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Syntheses, structures and spectra of β-$Mo_2X_4(dpcp)_2$ (X = Cl, Br, I), where dpcp is (±)-*trans*-1,2-bis(diphenylphosphino)cyclopentane. A study of several interesting effects of halogen atoms on the Mo–Mo quadruple bond

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Abstract

The complexes β-$Mo_2X_4(dpcp)_2$ (X = Br, I) were prepared by reaction of $Mo_2(O_2CCF_3)_4$, $(CH_3)_3SiX$ (X = Br, I) and (±)-*trans*-1,2-bis(diphenylphosphino)cyclopentane, dpcp, in THF at room temperature. β-$Mo_2Cl_4(dpcp)_2$ was prepared by reaction of $K_4Mo_2Cl_8$ and dpcp in boiling methanol. Their UV–Vis and NMR spectra have been recorded and the structures have been determined. The crystals of these three compounds are isotypic in the space group C2/c with four molecules per unit cell. They show no disorder of the Mo_2 units. Crystallographic data: β-$Mo_2Cl_4(dpcp)_2$: $a = 19.598$ (4), $b = 20.142(3)$, $c = 21.186(7)$ Å, $\beta = 112.12(2)°$, $V = 7748(6)$ Å^3; final residuals: $R = 0.0686$, $R_w = 0.0934$. β-$Mo_2Br_4(dpcp)_2$: $a = 19.772(7)$, $b = 20.094(6)$, $c = 21.154(6)$ Å, $\beta = 112.09(3)°$, $V = 7788(8)$ Å^3; final residuals: $R = 0.0694$, $R_w = 0.0904$. β-$Mo_2I_4(dpcp)_2$: $a = 20.141(12)$, $b = 20.140(10)$, $c = 21.543(9)$ Å, $\beta = 112.10(4)°$, $V = 8097(14)$ Å^3; final residuals: $R = 0.0562$, $R_w = 0.0844$. The structures of these three complexes have the same twist angle (P–Mo–Mo–P) of about 22°, and in all these the Mo–Mo distance is 2.155[5] Å. Some generalizations can be made for the series of complexes β-$Mo_2Cl_4(dpcp)_2$, β-$Mo_2Br_4(dpcp)_2$ and β-$Mo_2I_4(dpcp)_2$: (i) the Mo–X and Mo–P distances increase in the order $Cl < Br < I$, but the Mo–Mo distances and torsional angles are essentially unaffected: (ii) the absorption bands display marked sensitivities to the nature of the halogen atoms and the energies are red-shifted in the order $Cl < Br < I$; (iii) the diamagnetic anisotropies experienced by the cyclopentane protons appear to increase from X = Cl to X = I although detailed or quantitative analysis is not possible.

Introduction

Complexes containing metal–metal quadruple bonds have already been subjected to many studies of their structural and spectroscopic properties [1]. For complexes of the type β-$Mo_2X_4(PP)_2$, where PP is a diphosphine ligand and X is Cl, Br or I, properties of the Mo–Mo quadruple bond that have been investigated include: (i) the dependence of the Mo–Mo quadruple bond length on torsional angle [2, 3], which displays a linear relationship between cos (2χ) (where χ is the angle of twist away from the eclipsed conformation) and the Mo–Mo distance; (ii) the variation in $\delta \rightarrow \delta^*$ transition energies with δ-bond lengths [4, 5], which revealed a non-linear relationship between cos (2χ) and the $\delta \rightarrow \delta^*$ transition energy; (iii) the optical activity [6–9] of the Mo–Mo quadruple bond, in which a CD sign rule and the one electron static-coupling mechanism have been proposed or invoked to explain the observations; (iv) the effect of diamagnetic anisotropy of the Mo–Mo quadruple bond on the chemical shifts of the protons [10–13].

We report here an extension of the earlier studies that provides structural and spectroscopic data for a series of complexes β-$Mo_2X_4(dpcp)_2$ (X = Cl, Br, I). The new results are compared with those for $Mo_2X_4(PMe_3)_4$ (X = Cl, Br, I). The ^1H NMR spectra provide evidence that there is only one isomer or conformer present in solution, and also show that the diamagnetic anisotropy of the central $Mo_2X_4P_4$ unit varies with changes in the identity of X.

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Experimental

General procedures

All manipulations were carried out under an atmosphere of dry oxygen-free argon using Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. THF and n-hexane were purified by distillation from sodium–potassium/benzophenone and dichloromethane from P_2O_5. The UV–Vis absorption spectra of $Mo_2X_4(dpcp)_2$ (X = Cl, Br, I) were recorded on a Beckman DU 70 or Cary 17D spectrophotometer. ^1H NMR spectra were recorded on a Varian XL-200 or Varian Gemini-200 NMR spectrometer. CD spectra were recorded on a Cary-60 spectropolarimeter.

Starting materials

$Mo_2(O_2CCF_3)_4$ [14], $K_4Mo_2Cl_8$ [15] and (±)-*trans*-1,2-bis(diphenylphosphino)cyclopentane, dpcp [16] were prepared according to reported procedures. PCl_3, P_4 and PhMgCl were purchased from Aldrich Co.

Preparations

(±)-trans-1,2-Bis-(dichlorophosphino)cyclopentane

Phosphorus trichloride (68 ml), yellow P_4 (5.8 g) and cyclopentene (47 ml) were heated together in a Parr 300 ml 'mini' reactor at 215 °C, for 40 h. The resulting yellow–brown liquid was distilled under vacuum (b.p. 98–102 °C, 0.05 mmHg) to give approximately 24 g of the colorless liquid (±)-*trans*-1,2-bis-(dichlorophosphino)cyclopentane. ^1H NMR (200 Mz, $CDCl_3$): 1.28 (2H), 1.65 (4H), 2.36 (2H) ppm.

(±)-trans-1,2-Bis-(diphenylphosphino)cyclopentane

(±)-*trans*-1,2-Bis-(dichlorophosphino)cyclopentane (5 ml) was syringed into a 250 ml, three-necked flask equipped with a reflux condenser, gas inlet and dropping funnel. THF (50 ml) was added followed by the dropwise addition of PhMgCl (70 ml) at 0 °C. The dpcp was extracted from the filtered THF solution with hexane to give a white, air-stable product (m.p. = 135 °C). The parent ion peak of the mass spectrum appeared at *m/e* 438. This confirmed the molecular weight to be that of dpcp. ^1H NMR (200 Mz, $CDCl_3$): 1.66 (2H), 1.89 (2H), 2.27 (2H), 2.77 (2H), 7–7.5 (20H) ppm. ^{13}C NMR (200 Mz, $CDCl_3$): 24.19, 28.99, 39.59, 128.32, 133.53, 137.57 ppm. ^{31}P NMR (80 Mz, C_6H_6:THF(1:1)): proton decoupled, $\delta = -7.77$ ppm relative to H_3PO_4.

β-$Mo_2Cl_4(dpcp)_2$

$K_4Mo_2Cl_8$ (0.1 g, 0.158 mmol) and dpcp (0.14 g, 0.320 mmol) were placed in a flask equipped with a reflux condenser. Methanol (10 ml) was added and the mixture left to reflux for 20 h. The resulting green solution was filtered off and the residue dried. Yield: 0.06 g (31%). Solutions of this complex are slightly air-sensitive, but solid samples are air-stable. Crystals suitable for X-ray crystallographic analysis were obtained from a concentrated THF solution of β-$Mo_2Cl_4(dpcp)_2$, which was kept at 0 °C for 36 h.

β-$Mo_2Br_4(dpcp)_2$

A mixture of $Mo_2(O_2CCF_3)_4$ (0.25 g, 0.388 mmol) and dpcp (0.34 g, 0.776 mmol) was stirred in 13 ml of THF and 0.3 ml of $(CH_3)_3SiBr$. The reaction mixture first turned dark brown and a brown precipitate soon began to form. After 24 h the brown precipitate was isolated by filtration, washed by ether and then dried under vacuum. Yield: 0.11 g (20%). Crystals suitable for X-ray crystallographic analysis were obtained by layering the THF solution with 10 ml of hexane.

β-$Mo_2I_4(dpcp)_2$

In a 50 ml flask, $Mo_2(O_2CCF_3)_4$ (0.25 g, 0.388 mmol) and dpcp (0.34 g, 0.776 mmol) were dissolved in 12 ml of THF and then 0.3 ml of $(CH_3)_3SiI$ was added. The reaction mixture first turned purple and a brown precipitate soon began to form. After 6 h the brown precipitate was isolated by filtration, washed by ether and then dried under vacuum. Yield: 0.16 g (26%). Crystals suitable for X-ray diffraction measurement were obtained by hexane-induced crystallization from a THF solution.

Resolution of optical isomers of β-$Mo_2Cl_4(dpcp)_2$

β-$Mo_2Cl_4(dpcp)_2$ (0.05 g) was placed in a Schlenk tube, 5 ml of dried, degassed (*S*)-(−)-2-methyl-1-butanol was added and the mixture heated in a hot water bath. The alcohol dissolved a small portion of β-$Mo_2Cl_4(dpcp)_2$, and the resulting green solution was quickly filtered through a medium frit into another Schlenk tube. The alcohol was allowed to cool, giving a clear solution and the green solid of the partially resolved β-$Mo_2Cl_4(dpcp)_2$. The partially resolved β-$Mo_2Cl_4(dpcp)_2$ was washed with hexane and dried in vacuum.

X-ray crystallography

The structures of β-$Mo_2X_4(dpcp)_2$ (X = Cl, Br, I) were determined by a general procedure that has been fully described elsewhere [17].

β-$Mo_2Cl_4(dpcp)_2$

A green tetragonal prism was sealed inside a thin walled glass capillary and mounted on an Enraf-

Nonius CAD-4 instrument. The unit cell constants were determined from the geometrical parameters of 20 well-centered reflections with 2θ values in the range 15–27°. The unit cell constants and axial photographs were consistent with a monoclinic lattice. The intensities of all reflections with 2θ values in the range 4–45° were measured by the ω–2θ scan technique. The total number of reflections measured was 5333, of which 171 were intensity standards. Corrections were applied for Lorentz and polarization effects.

The positions of the molybdenum atoms were determined from a Patterson map. The positions of the other non-hydrogen atoms were located and refined by alternating difference Fourier maps and least-squares cycles. Anisotropic thermal parameters were employed for all atoms except those of the solvent molecule.The isotropic thermal parameters of the oxygen and four carbon atoms in the THF molecule were constrained to be 23 Å^2. Using the SHELX-76 program, the phenyl rings were idealized and refined as rigid bodies. The lengths of all the P–C single bonds were constrained. Bond lengths of 1.820 and 1.839 Å were assigned for the P–Ph and P–C (the bonds in the six-membered ring) bonds, respectively. The C–C bond lengths in the THF molecule was fixed at 1.54 Å and the O–C bond length was fixed at 1.50 Å. The site occupancy factors of all the atoms of the solvent molecule were fixed at 0.5. Refinement of this model gave a final R factor of 0.0686.

β-Mo_2Br_4(dpcp)$_2$

A dark green acicular crystal was sealed inside a glass capillary. Unit cell constants were determined using a Syntex P1 instrument and, together with the monoclinic symmetry, confirmed by axial photographs. The intensities of all reflections with 2θ values in the range 4–45° were measured by the ω–2θ scan technique. The total number of reflections measured was 4136. Corrections were applied for Lorentz and polarization effects. Absorption corrections [18] were made based on azimuthal scans of six reflections with χ angles near 90°.

The unit cell constants and the space group showed that this crystal was isomorphous with β-Mo_2Cl_4(dpcp)$_2$. The constraints applied for the positional and thermal parameters were the same. The atoms C(14), C(16) and C(20) could not be refined with anisotropic thermal parameters and were refined isotropically. The final R factor obtained on refining this model was 0.0694.

β-Mo_2I_4(dpcp)$_2$

A deep brown crystal of β-Mo_2I_4(dpcp)$_2$ was mounted inside a capillary with epoxy cement. Crystal quality was confirmed by a rotational photograph. The unit cell constants were determined from 25 reflections with 2θ values in the range 23–30°. These were consistent with a monoclinic crystal system.The diffraction data was collected on a Syntex P3 equivalent diffractometer at 20 ± 1 °C which was equipped with graphite monochromated Mo Kα ($\lambda_\alpha = 0.71037$ Å) radiation. Data reduction was carried out by standard methods with the use of well-established computational procedures*.

Routine ω–2θ data collection was used to scan a possible 6221 data points in the range of $4° < 2\theta < 46°$. Three check reflections monitored throughout the data collection displayed no significant gain or loss in intensity. The structure factors were obtained after a Lorentz and polarization correction. Empirical absorption corrections based on azimuthal (ψ) scans of reflections of Eulerian angle χ near 90° were applied to the data [18].

The direct methods program in SHELXS-86 [19] led to the location of the positions of the molybdenum atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. Anisotropic thermal parameters were used for all the atoms except those of the THF solvent. The positions of the hydrogen atoms were calculated and refined by the SHELXS-76 program. The final residuals of the refinement were $R = 0.0562$, $R_w = 0.0844$. The molecule refined has an S, S configuration.

Basic information pertaining to the crystal parameters and the structure refinement are summarized in Table 1. Tables 2, 3 and 4 list selected positional parameters for β-Mo_2Cl_4(dpcp)$_2$, β-Mo_2Br_4(dpcp)$_2$ and β-Mo_2I_4(dpcp)$_2$, respectively. Table 5 lists selected bond distances and angles of these three complexes.

Results and discussion

*Molecular structures of β-Mo_2X_4(dpcp)$_2$ ($X = Cl, Br, I$)***

The ligand, dpcp, Fig. 1, which is a racemic mixture of R,R-dpcp and S,S = dpcp, reacted with $Mo_2(O_2CCF_3)_4$ and $(CH_3)_3SiX$ ($X = Br$, I) in THF to give Mo_2X_4(dpcp)$_2$ ($X = Br$, I). β-Mo_2Cl_4(dpcp)$_2$ was prepared by reaction of $K_4Mo_2Cl_8$ and dpcp in boiling methanol. These three compounds form isotypic crystals in the space group $C2/c$ with four

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*Crystallographic computing was done on a local area VAX cluster, employing the VAX/VMS V4.6 computer.

**Further references to the β-Mo_2X_4(dpcp)$_2$ ($X = Cl$, Br, I) or $Mo_2X_4(PMe_3)_4$ ($X = Cl$, Br, I) series as a whole will be given as β-Mo_2X_4(dpcp)$_2$ or $Mo_2X_4(PMe_3)_4$, respectively.

TABLE 1. Crystal data for $Mo_2Cl_4(dpcp)_2 \cdot 0.5$ THF (**1**), $Mo_2Br_4(dpcp)_2 \cdot 0.5$ THF (**2**) and $Mo_2I_4(dpcp)_2 \cdot$THF (**3**)

	1	**2**	**3**
Formula	$Mo_2Cl_4P_4C_{58}H_{56} \cdot 0.5\ OC_4H_8$	$Mo_2Br_4P_4C_{58}H_{56} \cdot 0.5\ OC_4H_8$	$Mo_2I_4P_4C_{58}H_{56} \cdot OC_4H_8$
Formula weight	1246.73	1424.56	1648.59
Space group	*C2/c*	*C2/c*	*C2/c*
a (Å)	19.598(4)	19.772(7)	20.141(12)
b (Å)	20.142(3)	20.094(6)	20.140(10)
c (Å)	21.186(7)	21.154(6)	21.543(9)
β (°)	112.12(2)	112.09(3)	112.10(4)
V (Å^3)	7748(6)	7788(8)	8097(14)
Z	4	4	4
D_{calc} (g/cm^3)	1.069	1.215	1.352
μ(Mo Kα) (cm^{-1})	5.67	26.01	19.19
Temperature (°C)	22±3	22±3	20±1
Radiation monochromated in incident beam (Mo Kα, Å)	0.71073	0.71073	0.71073
R^a	0.0686	0.0694	0.0562
$R_w{}^a$	0.0934	0.0904	0.0844

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

TABLE 2. Selected positional and isotropic equivalent thermal parameters (Å^2) and their e.s.d.s. for $Mo_2Cl_4(dpcp)_2 \cdot 0.5$ THF

Atom	*x*	*y*	*z*	*B* (Å^2)^a
Mo(1)	0.0000	0.11611(7)	0.2500	3.22(4)
Mo(2)	0.0000	0.22328(7)	0.2500	3.27(4)
Cl(1)	−0.0873(2)	0.0827(2)	0.1404(2)	4.48(9)
Cl(2)	−0.0453(2)	0.2587(2)	0.1336(2)	4.58(9)
P(1)	0.0990(2)	0.0799(2)	0.2062(2)	3.93(9)
P(2)	0.1297(2)	0.2542(2)	0.2528(2)	3.96(9)
C(13)	0.1694(6)	0.1987(6)	0.2066(7)	4.8(4)
C(14)	0.2468(8)	0.2210(8)	0.2056(9)	7.2(6)
C(15)	0.271(1)	0.1528(8)	0.181(2)	15(1)
C(16)	0.2518(7)	0.0972(8)	0.2249(9)	7.0(6)
C(17)	0.1847(5)	0.1282(6)	0.2407(7)	4.4(4)

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

TABLE 3. Selected positional and isotropic equivalent thermal parameters (Å^2) and their e.s.d.s. for $Mo_2Br_4(dpcp)_2 \cdot 0.5$ THF

Atom	*x*	*y*	*z*	*B* (Å^2)^a
Mo(1)	0.0000	0.1226(1)	0.2500	2.68(7)
Mo(2)	0.0000	0.2298(1)	0.2500	2.77(7)
Br(1)	−0.0915(1)	0.0862(1)	0.1344(1)	4.29(7)
Br(2)	−0.0484(1)	0.2694(1)	0.1270(1)	4.61(7)
P(1)	0.0977(3)	0.0864(3)	0.2048(2)	3.3(2)
P(2)	0.1288(3)	0.2614(3)	0.2521(3)	3.6(2)
C(13)	0.167(1)	0.205(1)	0.205(1)	3.9(7)
C(14)	0.242(1)	0.227(1)	0.199(1)	5.8(6)^a
C(15)	0.271(2)	0.162(1)	0.185(2)	13(2)
C(16)	0.250(1)	0.108(1)	0.222(1)	5.6(6)^a
C(17)	0.1830(9)	0.136(1)	0.239(1)	4.2(7)

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

molecules per unit cell. Fig. 2 shows the ORTEP diagram of β-$Mo_2I_4(dpcp)_2$, a representative structure for the complexes β-$Mo_2X_4(dpcp)_2$. This molecule has approximate D_2 symmetry with one of the C_2 axes collinear with the Mo–Mo quadruple bond. This axis also coincides with the crystallographic C_2 axis. By inspection of the ligand geometry, it is found that the chirality of this ligand is *S*,*S*.

In this structure, two molybdenum, two phosphorus and two carbon atoms form a six-membered ring. The conformation of this six-membered ring can be assigned as λ or δ; if we assume that the center of the Mo–Mo bond is occupied by a single metal atom, i.e. we think of a mononuclear chelate complex with a five-membered ring [20], it can be shown that this ring has a δ configuration. Above this six-membered ring is a five-membered ring formed by five carbon atoms. It is noted from Tables 2, 3 and 4 that the thermal parameter of C(15) is 15 Å^2 in β-$Mo_2Cl_4(dpcp)_2$, 13 Å^2 in β-$Mo_2Br_4(dpcp)_2$ and 20 Å^2 in β-$Mo_2I_4(dpcp)_2$, which are larger than those of the other carbon atoms in the same ring. This can be regarded as a consequence of the in and out-of-plane (of paper) vibration or disorder of this atom.

TABLE 4. Selected positional and isotropic equivalent thermal parameters (Å^2) and their e.s.d.s. for $Mo_2I_4(dpcp)_2 \cdot THF$

Atom	*x*	*y*	*z*	*B* (Å^2)^a
I(1)	0.09699(6)	0.08602(6)	0.37159(6)	3.78(4)
I(2)	−0.05189(7)	0.28002(7)	0.12098(6)	4.13(4)
Mo(1)	0.000	0.1276(1)	0.250	2.78(6)
Mo(2)	0.000	0.2344(1)	0.250	2.99(6)
P(1)	0.0955(3)	0.0903(3)	0.2043(2)	3.5(1)
P(2)	0.1270(3)	0.2664(3)	0.2515(2)	3.8(1)
C(13)	0.179(1)	0.140(1)	0.235(1)	4.7(6)
C(14)	0.245(1)	0.114(2)	0.218(1)	8(1)
C(15)	0.272(2)	0.177(2)	0.201(3)	20(3)
C(16)	0.238(1)	0.231(1)	0.201(1)	8(1)
C(17)	0.161(1)	0.212(1)	0.202(1)	4.7(7)

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

Figure 3 is a view of the molecule with the Mo–Mo quadruple bond perpendicular to the plane of the paper. From this projection we can see that this molecule has a Λ configuration. The twist angles of these three complexes are about the same, with an average value in each case of about 22°. The nature of the halogen atoms has no effect on the twist angle. Since the space group of the crystal is centrosymmetric, there are two molecules in each cell that have ligands of *R,R* chirality and possess a central portion of Δ configuration, and two others of opposite chirality.

Table 5 lists selected bond distances and bond angles for β-$Mo_2X_4(dpcp)_2$. It is clear from this Table that these three complexes have the same Mo–Mo bond distances (2.15 Å). Similar insensitivity of the Mo–Mo bond distance to the nature of the halogen atoms has been found for the complexes $Mo_2X_4(PMe_3)_4$ [21]. The values of the bond distance, 2.15 Å, and torsional angle, 22°, are consistent with the prediction that the δ bond strength varies according to cos 2χ, where χ is the average of the four smallest torsional angles about the Mo–Mo quadruple bond. Also from Table 5 we can see that the Mo–X distances increase in the order $Cl < Br < I$ along with the small increase in the Mo–Mo–X angles. The increase of the Mo–X bond distances is due to the increase of the atomic radius from $X = Cl$ to $X = I$. In addition, the Mo–P distances also increase from $X = Cl$ to $X = I$. Table 6 shows the average bond distances and bond angles for β-$Mo_2X_4(dpcp)_2$ and $Mo_2X_4(PMe_3)_4$ [21]. Comparisons of these distances and angles show that the complexes β-$Mo_2X_4(dpcp)_2$ have the longer Mo–Mo and Mo–L bond distances and the larger Mo–Mo–L angles, but the Mo–X distances are shorter and the Mo–Mo–X angles are smaller than those of the complexes $Mo_2X_4(PMe_3)_4$. The shorter Mo–Mo distances for $Mo_2X_4(PMe_3)_4$ are due to their eclipsed configurations for the central portions. Molecules having the eclipsed configurations will have better d–d orbital overlaps and thus stronger Mo–Mo bonds (shorter Mo–Mo distances). A probable explanation for the shorter Mo–P distances in the complexes $Mo_2X_4(PMe_3)_4$ is that the Mo–P bonds are primarily P → Mo σ donor in nature and are stronger for the PMe_3 ligands which have three alkyl groups coordinated to each phosphorus atom than for the dpcp ligands which have two phenyl groups and one alkyl group coordinated to each phosphorus atom.

TABLE 5. Selected bond distances (Å) and angles (°) for $Mo_2X_4(dpcp)_2$ ($X = Cl$, Br, I)

Atom	Atom	Distances (Å)		
		X=Cl	X=Br	X=I
Mo(1)	Mo(2)	2.159(2)	2.155(4)	2.151(3)
Mo(1)	X(1)	2.405(3)	2.543(2)	2.744(1)
Mo(2)	X(2)	2.393(3)	2.539(2)	2.734(1)
Mo(1)	P(1)	2.552(4)	2.564(7)	2.580(6)
Mo(2)	P(2)	2.596(4)	2.609(6)	2.626(6)

Atom	Atom	Atom	Angles (°)		
			X=Cl	X=Br	X=I
Mo(2)	Mo(1)	X(1)	106.26(9)	106.73(8)	107.76(5)
Mo(1)	Mo(2)	X(2)	107.36(8)	108.24(8)	109.65(5)
Mo(2)	Mo(1)	P(1)	106.61(8)	106.5(1)	106.9(1)
MO(1)	Mo(2)	P(2)	103.86(8)	104.1(1)	104.2(1)

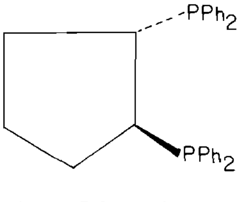

Fig. 1. Schematic structure of dpcp.

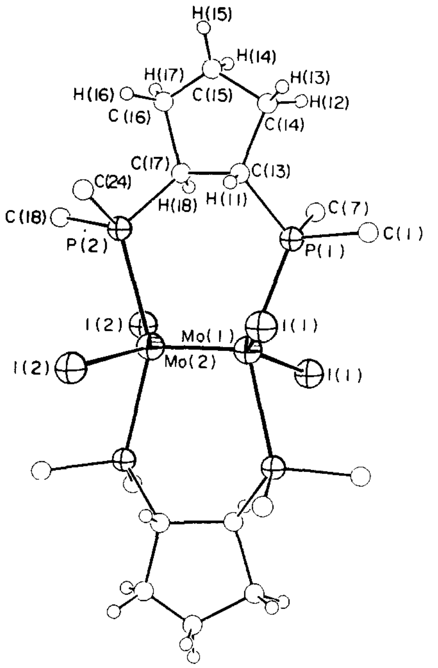

Fig. 2. ORTEP of $Mo_2X_4(dpcp)_2$, taken from the parameters of X = I.

It is notable that no disordering of the Mo_2 units within the ligand cages is seen in these compounds. In previous crystallographic studies of about twenty β-$Mo_2X_4(PP)_2$ compounds such disordering has been found in roughly half of them. We plan to examine this disordering in detail in a future publication, but we point out here that disordering appears to be disfavored by smaller twist angles. The average angle of 22° found in these compounds is one of the smallest known (not counting angles of *c*. 0° for $R_2PCH_2PR_2$ compounds). This low angle, as well, perhaps, as the conformational demands of the cyclic ligand and its shape, are in the aggregate not conducive to the occurrence of disorder.

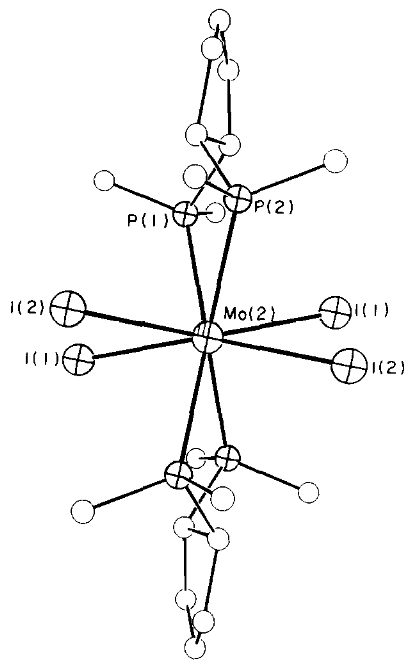

Fig. 3. View looking down the Mo–Mo bond of $Mo_2I_4(dpcp)_2$.

TABLE 6. Average bond distances (Å) and bond angles (°) for $Mo_2X_4(dpcp)_2$ (X = Cl, Br, I) and $Mo_2X_4(PMe_3)_4$ (X = Cl, Br, I)

X	L	Distances (Å)		
		Mo–Mo	Mo–X	Mo–L
Cl	dpcp	2.159(2)	2.399(3)	2.574(4)
Br	dpcp	2.155(4)	2.541(2)	2.587(7)
I	dpcp	2.151(3)	2.739(1)	2.603(6)
Cl	PMe_3	2.130(0)	2.414(1)	2.545(1)
Br	PMe_3	2.125(1)	2.549(1)	2.547(2)
I	PMe_3	2.127(1)	2.751(1)	2.565(2)
		Angles (°)		
		Mo–Mo–X		Mo–Mo–L
Cl	dpcp	106.81(9)		105.24(8)
Br	dpcp	107.49(8)		105.3(1)
I	dpcp	108.71(5)		105.6(1)
Cl	PMe_3	112.2(1)		102.3(1)
Br	PMe_3	113.5(1)		102.8(1)
I	PMe_3	115.1(1)		103.5(1)

The coordination ability (or flexibility) of this dpcp ligand is worthy of comment. The dihedral angle P–C–C–P of the free dpcp ligand was found [16] to be 161.8° and the distance between the two phosphorus atoms is 4.450 Å, so that at first it appears not to be a good chelating ligand. However in the complex [16] $NiBr_2(dpcp)$, the dihedral angle P–C–C–P was close to 53.7° and the distance between the two phosphorus atoms was shortened to 3.021 Å. In the case of β-$Mo_2X_4(dpcp)_2$, where the dpcp ligand acts as a bridging ligand, the dihedral angle P–C–C–P is found to be 85.34° for X = I, 85.75° for X = Br and 84.84° for X = Cl. The distance between the two phosphorus atoms is 3.678 Å for X = I, 3.646 Å for X = Br and 3.635 Å for X = Cl.

Spectroscopic studies

UV–Vis spectra

Figure 4 shows the absorption spectra of β-$Mo_2X_4(dpcp)_2$, which are typical for compounds of this type and each spectrum displays three distinct bands. The lowest energy band of β-$Mo_2I_4(dpcp)_2$ at 847 nm (11 806 cm^{-1}) was assigned to the $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition [7]. The second lowest band at 508 nm (19 685 cm^{-1}) can most probably be assigned [7] to the forbidden transition $\delta_{xy} \rightarrow \delta_{x^2-y^2}$.The third band at 445 nm (22 472 cm^{-1}) can perhaps be assigned to the $\pi_{yz} \rightarrow \delta_{xy}{}^*$ transition [7], although I → Mo charge transfer character is probably also mixed in. The assignments for the other two complexes are essentially the same. Table 7 lists the absorption band peak energies for β-$Mo_2X_4(dpcp)_2$. It is clear that the spectrum displays marked sensitivity to the nature of the halogen atoms and the energies of the three bands are red-shifted in the order $Cl < Br < I$. Specifically, the red shift of the $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition across the Cl, Br and I series is 1352 cm^{-1}, that of the $\delta_{xy} \rightarrow \delta_{x^2-y^2}$transition is 1960 cm^{-1}, and that of the $\pi_{yz} \rightarrow \delta_{xy}{}^*$ transition is 6099 cm^{-1}. The large difference of the energies of the $\pi_{yz} \rightarrow \delta_{xy}{}^*$ transition relative to that of the $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition suggests that the π_{yz} orbital is much more sensitive to the nature of the halogen atoms than the δ_{xy} orbital. This is supported by the results [22] of a calculation for $Mo_2Cl_4(PH_3)_4$. Assuming the torsional angle is 15°, the calculation showed that the contribution of the chlorine atoms to the δ_{xy} orbital is 15%, to the π_{yz} orbital is 39%. In contrast to this large difference, the small red shifts for the $\delta_{xy} \rightarrow \delta_{x^2-y^2}$and $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transitions suggest a similar dependency of the $\delta_{xy}{}^*$ orbital and the $\delta_{x^2-y^2}$orbital on the orbital contribution from the halogen atoms. From the same calculation [22], it was found that the $\delta_{xy}{}^*$ orbital has 13% and the $\delta_{x^2-y^2}$orbital has 20% of contributions from the chlorine atoms, which are consistent with the preceding remarks. In the discussion [21] of the red shift for $Mo_2X_4(PMe_3)_4$, it was found that the red shift of the second band across the series of Cl, Br and I is 5540 cm^{-1}, which is four times greater than that of the $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition, and it was assigned to the σ(M–P) → δ^* transition.

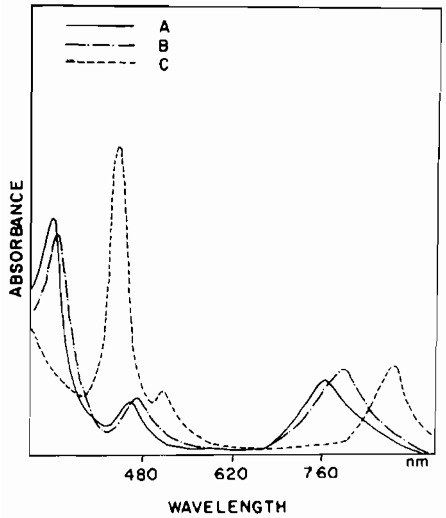

Fig. 4. UV–Vis spectra of: A, $Mo_2Cl_4(dpcp)_2$; B, $Mo_2Br_4(dpcp)_2$; C, $Mo_2I_4(dpcp)_2$ in CH_2Cl_2 solvents.

TABLE 7. Absorption energies (cm^{-1}) of β–$Mo_2X_4(dpcp)_2$ and $Mo_2X_4(PMe_3)_4$ ($X = Cl, Br, I$)

β–$Mo_2Cl_4(dpcp)_2$	13158	21645	28571
β–$Mo_2Br_4(dpcp)_2$	12987	21276	28169
β–$Mo_2I_4(dpcp)_2$	11806	19685	22472
$Mo_2Cl_4(PMe_3)_4$	17090	30860	
$Mo_2Br_4(Pme_3)_4$	16720	28990	
$Mo_2I_4(PMe_3)_4$	15720	25320	

Table 7 also shows the transition energies of the complexes $Mo_2X_4(PMe_3)_4$. It is clear from this Table that the $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition energies of the complexes $Mo_2X_4(PMe_3)_4$ are greater than those of β-$Mo_2X_4(dpcp)_2$. Since the twist angle of β-$Mo_2X_4(dpcp)_2$ is about 22° and that of $Mo_2X_4(PMe_3)_4$ is 90°, we would expect that the latter have stronger d orbital overlaps and thus greater $\delta_{xy} \rightarrow \delta_{xy}{}^*$ transition energies.

CD spectra

Four CD spectra of the partially resolved β-$Mo_2Cl_4(dpcp)_2$ were obtained in CH_2Cl_2 solvent over a period of three days. These are shown in Fig. 5. Spectrum A shows five Cotton effects in the range 625–270 nm. Spectra B and C show little or no change in the region 625–380 nm. The 350 nm band in spectrum B gains intensity and becomes negative in spectrum C, while the 330 nm band becomes less negative in spectrum B and finally becomes a positive shoulder in spectrum C. After two days and the addition of 1 ml of CH_2Cl_2, spectrum D was obtained. After three days, there was no further change in the spectrum. The amplitudes of all the bands in the CD spectra are approximately fifty times smaller than those of the corresponding bands in the CD spectrum of β-Mo_2Cl_4(*S*,*S*-dppb)$_2$ [7]. This is due to the fact that β-$Mo_2Cl_4(dpcp)_2$ is only partially resolved. We have no certain explanation for the observed changes in the bands at 350 and 330 nm. They might be due to the decomposition or to an isomerization happening in the period from spectrum A to spectrum D. Whether spectrum A or D is the more reliable one for the $Mo_2Cl_4(dpcp)_2$ molecule is thus uncertain. The most drastic changes in the

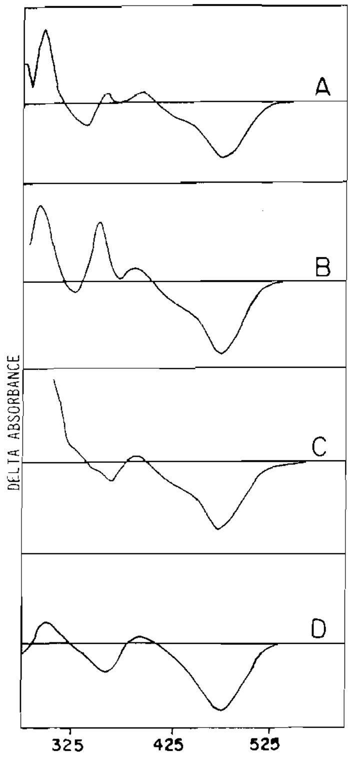

Fig. 5. CD spectra of partially resolved $Mo_2Cl_4(dpcp)_2$: (A) 0.25 h; (B) 24 h; (C) 48 h and (D) see text.

CD spectra occur in the range where the $\pi_{xy} \rightarrow \delta_{xy}$, $\pi_{xz} \rightarrow \delta_{xy}$ and $\pi_{yz} \rightarrow \delta_{x^2-y^2}$ transitions [7] occur.

A CD sign rule has been proposed [6] to predict the sign of the CD bands and has been verified [7, 8]. According to this rule the Λ and Δ complexes with torsional angles between 0 and 45° should show negative and positive CD bands, respectively, for the $\delta_{xy} \rightarrow \delta_{xy}^*$ transitions. The signs of the $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transitions are opposite to those of the $\delta_{xy} \rightarrow \delta_{xy}^*$ transitions.

From Fig. 5 it is clear that although the signs of other bands changed during this period, the sign of the band at about 460 nm remained negative. Since this transition can be assigned to the $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transition and shows a negative sign, we conclude that this partially resolved β-$Mo_2Cl_4(dpcp)_2$ was dominated by the Δ form complex with a ligand of *R,R* chirality.

NMR spectra

Figure 6 shows the ^1H NMR spectrum of β-$Mo_2Cl_4(dpcp)_2$ in $CDCl_3$ solution and Table 8 assembles data for the aliphatic resonances for the free ligand and each of the dimolybdenum complexes. The four aliphatic peaks have integrated intensities that are equal to one another and the total intensity in the aromatic region has a value of twenty relative to a value of two for each of the aliphatic peaks.

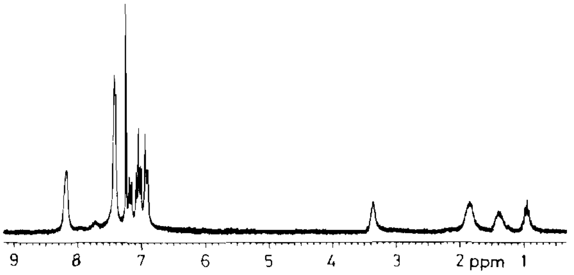

Fig. 6. Proton NMR spectrum of $Mo_2Cl_4(dpcp)_2$ in $CDCl_3$ solvent.

TABLE 8. Chemical shifts of the aliphatic protons for free dpcp and β-$Mo_2X_4(dpcp)_2$ (X = Cl, Br, I)

dpcp	2.75	2.25	1.86	1.65
β-$Mo_2Cl_4(dpcp)_2$	3.36	1.86	1.41	0.95
β-$Mo_2Br_4(dpcp)_2$	3.47	1.83	1.33	0.90
β-$Mo_2I_4(dpcp)_2$	3.68	1.90	1.30	0.83

The most important, and entirely unambiguous, inference that can be drawn from Fig. 6 is that only one isomer (not counting enantiomorphs) of β-$Mo_2Cl_4(dpcp)_2$ is present in solution, since it is extremely unlikely that the two isomers that are found in a disordered mixture in crystals of other compounds, such as β-$Mo_2Cl_4(dppe)_2$, could interconvert rapidly on the NMR time scale. Most likely there is the same isomer as the one seen in the crystal, but this cannot be said with certainty.

It must be recognized that because of the large conformational changes in the ligand on going from the free state to the coordinated state (as discussed earlier) we cannot attribute the changes in chemical shifts for the aliphatic protons in the coordinated ligands relative to those in the free ligand entirely to the diamagnetic anisotropy of the Mo≡Mo bond. There may also be small changes due to inductive effects attendant upon coordination of the phosphorus atoms as well.

Partial assignment of the NMR spectra can be made as follows. We shall identify the aliphatic protons in both the free and the coordinated ligands by the numbers shown in Fig. 2. A decoupling experiment on the free ligand showed that the protons responsible for the signals at 1.86 and 2.75 ppm are not coupled whereas the latter shows coupling to phosphorus (^2J(P–H) = 1.4 Hz). Thus we make the assignment

H(11), H(18)	2.75 ppm
H(14), H(15)	1.86 ppm
H(12), H(16) H(13), H(17)	1.65 and 2.25 ppm

We then suggest that in the complexes the signal at 3.36–3.68 ppm is due to H(11), H(18), the large downfield shift being attributed to their proximity to the midpoint of the Mo≡Mo bond. Similarly, the signal at 1.83–1.90 ppm may be assigned to the H(14), H(15) protons, which are farthest away from the Mo≡Mo bond. The other pair of signals may be tentatively assigned as shown in Table 8, assuming that in each case the upfield shifts should be similar because each type should experience the same inductive effect, similar conformational effects and similar influence from the diamagnetic anisotropy of the Mo≡Mo bond.

It should perhaps be reemphasized that these assignments are not completely certain and because of the participation of inductive and conformational effects it is not possible to make any quantitative assessment of the diamagnetic anisotropy of the Mo≡Mo bond.

Supplementary material

Complete tables of crystal data, positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, bond angles, and torsional angles for the central portion of the molecule (33 pages); and listings of observed and calculated structure factors (42 pages) are available from author F.A.C. upon request.

Acknowledgment

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