-dppm})_2I_4$ [1] are that this complex possesses a close relationship to its structurally characterized chloride and bromide analogues [2, 3]. We were able to grow the green iodide complex as thin plates from a $CH_2Cl_2-CH_3OH$ solution. While the crystal quality was relatively poor so that we were unable to carry out an especially accurate structure determination, nonetheless, the results are of sufficiently novelty and importance to warrant their publication at this time. Subsequently, the crystal structure of a different crystalline form of $Mo_2(\mu\text{-dppm})_2I_4$ that was grown from toluene has been determined [9].

The close structural similarity between $Mo_2(\mu\text{-dppm})_2I_4$ and its chloride and bromide analogues is confirmed in the present work. The dppm ligands are present in the usual intramolecular bridging mode with a transoid disposition to one another. Of special note is the existence of two independent types of molecule in the unit cell, one molecule resides on a center of symmetry while two others are in symmetry related general positions. The structural parameters

TABLE II. Positional Parameters for Non-hydrogen Atoms and their Estimated Standard Deviations[a]

Atom	*x*	*y*	*z*	*B* (Å^2)
Mo(1)	0.9329(1)	0.31884(9)	0.6236(1)	2.54(4)
Mo(2)	1.0740(1)	0.33831(9)	0.7786(1)	2.57(4)
Mo(3)	0.5302(1)	0.0306(1)	0.0867(2)	3.48(5)
I(1)	0.8761(1)	0.19963(8)	0.5230(1)	4.22(4)
I(2)	1.0913(1)	0.45555(8)	0.8856(2)	5.11(5)
I(3)	0.8748(1)	0.42400(8)	0.5679(1)	5.20(5)
I(4)	1.1633(1)	0.23954(8)	0.8192(1)	4.25(4)
I(5)	0.4428(2)	−0.0005(1)	0.2188(2)	7.64(6)
I(6)	0.6577(1)	0.12016(9)	0.0829(2)	6.40(6)
P(1)	1.0077(4)	0.3234(3)	0.4790(5)	3.1(1)
P(2)	1.1935(4)	0.3804(3)	0.6928(5)	3.3(2)
P(3)	0.8115(4)	0.3270(3)	0.7312(5)	3.3(2)
P(4)	1.0033(4)	0.3188(3)	0.9205(4)	2.9(1)
P(5)	0.5984(4)	−0.1007(3)	−0.0267(5)	3.5(2)
P(6)	0.6717(5)	−0.0273(3)	0.2167(6)	4.3(2)
C(1B)	1.106(1)	0.388(1)	0.544(2)	3.0(6)
C(2B)	0.894(1)	0.357(1)	0.889(2)	3.4(6)
C(3B)	0.627(2)	−0.104(1)	0.127(2)	3.6(6)
C(111)	0.917(1)	0.335(1)	0.338(2)	3.3(5)
C(112)	0.927(2)	0.390(1)	0.301(2)	4.0(6)
C(113)	0.847(2)	0.393(1)	0.188(2)	5.3(7)
C(114)	0.771(2)	0.346(1)	0.120(2)	4.8(7)
C(115)	0.761(2)	0.295(1)	0.161(2)	4.3(6)
C(116)	0.835(2)	0.289(1)	0.264(2)	4.6(7)
C(121)	1.065(2)	0.265(1)	0.428(2)	3.9(6)
C(122)	1.102(2)	0.222(1)	0.496(2)	3.3(6)
C(123)	1.154(2)	0.182(1)	0.464(2)	4.1(6)
C(124)	1.170(2)	0.178(1)	0.361(2)	5.3(8)
C(125)	1.137(2)	0.224(1)	0.300(2)	5.3(8)
C(126)	1.082(2)	0.267(1)	0.330(2)	4.1(7)
C(211)	1.289(1)	0.338(1)	0.675(2)	3.9(6)
C(212)	1.304(2)	0.330(1)	0.574(2)	5.5(8)
C(213)	1.385(2)	0.302(1)	0.564(3)	7.0(9)
C(214)	1.447(2)	0.286(2)	0.665(3)	8(1)

(continued)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)
C(215)	1.438(2)	0.294(1)	0.776(3)	7.2(9)
C(216)	1.359(2)	0.323(1)	0.773(2)	5.8(8)
C(221)	1.275(1)	0.453(1)	0.766(2)	3.6(6)
C(222)	1.278(2)	0.493(1)	0.692(3)	6.5(9)
C(223)	1.348(2)	0.548(2)	0.755(3)	10(1)
C(224)	1.405(3)	0.562(2)	0.874(4)	10(1)
C(225)	1.398(2)	0.524(2)	0.944(4)	8(1)
C(226)	1.322(2)	0.470(1)	0.884(3)	6.5(9)
C(311)	0.728(2)	0.259(1)	0.717(2)	4.2(7)
C(312)	0.710(2)	0.247(1)	0.811(2)	4.2(6)
C(313)	0.651(2)	0.195(1)	0.801(3)	5.8(8)
C(314)	0.600(2)	0.155(1)	0.688(3)	7(1)
C(315)	0.616(2)	0.170(1)	0.592(3)	6.1(9)
C(316)	0.679(2)	0.222(1)	0.606(2)	4.3(7)
C(321)	0.722(2)	0.379(1)	0.701(2)	3.7(6)
C(322)	0.283(2)	0.572(1)	0.215(2)	6.2(9)
C(323)	0.348(2)	0.537(1)	0.240(3)	9(1)
C(324)	0.427(2)	0.548(1)	0.360(3)	8(1)
C(325)	0.431(2)	0.591(2)	0.451(3)	8(1)
C(326)	0.353(2)	0.625(1)	0.420(2)	6.5(9)
C(411)	1.099(2)	0.352(1)	1.076(1)	3.0(5)
C(412)	1.179(2)	0.326(1)	1.122(2)	4.5(7)
C(413)	1.254(2)	0.354(1)	1.236(2)	6.5(9)
C(414)	1.233(2)	0.404(1)	1.297(2)	6.1(9)
C(415)	1.157(2)	0.428(2)	1.255(2)	7(1)
C(416)	1.079(2)	0.403(1)	1.142(2)	3.7(6)
C(421)	0.956(2)	0.244(1)	0.929(2)	3.6(6)
C(422)	0.938(2)	0.242(1)	1.027(2)	3.7(6)
C(423)	0.893(2)	0.188(1)	1.033(2)	5.2(7)
C(424)	0.868(2)	0.137(1)	0.939(2)	4.5(6)
C(425)	0.888(2)	0.140(1)	0.848(3)	5.6(8)
C(426)	0.934(2)	0.195(1)	0.838(2)	3.9(7)
C(511)	0.721(2)	−0.088(1)	−0.024(2)	4.0(6)
C(512)	0.769(2)	−0.135(1)	−0.038(2)	4.7(7)
C(513)	0.868(2)	−0.122(1)	−0.027(2)	6.3(9)
C(514)	0.912(2)	−0.070(2)	−0.015(4)	11(1)
C(515)	0.863(2)	−0.017(1)	0.014(4)	10(1)
C(516)	0.765(2)	−0.030(1)	−0.002(3)	8(1)
C(521)	0.552(2)	−0.179(1)	−0.110(2)	3.9(6)
C(522)	0.549(3)	−0.225(1)	−0.060(3)	8(1)
C(523)	0.528(3)	−0.284(2)	−0.128(3)	10(1)
C(524)	0.477(3)	−0.292(1)	−0.252(3)	9(1)
C(525)	0.502(4)	−0.246(2)	−0.301(3)	12(2)
C(526)	0.526(3)	−0.188(2)	−0.233(3)	9(1)
C(611)	0.673(2)	−0.036(1)	0.357(2)	5.8(7)
C(612)	0.651(2)	−0.090(1)	0.384(2)	6.4(8)
C(613)	0.650(3)	−0.089(2)	0.491(3)	10(1)
C(614)	0.690(2)	−0.031(2)	0.578(2)	12(1)
C(615)	0.702(2)	0.018(2)	0.545(3)	12(1)
C(616)	0.703(2)	0.021(2)	0.442(2)	8(1)
C(621)	0.806(2)	−0.013(1)	0.264(2)	5.1(8)
C(622)	0.868(2)	−0.059(2)	0.288(3)	7.2(9)
C(623)	0.970(2)	−0.041(2)	0.331(3)	8(1)
C(624)	1.008(3)	0.018(2)	0.345(5)	12(2)
C(625)	0.958(3)	0.060(2)	0.338(4)	15(2)
C(626)	0.844(2)	0.047(2)	0.294(4)	9(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

for these molecules are given in Tables III and IV; Mo(1)–Mo(2) and Mo(3)–Mo(3) signify the dimolybdenum units in general and special positions, respectively. ORTEP representations of these two molecules are shown in Figs. 1 and 2.

Both Mo–Mo bond distances found in this structure (2.152(2) and 2.178(3) Å) are somewhat longer than those previously determined for $Mo_2(\mu\text{-dppm})_2Cl_4\cdot 2(CH_3)_2CO$ and $Mo_2(\mu\text{-dppm})_2Br_4\cdot 2THF$ (2.138(1) Å) [2, 3], as well as for the salts of the $[Mo_2I_6(H_2O)_2]^{2-}$ anion [6, 7]. Nonetheless, these values are perfectly consistent with a quadruply bonded dimolybdenum(II) unit [10, 11]. The Mo–I and Mo–P bond lengths (Table III) average to 2.72 [1] and 2.61[3] Å,* respectively. As can be seen in Table V, where structural parameters are compared

TABLE III. Some Important Bond Distances (Å)[a]

Mo(1)–Mo(2)	2.152(2)	P(1)–C(121)	1.81(2)
Mo(1)–I(1)	2.717(2)	P(2)–C(1B)	1.86(1)
Mo(1)–I(3)	2.733(2)	P(2)–C(211)	1.85(2)
Mo(1)–P(1)	2.543(4)	P(2)–C(221)	1.83(2)
Mo(1)–P(3)	2.694(4)	P(3)–C(2B)	1.83(1)
Mo(2)–I(2)	2.735(2)	P(3)–C(311)	1.87(2)
Mo(2)–I(4)	2.728(2)	P(3)–C(321)	1.82(2)
Mo(2)–P(2)	2.664(4)	P(4)–C(2B)	1.83(1)
Mo(2)–P(4)	2.540(4)	P(4)–C(411)	1.87(1)
Mo(3)–Mo(3)	2.178(3)	P(4)–C(421)	1.86(2)
Mo(3)–I(5)	2.688(2)	P(5)–C(3B)	1.84(1)
Mo(3)–I(6)	2.726(2)	P(5)–C(511)	1.82(2)
Mo(3)–P(5)	2.548(5)	P(5)–C(521)	1.85(1)
Mo(3)–P(6)	2.688(5)	P(6)–C(3B)	1.84(1)
P(1)–C(1B)	1.82(1)	P(6)–C(611)	1.83(2)
P(1)–C(111)	1.82(1)	P(6)–C(621)	1.82(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE IV. Selected Bond Angles (deg)[a]

Mo(2)–Mo(1)–I(1)	112.45(6)	I(5)–Mo(3)–I(6)	141.83(8)
Mo(2)–Mo(1)–I(3)	109.16(6)	I(5)–Mo(3)–P(5)	86.2(2)
Mo(2)–Mo(1)–P(1)	95.2(2)	I(5)–Mo(3)–P(6)	81.9(1)
Mo(2)–Mo(1)–P(3)	98.6(1)	I(6)–Mo(3)–P(5)	84.9(2)
I(1)–Mo(1)–I(3)	137.72(6)	I(6)–Mo(3)–P(6)	96.4(1)
I(1)–Mo(1)–P(1)	86.5(1)	P(5)–Mo(3)–P(6)	162.2(1)
I(1)–Mo(1)–P(3)	96.6(1)	Mo(1)–P(1)–C(1B)	107.1(5)
I(3)–Mo(1)–P(1)	82.6(2)	Mo(1)–P(1)–C(111)	112.4(5)
I(3)–Mo(1)–P(3)	84.2(1)	Mo(1)–P(1)–C(121)	125.3(5)
P(1)–Mo(1)–P(3)	163.4(1)	C(1B)–P(1)–C(111)	106.9(7)
Mo(1)–Mo(2)–I(2)	105.62(6)	C(1B)–P(1)–C(121)	103.5(7)
Mo(1)–Mo(2)–I(4)	113.16(6)	C(111)–P(1)–C(121)	100.2(7)
Mo(1)–Mo(2)–P(2)	100.6(2)	Mo(2)–P(2)–C(1B)	104.1(5)
Mo(1)–Mo(2)–P(4)	95.9(2)	Mo(2)–P(2)–C(211)	121.6(6)
I(2)–Mo(2)–I(4)	140.62(6)	Mo(2)–P(2)–C(221)	120.9(6)
I(2)–Mo(2)–P(2)	85.3(2)	C(1B)–P(2)–C(211)	107.2(7)
I(2)–Mo(2)–P(4)	82.9(1)	C(1B)–P(2)–C(221)	105.6(7)
I(4)–Mo(2)–P(2)	94.0(1)	C(211)–P(2)–C(221)	96.2(7)
I(4)–Mo(2)–P(4)	86.5(1)	Mo(1)–P(3)–C(2B)	105.5(5)
P(2)–Mo(2)–P(4)	161.8(1)	Mo(1)–P(3)–C(311)	120.2(6)
Mo(3)–Mo(3)–I(5)	111.7(1)	Mo(1)–P(3)–C(321)	120.0(5)
Mo(3)–Mo(3)–I(6)	106.01(9)	C(2B)–P(3)–C(311)	107.8(8)
Mo(3)–Mo(3)–P(5)	95.6(1)	C(2B)–P(3)–C(321)	102.3(7)
Mo(3)–Mo(3)–P(6)	101.2(1)	C(311)–P(3)–C(321)	99.4(7)
Mo(2)–P(4)–C(2B)	106.9(6)	C(511)–P(5)–C(521)	102.3(8)
Mo(2)–P(4)–C(411)	109.4(5)	Mo(3)–P(6)–C(3B)	101.3(5)
Mo(2)–P(4)–C(421)	125.2(6)	Mo(3)–P(6)–C(611)	116.6(6)
C(2B)–P(4)–C(411)	108.9(7)	Mo(3)–P(6)–C(621)	128.3(7)
C(2B)–P(4)–C(421)	102.7(8)	C(3B)–P(6)–C(611)	102.2(9)
C(411)–P(4)–C(421)	103.0(7)	C(3B)–P(6)–C(621)	106.8(8)
Mo(3)–P(5)–C(3B)	107.3(6)	C(611)–P(6)–C(621)	98.8(8)
Mo(3)–P(5)–C(511)	123.6(5)	P(1)–C(1B)–P(2)	107.3(8)
Mo(3)–P(5)–C(521)	114.3(5)	P(3)–C(2B)–P(4)	105.8(7)
C(3B)–P(5)–C(511)	103.5(8)	P(5)–C(3B)–P(6)	107.1(8)
C(3B)–P(5)–C(521)	103.9(7)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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*Average values are arithmetic means. Numbers in brackets are the weighted deviations.

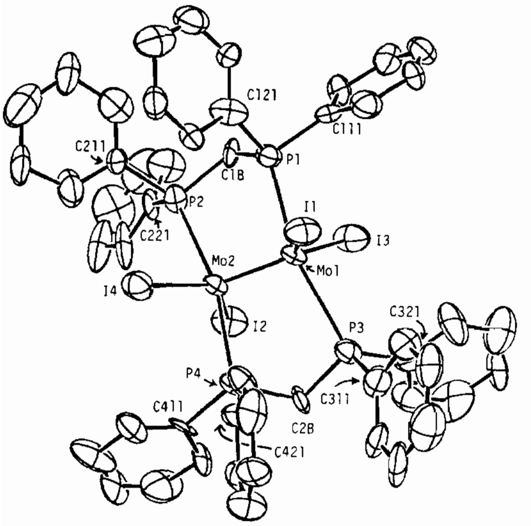

Fig. 1. ORTEP view of the molecules of $Mo_2(\mu\text{-dppm})_2I_4$ located in general positions. The thermal ellipsoids are drawn at the 50% probability level.

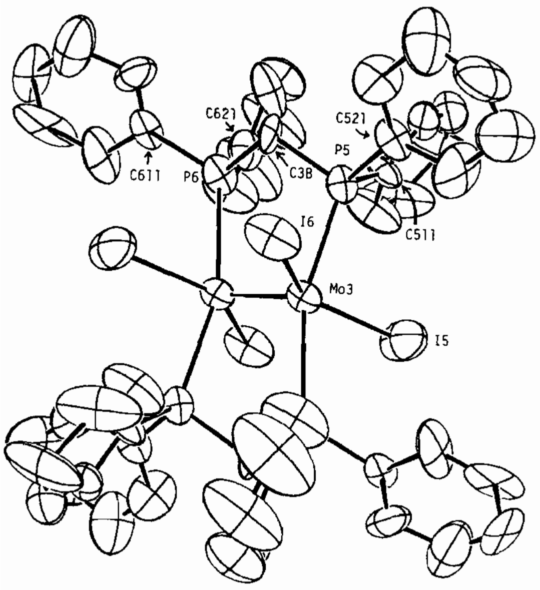

Fig. 2. ORTEP view of the molecule of $Mo_2(\mu\text{-dppm})_2I_4$ located in the special position. The thermal ellipsoids are drawn at the 50% probability level.

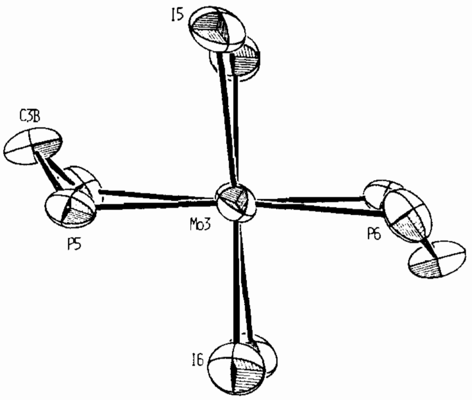

Fig. 3. The coordination and rotational conformation of the dimolybdenum unit Mo(3)–Mo(3) located in the special position.

for all three compounds of the type $Mo_2(\mu\text{-dppm})_2X_4$ (X = Cl, Br, or I), there is a close similarity between the related Mo–P distances and Mo–Mo–P and Mo–Mo–X angles in each of the complexes. The increase in the average Mo–Mo–X angles in the series I > Br > Cl reflects a small but systematic increase in intramolecular non-bonded X···X repulsions with an increase in the size of the X group.

Of most significance in this structure determination is a difference in the rotational geometry about the dimolybdenum unit in the two independent $Mo_2(\mu\text{-dppm})_2I_4$ molecules. In the structures of the related chloride and bromide analogues, in which the molecules reside on crystallographic inversion centers, the rotational conformation is eclipsed and therefore the average torsional angles (χ) are required by symmetry to be zero [2, 3].** In these two instances the appropriate X–Mo–Mo–X and P–Mo–Mo–P torsional angles are 2.6° and 6.1°, respectively, for X = Cl [2], and 6.2° and 8.1°, respectively, for X = Br [3]. In the case of the molecule of $Mo_2(\mu\text{-dppm})_2I_4$ which lies on the inversion center, and for which the average χ must be zero, the contributing angles are 7.4° and 9.3° (Fig. 3). In contrast, the

TABLE V. Comparison of some Structural Data for $Mo_2(\mu\text{-dppm})_2X_4$ (X = Cl, Br, or I)

	χ (deg)	Average Mo–P distance (Å)	Average Mo–X distance (Å)	Average Mo–Mo–P angle (deg)	Average Mo–Mo–X angle (deg)
$Mo_2(\mu\text{-dppm})_2Cl_4\cdot 2(CH_3)_2CO^a$	0	2.58[4]	2.394[6]	99[3]	106.9[13]
$Mo_2(\mu\text{-dppm})_2Br_4\cdot 2THF^b$	0	2.61[6]	2.535[3]	99[2]	108[5]
$Mo_2(\mu\text{-dppm})_2I_4$ eclipsed	0	2.62[7]	2.707[19]	98[3]	109[3]
$Mo_2(\mu\text{-dppm})_2I_4$ partially staggered	17(2)	2.61[4]	2.728[4]	98[1]	110[2]

[a] Data from ref. 2. [b] Data from ref. 3.

**For convenience in subsequent discussion we will refer to the rotational conformation as being eclipsed when $\chi = 0°$ and partially staggered when $0° < \chi < 45°$.

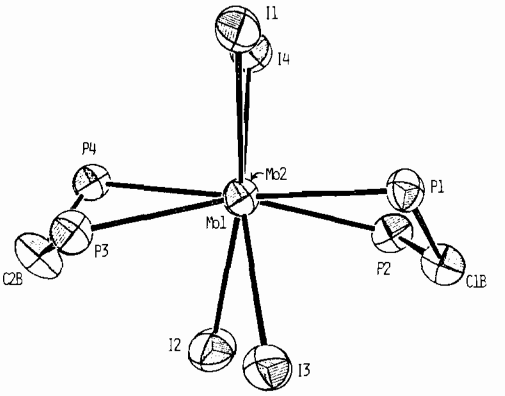

Fig. 4. The coordination and rotational conformation of the dimolybdenum units Mo(1)–Mo(2) located in the general positions.

TABLE VI. Torsional Angles (deg) in $Mo_2(\mu\text{-dppm})_2I_4$[a]

Planes defining the angle		
Atoms in plane 1	Atoms in plane 2	Angle
I(1)Mo(1)Mo(2)	Mo(1)Mo(2)I(4)	4.9(9)
I(3)Mo(1)Mo(2)	Mo(1)Mo(2)I(2)	19.7(2)
P(1)Mo(1)Mo(2)	Mo(1)Mo(2)P(2)	15.6(4)
P(3)Mo(1)Mo(2)	Mo(1)Mo(2)P(4)	17.2(2)
	Mean angle	17[2]

[a] Angles for the partially staggered molecules.

molecules residing on general positions exhibit a torsional angle of 17[2]° (Fig. 4 and Table VI), and in so doing resemble the thiocyanato complex $Mo_2(\mu\text{-dppm})_2(NCS)_4 \cdot 2(CH_3)_2CO$ [2] which has $\chi = 13.3°$. These differences are also reflected by the different conformations of the fused $\overline{Mo-Mo-P-C-P}$ rings (see Figs. 3 and 4) which in turn resemble the differences seen between eclipsed $Mo_2(\mu\text{-dppm})_2X_4$ (X = Cl or Br) [2, 3] and the partially staggered rotational geometry in $Mo_2(\mu\text{-dppm})_2(NCS)_4$ [2]. To our knowledge, this is the first instance where two quite different rotational geometries have been found in the solid state for the same crystal at least in the case of a halide compound of the type $M_2X_4(\text{bridge})_2$. However, since we completed this study we have learned that a similar effect is seen in the crystal structure of $\beta\text{-}Mo_2(\text{dppe})_2I_4$ (dppe = $Ph_2PCH_2CH_2PPh_2$) [12]. One important implication stemming from this result is that crystal packing forces can apparently have a far greater effect in determining the rotational geometry than may previously have been supposed.

A puzzling feature which emerges from this structure determination is that the $Mo_2(\mu\text{-dppm})_2I_4$ molecules which have the partially staggered rotational geometry have a shorter Mo–Mo bond distance than does the molecule with the eclipsed arrangement of ligands. This observation runs counter to the usual situation in which there is an inverse linear relationship between Mo–Mo bond length and the value of $\cos(2\chi)$ [5]. This result is especially surprising since the structure determination on the crystals of $Mo_2(\mu\text{-dppm})_2I_4$ grown from toluene [9] shows this molecule to be rigorously eclipsed (a zero average torsional angle) with a Mo–Mo distance of 2.139(1) Å *i.e.* statistically the same as in $Mo_2(\mu\text{-dppm})_2X_4$ (X = Cl or Br). Professor F. A. Cotton has suggested to us that the discrepancy between his results [9] and ours may lie in the presence of some residual chlorine in our crystals (our sample was prepared by reacting $Mo_2(\mu\text{-dppm})_2Cl_4$ with NaI in acetone). While the structural parameters for the molecules that are located in symmetry related general positions (molecules Mo(1)–Mo(2)) are quite normal, the eclipsed molecule in the special position shows an anomalously short Mo(3)–I(5) distance (Table III) and large temperature factors associated with I(5) and I(6) (Table II). Accordingly, we decided that any remaining chlorine (if present) must be associated with the dimolybdenum unit centered about the inversion center. Since there was no evidence from Fourier maps for chlorine in positions close to iodine, the chlorines were restrained to identical locations as I(5) and I(6) with fixed isotropic temperature factors of 4.5. The multiplicity of these two iodines were allowed to vary and the chlorine multiplicities were constrained to one minus the iodide multiplicity. The iodide multiplicities converged to 0.79 and 0.89 for I(5) and I(6), respectively. However, the maximum change in any bond distance was only 0.002 Å. The *R*-factors in this refinement lowered to 0.085 and 0.121 which is not a significant change [13]. For this reason the structure details are reported without the partial chlorine occupancy which, based on the preceding analysis, does not appear to exceed that of the average stoichiometry $Mo_2(\mu\text{-dppm})_2I_{3.8}Cl_{0.2}$ (*i.e.* 5%). Since the long Mo(3)–Mo(3) and short Mo(3)–I(5) distances appear to be artifacts of the partial chlorine occupancy and poor crystal quality, no special chemical significance should be attached to the 'anomalous' values of these parameters.

To obtain direct chemical evidence for the presence of chlorine we carried a series of comparative studies of the properties of samples of $Mo_2(\mu\text{-dppm})_2I_4$ prepared by our procedure [1] and that of Cotton *et al.* [9], *viz.* involving the reaction of $Mo_2(O_2CCH_3)_4$ with dppm and Me_3SiI in toluene. Bulk samples of complexes prepared by these two methods had identical electronic absorption spectra [λ_{max} in CH_2Cl_2 = 705, 565w, sh, 499w, sh, and 438 nm]*, both before and after recrystallization from

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*The spectrum reported previously [1] which had λ_{max} = 684 ($\epsilon \sim 3000$), ~480sh, 429 ($\epsilon \sim 3800$) and 400sh nm, may have been that of a contaminated sample.

CH_2Cl_2/MeOH and CH_2Cl_2/EtOH. These spectra are in turn essentially the same as that of the crystals used in the structure determination, with the exception that the weak features at 565 and 499 nm were obscurred by a broad low energy tail on the intense 438 nm absorption. Also, the cyclic voltammograms (measured in 0.1 M $Bu_4NPF_6-CH_2Cl_2$) of all samples (including the crystals) were the same as that reported previously for $Mo_2(\mu\text{-dppm})_2I_4$ [1]. While these measurements confirm that these samples are different batches of the same complex, one important difference emerged upon measuring their secondary ion mass spectra (SIMS) [14]. While samples of $Mo_2(\mu\text{-dppm})_2I_4$ prepared by Cotton's method [9] showed no Cl^- (at *m/z* 35, 37), those prepared using our procedure showed significant levels of Cl^- – these were greatest in the batch of crystals from which the crystal was selected for the structure determination. The source of chlorine is apparently from incomplete exchange of the $Mo_2(\mu\text{-dppm})_2Cl_4$ starting material, and the concentration of chlorine seems to maximize in the better formed crystals[†].

Supplementary Material

Listings of anisotropic thermal parameters (Table S1), bond distances for the phenyl rings (Table S2), bond angles for the phenyl rings (Table S3), observed and calculated structure factors, and illustrations showing the full atomic numbering schemes (Figs. S1 and S2) (55 pages) are available on request from P.E.F. or R.A.W.

Acknowledgements

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[†] We have now found that crystals of pure $Mo_2(\mu\text{-dppm})_2I_4$ prepared by the method of Cotton *et al.* [9] and grown from $CH_2Cl_2-CH_3OH$ index to the same unit cell as our crystals of $Mo_2(\mu\text{-dppm})_2I_{4-x}Cl_x$. Accordingly, the presence of low concentrations of chloride in the crystals does not apparently change the crystal structure.