New Dinuclear Molybdenum(V) Complexes With β′-Hydroxy-β-enaminones Containing a 4-Hydroxy-2-pyrone Ring[‡]

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New dinuclear molybdenum(V) complexes of the general formula $[Mo_2O_4L_2D_2]$, were prepared by the reaction of $[Mo_2O_3(acac)_4]$ (acac = acetylacetonate ion) with β′-hydroxy-β-enaminones (L). All prepared complexes consist of $Mo_2O_4^{2+}$ cores coordinated by two ligands L via two donor oxygen atoms as in the analogous β-diketonates. The usual octahedral coordination around the molybdenum atoms is completed by the monodentate solvent molecules D (methanol, ethanol, or 2-propanol). All compounds were characterized by elemental analyses, IR, one- and two-dimensional NMR spectra, and thermal analysis, and some of them by X-ray crystallography (**1a**, **4a**, **8b**, and **9a**).

Introduction

Metal complexes with 2-pyrone derivatives are of interest in coordination and bioinorganic chemistry because of their application in immunoassay procedures and in cytological investigations, as well as for their use as potential HIV protease inhibitors.[1–6] Dehydroacetic acid (dha = 3-acetyl-4-hydroxy-6-methyl-2-pyrone) containing a 4-hydroxy-2-pyrone ring is a frequently investigated compound due to its good complexing properties. However, only two crystal structures of complexes $[Re(dha)Cl_2(OPPh_3)(PPh_3)]\cdot EtOH$[7] and $[Co(dha)_2(dmf)_2]$[8] have been known so far. Furthermore, little is known about complexes with dehydroacetic derivatives such as the β′-hydroxy-β-enaminone, and to the best of our knowledge only the copper(II) complex $[Cu(acrp)_2(py)]\cdot H_2O$ [Hacrp = 4-hydroxy-6-methyl-3-(3-dimethylaminoacryloyl)-2*H*-pyran-2-one] has been structurally characterized.[9] Such complexes have been studied not only as models for the elucidation of interactions between flavonoides and metal ions, but they are also of interest when studying the correlation between their steric, electronic, and hydrogen bonding effects, as well as for their possible relevance to biological processes.[10,11] In addition, the enaminone derivatives are good analytical reagents for spectrofluorometric determination of beryllium.[12]

We have recently published syntheses and structures of several isomeric enaminones obtained by the reaction of ethyl 2-hydroxy-4-(4-hydroxy-6-methyl-2*H*-pyran-2-on-3-yl)-4-oxo-2-butenoate and corresponding amines (*n*-butylamine, aniline, *p*-anisidine, and α-naphthylamine).[13–16] Continuing this research, we describe here nine new dinuclear molybdenum(V) complexes obtained by the reaction of isomeric β′-hydroxy-β-enaminones and $[Mo_2O_3(acac)_4]$ (Scheme 1). All complexes have the general formula $[Mo_2O_4L_2D_2]$, where ligand L is coordinated to molybdenum in a bidentate manner through the deprotonated hydroxyl groups and ketone moieties. The typical octahedral coordination around the Mo atom is completed by the monodentate solvent molecules D.

All compounds were characterized by means of chemical analysis, high-resolution NMR and IR spectroscopy, and thermogravimetric analysis. Four of them were also characterized by X-ray crystallography (**1a**, **4a**, **8b**, and **9a**).

Results and Discussion

Synthesis and Characterization of Complexes

The reaction of ethyl 2-hydroxy-4-(4-hydroxy-6-methyl-2*H*-pyran-2-on-3-yl)-4-oxo-2-butenoate (**ehmpb**) with a suitable amine (*n*-butylamine, aniline, or α-naphthylamine)

[‡] This paper is part of our studies on molybdenum complexes with enaminones.[16]

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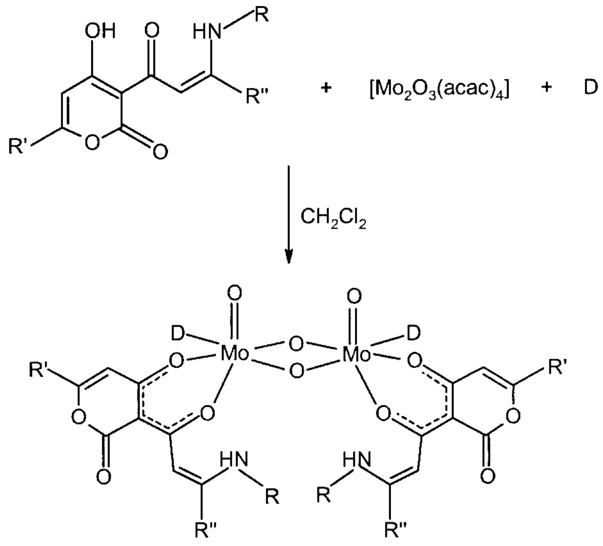
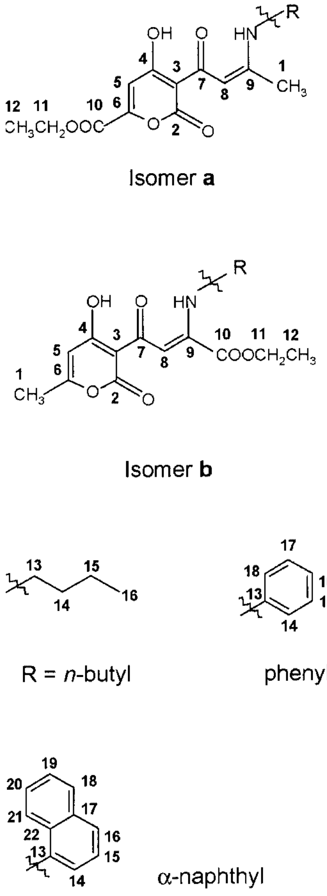


	R	R'	R''	D
1a	n-C$_4$H$_9$	CO$_2$C$_2$H$_5$	CH$_3$	CH$_3$OH
2a		CO$_2$C$_2$H$_5$	CH$_3$	CH$_3$CH$_2$OH
3a		CO$_2$C$_2$H$_5$	CH$_3$	(CH$_3$)$_2$CHOH
4a	C$_6$H$_5$	CO$_2$C$_2$H$_5$	CH$_3$	CH$_3$OH
4b		CH$_3$	CO$_2$C$_2$H$_5$	CH$_3$OH
5a		CO$_2$C$_2$H$_5$	CH$_3$	CH$_3$CH$_2$OH
5b		CH$_3$	CO$_2$C$_2$H$_5$	CH$_3$CH$_2$OH
6a		CO$_2$C$_2$H$_5$	CH$_3$	(CH$_3$)$_2$CHOH
6b		CH$_3$	CO$_2$C$_2$H$_5$	(CH$_3$)$_2$CHOH
7a	α-C$_{10}$H$_7$	CO$_2$C$_2$H$_5$	CH$_3$	CH$_3$OH
7b		CH$_3$	CO$_2$C$_2$H$_5$	CH$_3$OH
8a		CO$_2$C$_2$H$_5$	CH$_3$	CH$_3$CH$_2$OH
8b		CH$_3$	CO$_2$C$_2$H$_5$	CH$_3$CH$_2$OH
9a		CO$_2$C$_2$H$_5$	CH$_3$	(CH$_3$)$_2$CHOH
9b		CH$_3$	CO$_2$C$_2$H$_5$	(CH$_3$)$_2$CHOH

Scheme 1

resulted in the formation of two isomeric enaminones (Scheme 2), one with the 2-pyrone ring substituted at position 6 by ethoxycarbonyl group (isomer **a**) and the other one substituted by a methyl group (isomer **b**).[14,15] The reaction of **ehmpb** with n-butylamine gave both isomers **a** and **b**, but the obtained amount of isomer **b** was insufficient for further synthesis of molybdenum complexes.

New molybdenum(V) complexes of general formula [$Mo_2O_4L_2D_2$] were prepared by reaction of [$Mo_2O_3(acac)_4$] with enaminones (Scheme 1) variously substituted at the nitrogen atom (R = n-butyl, phenyl, or α-naphthyl). Both isomers **a** and **b** of the phenyl and α-naphthyl derivatives were used as starting reagents for the preparation of the corresponding molybdenum(V) complexes, whereas in the case of the n-butyl derivative only isomer **a** was used. Dichloromethane was chosen as the most suitable solvent for all preparations, followed by the addition of the corresponding alcohol D (methanol for the preparation of complexes **1**, **4**, and **7**, ethanol for **2**, **5**, and **8**, and 2-propanol for **3**, **6**, and **9**).



Scheme 2

In all complexes, ligand L was coordinated in a bidentate fashion to molybdenum through two oxygen atoms (as in the case of β-diketonates) and not through the nitrogen atom. One neutral solvent molecule D, acting as a monodentate ligand, completed the octahedral coordination of each Mo atom. Such behaviour was expected from the previous studies of molybdenum complexes with analogous ligands.[14,17,18]

Infrared Spectra and Thermal Analyses

All complexes were characterized by IR spectroscopy (selected spectroscopic data are given in Table 1). Two bands at 1735−1720 cm^{-1} and 1650−1700 cm^{-1} can be attributed to the stretching vibrations of the carbonyl group belonging to the ester $COOC_2H_5$ and 2-pyrone, respectively. The stretching frequencies at about 1570 and 1520 cm^{-1} attributed to the coordinated C···O groups and to C···C were observed at lower values compared to those found in the free ligands.[14,15] The single strong absorption maximum at about 950 cm^{-1} belongs to Mo−O (terminal), while the band at 730 cm^{-1} to the Mo−O (bridging) stretching frequencies. The remaining frequencies in the IR spectra are due to the vibrations within the ligands.

Thermal analyses of all prepared specimens revealed two main processes: (1) loss of solvent molecules, and (2) complex decomposition (Table 2). When heated, a weight loss

Table 1. Analytical and IR data for $[Mo_2O_4L_2D_2]$ complexes.

Formula *M*r	Complex	Analysis found (calcd.)				Yield (%)	Selected IR data (cm^{-1})
		%C	%H	%N	%Mo		
$C_{34}H_{48}Mo_2N_2O_{18}$ 964.63	**1a**	42.13 (42.33)	4.92 (5.01)	3.39 (2.90)	19.64 (19.89)	46	1724, 1651, 1594, 1522, 952, 738
$C_{36}H_{52}Mo_2N_2O_{18}$ 992.68	**2a**	43.13 (43.56)	5.29 (5.28)	2.77 (2.82)	18.72 (19.32)	40	1720, 1654, 1597, 1525, 957, 738
$C_{38}H_{56}Mo_2N_2O_{18}$ 1020.73	**3a**	44.25 (44.71)	5.17 (5.53)	2.32 (2.74)	18.28 (18.80)	35	1729, 1647, 1591, 1520, 952, 738
$C_{38}H_{40}Mo_2N_2O_{18}$ 1004.61	**4a**[a]	45.30 (45.43)	3.94 (4.01)	3.00 (2.79)	18.89 (19.10)	30	1733, 1686, 1573, 1504, 952, 735
	4b	45.36 (45.43)	3.88 (4.01)	3.07 (2.79)	19.30 (19.10)	33	1732, 1684, 1577, 1518, 958, 736
$C_{40}H_{44}Mo_2N_2O_{18}$ 1032.66	**5a**	46.75 (46.52)	3.88 (4.29)	2.64 (2.71)	18.27 (18.52)	35	1727, 1670, 1572, 1523, 961, 719
	5b	46.31(46.52)	4.37 (4.29)	2.63 (2.71)	18.21 (18.52)	34	1728, 1682, 1577, 1519, 959, 734
$C_{42}H_{48}Mo_2N_2O_{18}$ 1060.71	**6a**	46.88 (47.56)	3.86 (4.56)	2.29 (2.64)	17.84 (18.09)	40	1726, 1671, 1572, 1522, 962, 720
	6b	47.68 (47.56)	4.12 (4.56)	2.69 (2.64)	17.75 (18.09)	36	1731, 1681, 1574, 1519, 946, 728
$C_{46}H_{44}Mo_2N_2O_{18}$ 1104.72	**7a**	49.27 (50.01)	3.94 (4.01)	2.43 (2.54)	17.17 (17.37)	55	1720, 1696, 1568, 1499, 956, 712
	7b	49.30 (50.01)	3.96 (4.01)	2.38 (2.54)	17.28 (17.37)	57	1735, 1681, 1573, 1519, 961, 736
$C_{48}H_{48}Mo_2N_2O_{18}$ 1132.78	**8a**	50.47 (50.89)	3.95 (4.27)	2.50 (2.47)	17.16 (16.94)	59	1720, 1675, 1566, 1498, 951, 734
	8b*	50.23 (50.89)	4.12 (4.27)	2.54 (2.47)	16.71 (16.94)	58	1736, 1681, 1574, 1520, 960, 747
$C_{56}H_{68}Mo_2N_2O_{20}$ 1220.93	**9a**	51.78 (52.50)	5.28 (5.35)	2.05 (2.18)	15.36 (14.98)	61	1732, 1654, 1570, 1505, 946, 728
$C_{50}H_{52}Mo_2N_2O_{18}$ 1160.83	**9b**	51.55 (51.73)	4.31 (4.52)	2.15 (2.41)	16.21 (16.53)	60	1742, 1681, 1573, 1514, 957, 738

[a] According to the X-ray structure analysis, complex (**4a**) is solvated with two methanol molecules, while (**8b**) is solvated with two dichloromethane molecules. The crystals were readily loosing solvent at room temperature, so that they were left in a desiccator until constant weight, and analyzed as unsolvated species.

corresponding to the loss of solvated alcohol molecules was only observed in the case of **9a**, while all other complexes were loosing solvated molecules already at room temperature. The presence of solvated molecules in $[Mo_2O_4(C_{18}H_{16}O_6N)_2(CH_3OH)_2]\cdot 2CH_3OH$ (**4a**) and dichloromethane molecules in $[Mo_2O_4(C_{22}H_{18}O_6N)_2(CH_3CH_2OH)_2]\cdot 2CH_2Cl_2$ (**8b**) is established by the crystal structure determination. In general, the first weight loss could be attributed to the loss of coordinated alcohol and the complex conversion into a stable species of the formula $[Mo_2O_4L_2]$. On further heating, significant weight losses are indicative of complex decomposition resulting in the solid residues identified as MoO_3.

NMR Spectroscopy

^1H and ^{13}C resonances were assigned by using one-dimensional proton and carbon experiments as well as two-dimensional COSY sequence combined with $^1H-^{13}C$ correlation techniques through one bond- (HSQC) and multiple bond- (HMBC) procedures. Chemical shifts of the complexes are given in Table 3. A complete and unambiguous atom assignment for complex **4b** was not possible in

Table 2. Thermoanalytical data for $[Mo_2O_4L_2D_2]$ complexes

Formula	Complex	Loss of solvent			Decomposition		
		Temperature range (°C)	Δm (%) found	(calcd.)	Temperature range (°C)	Δm (%) found	(calcd.)
$[Mo_2O_4(C_{16}H_{20}NO_6)_2(CH_3OH)_2]$	**1a**	65−126	6.32	(6.64)	169−536	62.98	(63.52)
$[Mo_2O_4(C_{16}H_{20}NO_6)_2(CH_3CH_2OH)_2]$	**2a**	55−115	8.81	(9.28)	170−535	62.68	(61.72)
$[Mo_2O_4(C_{16}H_{20}NO_6)_2\{(CH_3)_2CHOH\}_2]$	**3a**	54−114	11.09	(11.77)	169−537	60.22	(60.03)
$[Mo_2O_4(C_{18}H_{16}NO_6)_2(CH_3OH)_2]$	**4a**[a]	85−161	5.75	(6.37)	187−514	65.19	(64.97)
	4b	40−138	5.84		189−533	65.35	
$[Mo_2O_4(C_{18}H_{16}NO_6)_2(CH_3CH_2OH)_2]$	**5a**	70−150	8.62	(8.92)	187−515	63.68	(63.20)
	5b	45−145	8.52		190−531	63.69	
$[Mo_2O_4(C_{18}H_{16}NO_6)_2\{(CH_3)_2CHOH\}_2]$	**6a**	50−137	10.89	(11.33)	186−515	60.94	(61.53)
	6b	48−138	10.79		188−532	61.82	
$[Mo_2O_4(C_{22}H_{18}NO_6)_2(CH_3OH)_2]$	**7a**	60−151	5.23	(5.80)	169−510	67.74	(68.15)
	7b	83−149	5.39		193−529	68.60	
$[Mo_2O_4(C_{22}H_{18}NO_6)_2(CH_3CH_2OH)_2]$	**8a**	50−142	7.58	(8.13)	167−508	66.89	(66.46)
	8b*	95-158	7.28		189−528	67.23	
$[Mo_2O_4(C_{22}H_{18}NO_6)_2\{(CH_3)_2CHOH)\}_2]\cdot 2(CH_3)_2CHOH$	**9a**	50−153	18.31	(14.77)	170−506	58.94	(58.77)
$[Mo_2O_4(C_{22}H_{18}NO_6)_2\{(CH_3)_2CHOH)\}_2]$	**9b**	114−174	9.63	(10.35)	190−528	63.06	(62.52)

[a] According to the X-ray structure analysis, complex (**4a**) is solvated with two methanol molecules, while (**8b**) is solvated with two dichloromethane molecules. The crystals were readily loosing solvent at room temperature, so that they were left in a desiccator until constant weight, and analyzed as unsolvated species.

Table 3. ^1H and ^{13}C NMR chemical shifts (ppm) of the compounds $[Mo_2O_4(C_{16}H_{20}NO_6)_2(CH_3OH)_2]$ (**1a**), $[Mo_2O_4(C_{18}H_{16}NO_6)_2(CH_3OH)_2]$ (**4a**), $[Mo_2O_4(C_{22}H_{18}NO_6)_2(CH_3OH)_2]$ (**7a**), and $[Mo_2O_4(C_{22}H_{18}NO_6)_2(CH_3OH)_2]$ (**7b**).

Compound	**1a**		**4a**		**7a**		**7b**	
atom	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1	1.97	20.49	2.28	21.30	1.86	21.71	2.11	19.61
2		161.81		160.36				162.06
3		102.10		106.47		102.11		99.53
4		179.41		176.02		179.86		181.93
5	6.94	114.07	6.37	111.10	6.27	113.91	5.38	107.25
6		148.38		150.12		148.16		163.25
7		180.22		179.52		183.49		187.23
8	6.45	96.11	6.89	99.10	6.46	98.33	6.70	99.53
9		168.69		171.12		167.38		153.07
10		160.37		159.26		160.89		165.28
11	4.39	62.70	4.39	63.12	4.47	62.68	3.96	62.04
12	1.38	14.27	1.39	14.30	1.48	14.51	0.78	13.65
13	3.16, 2.81	44.96		137.26		134.83		136.61
14	1.53, 1.43	31.76	7.21	125.60	7.33	125.70	7.05	122.15
15	1.14, 1.04	20.64	7.39	130.56	7.63		7.28	125.76
16	0.81	13.96	7.31	128.61	7.33	125.95	7.66	126.80
17			7.39	130.56		134.38		134.29
18			7.21	125.60	7.73	128.41	7.83	127.75
19					7.51	127.10	7.53	126.94
20					7.60	128.51	7.61	127.00
21					8.19	125.27	8.42	124.91
22						130.04		128.46
NH	9.98		12.21		11.58		10.48	

$[D_6]$acetone owing to its very low solubility in this solvent. In order to increase the solubility we added small amounts of DMSO, but the complex underwent rapid decomposition.

The chemical shift values listed in Table 3 are similar to those reported recently for related systems including molybdenum complexes.[13−16] Both proton and carbon chemical shifts are in the range expected for molybdenum complexes with ligands **a** and **b** [14,15] (Scheme 2). In that respect, the coordination-induced chemical shifts are the most pronounced for C-7 (up to 6 ppm), i.e. for one interacting site rather than for the other one, C-4.[14,15] The effects at C-7 atom are all upfield, as previously reported for related complexes.[16] The changes in chemical shifts for other carbon atoms are smaller and exhibit sign alternation as a consequence of the electron redistribution upon complexation with molybdenum.

All NMR spectroscopic data indicate that the ligand is in its enaminonic rather than iminoenolic form, which is in perfect agreement with the crystal structure determinations. The absence of hydroxyl proton resonances in the ^{1}H spectra confirms the complex formation. The marked downfield shifts of the NH protons ranging from 9.98 ppm up to 12.21 ppm (Table 3) are characteristic of strong hydrogen bonding in solution, as was found in the solid state.[11] The largest shift was observed for **4a**, indicating the strongest N−H···O bond in solution.

X-ray Analysis

Crystal structure determination was carried out for the nonsolvated compound $[Mo_2O_4(C_{16}H_{20}O_6N)_2(CH_3OH)_2]$, (**1a**), and for three solvated complexes $[Mo_2O_4(C_{18}H_{16}O_6N)_2(CH_3OH)_2]\cdot 2CH_3OH$ (**4a**), $[Mo_2O_4(C_{22}H_{18}O_6N)_2(CH_3CH_2OH)_2]\cdot 2CH_2Cl_2$ (**8b**), and $[Mo_2O_4(C_{22}H_{18}NO_6)_2\{(CH_3)_2CHOH)\}_2]\cdot 2(CH_3)_2CHOH$ (**9a**).

Selected interatomic distances and angles for complexes **1a**, **4a**, **8b**, and **9a** are given in Table 4−7, respectively. All four complex molecules contain the $[Mo_2O_4]^{2+}$ core, which displays a crystallographic twofold symmetry in **1a** and **9a** (Figure 1 and 4) but not in **4a** and **8b** (Figure 2 and 3). The Mo−Mo distances, ranging from 2.5319(6) Å in **9a** to 2.5561(5) Å in **4a**, correspond to a single bond between two molybdenum atoms, a result in agreement with the NMR spectroscopic data.[19,20] The molybdenum−to−molybdenum bonds established by structure analyses were confirmed by magnetic measurements.

Table 4. Selected interatomic distances (Å) and angles (°) for **1a**. Symmetry transformations used to generate equivalent atoms: *i* = −*x* + 1, *y*,−*z* + 3/2; *ii* = −*x* + 1,−*y*,−*z* + 1.

Mo1−Mo1^{i}	2.5341(6)		
Mo1−O7	1.688(1)	N1−C9	1.317(2)
Mo1−O8	1.921(1)	N1−C13	1.463(2)
Mo1−O8^{i}	1.934(1)		
Mo1−O3	2.086(1)	C1−C9	1.501(2)
Mo1−O4	2.138(1)	C2−C3	1.451(2)
Mo1−O9	2.212(1)	C3−C4	1.411(2)
		C3−C7	1.471(2)
O1−C6	1.349(2)	C4−C5	1.446(2)
O1−C2	1.409(2)	C5−C6	1.332(2)
O2−C2	1.207(2)	C6−C10	1.493(2)
O3−C4	1.280(1)	C7−C8	1.400(2)
O4−C7	1.293(1)	C8−C9	1.413(2)
O5−C10	1.321(2)		
O5−C11	1.466(2)		
O6−C10	1.210(2)		
O9−C17	1.376(2)		

Hydrogen bonding D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)
O9−H1···O6^{ii}	0.90	1.91	2.784(2)	160
N1−H2···O4	0.86	1.95	2.611(1)	133

Table 5. Selected interatomic distances (Å) and angles (°) for **4a**. Symmetry transformations used to generate equivalent atoms: *i* = *x* + 1/2, −*y* + 3/2, *z*; *ii* = *x* − 1/2, −*y* + 1/2, *z*; *iii* = *x*, *y* − 1, *z*; *iv* = −*x*, −*y* + 1, *z* + 1/2.

Mo1−Mo2	2.5561(5)		
Mo1−O17	1.679(2)	Mo2−O27	1.685(2)
Mo1−O18	1.929(2)	Mo2−O18	1.934(2)
Mo1−O28	1.946(2)	Mo2−O28	1.926(2)
Mo1−O13	2.096(2)	Mo2−O23	2.105(2)
Mo1−O14	2.145(2)	Mo2−O24	2.155(2)
Mo1−O19	2.191(2)	Mo2−O29	2.174(2)
O11−C106	1.350(4)	O21−C206	1.340(4)
O11−C102	1.398(3)	O21−C202	1.381(3)
O12−C102	1.217(3)	O22−C202	1.229(3)
O13−C104	1.292(3)	O23−C204	1.272(3)
O14−C107	1.297(2)	O24−C207	1.292(2)
O15−C110	1.329(4)	O25−C210	1.319(4)
O15−C111	1.469(4)	O25−C211	1.460(4)
O16−C110	1.198(4)	O26−C210	1.217(4)
O19−C119	1.404(4)	O29−C219	1.411(5)
N1−C109	1.338(3)	N2−C209	1.332(3)
N1−C113	1.421(3)	N2−C213	1.421(3)
C101−C109	1.492(4)	C201−C209	1.499(4)
C102−C103	1.436(3)	C202−C203	1.437(3)
C103−C104	1.403(3)	C203−C204	1.414(3)
C103−C107	1.473(3)	C203−C207	1.466(3)
C104−C105	1.445(3)	C204−C205	1.443(4)
C105−C106	1.334(4)	C205−C206	1.327(4)
C106−C110	1.499(4)	C206−C210	1.501(4)
C107−C108	1.398(3)	C207−C208	1.398(3)
C108−C109	1.402(3)	C208−C209	1.405(3)

Hydrogen bonding D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)
O19−H11···O22^{i}	0.93	1.76	2.673(3)	168
N1−H12···O14	0.86	1.94	2.618(3)	134
O29−H21···O1^{ii}	0.92	1.84	2.537(3)	130
N2−H22···O24	0.86	1.95	2.629(3)	135
O1−H4···O12^{iii}	0.82	1.86	2.675(3)	170
O2−H8···O18^{iv}	0.82	1.89	2.696(6)	168

Each molybdenum atom is in a distorted octahedral coordination, being bonded to one terminal and two bridging oxygen atoms, two oxygens from the bidentate ligand and one from the coordinated alcohol molecule. The shortest bond lengths with the terminal oxo−O, ranging from 1.679(2) Å in **4a** to 1.688(1) Å in **1a**, agree well with the value considered as $Mo{=}O_t$ double bond.[21] $Mo{-}O_b$ distances range from 1.914(2) Å in **8b** to 1.946(2) Å in **4a**. Two oxygen atoms from the bidentate ligand molecules are bonded at distances ranging from 2.073(3) to 2.105(2) Å (Mo−O3), and at 2.1380(10) to 2.1893(12) Å (Mo−O4). The $Mo{-}O_{alcohol}$ bond lengths range from 2.182(3) to 2.242(3) Å (both values observed in **8b**). In all four complexes, the characteristic bond lengths C8=C9, ranging from 1.365(5) to 1.413(2) Å, and C9−N1, from 1.317(2) to 1.344(5) Å, are indicative of the enamine C=C−N−H form of the ligand.

According to the values of the C−N−C13−C14 torsion angle: −165.3(1)° (**1a**), 50.1(4) and 55.0(4)° (**4a**), 41.8(5) and 45.7(6)° (**8b**), and 47.8(3)° (**9a**), the N-substituents have significant flexibility around the single N−C bonds. Moreover, in **4a** the ethyl groups adopt different conformations, with the torsion angles C110−O15−C111−C112 of −82.3(4)° and C210−O25−C211−C212 of 156.3(4)°.

Table 6. Selected interatomic distances (Å) and angles (°) for **8b**. Symmetry transformations used to generate equivalent atoms: *i* = −*x* + 2,−*y* + 1,−*z*; *ii* = −*x* + 2,−*y* + 1,−*z* + 1.

Mo1−Mo2	2.5438(7)		
Mo1−O17	1.684(3)	Mo2−O27	1.682(2)
Mo1−O18	1.914(2)	Mo2−O18	1.934(3)
Mo1−O28	1.934(2)	Mo2−O28	1.920(2)
Mo1−O13	2.086(3)	Mo2−O23	2.073(3)
Mo1−O19	2.182(3)	Mo2−O24	2.147(2)
Mo1−O14	2.185(2)	Mo2−O29	2.242(3)
O11−C106	1.361(5)	O21−C206	1.367(4)
O11−C102	1.379(4)	O21−C202	1.380(4)
O12−C102	1.220(4)	O22−C202	1.229(4)
O13−C104	1.283(4)	O23−C204	1.283(4)
O14−C107	1.283(4)	O24−C207	1.297(4)
O15−C110	1.325(5)	O25−C210	1.336(5)
O15−C111	1.474(5)	O25−C211	1.468(5)
O16−C110	1.201(5)	O26−C210	1.193(4)
O19−C123	1.447(5)	O29−C223	1.509(6)
N1−C109	1.342(4)	N2−C209	1.344(5)
N1−C113	1.419(4)	N2−C213	1.418(5)
C101−C106	1.492(5)	C201−C206	1.479(5)
C102−C103	1.442(5)	C202−C203	1.431(5)
C103−C104	1.418(5)	C203−C204	1.428(5)
C103−C107	1.456(5)	C203−C207	1.437(5)
C104−C105	1.435(5)	C204−C205	1.435(5)
C105−C106	1.324(6)	C205−C206	1.332(5)
C107−C108	1.418(5)	C207−C208	1.419(5)
C108−C109	1.373(5)	C208−C209	1.365(5)
C109−C110	1.521(5)	C209−C210	1.508(5)

Hydrogen bonding

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
O19−H11···O12^{i}	0.91	1.69	2.596(3)	177
N1−H12···O14	0.86	2.05	2.663(4)	128
O29−H21···O22^{ii}	0.94	1.76	2.673(4)	165
N2−H22···O24	0.86	2.02	2.633(4)	127

Table 7. Selected interatomic distances (Å) and angles (°) for **9a**. Symmetry transformations used to generate equivalent atoms: *i* = −*x*,*y*,−*z* + 1/2; *ii* = −*x*,−*y* + 2,−*z*.

Mo1−Mo1^{i}	2.5319(6)		
Mo1−O7	1.681(1)	N1−C9	1.337(2)
Mo1−O8	1.922(1)	N1−C13	1.427(2)
Mo1−O8^{i}	1.931(1)		
Mo1−O3	2.086(1)	C1−C9	1.507(2)
Mo1−O9	2.184(1)	C2−C3	1.451(2)
Mo1−O4	2.189(1)	C3−C4	1.413(2)
		C3−C7	1.466(2)
O1−C6	1.353(2)	C4−C5	1.448(2)
O1−C2	1.408(2)	C5−C6	1.326(2)
O2−C2	1.206(2)	C6−C10	1.488(2)
O3−C4	1.278(2)	C7−C8	1.411(2)
O4−C7	1.294(2)	C8−C9	1.386(2)
O5−C10	1.327(2)		
O5−C11	1.458(2)		
O6−C10	1.203(2)		
O9−C23	1.447(2)		

Hydrogen bonding

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)
O9−H1···O10	0.87	1.78	2.640(2)	172
N1−H2···O4	0.86	2.03	2.680(2)	131
O10−H27···O6^{ii}	0.82	2.00	2.765(2)	155

Owing to the strong N−H···O intramolecular hydrogen bonds, reinforced with π-delocalization along the heterodienic O=C−C=C−NH moiety [*d*(N···O) from 2.611(1) to 2.680(2) Å, *d*(H···O) from 1.95 to 2.05 Å], in all four structures, the enaminonic fragments adopt the form of a six-membered ring.[10,11] As seen from Table 4−7, all complex molecules in the crystal structures are interconnected as chains (along the *c*-axis in **1a**, **8b**, and **9a**, and along the *a*-axis in **4a**) realized through hydrogen bonds. These hydrogen bonds are formed between the coordinated methanol molecule and the carboxylato-oxygen [O9−H1···O6^{ii} of 2.784(2) Å] in **1a**, between ethanol and the keto-oxygens of 2-pyrone [O19−H11···O12^{i} of 2.596(3)

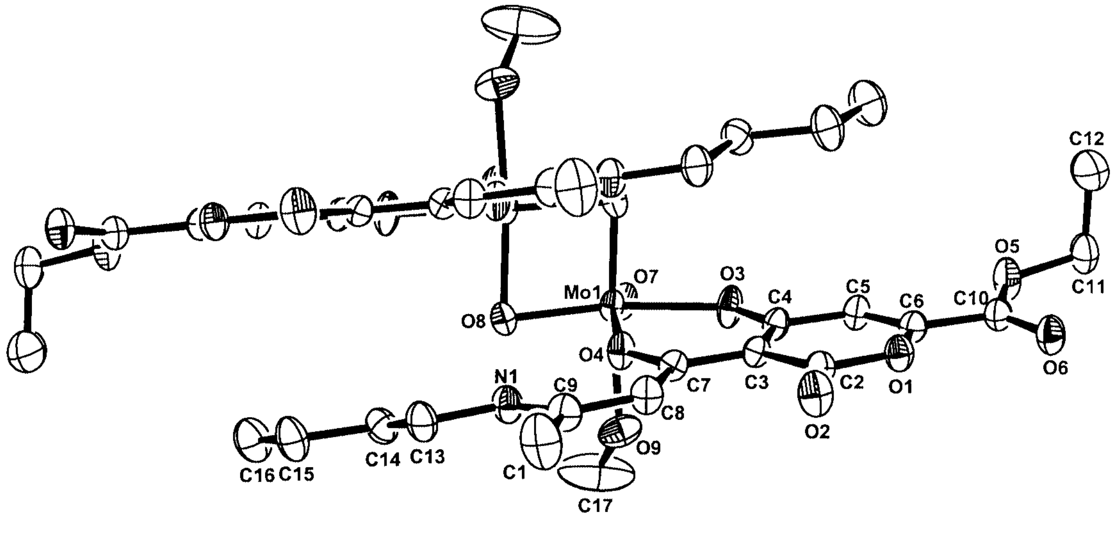


Figure 1. An ORTEP view of the dinuclear complex [$Mo_2O_4(C_{16}H_{20}NO_6)_2(CH_3OH)_2$] in **1a** (hydrogen atoms are omitted for clarity). Ellipsoids are shown at the 50% probability level.

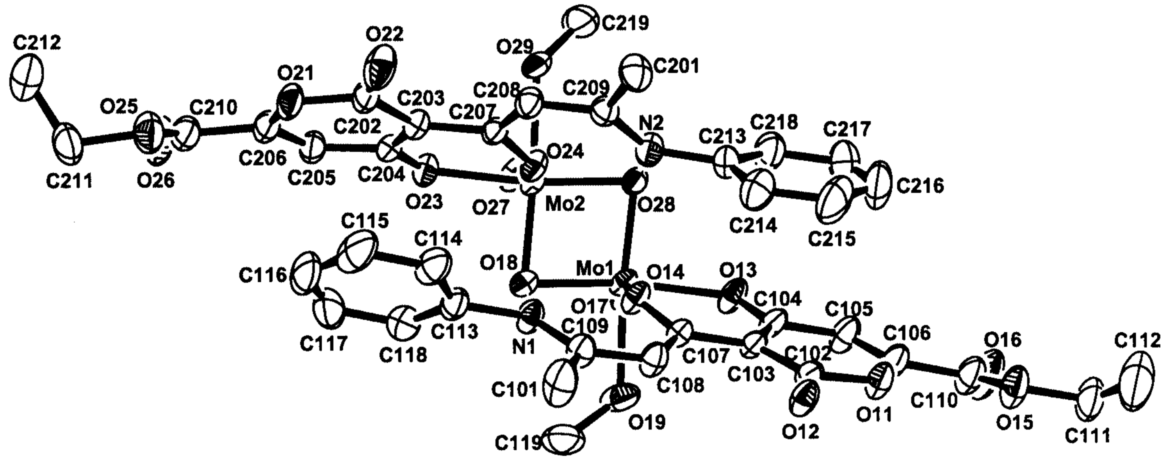


Figure 2. An ORTEP view of the dinuclear complex $[Mo_2O_4(C_{18}H_{16}NO_6)_2(CH_3OH)_2]$ in **4a** (hydrogen atoms are omitted for clarity). Ellipsoids are shown at the 50% probability level.

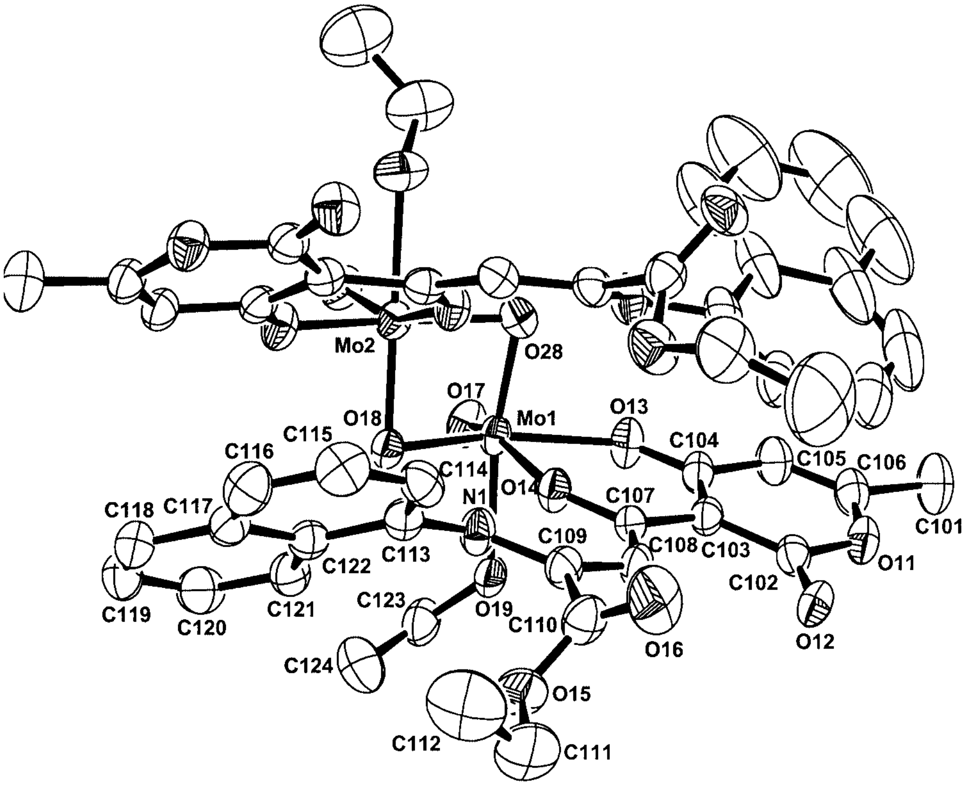


Figure 3. An ORTEP view of the dinuclear complex $[Mo_2O_4(C_{22}H_{18}NO_6)_2(CH_3CH_2OH)_2]$ in **8b**. Hydrogen atoms as well as the analogous labelling of upper part of the molecule are omitted for clarity. Ellipsoids are shown at the 50% probability level.

and O29−H21···O22^{ii} of 2.673(4) Å] in **8b**, and between methanol and the keto-oxygens [O19−H11···O22^{i} of 2.673(3) Å] in **4a**. The molecules in **4a** are further connected through solvent methanol molecule, acting as a proton donor when bonded to the keto group of the pyrone ring [O1−H4···O12^{iii} of 2.675(3) Å], and as a proton acceptor in a bond with coordinated methanol molecule [O29−H21···O1^{ii} of 2.537(3) Å]. In **9a** the complex molecules are interconnected through solvated 2-propanol molecules. Hydrogen bridges are formed between coordinated and solvated 2-propanol molecules [O9−H1···O10 of 2.640(2) Å], and between solvated 2-propanol molecule and ligand carboxylato-oxygen [O10−H27···O6^{ii} of 2.765(2) Å]. Observed values of O−H···O angles and H···O distances, ranging from 1.69 to 2.00 Å, are in the accordance with a proposed hydrogen bonding scheme. The crystal structures

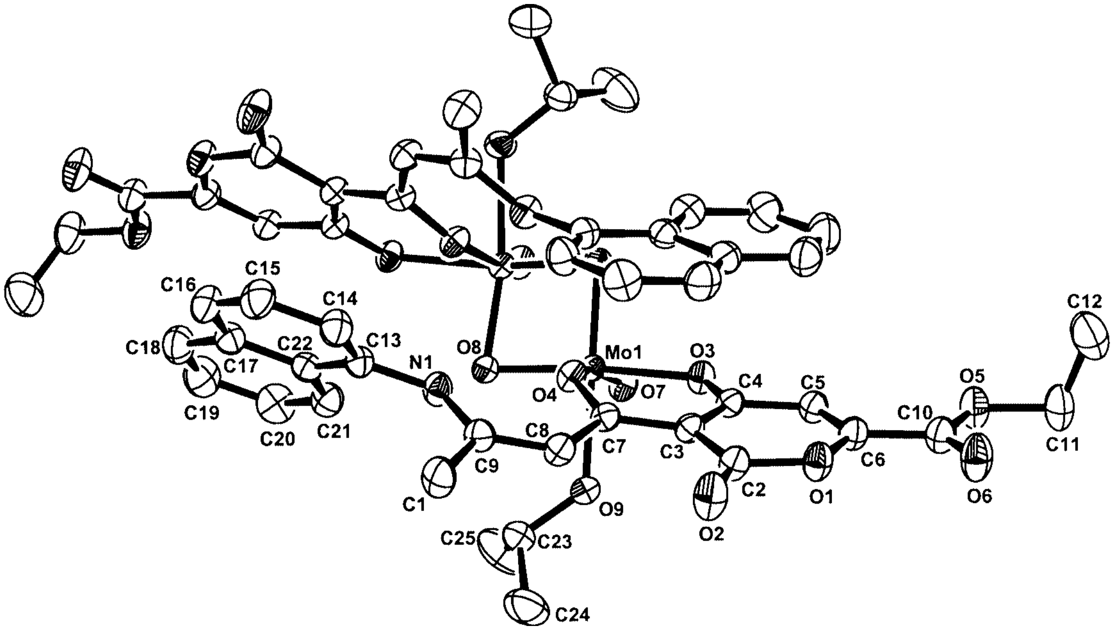


Figure 4. An ORTEP view of the $[Mo_2O_4(C_{22}H_{18}NO_6)_2\{(CH_3)_2CHOH)\}_2]$ dinuclear complex in **9a** (hydrogen atoms are omitted for clarity). Ellipsoids are shown at the 50% probability level.

of all compounds are additionally stabilized by C−H···O weak hydrogen bonds in the range from 2.745(2) to 3.358(5) Å.

Experimental Section

General: All chemicals and solvents were of reagent grade and used as purchased. The starting acetylacetonato complex $[Mo_2O_3(acac)_4]$ was prepared as described in the literature.[22,23] Ethyl 2-hydroxy-4-(4-hydroxy-6-methyl-2*H*-pyran-2-on-3-yl)-4-oxo-2-butenoate and isomeric enaminones (Scheme 2) were prepared according to previously described procedures.[13−16] Elemental analyses for C, H and N were provided by the Analytical Services Laboratory of Rudjer Bošković Institute, Zagreb. Molybdenum was determined using the usual procedure.[24] Infrared spectra were recorded in KBr with an FTIR 1600 Fourier transform spectrophotometer in the 4500−450 cm^{-1} region. Thermogravimetric (TG) analyses were measured on a Mettler TG 50 thermobalance using aluminum crucibles under oxygen atmosphere with a heating rate of 5 °C min^{-1}. For all experiments the temperature ranged from 30 to 600 °C. The results were developed by applying the GrafVare 2.1. program.

General Procedures for the Synthesis of Complexes

$[Mo_2O_3(acac)_4]$ (0.25 g, 0.4 mmol) was suspended in dry dichloromethane (25 mL) and appropriate ligand (0.4 mmol) was added. The mixture was gently warmed up for 0.5 h, the solution was filtered off, and corresponding alcohol (30 mL) added to the filtrate. Upon standing at room temperature for 5−10 days the obtained crystalline product was filtered off, washed with cold alcohol and dried. All complexes were orange-red crystalline solids very soluble in coordinating solvents such as DMF, DMSO, picoline, and pyridine, slightly soluble in dichloromethane, acetone, methanol, and ethanol. Elemental analyses, yields (based on $[Mo_2O_3(acac)_4]$) and selected IR data are given in Table 1. Thermal analysis data are given in Table 2. Since the crystals were easily loosing alcohol solvent, all analyses (elemental analyses, thermal analyses, IR, and NMR spectroscopy) were carried out with the samples left in a desiccator until constant weight.

NMR Spectra

NMR experiments were carried out on a Bruker Avance DRX500 spectrometer operating at 500.13 MHz for ^1H, with a 5 mm diameter inverse detection probe and a z-axis gradient coil. The solvent was $[D_6]$acetone and all experiments were performed at ambient temperature. TMS was used as the internal standard.

^1H NMR experiments were executed with a spectral width of 12500 Hz, 65 K data points and 8−32 scans. The sample concentration was 10−15 $mg.ml^{-1}$. The digital resolution was 0.2 Hz per point. In ^{13}C NMR spectra the spectral width was 31400 Hz, the number of data points 65 K, and the number of scans 2500−3000 per spectrum. The digital resolution was 0.5 Hz per point.

Two-dimensional absolute-value COSY spectra were recorded under the following conditions. Spectral width was 6600 Hz in both domains, 2 K data points were applied in time domain and 512 increments were collected for each data set with linear prediction and zero filling to 2 K. The relaxation delay was 1.5 s. Spectra were rocessed with sine or sine squared window functions. The digital resolution was 3.3 Hz per point in both f1 and f2 domains. The number of scans was 8.

Phase sensitive HSQC and absolute value HMBC spectra were recorded with a relaxation delay of 1.5 s and 32 scans per increment. The spectral width was 6600 Hz in acquisition domain f2 and 31000 Hz in time domain f1. Data were collected into 2048 × 256 acquisition matrix and processed by using a 2 K × 1 K transformed matrix with zero filling in f1 domain. Sine multiplication was performed prior to Fourier transformations. In HMBC spectra the delay for long range couplings was set to 60 ms.

Table 8. General and crystal data and summary of intensity data collection and structure refinement.

Compound	**1a**	**4a**	**8b**	**9a**
Formula	$C_{34}H_{48}Mo_2N_2O_{18}$	$C_{40}H_{48}Mo_2N_2O_{20}$	$C_{50}H_{52}Cl_4Mo_2N_2O_{18}$	$C_{56}H_{68}Mo_2N_2O_{20}$
M_r	964.62	1068.68	1302.62	1281.00
Crystal system and habit	Monoclinic, prism	Orthorhombic, prism	Triclinic, prism	Monoclinic, prism
Space group	$C2/c$	$Pna2_1$	$P\bar{1}$	$C2/c$
a [Å]	11.943(2)	21.252(4)	12.364(2)	20.352(4)
b [Å]	15.650(3)	9.623(2)	12.510(3)	10.184(2)
c [Å]	21.552(4)	21.524(4)	18.635(4)	28.548(6)
α [°]	90	90	89.60(3)	90
β [°]	99.26(3)	90	72.99(3)	98.20(3)
γ [°]	90	90	88.91(3)	90
Volume [Å^3]	3975.7(13)	4401.8(15)	2755.8(10)	5857(2)
Z	4	4	2	4
Density (calcd.) [gcm^{-3}]	1.612	1.613	1.570	1.453
μ (Mo-K_α) [mm^{-1}]	0.709	0.652	0.722	0.504
F(000)	1976	2184	1324	2648
2θ range for data collection [°]	5.4−66.3	4.2−66.2	4.6−52.6	4.6−66.2
h,k,l range	−18/18, −24/+23, −32/+33	−32/32, −14/14, −33/+33	−15/15, −15/15, −23/23	−31/30, −15/+12, −37/+40
Scan type	2° and ω scans	2° and ω scans	2° and ω scans	2° and ω scans
No. measured reflections	14098	16777	20231	15962
No. independent reflections	7490	16126	11114	10127
No. refined parameters	258	583	685	369
No. observed reflections, [$I \geq 2\sigma(I)$]	6575	13397	9003	8047
g_1, g_2 in w[a]	0.0288, 3.20	0.0427, 1.68	0.0615, 4.27	0.0296, 7.01
R[b], wR[c] [$I \geq 2\sigma(I)$]	0.0247, 0.0623	0.0359, 0.0812	0.0459, 0.1166	0.0348, 0.0769
R, wR [all data]	0.0305, 0.0660	0.0502, 0.0877	0.0602, 0.1257	0.0508, 0.0838
Goodness-of-fit on F^2, S[d]	1.030	1.025	1.011	1.012
Max., min. electron density [e Å^{-3}][e]	0.889, − 0.518	0.658, − 0.499	1.297, − 1.083	0.818, −0.744
Extinction coefficients	0.0014(2)	0.0005(1)		0.00025(8)
Maximum Δ/σ	0.006	0.006	0.001	0.001

[a] According to the X-ray structure analysis, complex **4a** is solvated with two methanol molecules, while **8b** is solvated with two dichloromethane molecules. The crystals were readily loosing solvent at room temperature, so that they were left in a desiccator until constant weight, and analyzed as unsolvated species. [b] $w = 1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$ where $P = (F_o^2 + 2F_c^2)/3$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma |F_o|$. [d] $wR = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [e] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})]^{1/2}$.

X-ray Crystallography

Single crystals of the complexes **1a**, **4a**, **8b**, and **9a** were grown by slow evaporation of solutions obtained from the above described preparations. The crystals so obtained were, however, unstable as they rapidly lost solvent and decomposed. Intensity data for all four structures were collected at 200 K on a Nonius−Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å), at crystal to detector distance of 28 mm and 50 s exposure time per frame. Data were reduced using DENZO program.[25]

Crystal data, experimental conditions, details of structure determination and final refinement parameters are summarized in Table 8.

Molybdenum atoms in all structures were located by the Patterson method. The remaining non-hydrogen atoms were found in subsequent difference Fourier maps. Refinements in which all non-hydrogen atoms were treated anisotropically were performed by the full-matrix least-squares method based on the F^2 values against all reflections. The last Fourier maps revealed positions of all H atoms but some with poor geometry. Therefore all hydrogen atoms attached to carbon and nitrogen atoms were generated on geometrical grounds. The hydrogen atoms bound to the oxygen atoms of coordinated alcohol molecules were kept fixed during the refinement.

Structure **4a** was refined in noncentrosymmetric space group $Pna2_1$. However, the value of the refined Flack parameter of 0.50(2) is indicative of a racemic twinning.

All calculations were performed on an IBM THINKPAD microcomputer (Pentium II processor, 300 MHz) using SHELXS-97[26] and SHELXL-97[27] programs, and ORTEP[28] to draw the structural diagrams.

CCDC-174217 (**1a**), -174218 (**4a**), -174219 (**8b**) and -174220 (**9a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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