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Synthesis and Complexes of Unsymmetrical Multidentate Ligands. Part IV.* Quadridentate Ligands and the Multidentate Chemistry of Manganese II. Part VII.*

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The synthesis and characterization is reported of a number of new unsymmetrical quadridentate ligands based on the interaction of o-aminophenol with mono-2-pyridylhydrazones of various α-diketones. The stability of the ligands has been confirmed by a study of their Mn(II) and Ni(II) compounds. The ligand derived from benzil was found to be particularly stable, and a further group of unsymmetrical quadridentates has been prepared, this set being based on the interaction of suitable primary amines with benzilmono-2-pyridylhydrazone. The ability of the ligands to act as stable planar ligands has been shown by preparation of various Mn(II) and Ni(II) complexes.

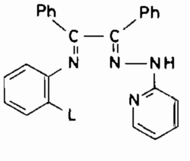
Introduction

In 1958 Lions and Martin [1] reported the preparation of the symmetrical quadridentate ligand obtained by the interaction of two molecules of 2-pyridylhydrazine with diacetyl, and in a subsequent paper Chiswell and Lions [2] described how this ligand could lose two protons when coordinated to a divalent metal atom in the reaction sequence:

$$M^{2+} + (H_2lig) \rightarrow [M(H_2lig)]^{2+} \xrightarrow{+OH^-} [M(lig)]^0$$

In a later paper [3], these latter workers noted the preparation of the mono-2-pyridylhydrazone of benzil. The presence of phenyl substituents upon the two carbonyl carbons in benzil reduces the ability of the α-diketone to form the bis-hydrazone, which is much more readily obtained when these substituents are protons or alkyl groups [4].

However, we have found that it is possible to condense both the carbonyl groups of benzil by reacting by primary amines with benzil mono-2-pyridylhydrazone to yield a range of unsymmetrical quadridentate ligands of structure I.



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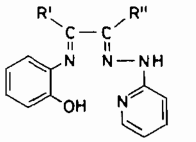

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(a) L = OH; (e) L = SH
(b) L = NH_2; (f) L = SMe
(c) L = COOH; (g) L = $AsMe_2$
(d) L = CHO;

(a) R′ = R″ = Ph
(b) R′ = R″ = H
(c) R′ = R″ = Me
(d) R′ = Me; R″ = H
(e) R′ and R″ in cyclohexane ring

In this paper we also report further on the work on unsymmetrical quadridentates, which commenced with ligands derived from glyoxal monophenylhydrazone [5].

Results and Discussion

Ligands

The seven unsymmetrical quadridentates of structure I were prepared by the Schiff base interaction of equi-molecular proportions of benzilmono-2-pyridylhydrazone and the required *o*-substituted aniline in ethanol solution. In each case, apart from ligand Id in which the *o*-substituent is an aldehydo-group, crystalline products were isolated, analysed, and treated by mass spectral analysis (see Table I). Ligand Id was characterized as its metal complexes (see Tables IIIb and IVb).

To study the effect of other than phenyl group substituents on the α-diketone carbon atoms, the ligands of structure II have been prepared. For these ligands, the mono-2-pyridylhydrazone of (a) benzil, (b) glyoxal, (c) diacetyl, (d) methylglyoxal and (e) 1,2-cyclohexanedione were first isolated, and subsequently in each case condensed with o-aminophenol. These ligands have all been isolated as solids, and analyses, melting points and mass spectral peaks are listed in Table II. Ligands Ia and IIa are of course identical.

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*Unfortunately reprints are not available.

TABLE I. Ligands of Structure I.

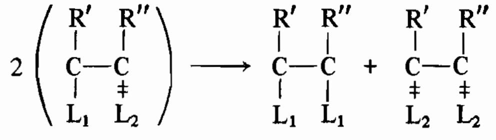
Ligand No.	L	Analysis %	C	H	N	M.p. °C	Parent m.s. peak
Ia	OH	Calc.	76.5	5.1	14.3	206°	392
		Found	76.6	5.3	14.3		
Ib	NH_2	Calc.	80.0	5.6	14.3	209°	391
		Found	79.7	5.8	14.5		
Ic	COOH	Calc.	74.3	4.8	13.3	221°	420
		Found	74.6	4.7	13.0		
Id	CHO	Not isolated as a crystalline product					
Ie	SH	Calc.	73.5	4.9	13.7	231°	408
		Found	73.4	4.7	13.4		
If	SCH_3	Calc.	73.9	5.2	13.3	242°	422
		Found	74.1	4.9	13.1		
Ig	$As(CH_3)_2$	Calc.	67.5	5.2	11.7	258°	480
		Found	67.5	5.4	11.6		

TABLE II. Ligands of Structure II.

Ligand No.	R′	R″	Analysis %	C	H	N	M.p. °C	Parent m.s. peak
IIa	C_6H_5	C_6H_5	See Ligand Ia - Table I.					
IIb	H	H	Calc.	65.0	5.0	23.3	207°	240
			Found	64.7	5.0	23.4		
IIc	CH_3	CH_3	Calc.	67.2	6.0	20.9	197°	268
			Found	67.3	6.1	21.2		
IId	CH_3	H	Calc.	66.1	5.5	22.0	216°	
			Found	66.4	5.8	22.0		
IIe	in cyclohexane ring		Calc.	69.4	6.1	19.0	184°	294
			Found	69.4	6.0	18.6		

As has been previously pointed out [6], the C=N (hydrazine) bond is more stable to dissociation than the C=N (imine) linkage. Thus, in all the above ligand preparations, the hydrazone was first prepared and purified, before condensation of the second carbonyl oxygen with the primary amine.

The inherent problem in the preparation of all these unsymmetrical ligands, is that associated with their tendency to disproportionate in solution to yield two different but symmetrical quadridentates:



$$2\left(\begin{matrix} R' & R'' \\ | & | \\ C & \!\!-\!\!C \\ | & \ddagger \\ L_1 & L_2 \end{matrix}\right) \longrightarrow \begin{matrix} R' & R'' \\ | & | \\ C & \!\!-\!\!C \\ | & | \\ L_1 & L_1 \end{matrix} + \begin{matrix} R' & R'' \\ | & | \\ C & \!\!-\!\!C \\ \ddagger & \ddagger \\ L_2 & L_2 \end{matrix}$$

In cases in which two different primary amines are condensed to the α-diketones, it has been found that this disproportionation proceeds rapidly in solution [7], however where at least one hydrazine residue is condensed, such reaction is relatively slow. Nevertheless, the ligands of structure II in which R′ and R″ are H or CH_3 groups (IIb, IIc and IId) will disproportionate markedly in 60 minutes in boiling ethanol. On the other hand, ligands IIa and IIe appear to be particularly stable, and for this reason it was decided to use benzilmono-2-pyridylhydrazone as the starting point for the preparation of the ligands of structure I.

Ligand IId has the potential to exist in two isomeric forms depending upon the carbonyl carbon atom used for the initial hydrazone condensation, however there seems little reason to doubt that such initial condensation takes place on the aldehyde rather than the ketone oxygen atom.

The nickel(II) and manganese(II) complexes of all the ligands have been studied. The former metal was used initially, as it is well-known to yield stable square compounds, and it was felt that such a property would prevent the ligands dissociating. However, the ligands proved to be more stable than expected, and manganese(II) compounds were then isolated as part of an ongoing study of the multidentate chemistry of Mn(II) [8].

Ni(II) Compounds

The interaction of nickel(II) acetate with all five quadridentates of structure II in aqueous ethanol solution yielded intensely coloured, green-red crystalline products of the general formula [Ni(lig)]$\cdot xH_2O$ (x = 0, 1 or 2), in which the ligand (lig) has functioned as a diabasic acid group, loosing the phenol and imine hydrogen atoms upon coordination. The hydrates of crystallisation could in each case be removed at 60 °C under vacuum, and the analytical results shown in Table IIIa are for the dehydrated products. All the compounds are diamagnetic*, and are presumed to be square planar. They are quite stable; the complex [Ni(ligIIa)], for example could be sublimed under vacuum.

With the unsymmetrical ligands of structure I, nickel(II) acetate also yielded square planar complexes similar to those obtained from ligands of structure II, for ligands Ib, Ic and Ie in which the donor group L has an acidic hydrogen (see Table IIIa). On the other hand, ligands Id, If and Ig gave amorphous impure products with nickel(II) acetate in aqueous ethanol. However the reaction of these latter three ligands with nickel(II) chloride in aqueous ethanol lead to the isolation of green non-deprotonated compounds of formula [Ni(Hlig)Cl$_2$] (see Table IIIb). These compounds are high spin (μ_{eff} = 3.1–3.2 B.M.), and are presumably octahedral in structure. The ligand entities of these complexes can be deprotonated in basic solution by the removal of the hydrazine residue proton, but such reaction was not very successful. Thus the compound [Ni(HligIg)Cl$_2$] reacted with sodium in dry ethanol to yield a small amount of [Ni(ligIg)$_2$], which is a deep green-red complex in which both ligand groups have lost a proton (see Table IIIc). The compound has a magnetic moment of 2.9 B.M., and is obviously octahedral. Although soluble, a chloroform solution sample gave a very poor N.M.R. spectrum, and it was not possible to prove which donor atoms on the ligands were uncoordinated.

Both [Ni(ligId and If)Cl$_2$] interacted with sodium ethoxide in ethanol to give decomposed ligand complexes; in both cases only a small amount of deep green-red [Ni(benzilmono-2-pyridylhydrazone)$_2$], in which each tridentate O–N–N ligand entity has been singly deprotonated, was obtained (see Table IIId). Obviously the primary amine Schiff base residue is hydrolysed from the ligand under these conditions.

TABLE III. Ni(II) Complexes of Unsymmetrical Ligands.

Ligand No.		Analysis %				Parent m.s. peak
		C	H	N	Ni	
(a) *Of formula* [*Ni(lig)*] [9]						
Ia = IIa	Calc.	66.8	4.0	12.5	13.1	449
	Found	66.5	4.0	12.0	13.4	
IIb	Calc.	52.5	3.4	18.9	19.8	297
	Found	52.6	3.1	19.1	20.0	
IIc	Calc.	55.4	4.3	17.2	18.1	325
	Found	55.3	4.1	17.0	18.5	
IId	Calc.	54.0	3.9	18.0	18.9	311
	Found	54.2	3.5	18.0	19.1	
IIe	Calc.	58.1	4.6	16.0	16.7	351
	Found	57.8	4.1	16.0	16.7	
Ib	Calc.	66.7	4.2	15.6	13.0	450
	Found	66.5	4.0	15.9	13.3	
Ic	Calc.	65.4	3.8	11.7	12.3	477
	Found	65.4	3.7	11.9	12.4	
Ie	Calc.	64.5	3.9	12.0	12.6	465
	Found	64.5	4.1	11.8	12.8	
(b) *Of formula* [*Ni(Hlig)Cl$_2$*] [9]						
Id	Calc.	58.4	3.7	10.5	11.0	534[a]
	Found	58.5	3.7	10.0	11.2	
If	Calc.	56.5	4.0	10.1	10.6	552[a]
	Found	56.0	3.7	9.7	11.0	
Ig	Calc.	53.1	4.1	9.2	9.6	610[a]
	Found	52.8	3.8	9.0	9.7	
(c) *Of formula* [*Ni(lig)*]$_2$ [9]						
Ig	Calc.	63.7	4.7	11.0	5.8	1018
	Found	64.1	4.8	11.3	5.8	
(d) *Of formula* [*Ni(benzilmono-2-pyridylhydrazone)$_2$*] [9]						
From Id	Calc.	69.2	4.2	12.7	8.9	659
	Found	69.0	4.0	12.9	9.2	
From If	Calc.	69.2	4.2	12.7	8.9	659
	Found	69.1	4.5	12.8	9.3	

[a] Very small parent peak obtained.

The nickel(II) complexes were subjected to mass spectral analysis to ensure that the required unsymmetrical quadridentate complex was present. The complexes of formula [Ni(lig)] all give one large parent peak at the required mass number (Table IIIa), as did the compound [Ni(ligIg)$_2$] (Table IIIc). However the compounds of formula [Ni(Hlig)Cl$_2$] gave only a small parent peak, indicating rapid breakdown (Table IIIb). The compound [Ni(benzilmono-2-

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*With a small residual paramagnetism attributed to the Second Order Zeeman Effect.

pyridylhydrazone)$_2$] gave a large peak for the required parent ion. There was no mass spectral evidence for any of these nickel compounds possessing dimeric structures; the parent peaks quoted in Table III are those of the highest a.m.u. peaks. Similar nickel(II) compounds of type [Ni(lig)] (lig = planar quadridentate) have been shown to form strong dimers [9].

Neither infrared spectra nor U.V.–visible spectra yielded much extra information on these nickel(II) compounds. The hydrazine residue proton of all the ligands has a clear infrared N–H stretch at about 3500 cm^{-1}, which vanishes in the deprotonated complexes [Ni(lig)], but is shifted to slightly lower frequencies in the protonated complexes [Ni(Hlig)Cl$_2$]. The U.V.–visible spectra of the Ni(II) compounds showed no peaks due to d–d transitions; but all compounds had a very intense peak at about 380 nm in the U.V. which has a large tail covering the visible region.

Mn(II) Compounds

The interaction of manganese(II) acetate with all five ligands of structure II in aqueous ethanol under nitrogen yielded deep red compounds of formula [Mn(lig)(H$_2$O)$_x$] (x = 1, 2 or 3), in which the ligand residue is doubly deprotonated. Drying of these compounds at 60 °C under vacuum gave the complexes of empirical formula [Mn(lig)(H$_2$O)] (Table IVa). These compounds are non-electrolytes in nitrobenzene solution, and possess molecular weights in this solvent which indicate that they are dimers. Mass spectral analysis of these compounds yielded only a small parent peak (the highest) for the formula [Mn(lig)(H$_2$O)]$_2$, but a major peak for the dehydrated dimer [Mn(lig)]$_2$. It would seem likely that dimer formation in these compounds is via the interaction of each ligand phenol oxygen with two manganese atoms in a manner similar to the manganese(II) atoms in [Mn(salen)] [10].

Ligands of structure I (apart from Ia = IIa) did not give pure isolable products when reacted under nitrogen with manganese(II) acetate in ethanol. With manganese(II) perchlorate in aqueous ethanol, a series of compounds of type [Mn(Hlig)(H$_2$O)](ClO$_4$)$_2$ (where Hlig = protonated ligand) were obtained for ligands Ib, Id, If and Ig (see Table IVb), but ligands Ic and Ie which possess acidic protons did not yield pure compounds. Furthermore, attempts to deprotonate the above perchlorates with sodium ethoxide in dry ethanol were unsuccessful.

To obtain the required deprotonated complexes, the six ligands Ib to Ig were interacted with decacarbonyldimanganese(0) in refluxing tetrahydrofuran under nitrogen with U.V. radiation, to obtain the compounds (see Table IVc):

(i) [Mn(ligIb)] in which ligand Ib has lost both a hydrazine and a phenol proton.

(ii) [Mn(ligIc)] in which ligand Ic has lost both a hydrazine and a carboxylic acid proton.

(iii) [Mn(ligIe)] in which ligand Ie has lost both a hydrazine and a thiol proton.

(iv) [Mn(ligIf)] in which ligand If has lost a hydrazine proton and a methyl group from the sulphur.

(v) [Mn(ligIg-Me)] in which ligand Ig has lost a hydrazine proton and a methyl group from the arsenic.

No pure compound could be isolated from the reaction of ligand Id with Mn$_2$(CO)$_{10}$, although a compound was obtained from the further interaction of the reaction mixture with *o*-aminophenol [7].

The five compounds of Table IVc are all deep violet in colour and appear stable to aerial oxidation in the solid state. Mass spectral analysis indicates that they are dimeric in the solid state, as they have a highest small parent peak at the dimer a.m.u. However, the major peak is observed in all cases at the a.m.u. for the monomer, and it appears that, unlike the complexes from ligands of structure II, the interactions between adjacent molecules are not particularly stable.

All the manganese(II) compounds are high spin, with the protonated compounds of Table IVb possessing magnetic moments in the range of 5.9–6.1 B.M. However, the deprotonated complexes of Table IVa and IVc, although high spin, have lower than spin-only values for the sextet ground state. These moments all lie within the range 4.8–5.4 B.M. It has already been noted [11] that complexes containing deprotonated 2-pyridylhydrazone residues often possess anomalous magnetic moments; the apparent dimer formation in the solid state may well give rise to metal–metal interaction of the antiferromagnetic type postulated in [Mn(salen)] [12].

Attempts to study N.M.R. spectra of these Mn(II) compounds were unsuccessful; their solutions give particularly broad unresolved spectra.

The interaction of solutions of the manganese(II) deprotonated compounds of Table IVa and IVc with oxygen are currently being studied.

Experimental

Ligands

All eleven ligands were prepared by adding one molecular proportion of 2-pyridylhydrazine [13] in ethanol to one molecular proportion of the required α-diketone in ethanol containing glacial acetic acid (2–3 ml). The mixture was heated to reflux, cooled overnight, and the required α-diketonemono-2-pyridylhydrazone which deposited was filtered off. This product was dissolved in ethanol with gentle warming, and treated with one molecular proportion

TABLE IV. Mn(II) Complexes of Unsymmetrical Ligands.

Ligand No.		Analysis %				Molecular Wt.		
		C	H	N	Mn	(a)	(b)	(c)
[a] *Of formula* $[Mn(lig)(H_2O)]_2$								
Ia = IIa	Calc.	64.8	4.3	12.1	11.9	895	926	890
	Found	64.5	4.0	11.8	11.8			
IIb	Calc.	50.1	3.9	18.0	17.7	580	622	586
	Found	50.0	3.7	18.0	17.9			
IIc	Calc.	53.1	4.7	16.5	16.2	652	678	642
	Found	52.8	4.5	16.0	15.8			
IId	Calc.	51.7	4.3	17.2	16.9	650	650	614
	Found	52.0	3.9	17.2	16.9			
IIe	Calc.	55.9	4.9	15.3	15.0	680	730	694
	Found	56.0	5.1	15.0	15.1			
[b] *Of formula* $[Mn(Hlig)(H_2O)](ClO_4)_2$								
Ib	Calc.	45.2	3.5	10.5	8.3	–	–	–
	Found	45.0	3.8	10.7	8.6			
Id	Calc.	46.1	2.9	8.3	8.1	–	–	–
	Found	45.9	3.1	8.0	8.0			
If	Calc.	44.9	3.5	8.1	7.9	–	–	–
	Found	45.0	3.8	8.0	8.0			
Ig	Calc.	43.0	3.6	7.4	7.3	–	–	–
	Found	43.0	3.8	7.2	7.0			
[c] *Of formula* $[Mn(lig)]$ [9]								
Ib	Calc.	67.6	4.3	15.8	12.4	–	888	444
	Found	67.6	4.1	15.6	12.4			
Ic	Calc.	66.0	3.8	11.8	11.6	–	946	473
	Found	65.7	3.5	11.9	11.8			
from Ie	Calc.	65.1	4.3	12.1	11.9	–	922	461
	Found	64.9	4.0	12.4	12.1			
from If	Calc.	65.1	4.3	12.1	11.9	–	922	461
	Found	65.3	3.9	12.0	11.7			
from Ig	Calc.	60.0	4.2	10.8	10.6	–	1040	520
	Found	59.9	3.9	10.8	10.6			

Molecular Weight: [a]From freezing pt. depression in nitrobenzene. [b]From mass spectrum; highest a.m.u. peak; peak small; represents $[Mn(lig)(H_2O)]_2$ for Table IV(a) and $[Mn(lig)]_2$ for Table IV(c). [c]From mass spectrum; largest peak; represents $[Mn(lig)]_2$ for Table IV(a) and $[Mn(lig)]$ for Table IV(c).

of the required purified amine in ethanol. The mixture was heated gently for 5 minutes and allowed to stand for 2–3 days to yield the required quadridentate. Only ligand Id could not be obtained as a crystalline product by this method. The analyses, melting points and mass spectra of the ligands are listed in Tables I and II.

Of the amines used in preparing the ligands, only *o*-aminobenzaldehyde [14] and *o*-(dimethylarsino)-aniline [15] had to be prepared. References are given for each of these preparations.

The stability of the ligands to disproportionation was tested by dissolving them in dry ethanol and refluxing the solution for 60 minutes under nitrogen. The solvent was then removed, and the solid product(s) subjected to mass spectral analysis. Ligands IIb, IIc and IId gave large parent peaks for the two symmetrical ligands, viz. α-diketonebis(2-

pyridylhydrazone) and α-diketone bis(*o*-substituted amine) and virtually no peak at the a.m.u. for the unsymmetrical ligand. On the other hand, ligands IIa (= Ia), IIe, Ib, Ic, Ie, If and Ig gave some evidence of disproportionation under these conditions, but the parent peak for the unsymmetrical ligand was still noticeably present.

Metal Complexes

Of type [Ni(lig)]

The required ligand (1 molecular proportion) in 95% aqueous ethanol was treated with stirring with nickel(II) acetate (1 molecular proportion) in aqueous ethanol. In all cases crystallisation of the required product took place immediately or on standing overnight. [Ni(ligId)] was prepared by using an aliquot from the reaction mixture of benzilmono-2-pyridylhydrazone and *o*-aminobenzaldehyde. The compounds were dried at 60 °C under vacuum.

Of type [Ni(Hlig)Cl$_2$]

The foregoing method was used replacing nickel(II) acetate with nickel(II) chloride.

Of type [Ni(lig)$_2$]

[Ni(HligIg)Cl$_2$] (mmol) in dry ethanol was treated with stirring with a solution of sodium (1 mmol) in dry ethanol. The green solution went deep red in colour, and upon standing overnight deposited a small amount (~0.1 g) of the required red-green product.

[Ni(benzilmono-2-pyridylhydrazone)$_2$]

Treatment of [Ni(HligId and If)Cl$_2$ by the foregoing method yielded this product.

Of type [Mn(lig)(H$_2$O)]

The method outlined under (i) above for [Ni(lig)] compounds was used, replacing nickel(II) by manganese(II) acetate.

Of type [Mn(Hlig)(H$_2$O)](ClO$_4$)$_2$

Again method (i) above was used, replacing the nickel(II) with manganese(II) perchlorate.

Of type [Mn(lig)]

These compounds were prepared by the method of Calderazzo *et al.* [16] for [Mn(salen)].

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