Tris(3,5-dimethylpyrazolyl)borato Molybdenum and Tungsten Nitrosyl Mentholates†

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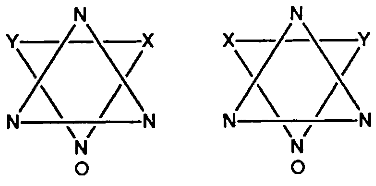
The complex [M(NO)L*X_2] [L* = tris(3,5-dimethylpyrazolyl)borate; M = Mo, X = Cl or I; M = W, X = Cl] reacted with (+)- and (−)-menthol ($C_{10}H_{19}OH$) affording diastereomeric mixtures of [M(NO)L*(X)($OC_{10}H_{19}$)]. These were separated by chromatography, and the structure of the diastereomer [Mo(NO)L*(Cl)({(−)-$OC_{10}H_{19}$}] determined crystallographically. The absolute configuration at the metal in this compound was determined to be *R*, and those of all other complexes [M(NO)L*(X)($OC_{10}H_{19}$)] related to it by comparison of their circular dichroism spectra.

We have long known that alcohols react with the prochiral molybdenum and tungsten nitrosyl dihalides [M(NO)L*X_2] [M = Mo or W, L* = tris(3,5-dimethylpyrazolyl)borate, X = Cl or I] affording a racemic mixture of enantiomeric monoalkoxides [M(NO)L*(X)(OR)].[1–3] Until recently we have not attempted to resolve these racemic mixtures, but our interest in obtaining pure enantiomers was stimulated because of the need to find a reliable route to chiral dipolar bimetallic species which might exhibit non-linear optical properties.

In designing materials capable of doubling the frequency of incident radiation a necessary feature is that the molecules comprising such a material contain a donor and an acceptor function separated by a polarisable bridge.[4] We knew that the {M(NO)L*} moiety was very powerfully electronegative[1,5,6] and could constitute a useful acceptor fragment if suitable donors could be attached. A further requirement for materials to show second-order non-linear optical effects is that the crystals are polar and non-centrosymmetric. The production of a pure diastereomer based on the [M(NO)L*(X)(OR)] system (OR = mentholate) would afford a non-centrosymmetric crystal, but we could not be sure that such a species would also crystallise in a polar space group. Accordingly, molecular design in the context of optical non-linearity is still subject to the somewhat adventitious nature of crystallisation and so has to be underpinned by crystallographic studies.

In developing this work with mentholate complexes we had two goals: determination of the absolute configuration of a key complex and correlation of its circular dichroism (CD) spectrum with that of related monosaccharide species; and formation of a series of chiral alkoxides which might be relatively easy to isolate as pure diastereomers. So far as we can determine there are relatively few reports of mentholate complexes. Among the best characterised species so far described are the chiral tetrahedral clusters [$MCo_2(CO)_6C(=O)$-{(+)-$OC_{12}H_{19}$}] [M = $Co(CO)_3$, Mo(η-C_5H_5)$(CO)_2$ and related fragments],[7] in fact carboxylato derivatives, and [Re_3(μ-$Cl)_2$(μ-$OC_{12}H_{19})_2$($OC_{12}H_{19})_5$].[8]

In this paper we describe the synthesis of monomeric molybdenum and tungsten nitrosyl mentholates, [M(NO)L*(X)-($OC_{10}H_{19}$)], the purification and isolation of some of the diastereomers, and the crystal, molecular structure and determination of the absolute configuration at the metal in one diastereomer of [Mo(NO)L*(Cl)($OC_{10}H_{19}$)]. The enantiomeric relationships of the metal co-ordination sphere are shown in Fig. 1, and the mentholate ligand, together with appropriate atom numbering, in Fig. 2. The substitution of X in these compounds by donor moieties bridged by polarisable groups, thereby affording dipolar molecules of NLO potential, will be described in subsequent publications.



A B

Fig. 1 Enantiomeric relationships of chiral [M(NO)L*(X)Y] (X = Cl, Y = mentholate) where the N_3 triangle represents the L* ligand

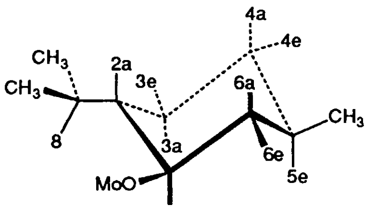


Fig. 2 The (−)-mentholate ligand

Experimental

The complexes [M(NO)L*X_2] (M = Mo, X = Cl or I; M = W, X = Cl) were prepared as described in the literature.[9] All other reagents were used as received and all reactions were carried out in dry solvents under nitrogen. Proton NMR and IR spectra were obtained using JEOL GX270 and Perkin-Elmer

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

PE237 spectrometers, and elemental analyses were determined by the Microanalytical Laboratory of the School of Chemistry, University of Birmingham. The UV/VIS spectral measurements were made with a Shimadzu spectrophotometer, and preliminary optical rotation measurements were carried out in dichloromethane solution using a PE241 polarimeter. Circular dichroism spectra were obtained using a Jobin-Yvon CNRS Dichrographe III, dichloromethane solutions being measured under nitrogen.

General Procedures for the Synthesis of [M(NO)L*(X)(OC$_{10}$H$_{19}$)] (M = Mo, X = Cl *or* I: M = W, X = Cl).—The complex [M(NO)L*X$_2$] (0.5 g; M = Mo, X = Cl or I; M = W, X = Cl) was dissolved in toluene (100 cm^3) and an excess (*ca.* 25%) of (+)- or (−)-menthol and NEt$_3$ (0.5 cm^3) were added. The mixture was stirred and refluxed until the full colour of the product had developed (M = Mo, X = Cl, blue; X = I, green; M = W, X = Cl, purple). The mixture was then cooled to −10 °C, filtered and the filtrate evaporated *in vacuo*. The residue was redissolved in dichloromethane and chromatographed on silica gel using dichloromethane–light petroleum (b.p. 40–60 °C) affording a mixture of diastereomers. The diastereomers were separated, where possible, using a long silica gel column and the same eluent. The diastereomer eluting first from the column was denoted **D1** and the second **D2**. Small aliquots were collected and checked by thin-layer chromatography (TLC), and those containing one nearly pure isomer were combined, the solvent evaporated *in vacuo* and the residue recrystallised from dichloromethane–hexane mixtures, affording the complexes as blue ({MoCl}), green ({MoI}) or purple ({WCl}) microcrystals. Repeated attempts to purify the diastereomers led to decomposition on the column, so complete purification was not always possible. The percentage composition of the mixture of **D1** and **D2** was determined by ^{1}H NMR spectroscopy, particularly using the double doublets due to the methyl signals of the Pr^i group (Table 1). The reactions attempted are listed in Table 1.

Table 1 Reactions of [M(NO)L*X$_2$] with (+)- and (−)-menthol

[M(NO)L*X$_2$]			
M	X	Menthol	Ratio **D1**:**D2**;[a] comments
1 Mo	I	(−)	2:1
2 Mo	I	(+)	5:1
3 Mo	Cl	(−)	16:1, crystals isolated[b]
4 Mo	Cl	(+)	12:1
5 Mo	Cl	(−)	Mostly **D2** as prisms, with small amounts of **D1** as needles[b,c]
6 W	Cl	(−)	Nearly pure **D2**[b]
7 W	Cl	(−)	2.5:1[b]

[a] Ratios established by NMR spectroscopy. [b] Relative ratios obtained by manipulation of reaction conditions/work-up procedure to obtain one diastereomer preferentially; reactions 3 and 5, and 6 and 7. [c] Isomer **D1** identified spectroscopically and confirmed by comparison of X-ray powder diffraction data with those for crystals of the material whose structure has been determined.

Crystallography of [Mo(NO)L*(Cl){(−)-OC$_{10}$H$_{19}$}].—*Crystal data.* C$_{25}$H$_{41}$BClMoN$_7$O$_2$, M_r = 613.8, orthorhombic, space group $P2_12_12_1$, a = 10.464(8), b = 16.893(10), c = 17.086(7) Å, U = 3020 Å^3, Z = 4, D_c = 1.350 g cm^{-3}, F(000) = 1280, μ(Mo-Kα) = 0.542 mm^{-1}, λ = 0.710 69 Å.

A dark blue crystal (0.3 × 0.2 × 0.2 mm), obtained by reaction of [Mo(NO)L*Cl$_2$] with (−)-menthol and isolated as

Table 3 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses and torsion angles (°). E.s.d.s for torsion angles are *ca.* 1.0°

Mo–Cl	2.369(1)	Mo–N(4)	2.159(4)
Mo–O(2)	1.875(3)	Mo–N(6)	2.220(4)
Mo–N(1)	1.765(5)	O(1)–N(1)	1.194(6)
Mo–N(2)	2.237(4)	O(2)–C(16)	1.437(5)
Cl–Mo–O(2)	102.2(1)	N(2)–Mo–N(4)	85.7(2)
Cl–Mo–N(1)	91.5(2)	Cl–Mo–N(6)	85.1(1)
O(2)–Mo–N(1)	97.9(2)	O(2)–Mo–N(6)	164.5(1)
Cl–Mo–N(2)	87.4(1)	N(1)–Mo–N(6)	95.6(2)
O(2)–Mo–N(2)	81.5(1)	N(2)–Mo–N(6)	85.2(1)
N(1)–Mo–N(2)	178.6(2)	N(4)–Mo–N(6)	77.0(1)
Cl–Mo–N(4)	161.3(1)	Mo–O(2)–C(16)	137.1(3)
O(2)–Mo–N(4)	94.0(2)	Mo–N(1)–O(1)	174.1(5)
N(1)–Mo–N(4)	95.6(2)		

N(1)–Mo–O(2)–C(16)	−7.7
Mo–O(2)–C(16)–C(17)	115.4
Mo–O(2)–C(16)–C(21)	−124.0
O(2)–C(16)–C(17)–C(18)	173.7
O(2)–C(16)–C(21)–C(20)	−176.3
C(23)–C(22)–C(17)–C(16)	−69.6
C(23)–C(22)–C(17)–C(18)	53.8
C(24)–C(22)–C(17)–C(16)	163.7
C(24)–C(22)–C(17)–C(18)	−72.9
C(22)–C(17)–C(16)–C(21)	−178.0
C(22)–C(17)–C(18)–C(19)	177.4
C(25)–C(20)–C(19)–C(18)	−177.0
C(25)–C(20)–C(21)–C(16)	177.6

Table 2 Fractional atomic coordinates (× 10^5 for Mo, × 10^4 for others) with estimated standard deviations (e.s.d.s) in parentheses for [Mo(NO)L*(Cl){(−)-OC$_{10}$H$_{19}$}]

Atom	x	y	z	Atom	x	y	z
Mo	−1 928(3)	13 703(2)	25 559(2)	C(8)	−2 054(6)	40(4)	690(4)
Cl	1 245(1)	1 972(1)	3 447(1)	C(9)	−991(5)	354(4)	324(3)
O(1)	−1 060(5)	290(3)	3 808(3)	C(10)	−612(7)	279(5)	−520(4)
O(2)	−1 598(2)	2 059(2)	2 592(2)	C(11)	2 277(6)	82(5)	3 427(4)
N(1)	−714(5)	693(3)	3 275(3)	C(12)	2 376(4)	248(3)	2 569(4)
N(2)	469(4)	2 251(2)	1 667(2)	C(13)	3 358(5)	55(4)	2 056(4)
N(3)	980(4)	2 007(3)	974(2)	C(14)	3 016(5)	340(3)	1 338(4)
N(4)	−923(4)	708(3)	1 572(2)	C(15)	3 743(6)	303(5)	576(4)
N(5)	−315(4)	756(3)	856(2)	C(16)	−2 833(4)	2 076(3)	2 959(3)
N(6)	1 486(4)	663(2)	2 179(2)	C(17)	−2 885(4)	2 759(3)	3 539(3)
N(7)	1 889(4)	702(3)	1 417(2)	C(18)	−4 254(5)	2 828(4)	3 858(3)
B	1 051(5)	1 126(4)	798(3)	C(19)	−5 219(5)	2 942(4)	3 194(3)
C(1)	70(6)	3 540(3)	2 328(4)	C(20)	−5 168(4)	2 267(3)	2 605(3)
C(2)	531(5)	3 050(3)	1 666(3)	C(21)	−3 799(4)	2 182(3)	2 299(3)
C(3)	1 081(6)	3 304(4)	970(3)	C(22)	−1 872(5)	2 682(4)	4 206(3)
C(4)	1 356(6)	2 640(4)	553(3)	C(23)	−2 147(7)	2 010(5)	4 779(3)
C(5)	2 046(10)	2 560(5)	−222(4)	C(24)	−1 682(7)	3 466(4)	4 634(4)
C(6)	−2 873(6)	34(4)	2 126(4)	C(25)	−6 085(5)	2 406(5)	1 921(4)
C(7)	−1 967(5)	253(3)	1 468(4)				

Table 4 Elemental analytical data obtained from mentholate complexes, $[M(NO)L^*X(OC_{10}H_{19})]$

Complex			Analysis (%)						
			Found			Calc.			
M	X	Ligand	C	H	N	C	H	N	Reaction*
Mo	Cl	$(-)$-$OC_{10}H_{19}$	49.0	6.8	15.7	48.9	6.7	16.0	3
Mo	Cl	$(+)$-$OC_{10}H_{19}$	48.4	6.7	15.9				4
Mo	I	$(+)$-$OC_{10}H_{19}$	42.8	5.7	13.6	42.6	5.9	13.9	2
Mo	I	$(-)$-$OC_{10}H_{19}$	42.3	6.0	13.6				1
W	Cl	$(-)$-$OC_{10}H_{19}$	42.9	5.7	14.2	42.8	5.9	14.0	6
W	Cl	$(-)$-$OC_{10}H_{19}$	42.9	5.8	14.2				7

* Reaction from which complex was obtained, as listed in Table 1.

D1 referred to in Table 1, was mounted on an Enraf-Nonius CAD-4 diffractometer; cell dimensions and intensities were measured by ω–2θ scans with graphite-monochromated Mo-Kα radiation. 4722 Reflections were scanned in the range $2 < \theta < 24°$, index range h − 11 to +11, k 0–19, l 0–19, and of these 3961 having $I > 2.5\sigma(I)$ were considered observed and used in the analysis. Bijvoet pairs were not merged. Three standard reflections measured every 2 h shows no significant variation in intensity.

The structure was determined by Patterson and Fourier methods and refined by least squares using anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions riding on their respective bonded atoms and only their isotropic thermal parameters were refined. Weights, $w = 1/[\sigma^2(F) + 0.0025F^2]$, were used in the least-squares refinement. The calculations were terminated when all shift/e.s.d. ratios were <0.1:1 and $R = 0.034$, $R' = 0.047$ for 3961 observed reflections. The residual electron density in the final difference map was within the range ± 0.8 e Å^{-3}. The inverse structure gave $R = 0.036$, $R' = 0.050$. The absolute configuration depicted in Fig. 3 is thus established[10] at better than the 99.5% probability level from consideration of anomalous scattering effects, in agreement with the known absolute configuration of the (−)-menthol used in the preparation of the complex.†

Complex neutral-atom scattering factors were employed. Computations were carried out on the University of Birmingham IBM 3090 computer and on the Amdahl 5890 at the Manchester Computing Centre with the SHELXS 86[11] and SHELX 76[12] packages. The molecular diagram was drawn using PLUTO.[13] Final atomic coordinates are listed in Table 2. Selected bond lengths and angles are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Reaction of $[M(NO)L^*X_2]$ (M = Mo, X = Cl or I; M = W, X = Cl) with an excess of (+)- or (−)-menthol, in the presence of triethylamine to facilitate elimination of HX, afforded mixtures of the desired diastereomeric monomentholates $[M(NO)L^*(X)(OC_{10}H_{19})]$ as green (M = Mo, X = I), blue (M = Mo, X = I) or purple (M = W, X = Cl) solids. Our attempts to separate the diastereomers by column chromatography were only partially successful, although mixtures containing no less than 60% of one component were invariably obtained. The species eluted first from the column we have labelled **D1** and that appearing second **D2**. The experiments carried out are described in the Experimental section (Table 1; analytical data in Table 4). In two cases we were able to obtain virtually pure diastereomers, *viz.* in reaction 5 between $[Mo(NO)L^*Cl_2]$ and (−)-menthol, giving predominantly the **D2** form as well formed prisms, and in reaction 6 between $[W(NO)L^*Cl_2]$ and (−)-menthol, giving the practically pure **D2** form also. We were also able to obtain needle-like crystals of **D1** from reaction 5, in spite of the predominance of **D2**, and these crystals were subsequently used in our X-ray crystallographic studies (see below). The relative ratios of the **D1** and **D2** forms in each reaction system were determined by ^{1}H NMR spectroscopy (see below).

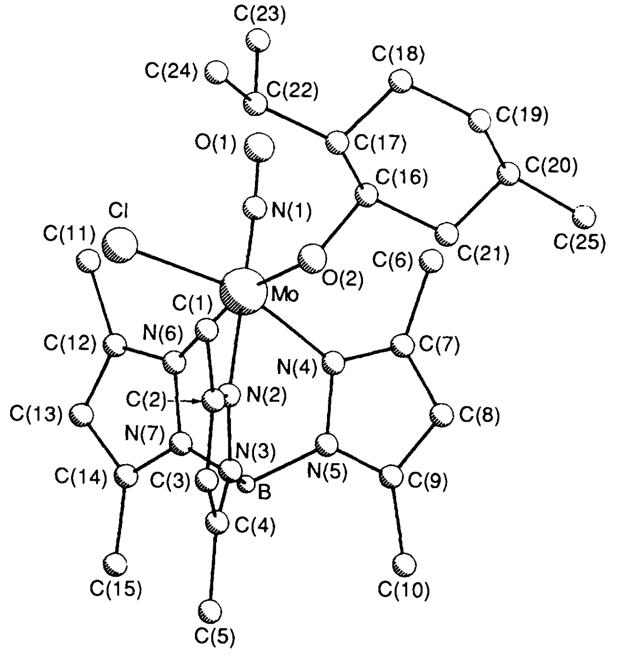

Fig. 3 View of $[Mo(NO)L^*(Cl)(OC_{10}H_{19})]$, hydrogen atoms being omitted for clarity

The IR spectra of the complexes (Table 5) exhibited absorptions characteristic of tris(3,5-dimethylpyrazolyl)borate, particularly ν(BH) at *ca.* 2210 cm^{-1}, and the NO stretching frequency occurred in the expected regions, between 1660 and 1680 cm^{-1} for the molybdenum species and at 1625 cm^{-1} for the tungsten species. These values are typical of monoalkoxides of this class of compound.[1–3,14]

The ^{1}H NMR spectra were characteristic of each diastereomer isolated (Table 5). Assignments were made of the mentholate resonances with the assistance of spin decoupling and the labelling scheme is shown in Fig. 2. Of the mentholate signals, that due to H(1a) is shifted significantly to low field in

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† Additional supports for the assignment comes from comparison of selected Bijvoet pairs. Considering Bijvoet pairs for which the ratios $F_{obs}(hkl)/F_{obs}(\bar{h}\bar{k}\bar{l})$ and $F_{calc}(hkl)/F_{calc}(\bar{h}\bar{k}\bar{l})$ are both either <0.95 or >1.05:1, in ten such pairs randomly selected, these ratios are all consistent with the assigned configuration.

Table 5 Infrared and ^{1}H NMR spectral data obtained from $[\mathrm{M(NO)L^*(X)(OC_{10}H_{19})}]$

Complex			IR[a]	^{1}H NMR data[b]		
	M[c]	X	$\nu_{NO}/\mathrm{cm^{-1}}$	δ[d]	Relative area	Assignment
D1	Mo[e]	Cl	1660	5.94	dt	H(1a), J = 10.0 and 3.5
				5.89	1s	$\mathrm{Me_2C_3}\mathit{H}\mathrm{N_2}$
				5.81	1s	
				5.76	1s	
				2.52	3s	$\mathrm{(C}\mathit{H}\mathrm{_3)_2C_3HN_2}$
				2.50	3s	
				2.38	3s	
				2.36	3s	
				2.35	3s	
				2.33	3s	
				ca. 2.5	1m	$\mathrm{C}\mathit{H}\mathrm{Me_2}$, overlapping with above signals, confirmed by spin decoupling
				1.75–1.00	8m	H(2a), H(3a), H(3e), H(4a), H(4e), H(6a), H(6e)
				ca. 1.6		H(5a), confirmed by spin decoupling
				1.09	3d	$\mathrm{CH(C}\mathit{H}\mathrm{_3)_2}$, J = 6.8
				0.89	3d	
				0.87	3d	$\mathrm{CH_3}$, J = 6.2
D2	Mo[f]	Cl		5.86	1s	$\mathrm{Me_2C_3}\mathit{H}\mathrm{N_2}$
				5.82	1s	
				5.74	1s	
				5.64	1dt	H(1a), $J(\mathrm{H^{1a}{-}H^{6a+2a}})$ = 10.4, $J(\mathrm{H^{1a}{-}H^{6e}})$ = 4.6
				3.07	1m	H(6e)
				2.52	3s	$\mathrm{(C}\mathit{H}\mathrm{_3)_2C_3HN_2}$
				2.44	3s	
				2.39	3s	
				2.38	3s	
				2.35	3s	
				2.33	3s	
				1.73	3m	H(5a), H(3e), H(4e)
				1.63	1m	$\mathrm{C}\mathit{H}\mathrm{Me_2}$
				1.39	2m	H(6a), H(2a)
				1.11	2m	H(3a), H(4a), peaks overlapping with signals from methyl group below
				1.07	3d	$\mathrm{CH_3}$, J = 6.4
				0.69	3d	$\mathrm{CH(C}\mathit{H}\mathrm{_3)_2}$, J = 7.0
				0.60	3d	
D1	Mo[g]	I	1675	5.85	1s	$\mathrm{Me_2C_3}\mathit{H}\mathrm{N_2}$
				5.82	1s	
				5.79	1s	
				5.85	1dt	H(1a), $J(\mathrm{H^{1a}{-}H^{6a}})$ = 10.3, $J(\mathrm{H^{1a}{-}H^{6e}})$ = 4.6
				2.53	3s	$\mathrm{(C}\mathit{H}\mathrm{_3)_2C_3HN_2}$
				2.45	3s	
				2.43	3s	
				2.41	3s	
				2.36	3s	
				2.32	3s	
				ca. 2.5	1m	$\mathrm{C}\mathit{H}\mathrm{Me_2}$, overlapped by above signals
				1.90–1.00	8m	H(2a), H(3a), H(3e), H(4a), H(4e), H(5a), H(6a), H(6e)
				1.00	3d	$\mathrm{CH(C}\mathit{H}\mathrm{_3)_2}$, J = 7.0
				0.89	3d	$\mathrm{CH_3}$, J = 6.4
				0.82	3d	
D2	Mo[h]	I		5.82	1s	$\mathrm{Me_2C_3}\mathit{H}\mathrm{N_2}$
				5.80	2s	
				5.04	1dt	H(1a), J = 11.1 and 4.9
				2.53	3s	$\mathrm{(C}\mathit{H}\mathrm{_3)_2C_3HN_2}$
				2.433	3s	
				2.427	6d	
				2.37	3s	
				2.34	3s	
				2.14	1d	H(6e), J = 12.5
				1.90–1.00	8m	H(2a), H(3a), H(3e), H(4a), H(4e), H(5a), H(6a) and $\mathrm{C}\mathit{H}\mathrm{Me_2}$
				1.07	3d	$\mathrm{CH_3}$, J = 6.4
				0.67	3d	$\mathrm{CH(C}\mathit{H}\mathrm{_3)_2}$, J = 6.9
				0.55	3d	
D1	W[i,j]	Cl	1625	5.92	1s	$\mathrm{Me_2C_3}\mathit{H}\mathrm{N_2}$
				5.82	2s	
				5.76	1m	H(1a)
				2.62	3s	$\mathrm{(C}\mathit{H}\mathrm{_3)_2C_3NH_2}$
				2.60	3s	
				2.40	3s	
				2.37	6s	
				2.31	3s	

Table 5 (*continued*)

Complex			IR[a]	^{1}H NMR data[b]		
	M[c]	X	ν_{NO}/cm^{-1}	δ[d]	Relative area	Assignment
				3.54	1m	CHMe$_2$
				1.80–0.90	8m	H(2a), H(3a), H(3e), H(4a), H(4e), H(5a), H(6a), H(6e)
				1.12	3d	CH(CH_3)$_2$, J = 7.0
				0.90	3d	
				0.85	3d	CH$_3$, J = 6.6
D2	W[i]	Cl	1625	5.89	1s	Me$_2$C$_3$$HN_3$
				5.83	1s	
				5.80	1s	
				5.41	1dt	H(1a), J(H^{1a}–H^{6a+2a}) = 10.6, J(H^{1a}–H^{1e}) = 4.6
				3.06	1m	
				2.60	3s	(CH_3)$_2$C$_3$HN$_2$
				2.58	3s	
				2.40	3s	
				2.38	3s	
				2.37	3s	
				2.33	3s	
				1.70	3m	H(5a), H(4e), H(3e)
				1.56	1m	CHMe$_2$
				1.31	2m	H(2a), H(6a)
				1.05	3d	CH$_3$, J = 6.2
				1.00	2m	H(3a), H(4a), peaks overlapping with above signals, and poorly resolved
				0.69	3d	CH(CH_3)$_2$, J = 7.0
				0.57	3d	

[a] In KBr discs. [b] Spectra of **D2** isomers normally obtained by subtraction of that of **D1** (when pure; J in Hz). [c] **D1** and **D2** refer to first and second eluates obtained in chromatographic separation of diastereomers: the spectra of the **D2** forms are usually the minor component of any mixture of diastereomers. [d] In CDCl$_3$ at 270 MHz. [e] From reaction 3. [f] From reaction 5 (cubes). [g] From reaction 2. [h] From reaction 1. [i] From reaction 6. [j] By subtraction of the spectrum of the **D2** eluate.

Table 6 UV/VIS spectral data obtained from [M(NO)L*(X)(OC$_{10}$H$_{19}$)] (M = Mo, X = Cl or I; M = W, X = Cl) in CH$_2$Cl$_2$

Complex	λ_{max}/nm, (ε/dm^3 mol^{-1} cm^{-1})	
[Mo(NO)L*(Cl)(OC$_{10}$H$_{19}$)][a]	560 (220)	300 (10 400)
[Mo(NO)L*(I)(OC$_{10}$H$_{19}$)][b]	600 (250)	323 (8800)
[W(NO)L*(Cl)(OC$_{10}$H$_{19}$)][c]	517 (180)	*ca.* 260 (sh) (18 000)

[a] From reaction 3. [b] From reaction 2. [c] From reaction 6.

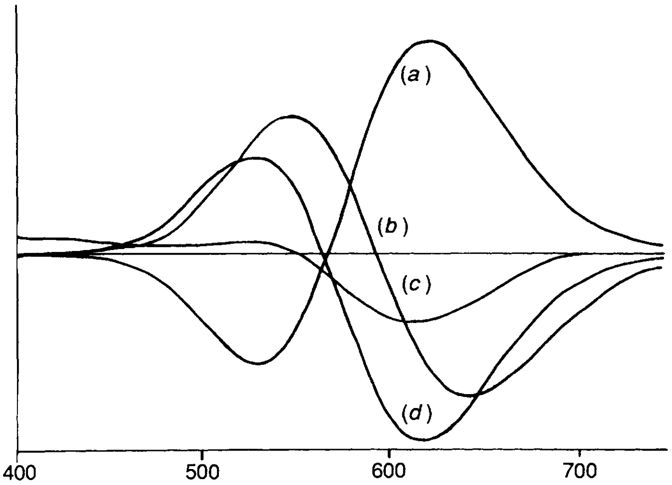

Fig. 4 CD spectra of [M(NO)L*(X)(OC$_{10}$H$_{19}$)]: (*a*) **D1**-[Mo(NO)L*(Cl){(–)-OC$_{10}$H$_{19}$}], structure determined; (*b*) **D2**-[Mo(NO)L*(Cl){(–)-OC$_{10}$H$_{19}$}], from reaction 5; (*c*) **D1**-[Mo(NO)L*(I){(+)-(OC$_{10}$H$_{19}$}], from reaction 2; (*d*) **D1**-[Mo(NO)L*(Cl){(+)-OC$_{10}$H$_{19}$}], from reaction 4

comparison with that in the uncomplexed alcohol because of the powerful electronegative influence of the {M(NO)L*(X)} group, an effect which has been described before.[1–3] The position of this signal is unique for each diastereomer, *e.g.* occurring as a doublet of triplets at δ 5.94 for the **D1** form of [Mo(NO)L*Cl(OC$_{10}$H$_{19}$)] and at higher field (δ 5.64) for the **D2** form. The same shift of this signal to higher field is observed for the **D2** diastereomer of the iodo complex and in its tungsten chloride analogue. Similar upfield shifts for the **D2** relative to the **D1** isomers were observed for the protons of the Pr^i group, whereas the opposite effect was found for methyl signals and for H(6e). These shifts, especially those of the double doublets of the methyl signals of the Pr^i group, were particularly useful when attempting to determine the relative percentages of each diastereomer in a given mixture in solution. In all complexes the protons attached to C(4) [C(3), C(8) and C(13) in Fig. 3] in the pyrazolyl rings appeared as three singlets, consistent with the overall lack of symmetry in these six-co-ordinate species.

The electronic spectra of the complexes were recorded in the visible region in dichloromethane (Table 6). The circular dichroism spectra of the products obtained from reactions 3–5 were recorded in dichloromethane (Fig. 4). A CD spectrum was also obtained of the product of the diastereomeric mixture isolated from reaction 2. It can be noted that the CD spectrum of the product of reactions 4 and 5, the former containing in excess of 90% of **D1**-[Mo(NO)L*(Cl){(+)-OC$_{10}$H$_{19}$}] and the latter essentially pure **D2**-[Mo(NO)L*(Cl){(–)-OC$_{10}$H$_{19}$}], are almost identical and therefore these complexes presumably have the same absolute configuration at the Mo atom. However, the CD spectrum of the product from reaction 3, which contains 94% of **D1**-[Mo(NO)L*(Cl){(–)-OC$_{10}$H$_{19}$}], indicates the metal has the opposite absolute configuration to that in the other two species. The CD spectrum of [Mo(NO)L*(I){(+)-OC$_{10}$H$_{19}$}] (from reaction 2), which contains 83% of the **D1** form, indicates that this species has the same absolute configuration as **D1**-[Mo(NO)L*(Cl){(+)-OC$_{10}$H$_{19}$}] and **D2**-[Mo(NO)L*(Cl){(–)-OC$_{10}$H$_{19}$}].

We were able to detect epimerisation only during reaction 3, but the conditions were not reproducible, and the interconversion of the diastereomers is being further investigated. Thus, so far, reliable evidence for the epimerisation of the diastereomers is lacking.

In order to relate the CD spectra reported above to the absolute configuration of each compound isolated we have determined the structure of **D1**-[Mo(NO)L*(Cl){(–)-$OC_{10}H_{19}$}] by X-ray crystallography. Selected bond lengths, angles and torsion angles are listed in Table 2. A stereoscopic view of the molecule is shown in Fig. 3 which also indicates the crystallographic atomic numbering scheme (this corresponds to **B** in Fig. 1).

The co-ordination about molybdenum is essentially octahedral, maximum angular deviation 18.7° [angle Cl–Mo–N(4) 161.3(1)], mean deviation 7.4°. The angles agree quite closely with those found in crystal structures of analogous compounds. Thus corresponding angles at molybdenum in the isopropoxo derivative [Mo(NO){HB(3,5-Me_2-4-$ClC_3N_2)_3$}Cl(OPr^i)][1] differ by only an average of 1.1° with a maximum difference of 2.3°. The Mo–N(pyrazolyl) bond lengths also follow the pattern observed previously.[1,5,15] The bond *trans* to the nitrosyl substituent is the longest of these, which may be attributed[15] to the *trans* influence of the strongly π-accepting nitrosyl group, whereas the bond *trans* to the chlorine atom is the shortest, reflecting the near single-bond character of molybdenum–halogen bonding. The high degree of π character of the Mo–N(nitrosyl) bonding results in this bond being by far the shortest of the molybdenum–nitrogen bonds (see Table 3), its length falling well within the range of values (1.744–1.804 Å) reported previously.[1,3,5,15,16] The Mo–Cl length [2.369(1) Å] is very slightly shorter than the lengths, 2.380(2)[1] and 2.408(2) Å,[16] observed in analogous structures.

The shortness of the Mo–O(2) bond, 1.875(3) Å, implies[1] significant p_π–d_π donation from oxygen to molybdenum. The large, 137.1(3)° Mo–O(2)–C(16) angle is consistent with π bonding. In comparable structures Mo–O lengths of 1.863(7),[1] 1.886(12),[5] 1.900(4),[3] and 1.908(4) Å[3] have been reported and the corresponding angles at oxygen range from 129.5 to 133.4°. Steric factors may, however, contribute to the large angle at O(2), as this would increase the N(1) ··· C(16) non-bonded distance, which at the observed value of 3.266(6) Å is close to the sum of the van der Waals radii[17] of nitrogen and carbon (3.25 Å). The relatively large O(2)–Mo–N(1) angle of 97.9(2)° also has the effect of increasing this distance. The near-eclipsed conformation of the N(1)–Mo–O(2)–C(16) moiety [torsion angle –8(1)°], which is the primary factor in the N(1) ··· C(16) steric interaction, is, however, energetically favourable in facilitating[3] the p_π–d_π ligand–metal interaction. Similarly small N(nitrosyl)–Mo–O–C torsion angles are invariably found[1,3,5] in this type of complex. Eclipsed conformations are also found[15] in amido complexes. The chloro substituent is effectively removed from steric interaction with the mentholate residue by the large, 102.2(1)°, Cl(1)–Mo–O(2) angle.

The mentholate ring adopts the normal, slightly flattened, cyclohexane chair conformation, ring torsion angles 54.9–58.0°. All substituents are equatorial. Pertinent torsion angles are listed in Table 3. The pyrazolyl rings are essentially planar and make dihedral angles of 114.7, 118.6 and 126.7° with one another. As has been noted previously[3,5,16] in analogous structures, the smallest of these angles is between the pair of rings [N(4),N(5),C(7)–(9) and N(6),N(7),C(12)–(14)] encompassing the relatively small nitrosyl group, while the largest angle is between the pair of rings encompassing the bulkiest substituent, here the mentholate residue. The absolute configuration of the mentholate ligand itself was found to be 1*R*-2*S*-5*R* (1 referring to the C atom bonded to oxygen, 2 to the C bonded to the Pr^i group and 5 to the C atom bound to Me).

According to the rules for assigning absolute configuration,[18] and from the structural arrangements established around the central metal atom, the diastereomer **D1**-[Mo(NO)L*(Cl){(–)-$OC_{10}H_{19}$}] has the absolute configuration *R* at the metal atom. Accordingly, from a consideration of the CD spectral data, we may deduce that the configurations at the central metal atom in **D1**-[Mo(NO)L*(Cl){(+)-$OC_{10}H_{19}$}], **D2**-[Mo(NO)L*(Cl)-{(–)-$OC_{10}H_{19}$}] and **D1**-[Mo(NO)L*(I){(+)-$OC_{10}H_{19}$}] are the same, whereas that in **D1**-[Mo(NO)L*(Cl){(–)-$OC_{10}H_{19}$}] is the opposite. Further, although we did not obtain a CD spectrum of **D2**-[W(NO)L*(Cl){(–)-$OC_{10}H_{19}$}], we believe that the absolute configuration of the tungsten atom will be identical to that in **D2**-[Mo(NO)L*(Cl){(–)-$OC_{10}H_{19}$}], *i.e. S*.

In conclusion, we have shown that is possible to detect enantiomers derived from [M(NO)L*(X)(OR)] and to separate some of the diastereomers derived from the mentholates virtually pure. Kurtz powder tests of *R*-[Mo(NO)L*(Cl){(+)-$OC_{10}H_{19}$}], undertaken to establish whether the mentholates species exhibited non-linear optical activity as solids, revealed[19] a secondary harmonic generator efficiency of 0.074 times that of the standard urea.† Such a low efficiency is not surprising since the mentholate is not a strongly polarisable donor even though {Mo(NO)L*(Cl)} is a powerful acceptor, and the molecule does not crystallise in a polar (non-centrosymmetric) space group. It should be possible, however, to substitute X by more powerful electron-donor substituents based on ferrocene, thereby affording species potentially capable of generating second-order non-linear optical effects, and some of our efforts in this direction have been described.[19,20]

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