Transition metal carbohydrate chemistry

Part 4 ☆. Homoleptic diacetoneglucose complexes of molybdenum and tungsten: chiral ligands associated with an M≡M triple bond

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Abstract

The synthesis of homoleptic 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (HL) complexes bound to metal triple bond moieties was achieved by their reaction with the corresponding molybdenum and tungsten dimethylamido derivatives. The products [Mo_2L_6] (1) and [W_2L_6] (2) were characterized by ^1H, ^{13}C NMR and IR spectroscopy; optical rotation values were measured and are briefly discussed. The X-ray structures of 1 and 2, determined at 118 and 293 K, respectively, are reported. Crystallographic details: [Mo_2L_6], monoclinic, space group $P2_1$, $a = 14.448(11)$, $b = 21.749(12)$, $c = 15.819(9)$ Å, $\beta = 115.07(5)°$, $Z = 2$ and $R = 0.0391$ for 13367 independent reflections; [W_2L_6], orthorhombic, space group $P22_12_1$, $a = 15.993(2)$, $b = 16.127(3)$, $c = 19.260(4)$ Å, $Z = 2$ and $R = 0.067$ for 6215 independent reflections.

Keywords: Glucose complexes; Metal–sugar compounds; Chiral ligands; Chiral metal–metal complexes

1. Introduction

Sugars are the building blocks for a large number of biological molecules. The assembly strategy is dictated by nature and is appropriate for various functions of the resulting aggregates.

Our approach consists of using transition metals with their different assembling properties (depending on the metal and its oxidation state, coordination number, d^n configuration, etc.) for the creation of novel architectures in coordination chemistry.

These molecules may provide (i) chiral metals (acids, bases, free radicals), (ii) chiral cavities, (iii) chiral precursors for aggregates via weak interactions, (iv) novel fragments in organometallic chemistry or (v) oxygen-rich cavities for alkali metal cations.

The assembly of sugar moieties using transition metals has recently been pursued in our laboratory [1–3].

The use of sugar fragments as ancillary ligands in organometallic chemistry has interesting precedent in compounds active in asymmetric syntheses [4,5]. Some complexes derived from amino sugars or their condensation compounds with salicylaldehyde have been used as ligands [6].

One of the most versatile assembling units in coordination chemistry is the [$M≡M$]$^{6+}$ [M = Mo, W] unit, and the chemistry associated with it. Alkoxo ligands provide the major entry into this chemistry, which renders sugars as appropriate binding units [7,8]. Some examples of the incorporation of ancillary chiral ligands in the M≡M unit have recently been reported [9,10].

2. Experimental details

2.1. General procedures

All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly distilled prior to use. Infrared

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spectra were recorded with a Perkin-Elmer Model 883 spectrophotometer, ^{1}H NMR spectra were measured on a Bruker 200-AC instrument, ^{1}H (200.13 MHz) and ^{13}C (50.32 MHz). The synthesis of $[M_2(NMe_2)_6]$ (M = Mo, W) has been carried out as reported in the literature [11].

2.2. Synthesis of [Mo₂L₆] (1)

A solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (HL) (11.38 g, 43.72 mmol) in toluene (200 cm^3) was added dropwise via a cannula to a stirred solution of $Mo_2(NMe_2)_6$ (3.33 g, 7.28 mmol) in toluene (50 cm^3) over 30 min. An immediate reaction occurred, accompanied by a colour change from yellow to red–brown. The mixture was stirred for over 12 h. Removal of volatiles under vacuum yielded a yellow–green powder, which was washed with hexane (50 cm^3), collected and dried in vacuo (9.16 g, 72%). Large orange prisms can be grown from a cool, saturated solution of octane. (Found: C, 49.45; H, 7.05. $C_{72}H_{114}Mo_2O_{36}$ requires C, 49.50; H, 6.55%). NMR: ^{1}H (200 MHz, C_6D_6), δ 1.21 (s, 18 H, Me), 1.41 (s, 18 H, Me), 1.49 (s, 18 H, Me), 1.52 (s, 18 H, Me), 4.16 (d, $J_{Hf,He}$ = 4.4 Hz, 12 H, H_f), 4.55 (m, 12 H, H_d, H_e), 5.06 (d, $J_{Hb,Ha}$ = 3.4 Hz, 6 H, H_b), 6.06 (s, br, 6 H, HC), 6.18 (d, $J_{Ha,Hb}$ = 3.4 Hz, 6 H, H_a); ^{13}C (50 MHz, C_6D_6), δ 26.3, 27.4, 26.6, 28.1, 68.8, 73.7, 84.6, 87.6, 87.9, 106.6, 110.8, 113.1. $[\alpha]_{589}^{30}$ = +53.4° (c = 0.0274 g cm^{-3} in THF). M.W. = 1507 by cryoscopy in benzene.

2.3. Synthesis of [W₂L₆] (2)

A solution of HL (9.25 g, 35.52 mol) in toluene (100 cm^3) was added dropwise via a cannula to a stirred solution of $W_2(NMe_2)_6$ (3.74 g, 5.92 mmol) in toluene (30 cm^3) over 10 min. The reaction mixture was stirred for 12 h to afford an orange–red solution. The volatiles were removed under reduced pressure. The resulting red–orange oily solid was washed with n-hexane (ca. 30 cm^3) to afford an orange–yellow solid and a red solution. The solid was collected and dried under vacuum (6.83 g, 60%). Orange cubes of [W₂L₆] can be obtained by cooling a saturated toluene solution to 0°C. (Found: C, 43.70; H, 5.90. $C_{72}H_{114}Mo_2O_{36}$ requires: C, 44.95; H, 5.95%). NMR: ^{1}H (200 MHz, C_6D_6), δ 1.29 (s, 18 H, Me), 1.49 (s, 18 H, Me), 1.50 (s, 18 H, Me), 1.70 (s, 18 H, Me), 3.82 (dd, $J_{Hf,Hf'}$ = 6.0 Hz, $J_{Hf,He}$ = 9.0 Hz, 6 H, H_f), 3.97 (m, 6 H, H_e), 4.29 (dd, $J_{Hf',He}$ = 2.0 Hz, $J_{Hf,Hf'}$ = 8.8 Hz, 6 H, $H_{f'}$), 4.58 (dd, $J_{Hd,He}$ = 1.8 Hz, $J_{Hd,Hf}$ = 9.2 Hz, 6 H, H_d), 5.12 (d, $J_{Hb,Ha}$ = 3.0 Hz, 6 H, H_b), 5.92 (d, $J_{Ha,Hb}$ = 3.0 Hz, 5 H, H_a), 6.47 (br,s, 6 H, H_c); ^{13}C (50 MHz, C_6D_6), δ 26.7, 29.0, 29.2, 29.4, 68.1, 73.2, 83.8, 87.6, 92.2, 106.8, 111.0), 114.0 $[\alpha]_{589}^{30}$ = −58.4° (c = 4.45 in THF).

2.4. X-ray crystallography for complexes 1 and 2

The crystals selected for study were sealed in Lindemann glass capillaries under nitrogen. Crystal data and details associated with data collection and with structure refinement are given in Table 1. No absorption correction was applied for **1**, while an empirical absorption correction, based on the ψ-scan method, was applied for **2** [12]. For complex **1**, the structure was solved by direct methods by SIR92 [13]. The absolute configuration was attributed assuming the D-configuration of the sugar ligands and confirmed by refining a chirality parameter [14]. Atoms O(5) in three (a, b, c) out of six sugar molecules showed positional disorder and an equal population for the two possible conformations was assumed. The high values of the displacement parameters of other atoms and the relatively high residual electron density indicate the presence of further disorder, which could not be resolved. A toluene molecule of crystallization was also found which is affected by some kind of disorder, as indicated by the high thermal parameters of the carbon atoms. For complex **2**, in the final difference Fourier map some peaks, less than 2 e Å^3 high, were found in holes of the crystal packing, but all attempts to identify these peaks as a recognizable solvent molecule failed and refinement of their positions as disordered carbon atoms proved very unstable. Some of the terminal methyl carbons have very high temperature factors, indicating that they are affected by structural disorder.

Table 1
Experimental data for the X-ray diffraction studies on complexes 1 and 2

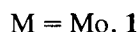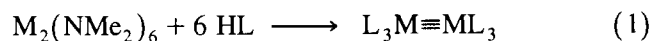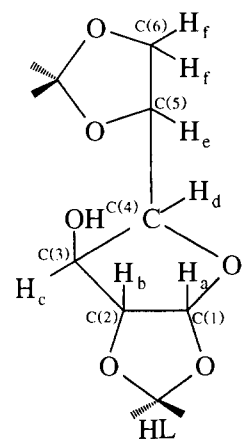|	Complex	
	1	2
Formula	$C_{79}H_{122}MoO_{36}$	$C_{72}H_{114}O_{36}W$
M	1839.6	1923.3
Space group	$P2_1$ (No. 4)	$P22_12_1$ (No. 18)
a (Å)	14.448(11)	15.993(3)
b (Å)	21.749(12)	16.127(3)
c (Å)	15.819(9)	19.260(4)
α (°)	90	90
β (°)	115.070(0)	90
γ (°)	90	90
U (Å³)	4503(5)	4967.7(15)
Z	2	2
D_c (g cm^{-3})	1.357	1.286
T (K)	118	293
λ (Å)	0.71073	
μ (mm^{-1})	0.362	0.386
Transmission coefficient	–	0.0468–0.0774
R ^{a}	0.0391	0.0611
wR ^{b}	0.045	0.0886

^{a} $R = \Sigma|\Delta F|/\Sigma|F_0|$.
^{b} $wR = \Sigma w^{1/2}|\Delta F|/\Sigma w^{1/2}|F_0|$.

Final atomic coordinates are listed in Tables 2 and 3 and selected bond distances and angles in Tables 4 and 5, for complexes 1 and 2, respectively [15].

3. Results and discussion

Utilizing the conventional synthetic approach we reacted $M_2(NMe_2)_6$ with the monoprotic ligand diacetoneglucose, 1,2 : 5,6-di-O-isopropylidene-α-D-glucofuranose (HL).

$$M_2(NMe_2)_6 + 6\ HL \longrightarrow L_3M\equiv ML_3 \qquad (1)$$

$$M = Mo,\ 1$$

$$M = W,\ 2$$
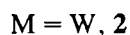
Characterization of the novel homoleptic compounds 1 and 2 was achieved by IR, ^1H and ^{13}C NMR spectroscopy, elemental analysis and X-ray structure determination. A preliminary inspection of the ^1H NMR spectra of complexes 1 and 2, which are temperature independent, revealed some interesting features. The relative resonances for the different protons of the sugar moiety could be unambiguously assigned by means of decoupling studies and will be briefly discussed. Doublets at 6.1 and 6.5 ppm for $[Mo_2L_6]$ and $[W_2L_6]$ are indicative of H_c (i.e. the proton α to the metal oxygen bond) and are deshielded by 1.8 and 2.2 ppm, respectively, compared with free HL (H_c resonance = 4.3 ppm). A similar trend is observed for other $[M_2(OR)_6]$ complexes [10]. On the other hand, H_a, i.e. the anomeric proton, is very little influenced by the two metals and appears in both compounds as a doublet at about 6.0 ppm (5.9 ppm in free HL); H_b is a doublet at 5.1 ppm (4.3 ppm in free HL); H_d a doublet of doublets at 4.6 ppm (4.3 ppm in free HL); H_e a doublet of doublets at 4.6 ppm and 4.3 ppm in Mo and W dimers, respectively (3.9 ppm in free HL); and finally the two diastereoisomeric protons H_f at 4.2 ppm as a doublet and at 4.0 ppm as a doublet of doublets in 1 and 2, respectively (3.9 ppm in free HL). Optical rotatory values $[\alpha]_D$ of 1 and 2 were recorded at various concentrations and in different solvents, and their values showed little or no

Table 2
Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficients ($\mathring{A}^2 \times 10^4$) for complex 1

Atom	x	y	z	U_{eq} [a]
Mo(1)	77759(2)	0	15586(2)	166(1)
O(1a)	73324(19)	8168(13)	11155(18)	223(9)
C(1a)	66350(29)	9443(19)	1782(25)	243(13)
C(2a)	55166(31)	9379(20)	360(30)	275(14)
O(2a)	53584(24)	15266(14)	3645(22)	329(12)
C(3a)	59483(35)	19688(21)	1703(33)	334(17)
C(4a)	67667(33)	16199(21)	−158(30)	302(15)
O(3a)	64742(29)	17014(17)	−9860(24)	466(15)
C(5a)	57213(45)	21844(27)	−13446(38)	496(22)
C(6a)	62062(57)	27657(32)	−14710(57)	754(38)
C(7a)	48841(73)	19519(41)	−21841(59)	1295(49)
O(4a)	53679(33)	22785(19)	−6579(31)	604(20)
C(8a)	52439(29)	4389(18)	5497(29)	271(14)
C(9a)	40898(31)	3908(22)	2739(35)	381(17)
O(5a)	37430(48)	−33(36)	−4801(45)	386(14)
O(5a′)	39172(49)	−2522(32)	1575(46)	364(14)
C(10a)	45610(34)	−4739(25)	−2606(38)	411(19)
C(11a)	43842(74)	−5184(40)	−12494(45)	1004(43)
C(12a)	46037(84)	−10924(38)	1383(56)	1086(53)
O(6a)	54924(22)	−1406(13)	2706(22)	309(11)
O(1b)	82954(19)	−5178(12)	8844(17)	210(9)
C(1b)	75610(28)	−8924(18)	1656(26)	213(12)
C(2b)	78740(30)	−9812(18)	−6295(27)	237(13)
O(2b)	86794(23)	−14263(14)	−2916(23)	331(12)
C(3b)	85595(31)	−18179(18)	3710(29)	259(14)
C(4b)	76731(30)	−15494(18)	5422(29)	255(14)
O(3b)	68207(21)	−19054(13)	−377(21)	275(11)
C(5b)	71987(32)	−25055(20)	−827(32)	301(16)
C(6b)	72370(41)	−28925(23)	7375(40)	444(22)
C(7b)	65648(41)	−27990(25)	−9893(38)	454(21)
O(4b)	82138(24)	−24036(14)	−91(25)	357(13)
C(8b)	82786(32)	−4109(19)	−8978(28)	268(14)
C(9b)	83953(36)	−4798(22)	−18069(30)	326(17)
O(5b)	74523(25)	−2357(15)	−24819(21)	356(12)
C(10b)	72110(31)	2600(23)	−20296(27)	309(14)
C(11b)	60544(34)	3346(32)	−24627(34)	489(20)
C(12b)	77684(40)	8435(23)	−20609(37)	409(20)
O(6b)	75425(23)	658(15)	−10807(19)	313(11)
O(1c)	71371(19)	−4367(13)	21990(18)	223(9)
C(1c)	74268(28)	−6923(18)	30989(26)	222(13)
C(2c)	64677(32)	−8922(18)	32109(30)	271(15)
O(2c)	61928(24)	−14709(13)	27315(23)	331(12)
C(3c)	70627(35)	−17655(20)	27590(33)	323(17)
C(4c)	79522(30)	−13089(18)	31419(27)	251(14)
O(3c)	84953(25)	−14855(15)	40886(21)	363(12)
C(5c)	83762(43)	−21401(24)	41102(36)	441(21)
C(6c)	91592(49)	−24650(28)	38635(45)	591(27)
C(7c)	84465(65)	−23168(33)	50505(46)	742(36)
O(4c)	73708(30)	−22598(16)	34166(28)	501(17)
C(8c)	55557(33)	−4637(21)	27472(37)	349(18)
C(9c)	46004(41)	−6673(26)	28635(48)	517(26)
O(5c)	46821(43)	−3319(27)	36947(40)	281(12)
O(5c′)	41419(97)	−1294(66)	28641(93)	1047(38)
C(10c)	50896(42)	2557(30)	35872(53)	631(29)
C(11c)	56083(68)	4450(38)	45530(59)	901(46)
C(12c)	43765(54)	7470(43)	30002(58)	939(39)
O(6c)	58130(25)	1172(15)	32091(30)	481(16)
Mo(2)	92654(2)	2762(2)	26866(2)	182(1)
O(1d)	97537(20)	−5318(13)	31262(19)	253(10)
C(1d)	107334(30)	−6909(21)	38309(28)	289(14)
C(2d)	114524(30)	−8673(21)	33878(31)	304(15)

Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficients ($\mathring{A}^2 \times 10^4$) for complex 1

Table 2 (continued)

Atom	x	y	z	U_{eq} [a]
Mo(1)	77759(2)	0	15586(2)	166(1)
C(3d)	118854(32)	1323(22)	39013(32)	373(17)
C(4d)	112963(32)	−1505(22)	44314(30)	344(16)
O(3d)	120772(26)	−3809(19)	52652(23)	473(14)
C(5d)	130118(37)	−728(29)	54425(37)	500(20)
C(6d)	131850(48)	4549(31)	61176(43)	621(26)
C(7d)	138652(44)	−5385(33)	75522(54)	736(30)
O(4d)	129012(25)	1820(23)	45718(25)	579(16)
C(8d)	109845(33)	−12249(22)	24904(32)	331(16)
C(9d)	117625(44)	−14001(28)	21090(42)	514(24)
O(5d)	122144(49)	−18973(31)	25784(45)	346(14)
O(5d')	116142(75)	−20978(48)	20055(69)	710(25)
C(10d)	113113(50)	−22742(25)	26474(42)	528(25)
C(11d)	119258(59)	−25209(31)	36155(48)	759(32)
C(12d)	107534(88)	−27556(42)	19762(65)	1479(62)
O(6d)	106347(25)	−18104(15)	26553(24)	386(13)
O(1e)	89366(20)	7620(14)	34983(18)	258(10)
C(1e)	80494(32)	9881(21)	35758(29)	302(15)
C(2e)	83349(38)	11324(22)	46105(31)	355(17)
O(2e)	87985(29)	17290(16)	47557(23)	443(14)
C(3e)	84808(37)	20534(22)	39222(35)	391(18)
C(4e)	77856(33)	16208(20)	31327(31)	325(16)
O(3e)	67984(27)	17914(17)	30062(29)	520(15)
C(5e)	68005(42)	24023(25)	33306(39)	482(21)
C(6e)	63907(53)	28597(30)	25235(46)	612(28)
C(7e)	62181(54)	24043(33)	39118(47)	676(31)
O(4e)	78479(31)	25548(20)	38698(34)	686(19)
C(8e)	90961(42)	7075(24)	52971(31)	413(19)
C(9e)	92629(61)	7925(33)	63156(37)	649(30)
O(5e)	94615(39)	2088(23)	67051(24)	736(21)
C(10e)	92060(48)	−2494(28)	59813(34)	497(22)
C(11e)	84192(53)	−6804(30)	60239(38)	597(28)
C(12e)	101612(54)	−5564(38)	60499(46)	720(32)
O(6e)	87292(30)	898(18)	51194(21)	483(15)
O(1f)	99393(20)	7214(14)	21035(19)	264(10)
C(1f)	98768(29)	8896(19)	12117(27)	253(13)
C(2f)	105072(36)	14766(20)	13217(31)	312(16)
O(2f)	115592(24)	12666(15)	17570(22)	364(12)
C(3f)	116095(31)	6747(21)	14217(30)	308(15)
C(4f)	104945(30)	4306(19)	9465(27)	265(14)
O(3f)	102428(20)	4744(14)	−216(19)	272(10)
C(5f)	111728(30)	4042(20)	−1203(29)	286(15)
C(6f)	114217(40)	−2705(23)	−1470(40)	435(21)
C(7f)	110556(37)	7473(26)	−9937(33)	411(19)
O(4f)	119244(22)	7007(16)	6811(21)	343(12)
C(8f)	103868(39)	19655(22)	19534(34)	380(19)
C(9f)	110301(45)	25500(24)	20541(41)	487(22)
O(5f)	103581(36)	30250(18)	20417(29)	573(19)
C(10f)	93503(47)	28214(22)	13840(37)	450(22)
C(11f)	92365(54)	29426(30)	4352(46)	631(31)
C(12f)	86104(59)	31254(30)	16737(57)	726(39)
O(6f)	93437(29)	21726(15)	15526(26)	422(15)
C(1)	40040(110)	23834(58)	46227(86)	1351(80)
C(2)	44365(127)	29059(53)	51758(124)	1454(102)
C(3)	43833(130)	34040(104)	47647(122)	1758(123)
C(4)	38953(80)	35340(47)	37725(137)	1602(95)
C(5)	35656(93)	30949(72)	33307(99)	1369(75)
C(6)	35798(78)	24331(55)	37422(80)	1064(60)
C(7)	42288(121)	18428(51)	52109(89)	1763(116)

[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 equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for complex **2**

Atom	x	y	z	U_{eq} [a]
W	10026(1)	10368(1)	9478(1)	36(1)
C(1a)	8260(14)	9775(12)	9001(11)	45(7)
C(2a)	7627(11)	10315(12)	8640(10)	44(6)
C(3a)	8138(16)	9504(16)	7736(10)	61(8)
C(4a)	8319(14)	9037(14)	8484(11)	56(7)
C(5a)	7226(17)	8403(16)	7834(11)	67(9)
C(6a)	7409(23)	7495(18)	7583(16)	108(14)
C(7a)	6333(21)	8608(23)	7826(19)	133(18)
C(8a)	7699(15)	11243(13)	8848(12)	62(8)
C(9a)	7032(20)	11756(15)	8461(13)	87(11)
C(10a)	6659(32)	11709(23)	9614(26)	129(19)
C(11a)	6120(17)	11026(35)	10000(20)	227(25)
C(12a)	6798(27)	12287(57)	9894(33)	738(112)
O(1a)	9045(9)	10134(11)	8984(9)	56(6)
O(2a)	7876(12)	10263(9)	7913(7)	60(6)
O(3a)	7577(11)	8546(9)	8516(7)	63(5)
O(4a)	7647(12)	8984(11)	7375(7)	76(6)
O(5a)	6335(12)	11770(14)	8906(10)	91(8)
O(6a)	7474(10)	11308(10)	9517(8)	65(5)
C(1b)	10156(14)	12087(10)	10230(8)	42(7)
C(2b)	10673(14)	12764(15)	10012(12)	55(7)
C(3b)	9261(14)	13088(13)	9732(10)	49(7)
C(4b)	9356(18)	12501(10)	10311(10)	65(8)
C(5b)	9017(15)	13856(13)	10721(9)	56(7)
C(6b)	8275(20)	14071(19)	11108(14)	94(12)
C(7b)	9695(21)	14445(15)	10976(16)	107(14)
C(8b)	11430(15)	12609(14)	9562(11)	67(8)
C(9b)	11868(20)	13369(16)	9263(15)	86(11)
C(10b)	12847(18)	12612(14)	9877(13)	69(9)
C(11b)	12920(29)	12932(30)	10656(18)	178(26)
C(12b)	13466(22)	11913(49)	9687(21)	351(66)
O(1b)	10081(13)	11508(7)	9695(6)	50(4)
O(2b)	10109(11)	13247(8)	9519(6)	56(5)
O(3b)	9300(11)	13022(8)	10902(7)	63(5)
O(4b)	8855(11)	13810(9)	9987(7)	71(5)
O(5b)	12747(16)	13167(18)	9356(14)	138(12)
O(6b)	12036(10)	12192(10)	9944(10)	80(6)
C(1c)	11647(12)	9491(13)	8874(9)	39(6)
C(2c)	11716(12)	9239(13)	8111(10)	43(6)
C(3c)	12516(16)	10470(19)	8249(12)	70(9)
C(4c)	12434(13)	10009(16)	8983(11)	54(7)
C(5c)	13811(22)	9786(23)	8550(19)	120(16)
C(6c)	14028(22)	9012(25)	8137(25)	187(25)
C(7c)	14496(19)	10150(27)	9172(32)	271(44)
C(8c)	10906(14)	9052(13)	7755(9)	55(7)
C(9c)	10993(18)	8785(13)	6984(9)	65(8)
C(10c)	10637(18)	7610(13)	7576(9)	62(8)
C(11c)	9882(31)	7272(16)	7291(12)	99(14)
C(12c)	11157(24)	6938(18)	8003(15)	109(15)
O(1c)	10950(9)	10019(10)	8968(8)	45(5)
O(2c)	12053(10)	9980(11)	7777(8)	56(5)
O(3c)	13125(11)	9495(11)	9025(10)	84(7)
O(4c)	13361(12)	10425(13)	8145(10)	95(8)
O(5c)	11222(12)	7930(9)	7049(6)	70(6)
O(6c)	10553(10)	8304(9)	8043(6)	59(5)

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

Table 4

Selected bond lengths (Å) and bond angles (°) for complex 1

Mo(1)–Mo(2)	2.218(2)	Mo(1)–O(1a)	1.918(3)
Mo(1)–O(1b)	1.910(3)	Mo(1)–O(1c)	1.890(4)
Mo(2)–O(1d)	1.912(3)	Mo(2)–O(1e)	1.873(4)
Mo(2)–O(1f)	1.870(4)	O(1a)–C(1a)	1.423(4)
O(1b)–C(1b)	1.435(4)	O(1c)–C(1c)	1.416(5)
O(1d)–C(1d)	1.424(4)	O(1e)–C(1e)	1.426(6)
O(1f)–C(1f)	1.423(6)		
Mo(2)–Mo(1)–O(1a)	95.9(1)	Mo(2)–Mo(1)–O(1b)	97.6(1)
Mo(2)–Mo(1)–O(1c)	103.4(1)	Mo(1)–Mo(2)–O(1d)	97.3(1)
Mo(1)–Mo(2)–O(1e)	105.2(1)	Mo(1)–Mo(2)–O(1f)	105.9(1)
O(1a)–Mo(1)–O(1b)	119.4(1)	O(1a)–Mo(1)–O(1c)	119.9(1)
O(1b)–Mo(1)–O(1c)	113.6(1)	O(1d)–Mo(2)–O(1e)	115.5(1)
O(1d)–Mo(2)–O(1f)	117.8(1)	O(1e)–Mo(2)–O(1f)	112.5(1)
Mo(1)–O(1a)–C(1a)	122.7(2)	Mo(1)–O(1b)–C(1b)	116.3(3)
Mo(1)–O(1c)–C(1c)	137.1(2)	Mo(2)–O(1d)–C(1d)	126.8(3)
Mo(2)–O(1e)–C(1e)	138.8(2)	Mo(2)–O(1f)–C(1f)	142.6(2)

Table 5

Selected bond lengths (Å) and bond angles (°) for complex 2

W–O(1a)	1.873(16)	W–O(1b)	1.887(11)
W–O(1c)	1.862(15)	W–W'	2.334(1)
C(1a)–O(1a)	1.383(27)	C(1b)–O(1b)	1.396(19)
C(1c)–O(1c)	1.413(25)		
O(1a)–W–O(1b)	110.4(8)	O(1a)–W–O(1c)	109.6(7)
O(1b)–W–O(1c)	112.0(7)	O(1a)–W–W'	109.6(5)
O(1b)–W–W'	107.7(3)	O(1c)–W–W'	107.5(5)
W–O(1a)–C(1a)	146.4(15)	W–O(1b)–C(1b)	145.0(10)
W–O(1c)–C(1c)	151.0(13)		

dependence on either concentration or solvent. A high positive value is found for [Mo$_2$L$_6$], [α]$_D$ = +53.4, whereas [α]$_D$ = −58.4 is found for [W$_2$L$_6$].

The structural characterization of [Mo$_2$L$_6$] (1) and [W$_2$L$_6$] (2) (see below) and comparison of their structures with that of [V(L$_3$(py)$_2$] [1] shows that in these structures the metal atoms reside in chirotopic, non-stereogenic positions.

The high energetic barrier to rotation around the metal–oxygen bond, in part due to the short M–O

distance (1.8–1.9 Å in both complexes), affords a single diastereoisomer in the reaction mixtures which cannot interconvert. Recently, a chiral version of alkoxy metal–metal triple bond was reported, namely two stable diastereoisomers of (+)-[W$_2$(mentholate)$_6$] [10].

The structure of 1 was determined by an X-ray analysis at 118 K and is reported in Fig. 1.

The molecule has no symmetry elements and is formed by two Mo atoms linked by a triple bond (2.218(2) Å). Each Mo atom binds three L moieties via their exocyclic oxygen atoms; the six ligands have been labelled with the letters a to f. The sugar molecules around each Mo are arranged in such a way that the Mo–O bonds form a calix with the Mo–Mo bond as a stem (see Fig. 2). All the sugar molecules have similar conformations. The oxygen atoms O(1n), when seen
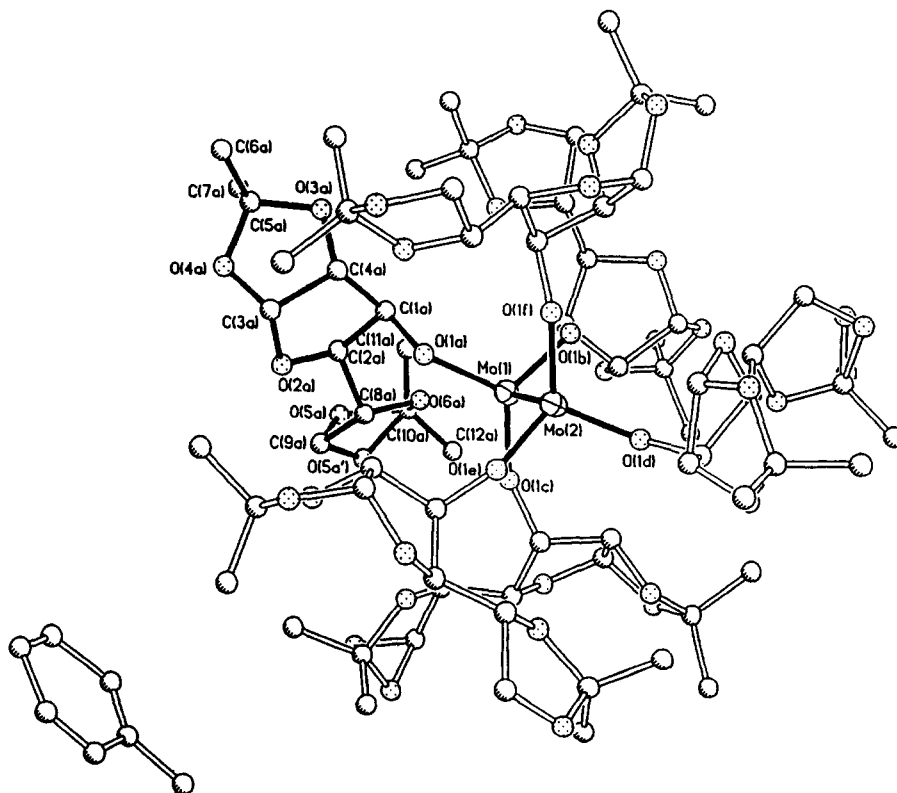

Fig. 1. View of complex 1 with the adopted labelling scheme, indicated in full for sugar a. The ellipsoids, shown only for the Mo atoms, are at the 80% probability level.
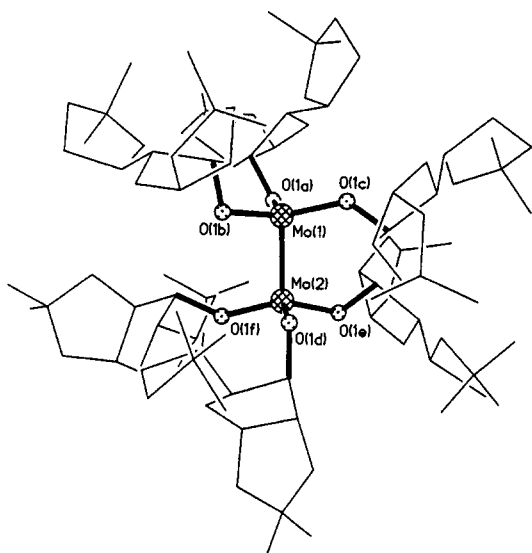
Fig. 2. Simplified view of complex **1** showing the calix arrangements of the sugar moieties around the Mo atoms.
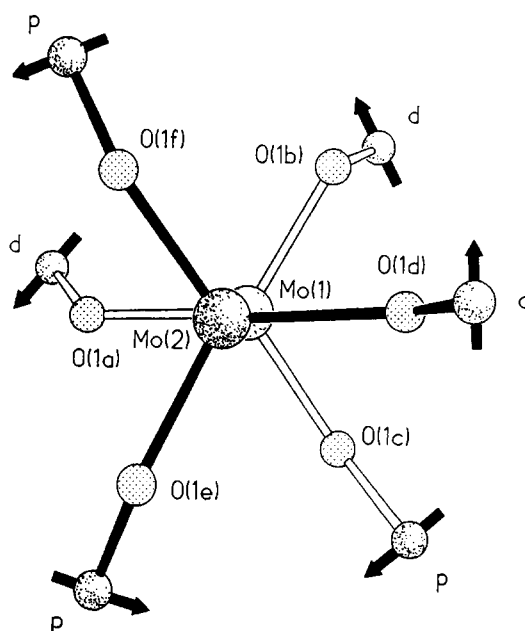

Fig. 3. View of the disposition of the O(1n) and C(1n) atoms seen along the Mo(1)–Mo(2) bond in complex **1**. The orientation of the sugar ligands is indicated by arrows going from the two fused rings to the single ring. The labels p and d indicate proximal and distal ligands, respectively.

along the Mo–Mo bond, have a staggered conformation (see Fig. 3); the values of the O(1m)–Mo–O(1n) angles vary from 113° to 120°. When the other sugar atoms are considered, and in particular C(1n), it may be seen that C(1a), C(1b) and C(1d) follow the same calix arrangement of O(1n) (distal, d), while C(1c), C(1e) and C(1f) are folded towards the stem of the calix (proximal, p). The two different arrangements are highlighted by different values of some geometrical parameters. The

Mo–O length is on average 1.913(3) Å for molecules *a*, *b* and *d* and 1.878(4) Å for molecules *c*, *e* and *f*. The first value is in keeping with the average value of 1.911
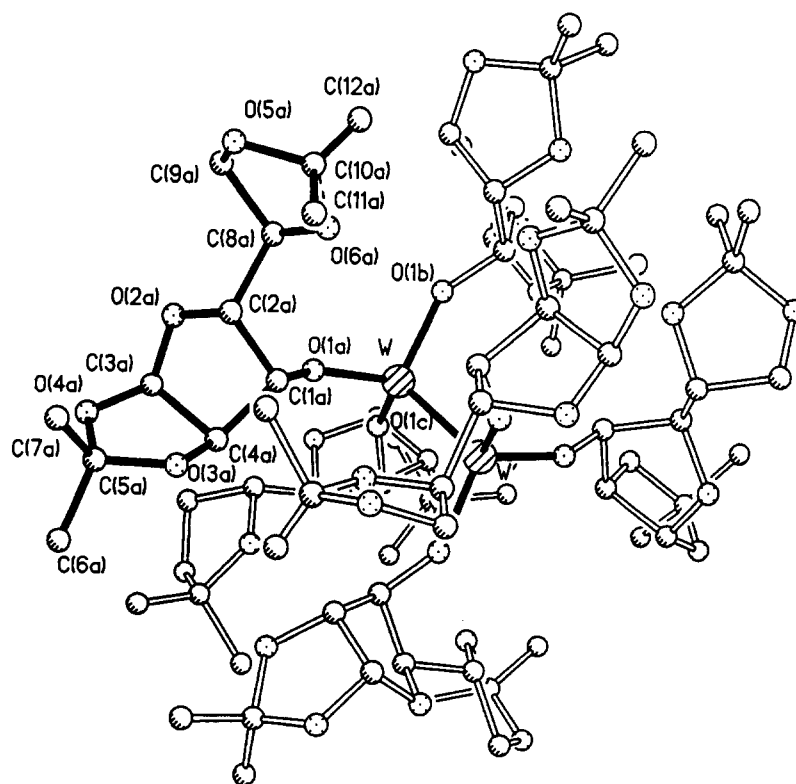

Fig. 4. View of complex **2** with the adopted labelling scheme, indicated in full for the sugar.

Å reported for alkoxy derivatives [16], whereas the second is lower. The Mo–Mo–O(1n) angles are also affected and vary from an average of 97° for *a*, *b* and *d* to an average of 105° for *c*, *e* and *f*. As a consequence, the oxygen calix is narrower around Mo(2) than around Mo(1). Nevertheless, the space-filling representation shows that Mo(2) is more exposed than Mo(1) because only molecule *d* folds towards it, whereas Mo(1) is obscured by the two sugar molecules, *a* and *b*. Also, the values of the angle Mo–O(1n)–C(1n) depend on the different arrangement of the ligands, being on average smaller (122°) for the distal ligands *a*, *b* and *d* and larger (140°) for the proximal ligands *c*, *d*, *e* and *f*.

The structure of **2** was determined by an X-ray analysis at room temperature and is illustrated in Fig. 4. The molecule possesses a crystallographic twofold axis, perpendicular to the W≡W bond (2.335(1) Å). The independent tungsten atom links three L moieties, which have been labelled with the letters *a*, *b* and *c*. In this case, the arrangement of the sugar molecules is such that W–O bonds form a calix (Fig. 5). The position of the twofold axis yields a staggered conformation of the O(1n) atoms around the W≡W bond (torsion angle O(1a)–W–W–O(1a)′ = −55°). When one considers the C(1n) atoms, a proximal disposition of all sugar moieties is revealed. Accordingly, the W–O(1n) lengths (average 1.87(1) Å), the W′–W–O(1n) angles (average 108.3(5)°) and the W–O(1n)–C(1n) angles (average 147(1)°) have a unimodal distribution, and in a space-filling representation the tungsten atoms are more exposed than both molybdenum atoms in complex **1**.

The stereochemistry of the two complexes may be compared with that of the similar homoleptic (+)-[W₂(mentholate)₆] complex [10]. The orientation of each sugar moiety may be described by an arrow going from the two fused five-membered rings to the single ring. These arrows are indicated in Fig. 3, where the letters d and p indicate distal and proximal sugars, respectively. It may be seen that around Mo(1) two arrows are counterclockwise and one is clockwise (d, d, p) and
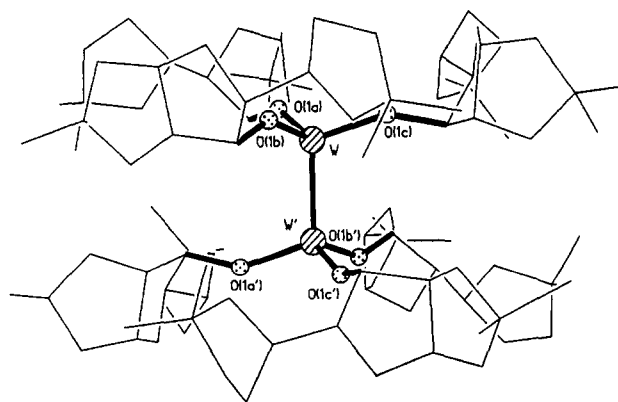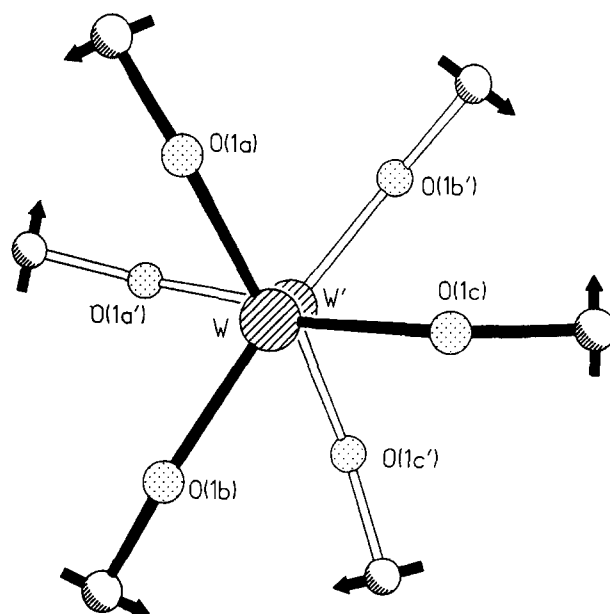

Fig. 6. View of the disposition of the O(1n) and C(1n) atoms seen along the W–W′ bond in complex **2**. The orientation of the sugar ligands, all proximal, is indicated by arrows going from the two fused rings to the single ring.

around Mo(2) all three arrows are counterclockwise (d, p, p). This arrangement is different from the two found in (+)-[W₂(mentholate)₆] [10], where the ligand is not as bulky.

With the aid of the simple force field provided by the MOLDRAW program [17], we analysed the energy profiles of the scans of the torsion angles M–M–O(1n)–C(1n) and M–O(1n)–C(1n)–C(2n) of both complexes (Fig. 6). In all cases the absolute minimum corresponds to the experimental value in the solid state; for the M–M–O(1n)–C(1n) angles, these are in the range −13 to 11° for proximal arrangements and in the range 153–176° for distal arrangements. The profiles of the scans of all the angles show deep and narrow minima with very high barriers. The situation is similar to that found in [VL₃(py)₂] [1] and is due to the steric hindrance of the bulky sugar ligands; this may be the reason why the Mo, W and V complexes afford a single diastereoisomer in the reaction mixture which cannot interconvert, in contrast with the behaviour of (+)-[W₂(mentholate)₆] [10].

The detectable disorder found for O(5n) of molecules *a*, *c* and *d* may be rationalized in terms of an envelope form of the five-membered ring in which the flap is up and down with respect to the plane of the other four atoms.

4. Conclusions

We have reported the easy access to mononuclear and dinuclear Mo and W derivatives containing only

Fig. 5. Simplified view of complex **2** showing the calix arrangement of the sugar moieties around the W atoms.

diacetoneglucose as an ancillary ligand. Their potential application to chemical reactivity, from asymmetric syntheses to other uses which can take advantage of the special nature of the glucose skeleton, is under investigation.

5. Supplementary material

Experimental data for the X-ray diffraction studies, fractional atomic coordinates for H atoms, anisotropic thermal parameters, bond distances and angles (Tables SI–SVI) and structure factor amplitudes (44 pages) for complexes 1 and 2 are available.

Acknowledgements

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