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A comparison of the solid-state structures of four crystallographically independent molecules of bis(pentamethylcyclopentadienyl)dioxodimolybdenum(VI) oxide, $[Cp^{\star}MoO_2]_2O$

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Abstract

Two previously undisclosed polymorphs of $[Cp^{\star}MoO_2]_2O$ have been crystallographically characterized: I: monoclinic, $P2_1/n$, a 8.145(4), b 9.193(3), c 15.263(5) Å, β 93.61 (3)°, V 1140.9(8) Å^3, $Z = 2$, $R(F) = 4.78\%$; II, monoclinic, $P2_1/n$, a 9.434(3), b 16.872(5), c 14.157(4) Å, β 97.19 (2)°, V 2235.7 (12) Å^3, $Z = 4$, $R(F) = 4.39\%$. A third polymorph (III, $Z = 6$) has recently been reported in two independent accounts [J.W. Faller and Y. Ma, *J. Organomet. Chem.*, 340 (1988) 59; P. Leoni, M. Pasquali, L. Salsini, C. di Bugno, D. Braga and P. Sabatino, *J. Chem. Soc., Dalton Trans.*, (1989) 155]. The existence of three polymorphs with four independent molecules containing six crystallographically independent, but chemically identical, Cp*Mo groups creates an unusual opportunity to examine the ranges of intramolecular bond parameters. Such knowledge is essential to a discussion of the extent to which intermolecular (crystal packing) factors affect these parameters. The Mo–O–Mo angle is found to vary from strict linearity (in I and III) to 172.7(3)° (in II). The range of terminal Mo=O distances exceeds the entire range seen in all previously known Mo(VI) structures containing Mo=O bonds.

Introduction

Polymorphism [1] in crystalline materials is undoubtedly a very common phenomenon. The infrequency with which examples are observed reflects only the very small fraction of known compounds which have been crystallographically characterized, and the inability of most research groups to perform routine unit-cell screening of crystalline products. When several polymorphic forms are encountered, an unusual opportunity exists to examine the extent to which bond parameters may be influenced by forces strictly limited to lattice packing effects. This knowledge is useful when bond parameters of different molecules are compared. Without knowledge of the possible ranges of packing effects, the potential exists to overemphasize the importance of chemical effects when "explaining" modest differences in bond parameters.

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During the course of our study of oxidative reactions of cyclic organoarsaoxanes, *cyclo*$(RAsO)_n$ ($n = 3$ or 4), with $[Cp^{\star}Mo(CO)_2]_2$ [2] we encountered four crystallographically independent forms of $[Cp^{\star}Mo(O)_2]_2O$ (**1**) in three polymorphic structures. Interest in Mo(VI) oxo structures has recently shown a marked increase; structures of 43 Mo(VI)-containing molecules with terminal Mo=O groups are included in a recent review [3]. From a structural perspective, the Mo=O group is particularly interesting as it is found in many examples of bond-stretch isomers. These are claimed to be separately isolable structures which differ only in distortions of their coordination spheres, a phenomenon discovered by Chatt [4] and more recently theoretically treated by Burdett, Hoffmann and coworkers [5].

We wish to present a brief comparison of the four structures of **1** in the three polymorphs (**I**, **II** and **III**). Two structural reports [6,7] of polymorph **III** have appeared; in this discussion we will use the data from ref. 7 because of the lower esd's and residuals for this analysis. Prior to both reports, we also determined the structure of **III**; our data closely agree with that found in ref. 7. The previous reports [6,7] include a thorough discussion of comparisons of **1** to related structures, which we will not repeat here.

Experimental

General procedures and materials

All reactions and manipulations were carried out in an atmosphere of purified N_2 or in evacuated Carius tubes. Melting points were measured on a Mel-Temp apparatus. Infrared (IR) spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer as solutions in $CDCl_3$. ^1H NMR spectra were obtained on a Bruker 250 MHz spectrometer with Me_4Si as an internal reference. Toluene was freshly distilled from sodium benzophenone ketyl, hexane and pentane from Na/K, methylene chloride from CaH_2 and ethyl acetate from P_2O_5. $Mo(CO)_6$ (Aldrich) was sublimed prior to use and pentamethylcyclopentadiene (Aldrich) was used as received. $[Cp^{\star}Mo(CO)_2]_2$ [8] and *cyclo*$(CH_3As)_5$ [9] were prepared by published procedures.

Preparation of $[Cp^{\star}Mo(O)_2]_2(\mu\text{-}O)$ (1)

$[Cp^{\star}Mo(CO)_2]_2$ (0.455 g, 0.793 mmol) was dissolved into 15 mL of a dry, degassed toluene solution containing 0.710 g (1.58 mmol) of *cyclo*$(CH_3As)_5$ (containing, by NMR integration, about 20% *cyclo*$(CH_3AsO)_4$) in a heavy-wall Carius tube (15 mm diam., 25 mL). The tube was evacuated with three freeze–pump–thaw cycles, flame-sealed under vacuum, and heated at 150 °C for 22 h in an oven. (**Caution**: pressures of 20–30 atm are generated during the heating process; therefore, the tube should be protected by an end-capped, perforated steel tube.) After cooling slowly to room temperature, the tube was opened with a moderate pop (pressurization by CO). The resulting deep-orange solution was evaporated to dryness and chromatographed on alumina.

Polymorph I. The reaction mixture was chromatographed on a deactivated alumina column with a 3 : 7 ethyl acetate/methylene chloride eluent and a brown-yellow band isolated. Crystals were grown by the slow diffusion of pentane into a methylene chloride solution.

Polymorph II. Isolation of this polymorph differed from **I** only in the eluent, in this case 1 : 9 methylene chloride/hexanes.

Polymorph III. Obtained as a later orange-red column fraction in the procedure for **II**. Although we have been unable to identify the precursor, apparently oxidative decomposition of another reaction mixture component on the column leads to the formation of **III**. In the two previous reports of this polymorph [6,7], **III** was obtained from the aerobic oxidation of Cp*Mo carbonyl precursors. Although we have no supporting evidence of their nature, the solution from which **III** was grown must contain impurities not present or in different proportions than were present when **II** was formed.

Solutions of the three polymorphs were spectroscopically identical to those previously reported for **III** [6,7].

Crystallographic characterization of polymorphs I and III.

Crystallographic data are collected in Table 1, including data for **III** from ref. 7. Both specimens used for data collection were mounted on fine glass fibers with epoxy cement. Photographic evidence and systematic absenses in the data uniquely determined the monoclinic space groups shown. Both data sets were empirically corrected for absorption. Unit-cell parameters were obtained from the least-squares fit of the angular settings of 25 reflections (22° $< 2\theta <$ 30°).

Both structures were solved using heavy-atom methods, and completed from subsequent difference Fourier syntheses. Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included as idealized isotropic contributions after a sufficient number were found to determine the rotational orientation relative to the Cp* plane.

Table 1

Crystallographic data for **I**, **II** and **III**

	I	II	III [7]
Formula	$C_{20}H_{30}O_5Mo_2$	$C_{20}H_{30}O_5Mo_2$	$C_{20}H_{30}O_5Mo_2$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	8.145(4)	9.434(3)	21.272(6)
b (Å)	9.193(3)	16.872(5)	9.248(1)
c (Å)	15.263(6)	14.157(4)	17.677(6)
β (deg)	93.61(3)	97.19(2)	101.68(2)
V (Å^3)	1140.9(8)	2235.7(12)	34.05.4(9)
Z	2	4	6
Color	yellow	yellow	brown-yellow
D_{calc} (g cm^{-3})	1.579	1.611	1.60
μ (Mo-K_α)(cm^{-1})	10.97	11.20	
Scan type	Wyckoff	Wyckoff	
2θ scan limits (deg)	4–45	4–54	
Reflections collected	1697	5247	
Independent reflections	1509	4873	
Observed data ($F_o \geq 5\sigma(F_o)$)	1095	3645	
$R(F)$	0.048	0.044	
$R(wF)$	0.054	0.055	
GOF	1.520	1.402	
N_o/N_v	8.8	12.82	
$\Delta(\rho)_{max}$ (e Å^{-3})	0.91	0.76	

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for **I**

	x	y	z	U^a
Mo	4017(1)	203.6(7)	6069.7(4)	74.6(4)
O(1)	5000	0	5000	102(4)
O(2)	5315(11)	1184(8)	6719(4)	144(4)
O(3)	2348(10)	1315(8)	5847(5)	139(4)
C(1)	2949(13)	−2246(9)	5879(5)	74(4)
C(2)	4520(11)	−2407(9)	6260(6)	70(3)
C(3)	4630(12)	−1808(10)	7068(6)	79(4)
C(4)	3080(14)	−1219(8)	7211(6)	87(4)
C(5)	2020(11)	−1531(11)	6465(8)	92(4)
C(6)	2346(17)	−2755(13)	4978(7)	156(7)
C(7)	5924(15)	−3212(13)	5843(9)	149(7)
C(8)	2577(28)	−496(12)	8048(8)	245(12)
C(9)	6043(17)	−1756(16)	7735(8)	186(8)
C(10)	214(14)	−1134(21)	6347(12)	266(13)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for **II**

	x	y	z	U^a
Mo(1)	4956.8(5)	7353.1(3)	2830.7(4)	46.7(2)
Mo(2)	5068.5(4)	5141.4(3)	2536.4(4)	48.5(2)
O(1)	4990(4)	6232(2)	2763(4)	71(2)
O(2)	4326(6)	7566(3)	3875(5)	84(2)
O(3)	3655(5)	7656(3)	1944(4)	80(2)
O(4)	5728(6)	5051(4)	1474(4)	96(2)
O(5)	6382(5)	4801(3)	3375(4)	85(2)
C(1)	7564(5)	7264(3)	3063(4)	48(2)
C(2)	7170(7)	7389(4)	2079(5)	62(2)
C(3)	6502(7)	8150(4)	1959(5)	69(2)
C(4)	6483(6)	8469(3)	2862(5)	56(2)
C(5)	7177(6)	7937(3)	3553(4)	48(2)
C(6)	8351(7)	6549(4)	3519(7)	84(3)
C(7)	7458(9)	6803(6)	1312(6)	109(4)
C(8)	5868(11)	8545(5)	1058(6)	117(4)
C(9)	5889(7)	9267(4)	3082(7)	103(4)
C(10)	7453(11)	8075(5)	4581(6)	90(4)
C(11)	2447(6)	5204(3)	2271(4)	48(2)
C(12)	2870(6)	4588(4)	1717(4)	52(2)
C(13)	3588(6)	4015(3)	2335(5)	59(2)
C(14)	3516(6)	4279(4)	3293(5)	62(2)
C(15)	2820(6)	5015(4)	3232(4)	54(2)
C(16)	1627(7)	5920(4)	1917(6)	75(3)
C(17)	2628(10)	4544(6)	647(5)	94(4)
C(18)	4220(8)	3257(4)	2015(9)	116(5)
C(19)	4104(10)	3814(5)	4150(7)	137(5)
C(20)	2489(8)	5520(5)	4068(5)	93(3)
C(19A)	3883(99)	4043(50)	4748(65)	149(33)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4

Selected bond distances and angles for **I**, **II**, **IIIa** [7] and **IIIb** [7]

	I	II	IIIa [7]	IIIb [7]
a. Bond distances (Å)				
Mo–O	1.873(1)	1.894(4)	1.871(1)	1.889(6)
		1.871(4)		1.855(6)
Mo=O	1.667(8)	1.700(6)	1.691(10)	1.701(7)
	1.717(8)	1.721(5)	1.680(9)	1.701(7)
		1.705(6)		1.689(7)
		1.705(5)		1.683(7)
Mo–CNT [a]	2.098(9)	2.107(6)	2.067(15)	2.080(17)
		2.105(6)		2.083(14)
b. Bond angles (deg)				
Mo–O–Mo	180.0	172.7(3)	180.0	179.2(4)
O–Mo=O	106.4(3)	105.4(2)	103.9(2)	105.3(3)
	105.3(3)	106.0(2)	106.2(3)	105.9(3)
		105.4(3)		106.1(3)
		104.6(2)		105.1(3)
O=Mo=O	105.1(4)	106.0(3)	106.2(4)	105.8(3)
		105.7(3)		105.6(3)
CNT–Mo=O	114.4(3)	114.3(2)	114.9(6)	114.5(7)
	114.4(3)	113.1(2)	115.2(6)	114.6(6)
		114.5(2)		115.4(5)
		115.1(2)		114.1(6)
CNT–Mo–O	110.5(2)	111.4(2)	110.9(4)	111.2(6)
		110.6(2)		110.5(5)
CNT–Mo–Mo–CNT	180.0	176.4(3)	180.0	179.1(5)

[a] CNT = centroid of Cp^* ring.

All software used the SHELXTL library (5.1 revision) (G. Sheldrick, Nicolet XRD, Madison, WI). The cell-reduction program TRACER was used to verify the independence of the three polymorphic structures.

The atomic coordinates for **I** and **II** are given in Tables 2 and 3, and selected bond distances and angles for all polymorphs are compared in Table 4. Additional crystallographic data, including structure factor tables may be obtained from one of the authors (A.L.R.).

Results and discussion

The asymmetric unit for polymorph **I** contains a half molecule on a $\bar{1}$ site, **II**, one whole molecule, and **III**, one and a half molecules with the half molecules on a $\bar{1}$ site. The molecular structures of **I** and **II** are shown in Figs. 1 and 2, respectively. The molecular parameters to be discussed are presented in Table 4.

Of the four independent molecules in the three polymorphs, **II** shows the most significant deviations from the averages of **I**, **IIIa** and **IIIb**. The Mo–O–Mo angle, while exactly or nearly linear in the other three molecules, is 172.7(3)° in **II**. Similarly, the CNT–Mo–Mo–CNT dihedral angle in **II** (176.4°) is the only one that deviates significantly from 180°. II also has the longest Mo=O bond; at 1.721(5) Å it is well outside the range for Mo(VI)=O values (1.67–1.69 Å) listed in

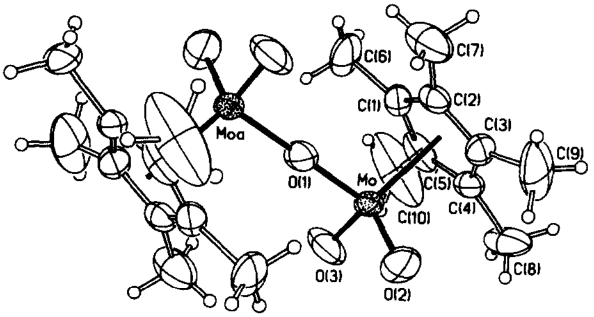

Fig. 1. Molecular structure of polymorph **I** of $[Cp^{\star}Mo(O)_2]_2O$.

ref. 3. The two independent Mo=O distances in I (1.667(8) and 1.717(8) Å) have the greatest range of values for a single structure; in no other structure do the values differ by more than 0.02 Å. The extreme values for the bridging Mo–O bonds also show a considerable range from 1.855(6) Å in **IIIb** to 1.894(4) Å in **II**.

Another of the structural features that could be affected by packing forces is the location of Mo relative to the centroid of the $Cp^{\star}$ rings. In polymorph **III**, it was found [7] that Mo was displaced from the centroid away from the bridging O atom in the three independent $Cp^{\star}Mo$ groups to roughly equal extents. All six independent $Cp^{\star}Mo$ groups in the three polymorphs are shown in Fig. 3. Although there are some minor variations in the rotational orientations of the $Cp^{\star}$ ring to the underlying MoO_3 projection, the displacement of Mo from the centroid is identical (within esd's) in all six, and hence is unlikely affected by packing. The range of Mo–C bond distances is broad; the shortest (2.344(9) Å) is found in **I** opposite the bridging Mo–O group, the longest, in **IIIb** (2.488(5) Å) adjacent to the Mo–O bridge. The same range of about 0.15 Å is seen in $[Cp^{\star}Mo(CO)_2(PPh_3)(L)]$ (L = NCO or N_3) complexes [7], but this range has been described as being large due to the bulk of the PPh_3 ligand. When all of the polymorphs of **1** are examined, there would appear to be no special steric effect attributable to the presence of the phosphine ligand in $[Cp^{\star}Mo(CO)_2(PPh_3)(L)]$ complexes in the context of Mo–O distances.

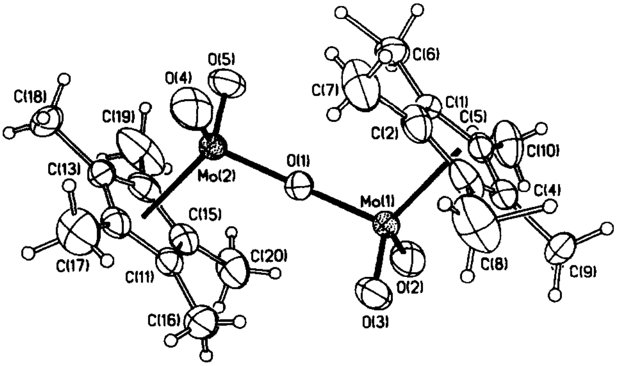

Fig. 2. Molecular structure of polymorph **II** of $[Cp^{\star}Mo(O)_2]_2O$.

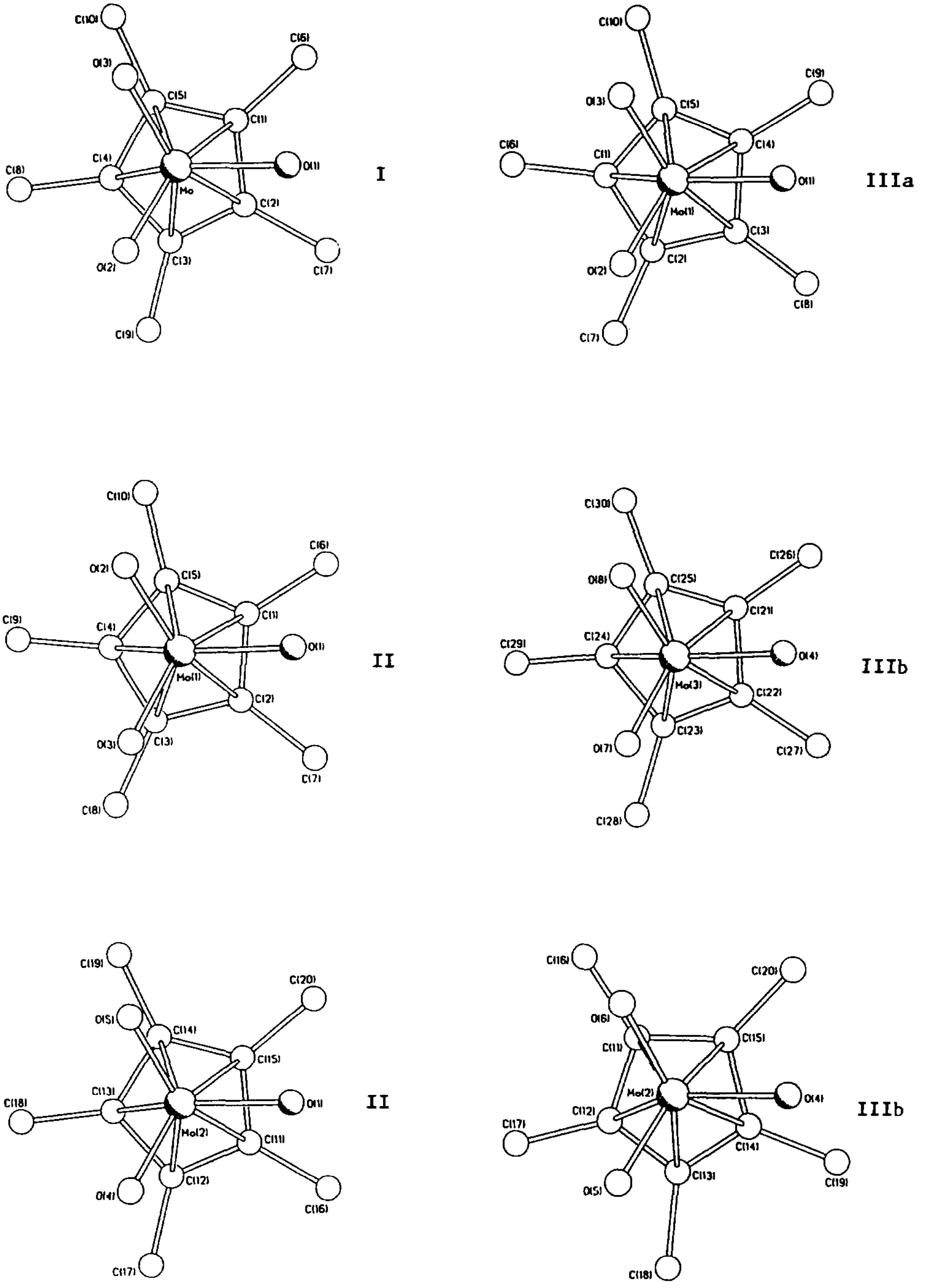

Fig. 3. The six crystallographically independent Cp*MoO$_3$ moieties in the three polymorphs of [Cp*Mo(O)$_2$]$_2$O. The shaded oxygen atom connects to Mo.

While the displacements of the methyl groups above or below the plane of the Cp* rings show a strong tendency to move away from Mo in all six Cp*Mo groups, the position of maximum displacement shows, when all six are examined, no consistency. Furthermore, at least one methyl group in each case is displaced toward

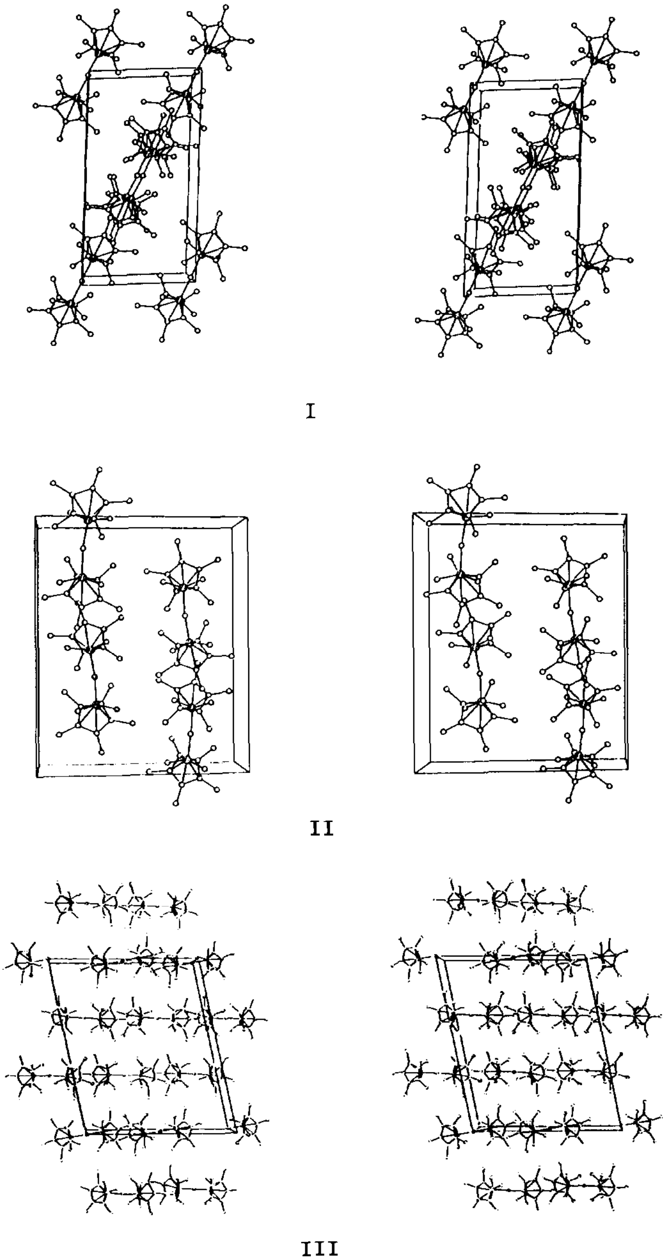

Fig. 4. Unit-cell packing diagrams for the three polymorphs of $[Cp^{*}Mo(O)_2]_2O$ as viewed down the ~ 9 Å axis.

the Mo atom, but, again, there is no consistency in the location. The methyl group with maximum displacement away from Mo is most often found in one of the locations more or less opposite the bridging Mo–O group, but there is at least one example of each position being the one most affected. In **1**, therefore, there would appear to be little intramolecular influence in determining methyl group displacements. (The same conclusions were presented in ref. 7 from the more limited data of a single polymorph.)

In Fig. 4, stereoviews of the unit cell packing of **I–III** are compared (the plot data for **III** come from our determination). Each is viewed down the ~ 9 Å axis which provides similar projections of the molecular structure of **1**. What is most striking about these packing diagrams is the *absence* of significant differences in the packing arrangements. All form chains of interleafed molecules in which the *trans* Cp* rings nest so as to maximize the attractive interactions between the terminal oxo atoms ($\delta-$) and the methyl-group hydrogen atoms ($\delta+$). The closest intermolecular C–H · · · O=Mo contact distances for all polymorphs are identical within esd's.

Conclusions

It is remarkable that these three separate polymorphs are isolable as the differences among the lattice energies must be extremely small. Only on the basis of the frequency with which **III** has been encountered, can we predict that it is the one most likely to be thermodynamically most stable. Crystals of each were grown from solutions that contained methylene chloride as the major solvent component. The effects responsible for the formation of the different polymorphs appear subtle, and may involve only differing concentrations of contaminants.

We have not been able to find previous studies containing as large of a structural polymorph database on a single organometallic compound as we report for $[Cp^{\star}MoO_2]_2O$. A comparison of two polymorphs of $[CpMo(CO)_2]_2(\mu,\eta^2\text{-}C{\equiv}NC_6H_5)$ [10] showed a much smaller variation range in the bond metrics. The maximum difference in bond distance (ca. 0.02 Å) and bond angle (ca. 2°) are less than half that found here. However, despite the relative isolation in which we find our work, there is little reason to suspect that the larger variations we find represent anything more than the presence of multiple *inter*molecular energy minima.

Crystallographic data are often used to parameterize theoretical calculations. But when confronted with a range of parameters to choose from, it becomes more difficult to decide which values are typical? An average will not be satisfactory if multiple *intra*molecular energy minima occur; in that case these polymorphs are better described as separate isomers. To address the question of whether these variations are intra- or intermolecular, we have initiated a collaborative theoretical studies (including *ab initio* calculations) that we will report on in a future paper.

Acknowledgment

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