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Inorganica Chimica Acta 342 (2003) 247-254

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Packing and compositional disorder with MoO₂Cl₂(OPMePh₂)₂, MoOCl₃(OPMePh₂)₂ and MoCl₄(OPMePh₂)₂ as assessed by single crystal X-ray diffraction

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Received 8 April 2002; accepted 23 May 2002

Abstract

The structures as determined by single crystal X-ray determinations of $MoO_2Cl_2(OPMePh_2)_2$ and various mixtures of $MoO_2Cl_2(OPMePh_2)_2$ (A), $MoOCl_3(OPMePh_2)_2$ (B) and $MoCl_4(OPMePh_2)_2$ (C) specifically in ratios 40.2/59.8; 30.8/69.2; 14/86; 4/96 in A/B, 100% B and 82/18 in B/C are reported. The structural data illustrate that both compositional and packing disorder afford mechanisms by which apparent long and different Mo–O bond distances can be obtained. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Packing and compositional disorder; MoO₂Cl₂ (OPMePh₂)₂; MoOCl₃(OPMePh₂)₂

1. Introduction

In 1971, the term 'distortional isomerism' was first proposed by Chatt, Manojlovic-Muir and Muir to explain the relationship between the green and blue complexes of *cis,mer*-MoOCl₂(PMe₂Ph)₃ [1-3]. X-ray structure analyses of these two compounds revealed that the green species has a significantly longer Mo=O bond (1.8 Å) compared with the typical value of (1.6 Å) [4,5] found in the blue species. Several other distortional isomers were reported after this first claim of 'possibility of a new type of isomerism' [6,7] but there was evidence of green complexes which contained short Mo=O bond lengths, specifically MoOCl₂(PMePh₂)₂ with $d_{(M_0-\Omega)} =$ 1.669 Å [8]. These isomers are compositionally and geometrically identical molecules but differ only by one or more bond lengths. In 1988, Hoffman et al. termed the isomers as 'bond-stretch isomers (BSI)' [9,10] and this described the phenomenon more accurately. Parkins' and Enemark's groups reinvestigated the cis,mer- $MoOCl_2(PR_3)_3$ in 1991, and reached the same conclu-

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sion which was that the BSI in these complexes was a consequence of mixtures of *cis,mer*-MoOCl₂(PR₃)₃ and the isostructural *mer*-MoCl₃(PR₃)₃ [11–13]. This phenomenon was appropriately described as compositional disorder and indeed verifiable cases of BSI are rare [14].

In the course of an investigation into the substitution of the chloride ligands on the heteronuclear quadruply bonded complex MoWCl₄(PMePh₂)₄ [15] with the amide NPh₂⁻ group, we obtained crystals of apparent stoichiometry MoO₂Cl₂(OPMePh₂)₂, which appeared to contain very long Mo-O bond distances $(d_{Mo-O} = 2.0)$ Å). With the now well-established fact of compositional disorder in mind [16] we considered that the co-crystallization of MoO2Cl2(OPMePh2)2 with some isostructural complex was the reason for the bond length variation. Here we report that the structure of pure MoO₂Cl₂(OPMePh₂)₂ contains Mo-O (oxo ligand) bond distances of 1.671(2) Å. Contamination of this material with MoOCl₃(OPMePh₂)₂ leads to an apparent lengthening of this bond due to the 'incorporation' of chloride into the oxo site both as a consequence of cocrystallization and packing disorder with MoOCl₃(OP-MePh₂)₂. In order to demonstrate the co-crystallization among the above three compounds, we deliberately grew crystals from the solution of mixtures of the above

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compounds and the crystals obtained revealed varied Mo-O bond lengths.

2. Experimental

2.1. Materials

Molybdenum pentachloride, methyldiphenylphosphine oxide, and lead molybdate were obtained from Aldrich Chemicals and used as received. Dichloromethane was dried over calcium hydride and distilled under nitrogen. Benzene and hexane were dried over sodium benzophenone ketyl and distilled under nitrogen. Methanol was dried over magnesium methoxide. All preparations were carried out using standard schlenk techniques under an inert atmosphere. Infrared spectra were obtained on a Mattson GL-3020 FT IR spectrometer. ¹H and ³¹P NMR data were recorded on a Varian XL-400 spectrometer.

2.2. Preparation of $MoO_2Cl_2(OPMePh_2)_2$ (A)

 $MoO_2Cl_2(OPMePh_2)_2$ (A) was synthesized according to the published procedure [17], except that OPMePh₂ was used instead of OPPh₃. The yield was 58%. The compound in the form of a white precipitate was filtered and dried under vacuum. The IR spectrum in the form of a Nujol mull contained two strong bands at 942 and 903 cm^{-1} which indicated the symmetric and asymmetric vibrations for the Mo=O bond, and agreed with that previous reported for the OPPh₃ analog [17,18]. ¹H NMR (CDCl₃): δ 2.23 (d, 3H, J = 13.2 Hz, Me), 7.39(m, 2H, J = 18.4 Hz, m-Ph), 7.49 (m, 1H, J = 8.8 Hz, p-Ph), 7.77 (m, 2H, J = 21.2 Hz, o-Ph). IR (Nujol mull) 942 (vs, Mo=O), 903 (s, Mo=O), 1155 (s, P-O), 1136 (s, P-O) cm⁻¹. ³¹P NMR (CDCl₃): δ 42.96 (br) relative to H_3PO_4 . Suitable crystals (labeled as 1) were obtained in 1 week by layering a THF solution of A with an equal volume of dried methanol.

2.3. Preparation of $MoOCl_3(OPMePh_2)_2$ (**B**)

Dichloromethane(2.5 ml) and freshly opened acetyl chloride (3.5 g, 0.042 mol) were added to lead molybdate (2.5 g, 6.8 mmol). The mixture was stirred for 30 min and then filtered. The addition of OPMePh₂ (3 g, 13.6 mmol), dissolved in a minimum quantity of dichloromethane, to the dark brown filtrate gave a green solution and white precipitate in high yields (i.e. > 70%). The mixture was stirred at room temperature (r.t.) for 3 h, and at the end contained a green precipitate. The product was collected by filtration, washed with benzene and dried under vacuum. The IR spectrum contained an absorption at 970 cm⁻¹ which has been previously assigned for the Mo(V)–O stretch-

ing mode in related compounds [19]. This peak was observed in other compounds of the type Mo(V)OCl₃L and not for those consisting of Mo(VI)O₂Cl₂LL' [20]. ¹H NMR (CHCl₃): δ 1.6 (br, 3H, Me), 7.27 (br, 2H, *m*-Ph), 7.42 (br, 1H, *p*-Ph), 7.76 (br, 2H, *o*-Ph). IR (Nujol mull) 970 (vs Mo(V)–O), 1146 (s, P–O), 1130 (s, P–O) cm⁻¹. ³¹P NMR (CHCl₃): δ 43.12 (br) relative to H₃PO₄.

2.4. Preparation of $MoCl_4(OPMePh_2)_2(C)$

A suspension of $MoCl_4(THF)_2$ (1.3 g, 3.4 mmol), which was prepared as previously reported [21], in benzene was treated with OPMePh₂ (1.6 g, 7.8 mmol). The mixture was stirred at r.t. for 5 h over which period the orange solution became yellow. The mixture was filtered, washed with benzene and dried under vacuum. The yield was 65%. IR (Nujol mull) 1081 (s, P–O), 1067 (s, P–O) cm⁻¹. We were unable to obtain crystals of this compound due to the instability of the compound in solution.

2.5. Preparation of co-crystals

Crystals of material labeled as 3 and 7 were obtained by layering the products obtained in the reaction of $MoWCl_4(PMePh_2)_4$ [15] and 4 equiv. of LiNPh_2 in benzene with hexanes. Crystal 1 was obtained from pure A; 2 was 33% each of A, B and C; 4 was 80% A, 20% B; 5 was 50% B 50% C; and 6 was from 'pure' C. These mixtures were dissolved in either dried dichloromethane or THF and then layered with hexanes or benzene. Suitable crystals for 2, 4, 5, and 6 grew in about 1 week (the most suitable were obtained from mixtures layered with benzene) and, except for 4, the compositions obtained were not the same as the initial mixtures.

2.6. X-ray diffraction studies

For 1-4 suitable crystals were chosen and removed from the mother liquor to a microscope slide where they were stabilized by immersion in a mixture of mother liquor and mineral oil. The crystals were then trimmed using a sharp scalpel, rolled in epoxy resin, and fixed on top of a thin glass fiber, which was anchored in a goniometer-mounting pin. Compounds 5 and 6 were mounted in 0.3 mm glass capillaries, which was filled with the solutions that the crystals grew from, and then capped with epoxy resin. All measurements were performed at r.t., except for 6 and 7, which were measured at 120 and 223 K, respectively. Except for compound 6, the diffractometer used was an Enraf-Nonius Diffractis 586 Turbo CAD4 X-ray diffractometer. The data collection and reduction were accomplished using procedures detailed previously [22]. The windows program WINGX was used as the interface for the solution and refinement of the models [23]. The data were first reduced and corrected for absorption using psi-scans [24] and then solved using the program SIR97 [25]. The model was refined with SHELXL97 [26] first with isotropic and then anisotropic thermal parameters to convergence. In those crystals where co-crystallization and/or disorder occurred, the percentage occupancies were determined by refinement of the site occupancies with the sum constrained to unity. Some sites could be modeled with anisotropic thermal parameters; others had to be defined with isotropic parameters. Compound 6 was collected on a KCCD (with Oxford Cryostream) at 120 K using ω -scans with κ offsets. The data was reduced and processed using the program COLLECT [27] and the solution and refinement was as detailed above for the other structures. Crystallographic data for 1-7 are given in Table 1. Selected bond distances and angles are listed in Table 2.

3. Results and discussion

3.1. Synthesis of A, B and C

The synthesis of A was based on well-established procedures [17] to prepare molybdenum (VI) compounds of the form $MoO_2X_2L_2$ (X = halide, L = monodentate ligand). This complex was identified by ¹H and ³¹P NMR, IR and (as crystals labeled as 1) by single Xray diffraction. The structure of the triphenylphosphine oxide analog, i.e. MoO₂Cl₂(OPPh₃)₂, was previously reported [29]. Compound **B** was prepared by adding the phosphine oxide ligand to the obtained filtrate from the reaction of lead molybdate and acetyl chloride in the quantities reported in the Section 2. We find that the nature of the product from this reaction is very sensitive to the quantities of acetyl chloride used and also works best if the container is freshly opened. This complex was identified on the basis of its IR, ¹H and ³¹P NMR spectra. A value of 967 cm⁻¹ has been assigned for the v(Mo(V)-O) stretching frequency [19,20]. With B, this stretch occurs at 970 cm⁻¹. Compound C, MoCl₄(OP-MePh₂)₂, was prepared by substitution of the THF ligands in MoCl₄(THF)₂ [21] with OPMePh₂. Unfortunately, we were not capable of producing crystals of this material.

3.2. Crystallographic results

Our interest in compositional disorder arose as a result of the structural determination of the material labeled as 3 and 7. It was not immediately apparent as to why different Mo to O atom distances ($d_{Mo-O} \approx 1.8$ and 2 Å) were being resolved in these structures, i.e. if the disorder is accounted for solely as an O atom. It occurred to us that this may be another case of

compositional disorder [12] and thus we set about deliberately preparing mixtures consisting of different quantities of 'pure' materials. For obvious reasons, it was important to establish the structural details of pure $MoO_2Cl_2(OPMePh_2)_2$ and thus crystals from A were grown and the data from this is listed as structure 1. An ORTEP-3 [30] representation of 1 is given in Fig. 1. Crystals of this compound did not contain any interstitial solvent molecules and Mo-O atom distances for the oxo ligand of 1.676(3) and 1.677(3) Å were obtained. Compound 1, which was the only molecule out of the seven studied herein to crystallize without lattice solvent, contained disorder in the arrangement of one of the phenyl rings as shown in Fig. 1 and was the only structure to contain this particular type of ligand disorder. Interestingly, this disorder is also present in the crystal structure of the tungsten analogue to A [31].

A drawing of 2 is displayed in Fig. 2. The distorted octahedral geometry displayed by 2 is typical of what remaining complexes 3-7 display, i.e. a *trans*-chloride, *cis*-phosphine oxide ligand arrangement. Compounds 2-7 all co-crystallized with a 1/2 mol of benzene, situated around an inversion point. This molecule of solvation was arranged in a disordered manner in 3 where it appeared to have crystallized in two orientations, which differed by a 30° rotation about the inversion point of the benzene molecule.

An examination of the occupancies for the O atom as listed in Table 1 reveals that varying occupancies were observed with the serendipitous results as afforded in the structures of 3 and 7 and in the different preparations consisting of mixing different quantities of A, B and C. The particular mixture of A, B and C that these occupancies represent is given by the compositional listing also in Table 1. Unfortunately, the tetrachloride compound C proved to be very unstable in solution affording the complex MoOCl₃(OPMePh₂)₂, (6), when we attempted to grow crystals of C directly. The structure of this compound was previously reported also as a benzene solvate but in this case 1 mol of benzene crystallized with 1 mol of MoOCl₃(OPMePh₂)₂ [32] instead of the 1/2 mol reported with 6, a situation which resulted in different unit cell parameters. A drawing of 6 is shown in Fig. 3. As 6 is believed to be composed entirely of MoOCl₃(OPMePh₂)₂·1/2C₆H₆, (and not a 50:50 mixture of A and C, based on IR evidence of the crystals where only **B** and no **A** was found) the disorder in the equatorial chloride and oxo ligands is caused by packing disorder. Interestingly, even this disorder can be accounted for by simply modeling each disordered atom site as an oxygen atom. However, this affords long Mo-O atom bond distances on the order of 2 Å and there is always substantial residual electron density near the O atoms on the opposite side of the Mo-O interaction. In all cases, the nature of the disorder was resolved by constraining the Mo-O

Table 1 Crystal data and structure refinement details for 1–7

	1	2	3	4	5	6	7	
Composition	MoO ₂ Cl ₂ (OPMePh ₂) ₂	40.2% MoO ₂ Cl ₂ (OP- MePh ₂) ₂ , 59.8% MoO ₁ - Cl ₃ (OPMePh ₂) ₂	30.8% MoO ₂ Cl ₂ (OP- MePh ₂) ₂ , 69.2% MoO ₁ - Cl ₃ (OPMePh ₂) ₂	14% MoO ₂ Cl ₂ (OP- MePh ₂) ₂ 86% MoO- Cl ₃ (OPMePh ₂) ₂	4% MoO ₂ Cl ₂ (OP- MePh ₂) ₂ 96% MoO- Cl ₃ (OPMePh ₂) ₂	100% MoOCl ₃ (OP- MePh ₂) ₂	82% MoOCl ₃ (OP- MePh ₂) ₂ 18% Mo- Cl ₄ (OPMePh ₂) ₂	
Disorder (O atom%)	100	70.1(7)	65.4(6)	56.7(6)	52.3(8)	49.1(5)	40.8(9)	
Formula M	$C_{26}H_{26}Cl_2Mo_1O_4P_2$	C ₂₉ H ₂₉ Cl _{2.60} Mo ₁ O _{3.40} P ₂ 682 0	C ₂₉ H ₂₉ Cl _{2.69} Mo ₁ O _{3.31} P ₂ 683.8	C ₂₉ H ₂₉ Cl _{2.86} Mo ₁ O _{3.14} P ₂ 687 1	C ₂₉ H ₂₉ Cl _{2.96} Mo ₁ O _{3.04} P ₂ 689 0	C ₂₉ H ₂₉ Cl ₃ Mo ₁ O ₃ P ₂ 689.8	C ₂₉ H ₂₉ Cl _{3.18} Mo ₁ O _{2.82} P ₂ 693 30	
Habit	yellow prism	green prism	green prism	green prism	green prism	light yellow-green	pale green prism	
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	
a (Å)	9.2615(16)	9.2624(19)	9.280(4)	9.2810(13)	9.3293(18)	9.2441(2)	9.2343(20)	
b (Å)	17.5140(40)	15.622(2)	15.624(4)	15.5960(3)	15.632(3)	15.4437(3)	15.5413(27)	
c (Å)	17.8060(40)	21.200(4)	21.181(4)	21.1770(33)	21.218(4)	21.0214(4)	21.1078(28)	
α (°)	90	90	90	90	90	90	90	
B (°)	104.959(17)	97.591(17)	97.65(2)	97.695(13)	97.727(15)	97,9807(8)	97.686(15)	
r () v (°)	90	90	90	90	90	90	90	
$V(\Lambda^3)$	2790 4(10)	3040 8(10)	30/3 5(16)	3037 7(9)	3066 2(10)	2072.01	3002 02(6)	
$V(\Lambda)$	0 71072	0.71073	0.71073	0.71073	0 71072	0.71073	0 71073	
radiation)	0.71075	0.71075	0.71075	0.71075	0.71075	0./10/5	0./10/3	
Temperature (K)	293	293	293	293	293	120	223	
Z	4	4	4	4	4	4	4	
$D_{\rm r} ({\rm g \ cm^{-3}})$	1.50	1 490	1 493	1 503	1 498	1 542	1 526	
F(000)	1280	1364	1364	1400	1400	1400	1400	
Monochromator	graphite	graphite	graphite	graphite	graphite	graphite	graphite	
Diffractomator	Enrof Nonjus	EN CADA	EN CADA	EN CADA	EN CADA	wCCD	EN CADA	
Diffactometer	Emai-Nomus	EIN CAD4	EIN CAD4	EIN CAD4	EIN CAD4	KCCD	EIN CAD4	
D:00	(EN) CAD4							
Diffraction	κ-geometry diffractometer	к	κ	κ	к		κ	
Type of scan	$\omega - 2\theta$ scans	$\omega - 2\theta$ scans	$\omega - 2\theta$ scans	$\omega - 2\theta$ scans	$\omega - 2\theta$ scans	multi-scan ^a	$\omega - 2\theta$ scans	
μ (Mo K α)	0.81	0.74	0 744	0.83	0.822	0.848	0.84	
μ (1010 Ku)	0.01	0.74	0.744	0.85	0.822	0.040	0.84	
(mm)	0.20 0.25 0.20	0.00 0.15 0.10	0.00 0.10 0.10	0.00 0.15 0.15	0.40 0.2 0.15	0.40 0.00 0.07	0.50 0.20 0.20	
Crystal size	$0.30 \times 0.25 \times 0.20$	$0.20 \times 0.15 \times 0.10$	$0.20 \times 0.18 \times 0.12$	$0.20 \times 0.15 \times 0.15$	$0.40 \times 0.2 \times 0.15$	$0.40 \times 0.08 \times 0.07$	$0.50 \times 0.30 \times 0.30$	
(mm)								
Number of	25	25	25	25	25	25	25	
reflections								
2θ Range (°)	16.2-24	20-30	20-30	19.56-27.78	19.38-27.7	5.1-64.08	20-30	
Some provided absorption coefficient b								
Semiempirical ab.	corplion coefficient	105	240	250	105		195	
number of ψ -	LLL	183	249	239	180		163	
scans								
Number of	6	5	7	7	5		5	
reflections								

Table 1 (Continued)

	1	2	3	4	5	6	7		
Transmission coefficients									
Min	0.730	0.8695	0.742	0.8681	0.6036	0.784	0.6788		
Max	0.851	0.9262	0.862	0.893	0.8635	0.936	0.7867		
$\theta \max(^{\circ})$	24.97	24.97	24.97	22.47	24.97	32.04	22.48		
Н	0-11	0-11	0-11	0-9	0-11	0-13	0-9		
Κ	0-20	0-18	0-18	0-16	0-18	-23 to 23	0-16		
L	-21 to 20	-25 to 24	-25 to 24	-22 to 22	-25 to 24	-31 to 31	-22 to 22		
Number of	4892	5338	5335	3945	5382	10136 °	3907		
reflections									
measured	measured								
Number of	2882	3075	3777	2822	3038	6347	2676		
observed data									
$[I > 2\sigma(I)]$									
Number of	311	353	349	352	352	329	353		
parameters									
R _{int}	0.024	0.030	0.020	0.022	0.049	0.031	0.027		
$R(F)^{d}$	0.041	0.071	0.054	0.041	0.070	0.066	0.057		
$wR(F^2)^{e}$	0.105 ^f	0.179 ^g	0.142 ^h	0.096 ⁱ	0.166 ^j	0.019 ^k	0.151 1		
Goodness-of-fit	0.997	1.037	1.039	1.021	1.02	1.169	1.045		
Max. (Δ/σ)	0.005	0.001	0.001	0.017	0.005	0.005	0.067		
Residual ΔO (e \mathring{A}^{-3})									
Max	0.297	1.287	1.299	0.513	0.941	0.935	1.252		
Min	-0.338	-1.033	-1.178	-0.645	-1.42	-1.383	-1.4		

Scattering factors from International Tables for Crystallography (Vol. C).

^a H.K.L. Scalepack ([24]).

^b North [24].

^b North [24]. ^c Denzo and Scalepack ([28]). ^d $R = \Sigma(F_o - F_c)/\Sigma(F_o)$. ^e $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. ^f $w = 1/[^2(F_o^2) + (0.0468 \times P)^2 + 0.4076P]$, where $P = (\max(F_o^2, 0) + 2 \times F_c^2)/3$. ^g $w = 1/[^2(F_o^2) + (0.0581 \times P)^2 + 12.4113P]$. ^h $w = 1/[^2(F_o^2) + (0.0519 \times P)^2 + 8.5275P]$. ⁱ $w = 1/[^2(F_o^2) + (0.0322 \times P)^2 + 5.3651P]$. ^j $w = 1/[^2(F_o^2) + (0.0137 \times P)^2 + 8.2246P]$. ^k $w = 1/[^2(F_o^2) + (0.0562 \times P)^2 + 15.6020P]$.

Table 2								
Selected	bond	lengths	(Å)	and	angles	(°)	for	1-7

	1	2	3	4	5	6	7
Bond lengths							
Mo1-O1	2.206(3)	2.139(5)	2.143(4)	2.116(4)	2.115(5)	2.116(2)	2.151(5)
Mo1-O2	2.160(3)	2.115(6)	2.121(4)	2.119(3)	2.122(5)	2.119(3)	2.114(6)
Mo1-Cl1	2.3962(15)	2.398(3)	2.3959(19)	2.3941(18)	2.398(2)	2.4004(10)	2.369(3)
Mo1-Cl2	2.3816(15)	2.367(3)	2.3703(19)	2.3750(18)	2.374(2)	2.3814(10)	2.399(3)
Mo1-O3	1.676(3)	1.735(5)	1.746(5)	1.748(5)	1.735(5)	1.754(5)	1.742(5)
Mo1-O4	1.677(3)	1.736(5)	1.761(5)	1.733(5)	1.7322(5)	1.725(5)	1.743(5)
Mo1-Cl3	~ /	2.316(5)	2.292(4)	2.282(4)	2.279(4)	2.266(2)	2.319(5)
Mo1-Cl4		2.313(5)	2.268(4)	2.250(4)	2.304(4)	2.196(3)	2.320(5)
Bond angles							
CH-Mol-Ol	83.92(9)	85.55(17)	85.61(12)	87.21(12)	87.72(16)	86.42(8)	85.84(17)
CH-Mo1-O2	85.49(9)	86.42(18)	86.91(13)	86.34(11)	86.60(15)	87.48(8)	85.09(18)
CH-Mo1-O3	94.18(15)	93.7(4)	93.6(4)	92.9(3)	92.0(4)	92.9(3)	93.6(4)
CH-Mo1-O4	94.70(13)	93.2(4)	92.5(3)	93.2(3)	92.3(5)	92.2(2)	93.7(3)
CH-Mo1-Cl2	166.08(5)	168.84(10)	169.53(7)	170.59(6)	171.55(8)	171.07(4)	168.80(9)
Cl2-Mo1-O1	85.64(9)	85.86(17)	86.13(12)	85.36(12)	85.85(16)	86.88(8)	85.40(17)
Cl2-Mo1-O2	83.33(9)	84.95(18)	85.27(13)	86.71(11)	86.99(15)	85.57(8)	86.40(18)
Cl2-Mo1-O3	94.38(15)	93.6(4)	93.5(4)	92.9(3)	93.8(4)	92.6(3)	93.9(4)
Cl2-Mo1-O4	94.27(12)	94.2(4)	94.5(3)	93.3(3)	93.2(5)	94.0(2)	93.6(3)
O1-Mo1-O3	169.35(14)	170.6(4)	170.7(4)	90.2(3)	173.1(4)	169.6(3)	170.5(4)
O1-Mo1-O4	88.81(14)	92.0(3)	93.7(3)	171.5(3)	90.0(5)	92.3(2)	92.5(4)
O1-P1-C10	113.4(2)	112.9(4)	113.1(3)	113.3(3)	113.2(4)	112.73(17)	112.9(4)
O2-P2-C20	113.1(2)	113.0(5)	113.3(3)	113.1(3)	113.0(4)	113.58(19)	112.6(4)
O3-Mo1-O4	101.80(16)	97.5(5)	95.6(5)	98.3(4)	96.9(6)	98.0(3)	97.1(5)
Mo1-O1-P1	139.59(18)	145.2(4)	145.3(3)	151.9(3)	151.3(4)	144.40(16)	144.6(4)
Mo1-O2-P2	156.5(2)	153.4(4)	152.3(3)	145.1(2)	146.0(3)	149.47(18)	152.6(4)
Cl3-Mo1-O1		169.9(3)	170.9(3)	90.2(3)	170.7(2)	170.60(9)	169.5(3)
Cl3-Mo1-O2		91.0(3)	91.2(3)	170.3(2)	89.7(2)	90.42(9)	90.5(3)
Cl3-Mo1-O4		98.1(4)	95.5(3)	97.6(4))	99.2(5)	97.0(2)	98.0(4)
Cl3-Mo1-C11		94.9(2)	94.2(2)	93.42(13)	92.64(17)	93.2(2)	92.54(7)
Cl3-Mo1-Cl2		92.3(2)	93.0(2)	92.45(13)	92.82(17)	93.10(7)	94.2(2)
Cl3-Mo1-Cl4		101.1(4)	100.4(3)	98.5(2)	98.4(2)	98.70(9)	100.9(3)
Cl4-Mo1-O1		89.0(3)	88.72(19)	90.89(16)	90.8(2)	90.68(10)	89.6(3)
Cl4-Mo1-O2		168.0(3)	168.3(2)	90.5(2)	172.0(2)	170.82(10)	168.6(3)
Cl4-Mo1-O3		100.4(5)	100.6(4)	99.2(4)	96.0(4)	99.7(3)	100.0(5)
Cl4-Mo1-Cl1		92.6(3)	92.79(16)	92.63(17)	92.95(17)	93.12(7)	94.0(3)
Cl4-Mo1-Cl2		94.4(3)	93.46(16)	93.77(17)	92.62(17)	92.86(7)	92.9(3)
O3-Mo1-O1		170.6(4)	170.7(4)	90.2(3)	173.1(4)	169.6(3)	170.5(1)
O3-Mo1-O2		91.6(4)	91.1(4)	170.3(3)	92.0(4)	89.4(3)	91.5(4)
O4-Mo1-O1		92.0(3)	93.7(3)	171.5(3)	90.0(5)	92.3(2)	92.5(4)
O4-Mo1-O2		170.9(3)	173.3(3)	91.5(3)	171.1(5)	172.5(3)	171.5(4)

distance to be approximately 1.7 Å, and the Mo–Cl distance was set at 2.37 Å. The occupancies were refined (as pointed out in the Section 2) allowing for a determination of the composition [26]. In all cases, the presence of the mixtures as suggested in Table 1 was confirmed qualitatively by obtaining the IR spectra of the compounds verifying that both MoO₂Cl₂(OP-MePh₂)₂ and MoOCl₃(OPMePh₂)₂ were present.

We believe that compounds labeled as 2-5 and 7 represent materials exhibiting compositional as well as packing disorder. This is a particularly noteworthy feature about these compounds. The composition data listed in Table 1 show that the quantity of MoO₂-Cl₂(OPMePh₂)₂ (**A**), to MoOCl₃(OPMePh₂)₂ (**B**), decreases from 40.2/59.8 in **2** to 4/96 in **5**. Essentially, all of

these structures display a similar geometry to that displayed for 2 and 6 in Figs. 2 and 3, respectively. The packing disorder in these structures is due to the disordered arrangement of compound **B**.

As the experimental and crystallographic data indicate, we were not successful in obtaining material containing the tetrachloride $MoCl_4(OPMePh_2)_2$ (C). Despite our precautions regarding drying solvents and exclusion of moist air, mixtures initially containing C resulted in crystals where C transformed into MoO- $Cl_3(OPMePh_2)_2$ (B). Evidence of C was only found for the crystals labeled as 7 produced in the reaction between of MoWCl₄(PMePh₂)₄ [15] and 4 equiv. of LiNPh₂, which had also produced (in a different experimental run) material of composition labeled as



Fig. 1. ORTEP-3 [30] representation of 1 with 20% probability ellipsoids. Spheres of arbitrary radii represent H atoms. The major orientation (68.2(5)%) in the disordered phenyl ring on the right of the drawing is the one almost perpendicular to the plane of the paper.



Fig. 2. ORTEP-3 [30] representation of **2** at 50% probability ellipsoids, without the benzene molecule of solvation. H atoms are not shown.



Fig. 3. ORTEP-3 [30] representation of 6 at 50% probability ellipsoids, without the benzene molecule of solvation. Spheres of arbitrary radii represent H atoms.

3. The IR of this mixture clearly indicated the presence of **B** and did not indicate **A**. The only way (assuming refining occupancies is meaningful in all cases) to account for the below 50% occupancy of the O atom (as determined crystallographically) is to have compositional disorder with **B** and **C**.

There are some noteworthy differences in the geometries of complexes 1–7, see Table 2. First, the two Mo– O atom bond distances for the O atom in the phosphine oxide ligand at 2.160(3) and 2.206(3) Å are significantly different in 1. In some cases, namely 4–6, these distances are not significantly different but the distances in 1 are longer than the corresponding distances in 2–7. This difference is reflected in the Mo–O–P angles where those in 1 again display the largest range at 139.59(18) and 156.5(2)°. The smaller angle in complexes 2–7 ranges from 144.40(6) to 146.0(3)° and the larger one ranges from 149.47(18) to 153.4(4)°. The corresponding angles in 1 are significantly different from those in 2–7.

There are some slight differences in the axial *trans*chloride ligands distances and angles, i.e. Cl1–Mo–Cl2. This angle ranges from $166.08(5)^{\circ}$ in **1** to $171.55(8)^{\circ}$ in **5** similar to bond angles in related structures [32,33]. The two oxo ligands complete the coordination sphere in **1** and, the Mo–O(oxo) bond distances here, as expected, are the shortest. In the other structures, this distance ranges from 1.725(5) to 1.761(5) Å which is no doubt a consequence of the packing and compositional disorder. This disorder also results in shorter Mo–Cl_(eq) bond distances compared with the Mo–Cl_(ax) bond distances.

In summary, a variety of disorder was found in these crystallographic studies ranging from solvent, ligand, packing and compositional disorder. The refinement suggests that complexes A and B can co-crystallize and evidence was found for B and C on one occasion. As of this moment, we do not have evidence that A and C can co-crystallize or that ternary mixtures can be produced [16c] with these series of compounds. Attempts to define this were thwarted by the unfortunate decomposition of C.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 182926–182932 for compounds 1–7, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac. uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank Michigan Technological University and the NSF (CHE-0079158) for generous support.

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