

# Synthesis and Structural Characterisation of Glucofuranoside and Galactopyranoside Derivatives of [Tris(3,5-dimethylpyrazolyl)borato]-molybdenum and -tungsten Nitrosyls†

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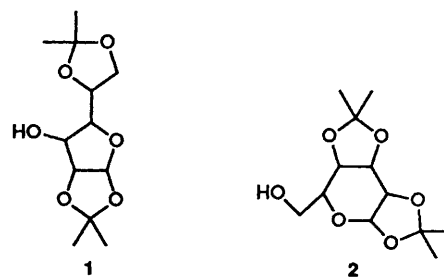
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The complex  $[M(NO)L^*X_2]$  [ $L^*$  = tris(3,5-dimethylpyrazolyl)borate;  $M$  = Mo,  $X$  = Cl or I;  $M$  = W,  $X$  = Cl] reacted with 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranose ( $HG_f$ ) and with 1,2:3,4-di-*O*-isopropylidene- $\alpha$ -D-galactopyranose ( $HG_p$ ) to give diastereomers of  $[M(NO)L^*(X)G_f]$  and  $[M(NO)L^*(X)G_p]$ . The structure of the thermodynamically stable diastereomer of  $[Mo(NO)L^*(I)G_f]$  was determined by a single-crystal X-ray diffraction study, which showed the absolute configuration at the Mo atom to be *S*, in agreement with the known configuration of the mentholate *R*- $[Mo(NO)L^*(Cl)\{(-)-OC_{10}H_{19}\}]$  and the circular dichroism (CD) spectra. The absolute configurations of the other isolated diastereomers were related to this complex and to *R*- $[Mo(NO)L^*(Cl)\{(-)-OC_{10}H_{19}\}]$  by comparison of their CD spectra.

The reactions of prochiral  $[M(NO)L^*X_2]$  [ $L^*$  = tris(3,5-dimethylpyrazolyl)borate;  $M$  = Mo,  $X$  = Cl or I;  $M$  = W,  $X$  = Cl] with alcohols to give monoalkoxides have been well documented.<sup>1</sup> As reported in our earlier paper describing optically resolved mentholate complexes *R*- and *S*- $[M(NO)L^*(X)(OC_{10}H_{19})]$  ( $M$  = Mo or W,  $X$  = Cl or I),<sup>2</sup> we have recognised that these monoalkoxides can exist in enantiomeric pairs, but had never previously observed the independent existence of one of these isomers since the products of the alcoholysis reactions are always racemic mixtures. However, since the precursors and products are kinetically stable, reaction of the dihalides with chirally resolved alcohols must afford stable diastereomeric pairs of alkoxides which should be separable and amenable to spectroscopic and X-ray crystallographic characterisation. Apart from the intrinsic interest in producing optically pure compounds containing the  $\{M(NO)\}^{3+}$  system, a further impetus to this work has been our desire to find reliable routes to chiral acceptor molecules as part of a programme of design of dipolar bimetallic species exhibiting non-linear optical properties,<sup>3</sup> also as described earlier.<sup>2</sup>

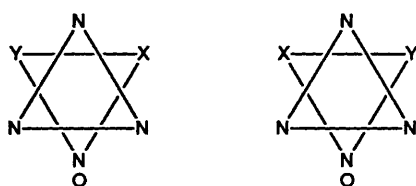
Mono- and poly-saccharides can be obtained optically pure and should be good vehicles for the production of chiral complexes from prochiral precursors. However, while saccharides have been known for many years to form complexes with transition metals, e.g. Cu and Fe,<sup>4</sup> their nature and structures have not been satisfactorily established. The lack of detailed spectroscopic and crystallographic information may perhaps be due to the formation of complexes containing unco-ordinated OH groups, with concomitant difficulties in removing hydrogen-bonded solvents, or to the generation of oligo- or poly-meric species. The potential for saccharides to engage in polyligation can, of course, be reduced by protection of all but one of the hydroxyl groups. This condition is fulfilled in the mono-



saccharides 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranose (**1**,  $HG_f$ ) and 1,2:3,4-di-*O*-isopropylidene- $\alpha$ -D-galactopyranose (**2**,  $HG_p$ ), which are readily available. The former is a secondary and the latter a primary alcohol, and both should form alkoxides of the type  $[M(NO)L^*(X)G_f]$  and  $[M(NO)L^*(X)G_p]$ .

Among the various types of 'sugar' complexes recently adequately characterised are a series of metal carbonyl derivatives obtained by treatment of halogenoglucose with carbonylate ions {e.g.  $[Mn(CO)_5]^-$ ,  $[Fe(CO)_2(\eta^5-C_5H_5)]^-$  and  $[Co(CO)_4]^-$ }, and complexes of amino or thio 'sugars' with  $Pd^{II}$  and  $Pt^{II}$ .<sup>5</sup> Nickel(II) complexes containing N-glucosidic ligands can be derived by reaction of  $[Ni(en)_3]^{2+}$  ( $en$  = 1,2-diaminoethane) with D-glucosamine (2-amino-2-deoxy-D-glucopyranose), D-galactosamine and D-mannosamine.<sup>6</sup> However, in none of these has the sugar been employed as a simple alkoxide. Using previously established techniques, coupled to very careful chromatographic separation, we have been able to isolate a number of diastereoisomers of  $[M(NO)L^*(X)G_f]$  and  $[M(NO)L^*(X)G_p]$ , to establish by crystallographic techniques the absolute configuration of  $[Mo(NO)L^*(I)G_f]$  and so determine the configuration at the metal in all other species which we could detect in characterisable quantities. The enantiomeric relationships of the metal co-ordination sphere are shown in Scheme 1.

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1

### 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,<sup>7</sup> and all other reagents were used as supplied. 1,2:5,6-Di-*O*-isopropylidene- $\alpha$ -D-glucopyranose and 1,2:3,4-di-*O*-isopropylidene- $\alpha$ -D-galactopyranose were obtained from Aldrich. Infrared spectra were obtained using a Perkin Elmer (PE) 237 spectrophotometer,  $^1H$  NMR spectra using a JEOL GX270 instrument. Optical rotation measurements were carried out in dichloromethane solution using a PE 241 polarimeter. Circular dichroism (CD) spectra were recorded using a Jobin-Yvon CNRS Dichrographe III, dichloromethane solutions being measured under nitrogen. Elemental analyses (Table 1) were performed by the Microanalytical Laboratory of the School of Chemistry, University of Birmingham.

**General Procedures for the Synthesis of  $[Mo(NO)L^*(X)Y]$  ( $X = Cl$  or  $I$ ) and  $[W(NO)L^*(Cl)Y]$  ( $Y = G_r$  or  $G_p$ ).**—The complex  $[M(NO)L^*X_2]$  ( $M = Mo$ ,  $X = Cl$  or  $I$ ;  $M = W$ ,  $X = Cl$ ) (0.5 g) was dissolved in dry toluene (100 cm<sup>3</sup>) and an excess of the appropriate (+)-sugar and  $NEt_3$  (0.5 cm<sup>3</sup>) was added. The mixture was stirred and refluxed until the colour of the solution characteristic of the final products developed fully:  $[Mo(NO)L^*(Cl)Y]$ , blue;  $[Mo(NO)L^*(I)Y]$ , green;  $[W(NO)L^*(Cl)Y]$ , purple. The reaction mixture was then cooled to room temperature, pentane added and the mixture further cooled to  $-10^\circ C$ . The  $[NH_4]X$  which had precipitated was filtered off and the filtrate was evaporated *in vacuo*. If the thermodynamically stable isomer **A** was required no special care was taken at this stage to keep the solvents cool. However, if an attempt was made to purify and isolate the unstable diastereoisomer **B**, the evaporation of solvents had to be accomplished using cool water-baths (room temperature or slightly below if possible). The crude product was purified by column chromatography on silica gel using dichloromethane–light petroleum (b.p.  $40$ – $60^\circ C$ ) as eluent.

The diastereoisomers were separated using a long silica gel column. Small aliquots were collected and checked by TLC. Those containing one pure isomer were combined, the solvent evaporated *in vacuo*, and the residue recrystallised from diethyl ether–hexane or dichloromethane–hexane mixtures to afford the complexes as blue, green or purple crystals, respectively. The yields of the complexes varied between 5 and 35%, but were always relatively low because of the losses sustained during careful and extensive purification, particularly for the **B** diastereoisomers.

**Crystal and Molecular Structure and Absolute Configuration of  $[Mo(NO)L^*(I)G_r]$ .**—*Crystal data.*  $C_{27}H_{41}BIMoN_7O_7$ ,  $M = 809.3$ , green block of dimensions  $0.2 \times 0.3 \times 0.5$  mm, monoclinic, space group  $P2_1$ ,  $a = 10.069(9)$ ,  $b = 16.573(6)$ ,  $c = 21.734(6)$  Å,  $\beta = 101.65(2)^\circ$ ,  $U = 3552$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.52$  g cm<sup>-3</sup>,  $F(000) = 1632$ , graphite-monochromated  $Mo-K\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\mu = 12.9$  cm<sup>-1</sup>.

All measurements were performed using an Enraf-Nonius CAD4 diffractometer at room temperature. 7365 Independent reflections (including 1064 Friedel pairs) with  $2\theta < 55^\circ$  were collected by the  $2\theta$ – $\theta$  scan method. 5292 Reflections with  $I > 2\sigma(I)$  (including 960 Friedel pairs) were used in the calculations, their intensities being corrected for absorption by the semiempirical (azimuthal scan) method. The structure was solved by direct methods and refined by least squares using the

SHELXTL PLUS set of programs and a MicroVax II computer. All non-hydrogen atoms were refined with anisotropic displacement parameters, except C(6'), C(61'), C(62'), C(8'), O(8'), C(9') and C(91') which are probably disordered (which could not be rationalised) and therefore were treated in isotropic approximation. The biggest residual features of the final Fourier difference map (varying from 0.79 to  $-0.58$  e Å<sup>-3</sup>) were observed in the proximity of these atoms. Hydrogen atoms were included in the riding model. Fourier difference maps revealed the presence of the solvent of crystallisation, which was included in the refinement as two oxygen atoms, O(1W) and O(2W) (*i.e.* water molecules), with occupancy factors of 0.25. The weighting scheme  $w^{-1} = \sigma^2(F) + 0.0003F^2$  was used.

The refinement of both enantiomeric models converged at  $R = 0.0484$ ,  $R' = 0.0473$  and goodness of fit  $S = 1.11$  for the absolute configuration corresponding to that known for  $\alpha$ -D-glucopyranose,<sup>8</sup> and at  $R = 0.0515$ ,  $R' = 0.0518$  and  $S = 1.21$  for the inverted structure. Refinement of the former structure with the Cruickshank multiplier of the anomalous dispersion corrections  $\Delta f''$  as a variable, yielded the latter as 0.93(5), *i.e.* essentially equal to 1, thus confirming the absolute structure. The atom coordinates, relevant bond distances and angles are listed in Tables 2, 3 and 4, respectively.

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

### Results and Discussion

**Synthetic Studies.**—Reaction of  $[M(NO)L^*X_2]$  with the appropriate sugar,  $HG_r$  or  $HG_p$ , in refluxing toluene containing triethylamine afforded the desired alkoxides,  $[M(NO)L^*(X)G_r]$  and  $[M(NO)L^*(X)G_p]$  (elemental analyses, Table 1). The complexes with  $M = Mo$ ,  $X = Cl$  were blue, those with  $M = Mo$ ,  $X = I$  green and those with  $M = W$ ,  $X = Cl$  purple. They were initially purified on a short silica gel column, and the diastereoisomers, which have opposite configurations at the metal atom and which were always observed, were separated, where possible, using long columns. We were almost always able to isolate the thermodynamically stable diastereomer (denoted throughout this paper as **A**). In order to obtain the less thermodynamically stable diastereomer **B** the eluted solutions obtained after chromatography had to be kept cool to minimise epimerisation, and we were not always successful in obtaining this isomer pure.

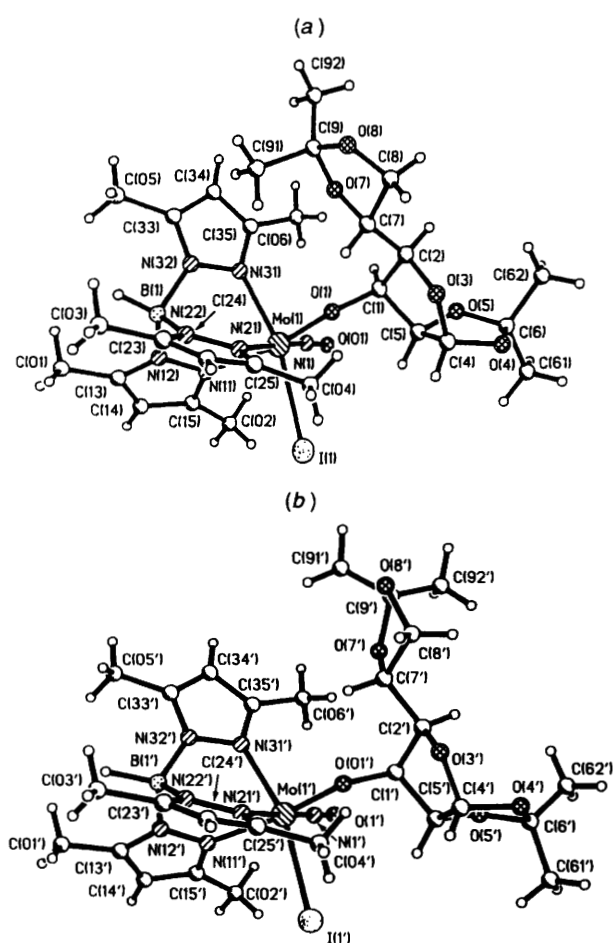
By monitoring the reaction progress by thin-layer chromatography (TLC) we were able to follow broadly the course of the reactions producing the two diastereoisomers **A**- and **B**- $[Mo(NO)L^*(Cl)G_r]$ . In general, it appears that both are produced very rapidly (within a few minutes of commencement of the reaction), that the **B** is in excess initially but that **A** soon dominates the reaction mixture. Thus, in this case, **A** is the more stable thermodynamically and it proved impossible to isolate **B** pure. The virtually complete epimerisation of the **B** to the **A** isomer permitted us to isolate **A**- $[Mo(NO)L^*(Cl)G_r]$  pure as blue crystals after careful column chromatography and crystallisation.

Using  $^1H$  NMR spectral monitoring, the course of the reaction between  $[Mo(NO)L^*I_2]$  and  $HG_r$  could be followed in more detail. Our method of sampling was to start the reaction in refluxing toluene containing  $NEt_3$ , then cool it after a prescribed interval, evaporate the solvent, rapidly chromatograph the mixture on a very short column to remove very polar side products, and record the NMR spectrum of the isolated mixture in  $CDCl_3$ . Thus after refluxing the mixture in toluene for 3 min and extracting the products as described above, both diastereoisomers (**A** and **B**) were observed in the ratio 1:1. After a further 3 min **B** disappeared, having been converted to **A**. If the reaction was carried out at  $50^\circ C$ , however, maximum conversion to **A**- and **B**- $[Mo(NO)L^*(I)G_r]$  is only complete after 1 h, and after a further 1 h, **B** was mostly converted to **A**. If the

**Table 1** Analytical data obtained from the diastereomers of  $[M(NO)L^*(X)Y]$ 

Isomer <sup>a</sup>	M	X	Y	Analysis (%)					
				Found			Calc.		
				C	H	N	C	H	N
A, <i>R</i>	Mo	Cl	G <sub>r</sub>	45.1	5.9	13.9	45.2	5.8	13.7
A, <i>S</i>	Mo	I	G <sub>r</sub>	39.8	5.2	12.0	40.1	5.1	12.1
A/B	Mo	I	G <sub>r</sub>	40.3	4.8	11.8	40.1	5.1	12.1
A, <i>R</i>	W	Cl	G <sub>r</sub>	39.2	5.8	10.7	40.2	5.1	12.2
B, <i>S</i>	W	Cl	G <sub>r</sub>	40.4	5.6	11.9	40.2	5.1	12.1
A/B	Mo	Cl	G <sub>p</sub>	44.9	5.7	13.9	45.2	5.8	13.7
A/B	Mo	I	G <sub>p</sub>	40.4	5.1	12.3	40.1	5.1	12.1
A/B	W	Cl	G <sub>p</sub>	40.5	5.4	11.9	40.2	5.1	12.2

<sup>a</sup> Diastereomeric mixture indicated by A (the more thermodynamically stable) and B; absolute configuration indicated as *R* or *S*.



**Fig. 1** Molecular structures of the two independent molecules **A1** (a) and **A2** (b) of  $A-[Mo(NO)L^*(I)G_r]$ , showing the numbering scheme

reaction was carried out in boiling dichloromethane, however, more products were observed, some of which may have been due to decomposition. After 15 min, conversion of the diiodide to *A*- and *B*- $[Mo(NO)L^*(I)G_r]$  was *ca.* 20% and the two diastereomers were present in roughly equal amounts. Later, the amount of **B** diminished and some new products, including the chloro species *A*- $[Mo(NO)L^*(Cl)G_r]$ , were observed. On some occasions, traces of *A*- $[Mo(NO)L^*(Cl)G_r]$  could also be detected in solutions obtained from the monitoring of reactions in toluene. Attempts to separate and purify *B*- $[Mo(NO)L^*(I)G_r]$  were unsuccessful.

We can say little at the moment regarding the mechanism of formation of *A*- $[Mo(NO)L^*(Cl)G_r]$  in the reaction involving

iodo-species. The product must arise by I/Cl exchange through contact with a chlorinated hydrocarbon. This could arise either *via* use of  $CD_2Cl_2$  or  $CDCl_3$  as NMR solvents, or by carrying out the reaction in these solvents when, indeed, the yields of *A*- $[Mo(NO)L^*(Cl)G_r]$  increased significantly. We were able to isolate the complex by purification of the products obtained from reaction in  $CH_2Cl_2$ . It seems that this chloro-complex does not appear in detectable amounts until after the appearance of *A*- and *B*- $[Mo(NO)L^*(I)G_r]$ , and its formation seems to be temperature dependent and to need the presence of  $NEt_3$  [hexamine (hexamethylenetetramine,  $C_6H_{12}N_4$ ) does not affect this exchange]. We know that  $[Mo(NO)L^*I_2]$  reacts with hot  $CCl_4$  or with  $PhCH_2Cl$  to afford  $[Mo(NO)L^*Cl_2]$ .<sup>9,10</sup>

The reaction between  $[W(NO)L^*Cl_2]$  and  $HG_r$  gave the two expected diastereomers, and we observed that *B*- $[W(NO)L^*(Cl)G_r]$  was kinetically relatively more stable than its molybdenum analogue, and so were able to isolate it totally free from the *A* diastereomer.

In general, similar results were obtained from the reactions of  $[M(NO)L^*Cl_2]$  with the galactopyranose, but we were unable to obtain sufficient quantities of the pure thermodynamically unstable diastereomer *B*- $[Mo(NO)L^*(Cl)G_p]$  to make satisfactory circular dichroism measurements. However, *A*- $[Mo(NO)L^*(Cl)G_p]$  and *A*- and *B*- $[W(NO)L^*(Cl)G_p]$  were isolated pure. Reaction between  $[Mo(NO)L^*I_2]$  and  $HG_p$  afforded only the two expected diastereomers, and there was no evidence for I/Cl exchange.

**Crystal Structure of *A*- $[Mo(NO)L^*(I)G_r]$ .**—The asymmetric unit of the structure contains two independent molecules (**A1** and **A2**, see Scheme 1), differing substantially in the conformation of the glucofuranose ligand. However, this difference does not significantly affect the co-ordination geometry about the Mo atoms, which have a distorted-octahedral environment and bond distances similar to those found in  $[Mo(NO)\{HB(cdmpr)\}Cl(OPr^i)]$  ( $cdmpr$  = 4-chloro-3,5-dimethylpyrazolyl).<sup>9</sup> According to the current rules,<sup>11</sup> the absolute configurations of the metal atoms in *A*- $[Mo(NO)L^*(I)G_r]$  should be described as *S*, and therefore the unstable **B** isomer should have an *R* configuration.

In both molecules (**A1** and **A2**) the Mo–N(L\*) bond in the *trans* position to the NO ligand is slightly longer than the others, indicating the relatively strong *trans* influence of the NO group. It is known<sup>12</sup> that in molybdenum nitrosyl thioalkoxy complexes with filled metal  $d_{xz}$  and  $d_{yz}$  orbitals the torsion angles (O)N–Mo–S–C adopt values near 0 or 180° to maximise the  $d_{xy}$ -p overlap between the empty metal orbital and the lone electron pairs on the S atom. Similar effects appear in the present structure, the (O)N–Mo–O–C torsion angles being close to 0° (4.8 and –6.8° in **A1** and **A2**, respectively).

The absolute configuration of  $[Mo(NO)L^*(I)G_r]$ , as determined by the X-ray method, is consistent with that assigned by



**Table 2** Atomic coordinates ( $\times 10^4$ ) for **A**-[Mo(NO)L\*(I)G<sub>r</sub>]

Atom	x	y	z	Atom	x	y	z
Mo(1)	4283(1)	1171(1)	4003(1)	Mo(1')	4172(1)	6058(1)	1259(1)
I(1)	6005(1)	1699	3248(1)	I(1')	2744(1)	5787(1)	2197(1)
N(1)	3795(9)	361(7)	3504(4)	N(1')	2991(9)	6796(8)	926(5)
O(1)	2768(7)	1827(5)	3685(3)	O(1')	3419(8)	5212(5)	719(4)
O(01)	3475(9)	-159(6)	3120(5)	O(01')	2183(9)	7294(7)	687(5)
C(1)	1563(10)	1693(8)	3228(5)	C(1')	2236(11)	5167(8)	256(6)
C(2)	558(11)	2380(8)	3273(6)	C(2')	2350(14)	4520(9)	-227(6)
O(3)	925(9)	3017(5)	2898(4)	O(3')	2216(9)	3789(6)	93(4)
C(4)	1599(14)	2707(9)	2443(6)	C(4')	1179(15)	3898(9)	462(7)
O(4)	814(11)	2763(7)	1839(5)	O(4')	-95(10)	3644(7)	121(6)
C(5)	1786(11)	1836(9)	2572(5)	C(5')	1083(11)	4797(10)	538(7)
O(5)	701(9)	1456(6)	2144(4)	O(5')	-175(9)	5028(6)	141(5)
C(6)	279(14)	1984(10)	1641(7)	C(6')	-1009(18)	4322(13)	33(9)
C(61)	816(18)	1747(11)	1067(7)	C(61')	-1899(20)	4225(14)	505(9)
C(62)	-1264(14)	1988(13)	1514(8)	C(62')	-1703(22)	4344(15)	-587(11)
C(7)	649(11)	2702(8)	3923(6)	C(7')	3694(17)	4503(10)	-455(7)
O(7)	406(8)	2097(5)	4340(4)	O(7')	3684(12)	5165(7)	-879(5)
C(8)	-435(11)	3313(8)	4026(6)	C(8')	3866(17)	3747(12)	-856(8)
O(8)	-388(9)	3291(6)	4651(4)	O(8')	4653(12)	4131(9)	-1287(6)
C(9)	36(14)	2497(10)	4863(7)	C(9')	4042(18)	4889(13)	-1439(9)
C(91)	1288(17)	2562(9)	5382(7)	C(91')	5246(19)	5422(15)	-1548(9)
C(92)	-1065(17)	2008(12)	5052(8)	C(92')	2861(23)	4890(15)	-1930(11)
B(1)	5490(13)	1275(9)	5530(6)	B(1')	7463(13)	6162(11)	1744(6)
N(11)	6014(9)	552(6)	4586(4)	N(11')	5419(10)	6930(6)	1923(4)
N(12)	6388(8)	721(6)	5215(4)	N(12')	6771(9)	6781(7)	2105(4)
C(13)	7469(11)	276(8)	5483(6)	C(13')	7338(14)	7353(10)	2519(6)
C(01)	8104(11)	339(9)	6152(6)	C(01')	8832(15)	7336(12)	2820(8)
C(14)	7836(11)	-184(8)	5025(6)	C(14')	6304(15)	7851(9)	2606(7)
C(15)	6958(11)	-21(7)	4480(6)	C(15')	5134(15)	7607(9)	2221(6)
C(02)	6856(13)	-404(9)	3839(6)	C(02')	3741(15)	7946(10)	2127(7)
N(21)	4914(8)	2249(6)	4619(5)	N(21')	5662(10)	5097(7)	1674(5)
N(22)	5427(9)	2124(6)	5250(5)	N(22')	6999(9)	5316(7)	1856(5)
C(23)	5757(13)	2832(9)	5549(7)	C(23')	7706(13)	4691(10)	2119(6)
C(03)	6320(15)	2881(10)	6231(7)	C(03')	9239(14)	4730(11)	2385(8)
C(24)	5464(13)	3397(10)	5109(8)	C(24')	6862(13)	4035(10)	2100(7)
C(25)	4933(12)	3048(8)	4527(6)	C(25')	5573(13)	4313(9)	1830(6)
C(04)	4489(12)	3471(8)	3910(6)	C(04')	4282(14)	3851(10)	1691(9)
N(31)	3409(8)	714(6)	4760(4)	N(31')	5685(8)	6416(5)	753(4)
N(32)	4027(8)	883(6)	5379(4)	N(32')	7033(8)	6391(5)	1043(4)
C(33)	3333(11)	572(8)	5774(6)	C(33')	7781(11)	6673(9)	647(6)
C(05)	3736(13)	641(10)	6490(6)	C(05')	9281(10)	6798(10)	807(6)
C(34)	2196(12)	191(8)	5412(6)	C(34')	6922(12)	6895(8)	111(6)
C(35)	2321(11)	273(8)	4808(6)	C(35')	5610(12)	6749(9)	190(5)
C(06)	1339(12)	-34(8)	4256(6)	C(06')	4301(11)	6899(9)	-272(6)
				O(1W)	-41(33)	9479(23)	2835(16)
				O(2W)	137(32)	8710(25)	1731(17)

comparison with the mentholate complex **R**-[Mo(NO)L\*(Cl)-(OC<sub>10</sub>H<sub>19</sub>)]<sup>2</sup> and from CD spectral studies (see below).

**Spectral Studies.**—The IR spectra of the new complexes exhibited  $\nu_{\text{NO}}$  (Table 5) at positions typical of monoalkoxides, e.g. 1670–1680 cm<sup>-1</sup> for [Mo(NO)L\*(X)(sugar)] and 1630–1640 cm<sup>-1</sup> for [W(NO)L\*(Cl)(sugar)].<sup>1</sup>

The <sup>1</sup>H NMR spectra are summarised in Table 5. In general, they are consistent with our formulations and indicate the expected patterns for complexes of the general type [M(NO)L\*(X)Y]. Thus, the protons attached to C(4) of the pyrazolyl rings normally appear as three singlets due to the asymmetry of the complexes. These resonate in the region  $\delta$  5.7–6.0, whereas the signals due to the pyrazolyl 3- and 5-methyl groups occur in the region  $\delta$  2.2–2.6. Accidental degeneracy occasionally occurred, as for **A**-[Mo(NO)L\*(I)G<sub>r</sub>] where the pyrazolyl [C(4)] protons appeared as a singlet, and such behaviour has been observed before. For these particular complexes the methyl signals associated with the protecting (O<sub>2</sub>CMe) groups occurred usually as four singlets in the range  $\delta$  1.2–1.6. Since the basic M(NO)L\*(X) group is powerfully electronegative, a proton attached to the carbon atom  $\alpha$  to the O atom of the alkoxide residue normally resonates at relatively low fields.<sup>11</sup> In

the glucofuranosides this proton is assigned as H(3) ( $\delta_{\text{av}}$  6.39) and in the galactopyranosides they are assigned as H(6,6') ( $\delta_{\text{av}}$  5.98) and may appear as an AB pair ( $J = 11$ –12 Hz). This deshielding phenomenon has been commented on before.<sup>1,9</sup>

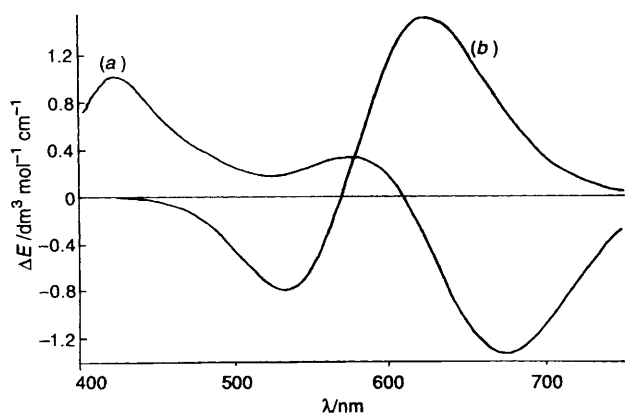
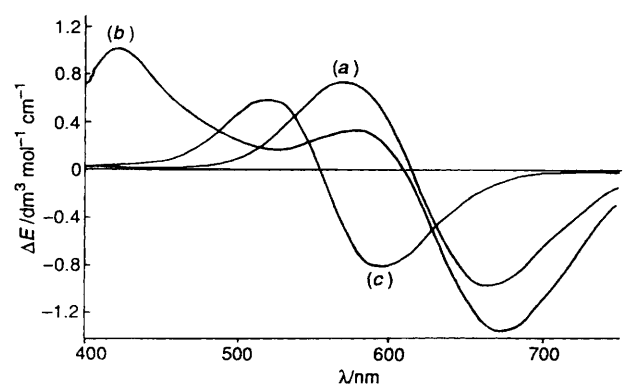
From a comparison of the <sup>1</sup>H NMR spectrum of **A**-[Mo(NO)L\*(Cl)G<sub>r</sub>] and that of **A**-[W(NO)L\*(Cl)G<sub>r</sub>], particularly in the range  $\delta$  4–6, it seems very probable that the two **A** forms have similar configurations at the metal and within the carbohydrate residues. The same conclusions may be drawn from a spectral comparison of **B**-[Mo(NO)L\*(Cl)G<sub>r</sub>] with **B**-[W(NO)L\*(Cl)G<sub>r</sub>], but their spectra are significantly different to those of the **A** diastereomers. In general, similar results are obtained from the galactopyranosides. It should be noted, however, that the spectra of a number of **B** isomers could only be obtained by computer 'subtraction' of the spectra of the pure **A** isomers from those of mixtures of the two diastereomers.

The UV/VIS spectra bands of the complexes are reported in Table 6 and show two main absorptions: one in the range 270–340 nm which is thought to be a predominantly metal-based transition, and one between 540 and 631 nm.

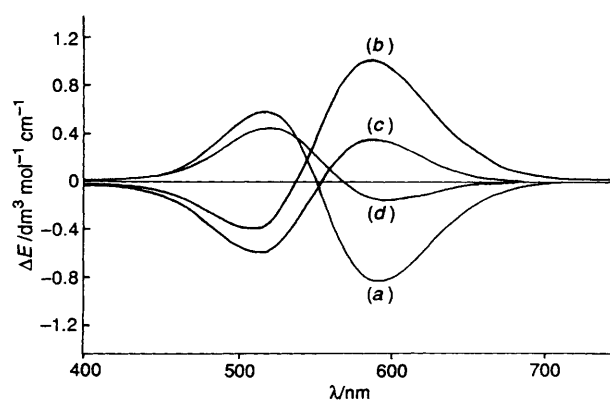
The CD spectra of the stable diastereomers are reported in the region 450–700 nm (Figs. 2–4). Since the signs of the CD curve obtained from **A**-[Mo(NO)L\*(I)G<sub>r</sub>] (Fig. 2) are opposite

**Table 3** Bond lengths (Å) in two independent molecules of A-[Mo(NO)L\*(I)G<sub>r</sub>]

	A1	A2		A1	A2
Mo(1)–I(1)	2.759(3)	2.758(3)	Mo(1)–N(1)	1.732(10)	1.756(11)
Mo(1)–O(1)	1.887(7)	1.888(8)	Mo(1)–N(11)	2.192(9)	2.238(9)
Mo(1)–N(21)	2.247(10)	2.249(11)	Mo(1)–N(31)	2.154(10)	2.135(9)
N(1)–O(01)	1.199(14)	1.201(15)	O(1)–C(1)	1.421(11)	1.397(13)
C(1)–C(2)	1.540(17)	1.521(20)	C(1)–C(5)	1.505(16)	1.546(19)
C(2)–O(3)	1.427(16)	1.417(18)	C(2)–C(7)	1.496(18)	1.532(24)
O(3)–C(4)	1.406(18)	1.451(19)	C(4)–O(4)	1.392(15)	1.410(17)
C(4)–C(5)	1.476(21)	1.504(23)	O(4)–C(6)	1.430(19)	1.440(22)
C(5)–O(5)	1.430(14)	1.434(14)	O(5)–C(6)	1.400(17)	1.432(22)
C(6)–C(61)	1.508(23)	1.500(30)	C(6)–C(62)	1.523(20)	1.389(27)
C(7)–O(7)	1.405(15)	1.431(20)	C(7)–C(8)	1.538(18)	1.558(26)
O(7)–C(9)	1.429(18)	1.412(24)	C(8)–O(8)	1.350(17)	1.486(24)
O(8)–C(9)	1.431(19)	1.409(25)	C(9)–C(91)	1.516(20)	1.556(30)
C(9)–C(92)	1.495(25)	1.429(27)	B(1)–N(12)	1.542(17)	1.540(20)
B(1)–N(22)	1.529(18)	1.514(21)	B(1)–N(32)	1.582(15)	1.544(16)
N(11)–N(12)	1.372(12)	1.361(13)	N(11)–C(15)	1.395(15)	1.356(18)
N(12)–C(13)	1.347(14)	1.352(18)	C(13)–C(01)	1.469(16)	1.515(19)
C(13)–C(14)	1.364(18)	1.371(22)	C(14)–C(15)	1.354(15)	1.362(19)
C(15)–C(02)	1.517(18)	1.485(21)	N(21)–N(22)	1.380(13)	1.373(13)
N(21)–C(25)	1.339(16)	1.350(19)	N(22)–C(23)	1.349(18)	1.320(18)
C(23)–C(03)	1.480(20)	1.537(18)	C(23)–C(24)	1.328(22)	1.375(22)
C(24)–C(25)	1.396(20)	1.390(18)	C(25)–C(04)	1.499(18)	1.486(20)
N(31)–N(32)	1.391(12)	1.377(10)	N(31)–C(35)	1.338(15)	1.331(15)
N(32)–C(33)	1.317(17)	1.337(16)	C(33)–C(05)	1.531(17)	1.494(15)
C(33)–C(34)	1.401(16)	1.355(16)	C(34)–C(35)	1.351(20)	1.388(18)
C(35)–C(06)	1.482(17)	1.507(15)			

**Fig. 2** The CD spectra of A-[Mo(NO)L\*(I)G<sub>r</sub>] (a) and R-[Mo(NO)L\*(Cl){(-)OC<sub>10</sub>H<sub>19</sub>}] (b)**Fig. 3** The CD spectra of A-[Mo(NO)L\*(Cl)G<sub>r</sub>] (a) A-[Mo(NO)L\*(I)G<sub>r</sub>] (b) and A-[W(NO)L\*(Cl)G<sub>p</sub>] (c)

to those of R-[Mo(NO)L\*(Cl){(-)OC<sub>10</sub>H<sub>19</sub>}], it is probable that the former has the absolute configuration *S* at the metal atom (following the element sequence rules).<sup>11</sup> It is therefore possible to assign the absolute configurations at the metal of almost all related complexes. The CD spectra of the three A diastereomers of [M(NO)L\*(X)G<sub>r</sub>] are very similar (Fig. 3),

**Fig. 4** The CD spectra of A-[W(NO)L\*(Cl)G<sub>r</sub>] (a), B-[W(NO)L\*(Cl)G<sub>r</sub>] (b), A-[W(NO)L\*(Cl)G<sub>p</sub>] (c) and B-[W(NO)L\*(Cl)G<sub>p</sub>] (d)

and thus the configuration at the metal in each must also be the same; for the chloro-complexes this is *R* because of the element preference rule.<sup>11</sup> It can be seen from Fig. 4 that the CD spectrum of B-[W(NO)L\*(Cl)G<sub>r</sub>] is the inverse of that of the A diastereomer. Therefore, the absolute configuration at the metal in B-[W(NO)L\*(Cl)G<sub>r</sub>] must be the opposite of that in A-[Mo(NO)L\*(I)G<sub>r</sub>], i.e. *S*. It follows that the absolute configuration at the metal in B-[Mo(NO)L\*(I)G<sub>r</sub>] is *R*. We were able to obtain CD spectra only from the diastereomeric pair A- and B-[W(NO)L\*(Cl)G<sub>p</sub>] as the other species could not be separated satisfactorily. By comparison with the CD spectrum of A-[Mo(NO)L\*(I)G<sub>r</sub>] we may conclude that B-[W(NO)L\*(Cl)G<sub>p</sub>] has the same configuration at the metal (i.e. *R*), whereas the other species, A-[W(NO)L\*(Cl)G<sub>p</sub>], is *S*. In other words, in this system the apparently more thermodynamically stable form has the opposite absolute configuration at molybdenum to that of the thermodynamically stable diastereomer of [Mo(NO)L\*(Cl)G<sub>r</sub>].

In summary, we have shown that, of the diastereomers produced in this work, the following have the same configuration at the metal: the thermodynamically stable A-[M(NO)L\*(X)G<sub>r</sub>] where M = Mo and X = Cl or I, and M = W and X = Cl, and B-[W(NO)L\*(Cl)G<sub>p</sub>]. The following species have

**Table 4** Bond angles (°) in two independent molecules of A-[Mo(NO)L\*(I)G<sub>r</sub>]

	A1	A2		A1	A2
I(1)–Mo(1)–N(1)	90.4(3)	90.4(4)	I(1)–Mo(1)–O(1)	99.1(2)	97.8(3)
N(1)–Mo(1)–O(1)	96.4(4)	96.2(4)	I(1)–Mo(1)–N(11)	88.3(3)	86.4(3)
N(1)–Mo(1)–N(11)	95.2(4)	93.5(4)	O(1)–Mo(1)–N(11)	166.2(3)	169.4(4)
I(1)–Mo(1)–N(21)	88.1(3)	89.6(3)	N(1)–Mo(1)–N(21)	178.0(4)	178.9(5)
O(1)–Mo(1)–N(21)	82.6(3)	82.8(4)	N(11)–Mo(1)–N(21)	86.1(3)	87.5(4)
I(1)–Mo(1)–N(31)	165.5(2)	163.5(2)	N(1)–Mo(1)–N(31)	95.6(4)	95.1(4)
O(1)–Mo(1)–N(31)	93.3(3)	97.1(4)	N(11)–Mo(1)–N(31)	78.1(3)	77.7(4)
N(21)–Mo(1)–N(31)	86.2(4)	85.2(4)	Mo(1)–N(1)–O(01)	174.6(10)	178.8(9)
Mo(1)–O(1)–C(1)	132.8(7)	131.6(8)	O(1)–C(1)–C(2)	108.6(9)	111.3(10)
O(1)–C(1)–C(5)	111.6(9)	109.6(10)	C(2)–C(1)–C(5)	99.8(10)	99.3(11)
C(1)–C(2)–O(3)	105.1(10)	103.7(11)	C(1)–C(2)–C(7)	114.2(9)	115.4(12)
O(3)–C(2)–C(7)	107.6(10)	108.7(12)	C(2)–O(3)–C(4)	110.5(10)	108.4(11)
O(3)–C(4)–O(4)	112.1(11)	110.6(12)	O(3)–C(4)–C(5)	106.5(11)	104.7(12)
O(4)–C(4)–C(5)	105.7(11)	106.3(11)	C(4)–O(4)–C(6)	109.4(11)	109.0(12)
C(1)–C(5)–C(4)	107.2(11)	106.2(12)	C(1)–C(5)–O(5)	107.8(10)	107.4(11)
C(4)–C(5)–O(5)	104.8(9)	105.5(11)	C(5)–O(5)–C(6)	107.7(10)	107.3(12)
O(4)–C(6)–O(5)	107.0(10)	106.2(12)	O(4)–C(6)–C(61)	108.0(13)	106.3(16)
O(5)–C(6)–C(61)	112.4(13)	112.8(16)	O(4)–C(6)–C(62)	111.1(14)	109.4(17)
O(5)–C(6)–C(62)	106.3(13)	107.4(17)	C(61)–C(6)–C(62)	112.0(12)	114.4(17)
C(2)–C(7)–O(7)	111.6(10)	107.6(13)	C(2)–C(7)–C(8)	117.5(9)	113.6(13)
O(7)–C(7)–C(8)	99.0(10)	104.0(13)	C(7)–O(7)–C(9)	106.7(10)	109.7(13)
C(7)–C(8)–O(8)	104.2(10)	98.2(14)	C(8)–O(8)–C(9)	107.2(11)	105.5(14)
O(7)–C(9)–O(8)	106.2(11)	105.2(15)	O(7)–C(9)–C(91)	108.2(12)	106.9(15)
O(8)–C(9)–C(91)	108.8(12)	103.0(15)	O(7)–C(9)–C(92)	107.1(13)	109.0(17)
O(8)–C(9)–C(92)	113.4(13)	115.7(18)	C(91)–C(9)–C(92)	112.6(13)	116.2(18)
N(12)–B(1)–N(22)	110.6(10)	110.4(11)	N(12)–B(1)–N(32)	105.6(9)	105.8(11)
N(22)–B(1)–N(32)	109.5(9)	110.6(10)	Mo(1)–N(11)–N(12)	120.4(7)	117.9(8)
Mo(1)–N(11)–C(15)	135.5(7)	134.2(8)	N(12)–N(11)–C(15)	104.1(8)	107.9(10)
B(1)–N(12)–N(11)	119.8(8)	120.1(9)	B(1)–N(12)–C(13)	129.0(9)	129.2(10)
N(11)–N(12)–C(13)	110.8(9)	109.2(11)	N(12)–C(13)–C(01)	122.8(11)	121.6(14)
N(12)–C(13)–C(14)	107.7(10)	106.5(11)	C(01)–C(13)–C(14)	129.4(11)	131.8(14)
C(13)–C(14)–C(15)	107.5(11)	108.9(13)	N(11)–C(15)–C(14)	109.8(11)	107.4(12)
N(11)–C(15)–C(02)	120.9(9)	122.2(11)	C(14)–C(15)–C(02)	129.1(11)	130.4(13)
Mo(1)–N(21)–N(22)	118.5(7)	117.6(8)	Mo(1)–N(21)–C(25)	135.1(8)	135.2(8)
N(22)–N(21)–C(25)	106.5(9)	107.0(10)	B(1)–N(22)–N(21)	120.7(9)	121.0(10)
B(1)–N(22)–C(23)	128.5(11)	129.8(10)	N(21)–N(22)–C(23)	110.7(10)	109.2(11)
N(22)–C(23)–C(03)	122.6(13)	122.8(14)	N(22)–C(23)–C(24)	105.7(13)	109.4(11)
C(03)–C(23)–C(24)	131.7(15)	127.8(14)	C(23)–C(24)–C(25)	110.3(14)	105.6(13)
N(21)–C(25)–C(24)	106.8(12)	108.7(12)	N(21)–C(25)–C(04)	125.8(11)	123.0(12)
C(24)–C(25)–C(04)	127.3(12)	128.2(14)	Mo(1)–N(31)–N(32)	119.7(6)	119.7(6)
Mo(1)–N(31)–C(35)	135.9(8)	132.5(7)	N(32)–N(31)–C(35)	104.4(9)	107.6(9)
B(1)–N(32)–N(31)	119.9(9)	120.9(9)	B(1)–N(32)–C(33)	128.3(9)	129.7(8)
N(31)–N(32)–C(33)	111.0(9)	109.0(8)	N(32)–C(33)–C(05)	124.6(11)	125.0(10)
N(32)–C(33)–C(34)	106.9(11)	107.7(10)	C(05)–C(33)–C(34)	128.5(12)	127.0(12)
C(33)–C(34)–C(35)	105.9(12)	107.7(11)	N(31)–C(35)–C(34)	111.6(10)	107.9(9)
N(31)–C(35)–C(06)	123.2(12)	124.1(11)	C(34)–C(35)–C(06)	125.0(11)	128.0(11)

the configuration at the metal opposite to that in A-[Mo(NO)L\*(I)G<sub>r</sub>]: the thermodynamically unstable diastereomers B-[M(NO)L\*(X)G<sub>r</sub>] and the stable A-[W(NO)L\*(Cl)G<sub>r</sub>]. From the general synthetic and NMR spectral behaviour of the molybdenum galactopyranosides, it is possible that the B diastereomers have the same configuration as that of A-[Mo(NO)L\*(I)G<sub>r</sub>], but we are unable to support this *via* CD spectral measurements.

It is clearly possible to form diastereomers in the reactions between [M(NO)L\*X<sub>2</sub>] and the protected monosaccharides D-glucofuranose and D-galactopyranose. From simple studies of the formation of the glucofuranose species, it seems probable that the B diastereomer is produced almost immediately, that the A form may also be formed but more slowly and presumably has its origin in the epimerisation of B-[M(NO)L\*(X)G<sub>r</sub>], and that the B diastereomer epimerises at a rate apparently dependent on temperature, affording eventually relatively pure A-[M(NO)L\*(X)G<sub>r</sub>]. Bearing in mind our objective of using optically resolved metal fragments to design bimetallic dipolar molecules potentially capable of exhibiting non-linear optical properties, we have investigated the ability of R-[Mo(NO)L\*(I)G<sub>r</sub>] to exhibit secondary harmonic generation (a simple test for molecules with significant second hyperpolaris-

abilities which form solids with substantial second-order susceptibilities). Kurtz powder tests of R-[Mo(NO)L\*(Cl)-{(+)-OC<sub>10</sub>H<sub>19</sub>}] revealed a secondary-harmonic generation efficiency of 0.074 times that of the standard urea.† Such a low efficiency is not surprising since the 'sugar' residue is not a particularly good donor even though {Mo(NO)L\*Cl} is a powerful acceptor, and there is no highly polarisable conjugated or aromatic bridge linking the donor and acceptor fragments. However, it should be possible to replace I in R-[Mo(NO)L\*(I)G<sub>r</sub>] by a bridging group such as –C<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>4</sub>– attached to a good donor fragment such as ferrocenyl.

#### Acknowledgements

We are grateful to the SERC for providing funds to assist in this work (S. S. K.) and to the Royal Society for a Visiting Fellowship (A. S. B.). We wish particularly to thank the British Council for travel funds to assist in the collaboration through a Tripartite

† We are grateful to Professor D. Bloor, Materials Centre, University of Durham, and Drs. P. V. Kolinsky and R. J. Jones of the Hirst Research Centre, GEC, for these preliminary measurements.

**Table 5** Infrared and <sup>1</sup>H NMR spectral data obtained from the diastereomers of [M(NO)L\*(X)Y] in CDCl<sub>3</sub>

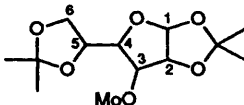
Complex				IR <sup>a</sup> /cm <sup>-1</sup> ν <sub>NO</sub>	NMR <sup>b</sup>							
M	X	Y	δ		Rel. area	Assignments						
Glucofuranosides												
												
A, R	Mo	Cl	G <sub>f</sub>	1680	6.54	1d	H <sup>3</sup> from G <sub>f</sub> ; $J(\text{H}^3\text{H}^4) = 2.5$					
					5.88	1s						
					5.86	1s	C <sub>3</sub> HN <sub>2</sub> Me <sub>2</sub>					
					5.75	1s						
					5.83	1s	H <sup>1</sup> from G <sub>f</sub> ; $J(\text{H}^1\text{H}^2) = 3.8$					
					5.82	1d		H <sup>2</sup> from G <sub>f</sub> ; $J(\text{H}^1\text{H}^2) = 3.8$				
					4.44	1dd	H <sup>4</sup> from G <sub>f</sub> ; $J(\text{H}^3\text{H}^4) = 2.5$ , $J(\text{H}^4\text{H}^5) = 6.7$					
					3.84	2m		H <sup>5,6</sup> from G <sub>f</sub> ; poorly resolved AB pair				
					3.57	1m	H <sup>6</sup> from G <sub>f</sub>					
					2.49 <sub>4</sub>	3s						
					2.48 <sub>6</sub>	3s						
					2.39	3s	C <sub>3</sub> HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>					
					2.37	6s						
					2.25	3s						
					1.60	3s						
					1.57	3s	O <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> from G <sub>f</sub>					
					1.41	3s						
					A, S	Mo	I	G <sub>f</sub>	1675	6.24	1dd	H <sup>3</sup> from G <sub>f</sub> ; $J(\text{H}^3\text{H}^4) = 2.3$
5.83	3s	C <sub>3</sub> HN <sub>2</sub> Me <sub>2</sub>										
5.78	1d		H <sup>1</sup> from G <sub>f</sub> ; $J(\text{H}^1\text{H}^2) = 3.6$									
5.70	1d	H <sup>2</sup> from G <sub>f</sub> ; $J(\text{H}^1\text{H}^2) = 3.6$										
4.41	1dd		H <sup>4</sup> from G <sub>f</sub> ; $J(\text{H}^3\text{H}^4) = 2.3$ , $J(\text{H}^4\text{H}^5) = 6.7$									
3.78	2m	H <sup>5,6</sup> from G <sub>f</sub> ; poorly resolved AB pair										
3.54	1m		H <sup>6</sup> from G <sub>f</sub>									
2.49	3s											
2.46	3s											
2.42	3s	C <sub>3</sub> HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>										
2.36	6s											
2.34	3s											
1.59	3s											
1.40	3s	O <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> from G <sub>f</sub>										
1.33	3s											
A <sup>c</sup>	Mo	I	G <sub>f</sub>	—						0.97	3s	H <sup>3</sup> from G <sub>f</sub> ; $J(\text{H}^3\text{H}^4) = 1.8$
										6.31	1d	
										5.90	1s	C <sub>3</sub> HN <sub>2</sub> Me <sub>2</sub>
					5.82	1s						
					5.81	1s						
					5.78	1d	H <sup>1</sup> from G <sub>f</sub> ; $J(\text{H}^1\text{H}^2) = 3.7$					
					4.29	2m		H <sup>4,5</sup> from G <sub>f</sub>				
					4.22	1d	H <sup>2</sup> from G <sub>f</sub> ; $J(\text{H}^1\text{H}^2) = 3.8$					
					4.00	2m		H <sup>6,6'</sup> from G <sub>f</sub> ; poorly resolved AB pair				
					2.54	3s						
					2.52	3s						
					2.42	6s	C <sub>3</sub> HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>					
					2.36	3s						
					2.33	3s						
					1.55	3s						
					1.51	3s	O <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> from G <sub>f</sub>					
					1.47	3s						
					A,R	W	Cl	G <sub>f</sub>	1640	1.25	3s	H <sup>3</sup> from G <sub>f</sub> ; $J(\text{H}^3\text{H}^4) = 2.4$
6.41	1d											
5.89	1s	C <sub>3</sub> HN <sub>2</sub> Me <sub>2</sub>										
5.87	1s											
5.82	1s											
5.81	1d	H <sup>1</sup> from G <sub>f</sub> ; $J(\text{H}^1\text{H}^2) = 4.0$										
5.42	1d		H <sup>2</sup> from G <sub>f</sub> ; $J(\text{H}^1\text{H}^2) = 4.0$									
4.39	1m	H <sup>4</sup> from G <sub>f</sub> ; $J(\text{H}^4\text{H}^5) = 6.6$										
3.83	2m		H <sup>5,6</sup> ; poorly resolved AB pair									
3.58	1m	H <sup>6</sup> from G <sub>f</sub>										
2.62	3s											
2.58	3s											
2.37	6s	C <sub>3</sub> HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>										
2.34	3s											
2.31	3s											
1.58	3s											
1.40	3s	O <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> from G <sub>f</sub>										
1.43	3s											
	1.02	3s										

Table 5 (continued)

Complex				NMR <sup>b</sup>			
	M	X	Y	IR <sup>a</sup> /cm <sup>-1</sup>	δ	Rel. area	Assignments
B,S	W	Cl	G <sub>r</sub>	1640	6.43	1d	H <sup>3</sup> from G <sub>r</sub> ; $J(\text{H}^3\text{H}^4) = 2.2$
					5.97	1s	C <sub>3</sub> HN <sub>2</sub> Me <sub>2</sub>
					5.86	1s	
					5.80	1s	
					5.77	1d	
					4.44	1m	H <sup>5</sup> from G <sub>r</sub>
					4.29	1dd	H <sup>4</sup> from G <sub>r</sub> ; $J(\text{H}^4\text{H}^5) = 8.1$
					4.15	1d	H <sup>2</sup> from G <sub>r</sub> ; $J(\text{H}^1\text{H}^2) = 3.6$
					4.10	1dd	H <sup>6</sup> from G <sub>r</sub> ; $J(\text{H}^5\text{H}^6) = 6.4$
					3.91	1dd	H <sup>6'</sup> from G <sub>r</sub> ; $J(\text{H}^5\text{H}^6') = 6.1, J(\text{H}^6\text{H}^6') = 8.2$
					2.70	3s	C <sub>3</sub> HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>
					2.60	3s	
					2.38	3s	
					2.37	3s	
					2.36	3s	
					2.33	3s	
					1.53	9s	O <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> from G <sub>r</sub>
					1.24	3s	
Galactopyranosides							
A <sup>c,d</sup>	Mo	Cl	G <sub>p</sub>	1675	6.24	1dd	H <sup>6</sup> from G <sub>p</sub> ; $J(\text{H}^5\text{H}^6) = 4.8, J(\text{H}^6\text{H}^6') = 12.0$
					5.95	1m	
					5.88	1s	C <sub>3</sub> HN <sub>2</sub> Me <sub>2</sub>
					5.86	1s	
					5.73	1s	
					5.56	1d	
					4.63	1dd	H <sup>3</sup> from G <sub>p</sub>
					4.47	1dd	H <sup>4</sup> from G <sub>p</sub>
					4.33	1d	H <sup>2</sup> from G <sub>p</sub>
					4.22	1m	H <sup>5</sup> from G <sub>p</sub>
					2.52	3s	C <sub>3</sub> HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>
					2.46	3s	
					2.38	3s	
					2.36	6s	
					2.34	3s	
					1.48	6s	O <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> from G <sub>p</sub>
					1.38	3s	
					1.31	3s	
B <sup>c</sup>	Mo	Cl	G <sub>p</sub>	1675	5.95	2m	H <sup>6,6'</sup> from G <sub>p</sub>
					5.90	1s	C <sub>3</sub> HN <sub>2</sub> Me <sub>2</sub>
					5.86	1s	
					5.74	1s	
					5.61	1d	H <sup>1</sup> from G <sub>p</sub>
					4.60	1dd	H <sup>3</sup> from G <sub>p</sub>
					4.35	3m	H <sup>2</sup> , H <sup>4</sup> , H <sup>5</sup> from G <sub>p</sub>
					2.50	3s	C <sub>3</sub> HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>
					2.45	3s	
					2.38	3s	
					2.36	3s	
					2.35	3s	
					2.34	3s	
					1.58	3s	O <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> from G <sub>p</sub>
					1.48	3s	
					1.34	3s	
					1.29	3s	
					A, R	Mo	I
5.84	2s	C <sub>3</sub> HN <sub>2</sub> Me <sub>2</sub>					
	1s						
ca. 5.8	1m		Overlap with signals due to H <sup>6'</sup>				
5.55	1m	H <sup>1</sup> from G <sub>p</sub> ; $J(\text{H}^1\text{H}^2) = 5.0$					
4.62	1dd	H <sup>3</sup> from G <sub>p</sub> ; $J(\text{H}^2\text{H}^3) = 1.9$					
4.41	1dd	H <sup>4</sup> from G <sub>p</sub> ; $J(\text{H}^3\text{H}^4) = 7.9$					
4.31	1dd	H <sup>2</sup> from G <sub>p</sub> ; $J(\text{H}^1\text{H}^2) = 5.0$					
4.25	1m	H <sup>5</sup> from G <sub>p</sub>					
2.51	3s	C <sub>3</sub> HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>					
2.49	3s						
2.39	3s						
2.35	9s						

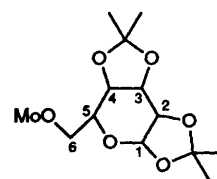




Table 5 (continued)

Complex				IR <sup>a</sup> /cm <sup>-1</sup> ν <sub>NO</sub>	NMR <sup>b</sup>		
M	X	Y			δ	Rel. area	Assignments
A, S	W	Cl	G <sub>p</sub>	1630	1.47	6s	O <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> from G <sub>p</sub>
					1.36	3s	
					1.30	3s	
					6.21	1dd	H <sup>6</sup> from G <sub>p</sub> ; <i>J</i> (H <sup>5</sup> H <sup>6</sup> ) = 3.7, <i>J</i> (H <sup>6</sup> H <sup>6'</sup> ) = 11.5
					5.90	1s	
					5.86	1s	
					5.78	1s	C <sub>3</sub> HN <sub>2</sub> Me <sub>2</sub>
					5.83	1dd	
					5.55	1d	
					4.62	1dd	H <sup>1</sup> from G <sub>p</sub> ; <i>J</i> (H <sup>1</sup> H <sup>2</sup> ) = 5.0
					4.43	1dd	H <sup>3</sup> from G <sub>p</sub> ; <i>J</i> (H <sup>2</sup> H <sup>3</sup> ) = 2.3
					4.43	1dd	H <sup>4</sup> from G <sub>p</sub> ; <i>J</i> (H <sup>3</sup> H <sup>4</sup> ) = 8.0
					4.30	1dd	H <sup>2</sup> from G <sub>p</sub> ; <i>J</i> (H <sup>1</sup> H <sup>2</sup> ) = 5.0
					4.16	1m	H <sup>5</sup> from G <sub>p</sub>
					2.60	6s	C <sub>3</sub> HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>
					2.47	3s	
					2.34	6s	
B, R	W	Cl	G <sub>p</sub>	1630	2.33	3s	O <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> from G <sub>p</sub>
					1.51	3s	
					1.45	3s	
					1.36	3s	C <sub>3</sub> HN <sub>2</sub> Me <sub>2</sub>
					1.31	3s	
					5.91	1s	
					5.86	1s	H <sup>6,6'</sup> from G <sub>p</sub>
					5.80	1s	
					5.85	2m	
					5.59	1d	H <sup>1</sup> from G <sub>p</sub> ; <i>J</i> (H <sup>1</sup> H <sup>2</sup> ) = 5.1
					4.60	1dd	H <sup>3</sup> from G <sub>p</sub> ; <i>J</i> (H <sup>3</sup> H <sup>4</sup> ) = 2.1
					4.31	3m	H <sup>2</sup> , H <sup>4</sup> , H <sup>5</sup> from G <sub>p</sub>
					2.59	6s	C <sub>3</sub> HN <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>
					2.42	3s	
					2.36	3s	
					2.36	3s	O <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> from G <sub>p</sub>
					2.35	3s	
					1.57	6s	
					1.34	3s	
					1.29	3s	

<sup>a</sup> In KBr discs. <sup>b</sup> In CDCl<sub>3</sub> solution at 270 MHz, *J* in Hz. <sup>c</sup> Spectrum obtained by subtraction from total spectrum of unseparated diastereomeric mixture. <sup>d</sup> The more concentrated species.

Table 6 UV/VIS spectra and specific rotations of [M(NO)L\*(X)Y] in dichloromethane, indicating diastereomer stability and absolute configuration

Compound	λ <sub>max</sub> /nm (ε/dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )		α/° g cm <sup>3</sup> dm <sup>-1</sup>	
			546	589 nm
[Mo(NO)L*(Cl)G <sub>r</sub> ] <sup>a</sup>	340 (8300)	631 (330)		
A-[Mo(NO)L*(Cl)G <sub>r</sub> ] <sup>a</sup> ( <i>R</i> )			-320	+1020
[Mo(NO)L*(I)G <sub>r</sub> ] <sup>a</sup>	320 (9000)	600 (300)		
A-[Mo(NO)L*(I)G <sub>r</sub> ] <sup>a</sup> ( <i>S</i> )			-740	+1250
[W(NO)L*(Cl)G <sub>r</sub> ] <sup>a</sup>	280 (13 600)	550 (250)		
A-[W(NO)L*(Cl)G <sub>r</sub> ] <sup>a</sup> ( <i>R</i> )			+1170	+955
B-[Mo(NO)L*(Cl)G <sub>r</sub> ] <sup>a</sup>			-330	-10
[Mo(NO)L*(Cl)G <sub>p</sub> ] <sup>a</sup>	310 (9800)	600 (230)		
[Mo(NO)L*(I)G <sub>p</sub> ] <sup>a</sup>	337 (7600)	627 (300)		
A-[Mo(NO)L*(Cl)G <sub>p</sub> ] <sup>a</sup> ( <i>S</i> )			-580	<sup>b</sup>
A-[Mo(NO)L*(I)G <sub>p</sub> ] <sup>a</sup> ( <i>R</i> )			-130	-350
[W(NO)L*(Cl)G <sub>p</sub> ] <sup>a</sup>	275 (9300)	540 (210)		
A-[W(NO)L*(Cl)G <sub>p</sub> ] <sup>a</sup> ( <i>S</i> )			-850	-600
B-[W(NO)L*(Cl)G <sub>p</sub> ] <sup>a</sup> ( <i>R</i> )			+600	+720

<sup>a</sup> Diastereomeric mixture. <sup>b</sup> Unreliable results because of strong light absorption.

Acciones Integradas (UK, Spain and Poland) and the Politechnika Krakowska and the Universities of Birmingham and Bristol for enabling the collaboration to be carried out effectively. We are grateful to Drs. T. A. Hamor and A. J. Edwards for early advice regarding the X-ray structural determination, Professor R. D. Gillard and Dr. P. Williams of the Chemistry Department, University of Cardiff, for help in measuring CD spectra, and to Drs. C. J. Jones and B. J. Coe for

discussions concerning non-linear optical properties of metal-organic compounds.

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Received 16th October 1992; Paper 2/05530I