Note

Tridentate coordination of dioxomolybdenum(VI) with some potentially quinquedentate (N$_2$O$_3$) Schiff base ligands

James H. Cameron and John A. McEwan

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS (UK)

Abstract

Three complexes of molybdenum(VI) **4–6** have been prepared and characterised using potentially quinquedentate ligands derived from Schiff base condensations using 1,3-diamino-2-hydroxypropane. From NMR spectroscopic evidence it is clear that the ligands bind to the metal ion in a terdentate manner, leaving two of the possible ligand donor atoms uncoordinated. This represents a new coordination mode for monomeric complexes of these ligands with a transition metal ion. In solution, the sixth coordination site of the MoO$_2^{2+}$ ion is occupied by a solvent molecule while in the solid state, the ^{13}C NMR spectrum of **4** suggests that the sixth coordination site of MoO$_2^{2+}$ is occupied by a phenolic oxygen, probably via an intermolecular interaction between the complexes.

In recent years there has been considerable interest in the coordination chemistry of the ligand formed by the Schiff base condensation of 1,3-diamino-2-hydroxypropane with two equivalents of salicylaldehyde, L$_1$ [1]. This ligand has five groups potentially available to act as donor atoms to metal ions and the range of structures displayed by the complexes of L$_1$ is very broad and encompasses both a variable metal:ligand ratio and variable denticity of the ligand. For example the literature reports monomeric Cu(II) and Ni(II) species where L$_1$ coordinates in a square planar fashion, with the secondary hydroxyl group remaining uncoordinated [2]. Alternatively, there are numerous reports of bimetallic systems, particularly with Cu(II), of stoichiometry [M$_2$(L$_1$)$_1$], where the complex has an endogenous alkoxy anion and various exogenous groups bridging the two metal centres [3]. The coordination versatility of this ligand is further well demonstrated

by several reports where the structure of the product is controlled by varying the conditions of complex synthesis, producing monomeric, dimeric and even polymeric products, for example involving Mn(III) [4], Fe(III) [5], Tc(V) and Re(V) [6] and V(IV) [7].
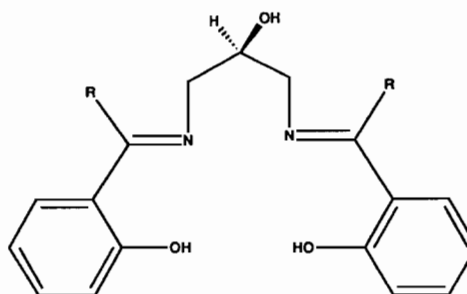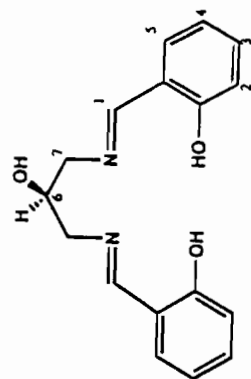

L$_1$, R = H
L$_3$, R = Me
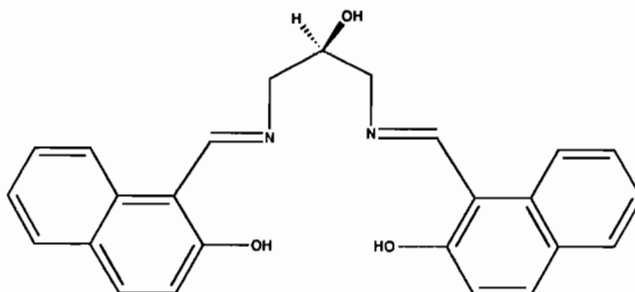
L$_2$

It was of interest to examine the coordination chemistry of L$_1$ and two related ligands (L$_2$, L$_3$) with the [MoO$_2$]$^{2+}$ cation and to try to identify the mode of binding of these potentially quinquedentate ligands with an ion requiring only four donor atoms to complete its coordination sphere. The [MoO$_2$]$^{2+}$ complex of L$_1$ had been reported previously in the literature, but no structural information was given [8].

The ligands were prepared in good yield by condensation of two equivalents of the appropriate aldehyde or ketone with one equivalent of 2-hydroxy-1,3-diaminopropane, using methanol as solvent. Relevant spectroscopic data for all three ligands are included in Tables 1 and 2 and are entirely consistent with the proposed structures. L$_1$ is a well known compound and the spectroscopic results obtained in this work were in good agreement with those reported previously [3]. A Chemical Abstracts report of the preparation of L$_2$ arose due to an error in abstracting. For compound L$_2$, the imine hydrogen atom coupled to the phenolic
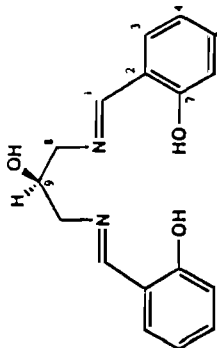
TABLE 1. NMR data^{a,b}

^1H data

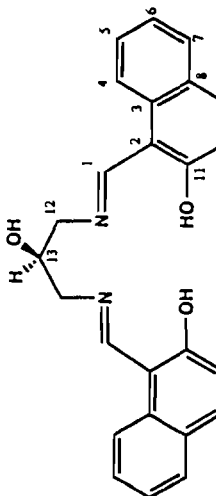| Compound	1^c	2	2'	3	3'	4	4'	5	5'	6	7	7'	Aromatic-OH	Alcoholic-OH	Me	Me'
L$_1^d$	8.40 (s, 2H)	6.97 (d, 2H)		7.33 (dt, 2H)		6.90 (dt, 2H)		7.27 (dd, 2H)		4.28 (m, 1H)	3.80 (dABq, 4H)					
L$_1$	8.55 (s, 2H)	6.90* (m, 2H)		7.37 (dt, 2H)		6.90* (m, 2H)		7.48 (dd, 2H)		4.10 (br, 1H)	3.70 (dABq, 4H)		13.55 (br, 2H)	5.30 (br, 1H)		
4	8.80 (s, 1H); 8.55 (s, 1H)	6.88* (m, 1H)	6.88* (m, 1H)	7.34 (dt, 1H)	7.48 (dt, 1H)	6.95 (dt, 2H)	6.88* (m, 1H)	7.45 (dd, 1H)	7.55 (dd, 1H)	4.60 (sx, 1H)	3.85* (m, 2H)	3.85, 4.27 (m, 1H; dd, 1H)	13.45 (s, 1H)			
L$_2$		6.80 (d, 2H)		7.25 (dt, 2H)		6.79 (dt, 2H)		7.65 (dd, 2H)		4.13 (br, 1H)	3.69 (m, 4H)		16.45 (s, 2H)	5.35 (br, 1H)	2.40 (s, 6H)	
6		6.80 (d, 1H)	6.85 (d, 1H)	7.30 (dt, 1H)	7.40 (dt, 1H)	6.78 (t, 1H)	6.95 (t, 1H)	7.68 (dd, 1H)	7.80 (dd, 1H)	4.70 (sx, 1H)	3.68, 3.85* (dd, 1H; m, 1H)	3.85*, 4.22 (m, 1H; dd, 1H)	16.30 (s, 1H)		2.40 (s, 3H)	2.57 (s, 3H)
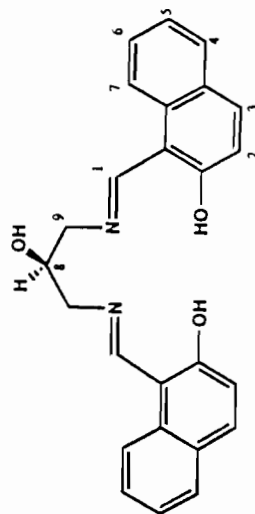
Compound	1	1'	2	2'	3,3',4,4',7,7'	5,5',6,6'	8	9	9'	Aromatic-OH	Alcoholic-OH
L$_2$	9.10 (d, 2H)		6.75 (d, 2H)		8.03 (d, 2H); 7.74 (d, 2H); 7.63 (d, 2H)	7.40 (t, 2H); 7.20 (t, 2H)	4.02 (br, 1H)	3.78 (m, 4H)		14.04 (br, 2H)	
5	9.06 (d, 1H)	9.70 (s, 1H)	6.73 (d, 1H)	7.13 (d, 1H)	8.05* (d, 1H); 8.42 (d, 1H); 7.74 (d, 1H); 7.74 (d, 1H); 8.05* (d, 1H); 7.90 (d, 1H)	7.61* (t, 1H); 7.43* (t, 1H); 7.61* (t, 1H); 7.43* (t, 1H)	4.70 (sx, 1H)	3.95* (m, 2H)	3.95*, 4.45 (m, 1H; dd, 1H)	13.95	5.70 (d, 1H)

(continued)

TABLE 1. (continued)

(Structures: top — a chiral diamine backbone bearing two salicylaldimine (CH=N / C–OH) aromatic units, with labelled positions 1, 8, 9 and ring carbons 2–6; bottom — a bis(2‑hydroxy‑1‑naphthylidene) Schiff base with labelled positions 1–11 on the naphthalene units and 12, 12', 13 on the backbone.)

¹³C data

	1	1'	7	7'	3	3'	5	5'	2	2'	4	4'	6	6'	9	8	8'	10	10'
L₁	167.0		160.8		131.6		132.2		118.7		118.3		116.5		69.4	62.7			
4	167.5	164.2	160.8	161.5	131.7	134.8	132.4	133.9	118.7	121.0	118.5	119.4	116.5	119.3	80.0	63.1	61.0		
4ᵉ	168.4	164.9	173.5	161.1	135.3	139.5	137.6*	137.6*	114.6	120.2	121.8*	121.8*	115.8	121.8*	76.2	64.0	50.5	14.5	
L₃	163.8		173.0		128.7		132.3		118.9		118.1		116.5		69.7	52.9			
6	163.5	161.3	173.3	170.2	128.7	133.2	132.4	130.0	119.0	124.4	118.0	119.3*	116.7	119.3*	80.6	52.0	58.1	14.6	19.5

	11	11'	1	1'	2,2';3,3';8,8'	4,4';5,5';6,6';7,7';9,9';10,10'	13	12	12'
L₂	176.8		159.8		136.9 134.2 125.1 105.9 125.2	127.7 128.7	68.8	54.9	
5	177.2	162.4	160.0		137.3 135.7 134.3 132.9 125.3 123.9 106.0 112.2	125.4 127.8 128.0 128.8 127.7 128.9 121.5 122.3 118.4 120.9	79.0	53.4	63.0

TABLE 2. Analytical and spectral data

Compound	Microanalytical data (%)[a]				Electronic spectrum (nm)			Selected IR bands (cm^{-1})		
	C	H	N	Mo	λ_{max} (log ϵ)			ν(OH)	ν(C=N)	ν(Mo=O)
L$_1$					312 (3.82)	267 (4.30)		3389 (br)	1630, 1610, 1576	
L$_2$	75.5 (75.4)	5.7 (5.5)	7.1 (7.0)		426 (4.24)	405 (4.18)	272 (4.92)	3150 (br)	1638, 1540	
L$_3$					396 (3.35)	320 (3.72)		3142	1613, 1540	
4	47.8 (48.1)	3.5 (3.8)	6.6 (6.6)	22.3 (22.6)	310(sh) (3.90)	267 (4.37)			1645, 1600	917, 888
5	55.8 (56.1)	4.05 (4.3)	5.05 (5.0)	15.5 (17.3)	423 (4.04)	402 (4.10)	306 (4.41)		1631, 1545	916, 892
6	50.3 (50.5)	4.2 (4.4)	6.0 (6.2)	18.5 (21.2)	410(sh) (3.0)	323 (3.72)			1629, 1609, 1550	920, 882

[a]Expected figures in brackets.

hydrogen atom, implying strong hydrogen bonding of the phenolic –OH to the imine nitrogen, and this was supported both by broadening of the O–H stretching band in the IR spectrum of L$_2$ and a shift of the maximum to 3150 cm^{-1} (relative to L$_1$ at 3389 cm^{-1}). In compound L$_3$ the situation is less clear cut. While the IR spectrum resembled that of L$_2$, with a broad band at 3142 cm^{-1}, the position of the phenolic hydrogens in the ^{1}H NMR spectrum (16.45) indicated significant deshielding relative to both L$_1$ and L$_2$ which implies that hydrogen bonding is less significant in compound L$_3$.

Reaction of the ligands, in methanol solution at reflux, with one equivalent of MoO$_2$(acac)$_2$ (where acac is the acetylacetonate ion), resulted in formation of yellow, microcrystalline precipitates, of low solubility in all but DMSO solution, which gave satisfactory microanalytical results (Table 2), characterising them as species of general formula MoO$_2$L, (although complex 5 was isolated as the methanol solvate). The complex of L$_1$ had been reported previously as being a light brown solid but only analytical results were given, without any discussion of its spectra or its possible structure [8]. The IR spectra of the complexes (Table 2) had a number of interesting features: there were no distinct bands in the hydroxyl stretching region; all spectra showed slight shifts in the position of the bands ascribed to the imine group, relative to those of the free ligands, consistent with imine involvement in complex formation; characteristic bands at c. 920 and 885 cm^{-1}, assigned to the stretching of the cis-dioxomolybdenum(VI) group, were observed.

The ^{1}H and ^{13}C NMR spectra of the complexes (Table 1) proved very useful in the ascribing of structures

to the products. It was immediately apparent that the ligands were binding as dianions, with loss of the signals due to the alcoholic proton and only one of the phenolic protons. Most of the remaining signals were doubled, with one set appearing at exactly the same chemical shift as the starting free ligands and a second set appearing slightly shifted, generally to lower field. This behaviour is entirely consistent with the potentially quinquedentate ligands binding as tridentate NO$_2$ donor species, utilising one phenoxide oxygen, an imine nitrogen and an alkoxide oxygen as the donor set, producing small shifts in the NMR resonance positions of adjacent atoms, while the second iminophenol group remains uncoordinated, displaying no NMR shift from the free ligand resonance positions. Normally it is expected that dioxomolybdenum(VI) complexes will be six-coordinate in nature and in the solution phase it is believed that coordination of complexes 4 and 6 is completed by a molecule of dimethyl sulfoxide while complex 5 contains a molecule of coordinated methanol, which is observed in both the ^{1}H and ^{13}C NMR spectra. The structure of these complexes is therefore believed to be similar to complexes of terdentate, NO$_2$ donor Schiff base ligands reported by Rajan and Chakravorty and by Topich [9], which also have a solvent molecule bound to the metal ion. Terdentate coordination of L$_1$ has been reported in a complex of the Ph$_2$Sn(IV) ion [10] but, to our knowledge, this is the first reported incidence of this mode of binding with a transition metal ion.

It was of interest to examine the coordination of L$_1$ in complex 4 in the absence of solvent, using solid state ^{13}C NMR spectroscopy to determine the nature of the donor atom completing the six coordination of the metal
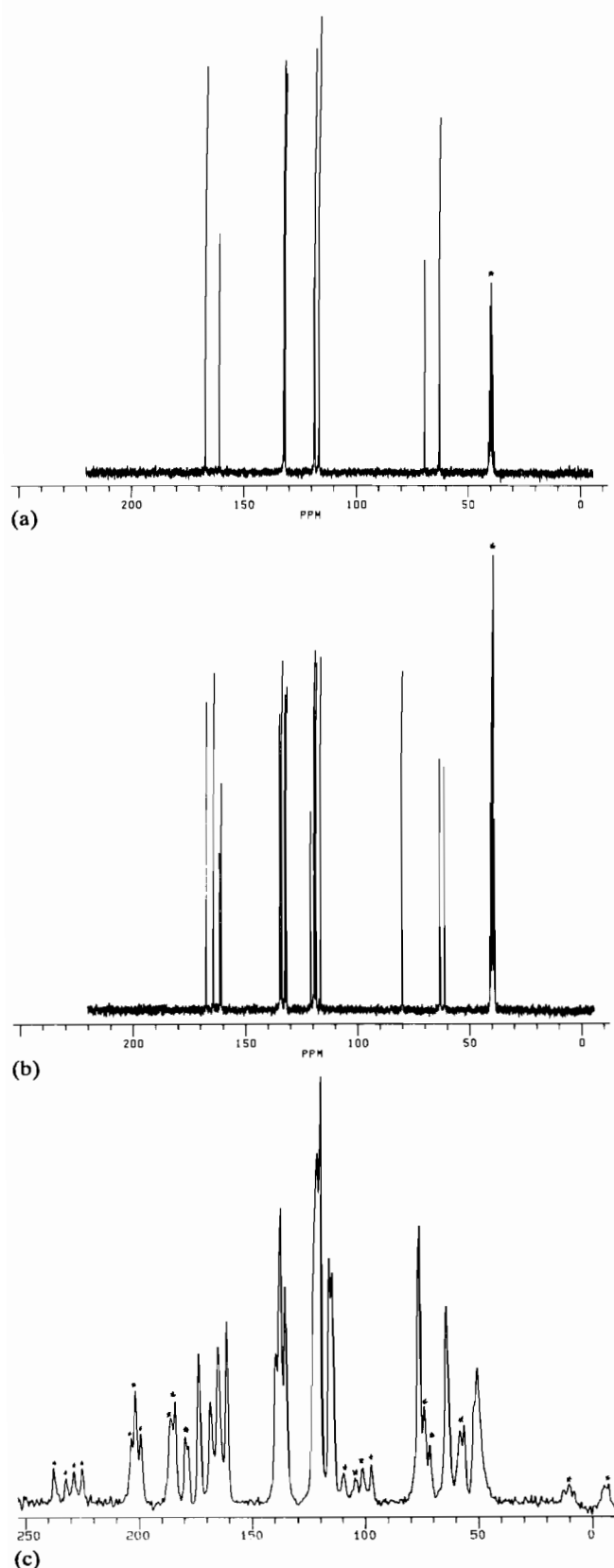
Fig. 1. ^{13}C NMR spectra of: (a) L$_1$ in d^6-DMSO solution; (b) 4 in d^6-DMSO solution; (c) 4 in the solid state. *Indicates solvent peak or spinning side bands.

centre. The results are listed in Table 1. By far the most significant difference between the solution and solid state spectra was the shift in the position of the resonance ascribed to the aromatic carbon atom bearing the phenolic hydroxyl group (Fig. 1). In solution the signal of the carbon atom of this uncoordinated group appeared at 160.8 ppm, the same position as in the free ligand, while in the solid state, the signal of the same carbon atom appeared at 173.5 ppm. The only other major difference observed was a 10 ppm upfield shift of the resonance ascribed to one of the methylene carbons, although the origin of this shift is unknown.

On the basis of the results from the solid state spectrum, it is reasonable to propose that the Mo(VI) ion is six-coordinate, with cis-related dioxo groups, an NO$_2$ coordinated Schiff base ligand and the final site occupied by the oxygen atom of a phenolic hydroxyl group. From structural models it is physically possible to construct a complex with intramolecular coordination of the phenolic hydroxyl but it is believed more likely that, on steric grounds, the phenolic hydroxyl group is actually associating with the molybdenum ion via an intermolecular mechanism, leading to polymeric chains of complexes in the solid state. Attempts are under way to establish the structure of this molybdenum(VI) complex using an X-ray powder diffraction technique.

Since in solution the ligands bind to the molybdenum ions as terdentate species, two donor atoms are potentially available to bind to another metal centre and the possibility exists of using the molybdenum complexes in the preparation of new multinuclear complexes. To this end, solutions of 4 were allowed to react with solutions containing nickel acetate tetrahydrate, under varying conditions. The products were all paramagnetic, lime green solids of limited solubility, dissolving only sparingly in DMSO to produce orange solutions. Microanalytical and spectroscopic results reveal that the products do indeed contain molybdenum(VI) and nickel(II), and ligand, L$_1$, however the overall stoichiometry of the products is dependent upon the reaction conditions. The physical and chemical properties of these novel bimetallic species will form the basis of a separate report.

Acknowledgements

References

1 Y. Nishida and S. Kida, *Inorg. Chem., 27* (1988) 447.

2 R.J. Butcher, G. Diven, G. Erickson, G.M. Mockler and E. Sinn, *Inorg. Chim. Acta, 111* (1986) L55; W. Mazurek, A.M. Bond, M.J. O'Connor and A.G. Wedd, *Inorg. Chem., 25* (1986) 906.

3 R.J. Butcher, E. Sinn and G.M. Mockler, *Proc. Ind. Acad. Sci., Chem. Sci., 102* (1990) 209; Y. Nishida and S. Kida, *J. Chem. Soc., Dalton Trans.,* (1986) 2633; W. Mazurek, B.J. Kennedy, K.S. Murray, M.J. O'Connor, J.R. Rodgers, M.R. Snow, A.G. Wedd and P.R. Zwack, *Inorg. Chem., 24* (1985) 3258; Y. Nishida and S. Kida, *Chem. Lett.,* (1985) 631; W. Mazurek, K.J. Berry, K.S. Murray, M.J. O'Connor, M.R. Snow and A.G. Wedd, *Inorg. Chem., 21* (1982) 3071.

4 J.A. Bonadies, M.L. Kirk, M.S. Lah, D.P. Kessissoglou, W.E. Hatfield and V.L. Pecoraro, *Inorg. Chem., 28* (1989) 2037; J.A. Bonadies, M.J. Maroney and V.L. Pecoraro, *Inorg. Chem., 28* (1989) 2044.

5 G.D. Fallon, A. Markiewicz, K.S. Murray and T. Quach, *J. Chem. Soc., Chem. Commun.,* (1991) 198.

6 F. Tisato, F. Refosco, U. Mazzi, G. Bondoli and A. Dolmella, *Inorg. Chim. Acta, 164* (1989) 127.

7 J.C. Dutton, K.S. Murray and E.R.T. Tiekink, *Inorg. Chim. Acta, 166* (1989) 5.

8 K. Dey, R.K. Maiti and J.K. Bhar, *Transition Met. Chem. (Weinheim), 6* (1981) 346.

9 O.A. Rajan and A. Chakravorty, *Inorg. Chim. Acta, 37* (1979) L503; J. Topich, *Inorg. Chem., 20* (1981) 3704.

10 J.N.R. Ruddick and J.R. Sams, *J. Organomet. Chem., 60* (1973) 233.