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Syntheses and Complexes of Unsymmetrical Multidentate Ligands.
Part II. Tridentate Ligands

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The synthesis is reported of some new tridentate ligands which are possible precursors to the preparation of highly unsymmetrical quadridentates. These tridentates have been prepared by (A) the interaction of glyoxalmonophenylhydrazone and (i) o*-aminophenol, (ii)* o*-phenylenediamine, and (iii) benzoylhydrazine, and (B) the interaction of* o*-aminobenzaldehyde and 2-pyridylhydrazine.*

Introduction

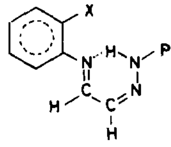
A previous paper [1] illustrated the possibility of the synthesis of unsymmetrical bidentate ligands by the condensation of two different primary amine groups upon the one molecule of glyoxal.

This paper extends this earlier work to demonstrate how unsymmetrical tridentates can be obtained by the above synthetic process. It was hoped that further condensation upon such tridentate ligands could yield highly unsymmetrical quadridentates. Such attempts were only successful in the presence of metal ion, and a new line of approach to the synthesis of highly unsymmetrical multidentates, based on *o*-aminobenzaldehyde as a starting point, is described.

A further paper dealing with the synthesis of unsymmetrical quadridentate Schiff-base ligands, from tridentates derived from glyoxalmonophenylhydrazone and *o*-aminobenzaldehyde, is currently in preparation.

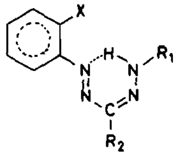
The interaction of *o*-phenylediamine or *o*-aminophenol with glyoxalmonophenylhydrazone yields unsymmetrical tridentates of type (I), which are similar to the tridentate formazans (II).

The chemistry of tridentate formazans appears well established. These formazans oxidise under a variety of conditions to tetrazolium salts while with metal ions under appropriate conditions, metal complexes result [2]. For example, the tridentate formazans (II) form copper(II) complexes with a 1:1 metal–ligand stoichiometry. The copper(II) complex from the formazan where X = OH, possesses an abnormal magnetic moment compatible with a dimeric structure involving a Cu_2O_2 bridging system. On the other hand the copper(II) complex from the formazan where X = COOH, which is also considered to be dimeric, possesses a normal magnetic moment. The difference between these two copper(II) complexes reflects the differing extent of the antiferromagnetic exchange between the two paramagnetic centres in the complexes.



I

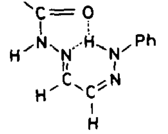
X = NH_2, OH



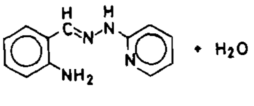
II

X = OH, COOH

$R_1 = R_2 =$ phenyl



III



IV

No tridentate or potential tridentate glyoxalanil-(1)-arylhydrazone-(2) ligands of the type (I) nor potential tridentate systems of type (III) derived from glyoxalmonophenylhydrazone appear to have been previously reported. By analogy with the formazans, similar tridentate systems should exist and exhibit behaviour similar to the analogous formazans with respect to oxidation and the formation of metal complexes.

Unsymmetrical tridentate ligands can readily be obtained from *o*-aminobenzaldehyde, and this work

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deals with the preparation of such a ligand (IV), obtained by condensation of the aldehyde group with a primary amine.

Experimental

Anil-hydrazone Ligands (I)

These were prepared by direct reaction of freshly sublimed [3] *o*-aminophenol or recrystallised *o*-phenylenediamine dissolved in a minimum of hot methanol or ethanol with the stoichiometric amount of glyoxalmonophenylhydrazone dissolved in a minimum of hot methanol or ethanol. This preparative procedure is the same as that used for the preparation of the bidentate anil-hydrazones described previously [1]. *Analyses.* (i) *o*-aminophenol derivative: Found: C, 70.46; H, 5.72; N, 17.6. Calc. for $C_{14}H_{13}NO$: C, 70.29; H, 5.44; N, 17.6%. (ii) *o*-phenylenediamine derivative: Found: C, 70.10; H, 6.11; N, 23.4 Calc. for $C_{14}H_{14}N_4$: C, 70.59; H, 5.88; N, 23.5%.

Glyoxalmonophenylhydrazonemonobenzoylhydrazone(III)

This potentially tridentate derivative of glyoxalmonophenylhydrazone was prepared by direct reaction of the stoichiometric amounts of glyoxalmonophenylhydrazone dissolved in a minimum of hot methanol or ethanol with benzolhydrazine [4] dissolved in a minimum of hot methanol or ethanol. The preparation procedure is similar to that used for the preparation of bidentate anil-hydrazones [1]. The reaction produce appeared immediately on mixing the reagents, the analytical sample being recrystallised from hot methanol. M.Pt. 236 °C. *Analysis.* Found: C, 67.33; H, 5.31; N, 21.1. Calc. for $C_{15}H_{14}N_4O$: C, 67.67; H, 5.26; N, 21.0%.

o-Aminobenzaldehyde-(2'-pyridyl)hydrazone(IV)

Freshly prepared *o*-aminobenzaldehyde (22 mmol) in ethanol was filtered into a refluxing solution of 2-pyridylhydrazine (22 mmol) and glacial acetic acid (5 ml) in ethanol (200 ml). Upon cooling, light yellow needles separated. The solid was filtered off, washed with cold ethanol and air-dried. Yields 80–90%. M.Pt. 180 °C. *Analysis.* Found: C, 67.84; H, 5.90; N, 26.1. Calc. for $C_{12}H_{12}N_4$: C, 67.92; H, 5.66; N, 26.4%.

Glyoxal-(2-hydroxyphenyl)-anil-(1)-phenylhydrazinato-(2)-copper(II)

This metal complex may be prepared by either an *in-situ* formation of the ligand in methanol or ethanol followed by reaction of the ligand solution with a hot aqueous methanol solution of copper(II) acetate or by direct reaction of the ligand dissolved in a minimum of hot methanol or ethanol with a hot aqueous methanol solution of copper(II) acetate. The preparative procedures are essentially the same as those used for the preparation of deprotonated copper(II) complexes of the bidentate anil-hydrazone ligands. *Analyses.* Found: C, 56.30 (55.26); H, 3.89 (3.88); N, 13.7 (13.9); Cu, 21.27 (20.18). Calc. for $C_{15}H_{12}N_4OCu$: C, 55.91; H, 3.66; N, 13.9; Cu, 21.13%. Figures in brackets indicate analysis of product obtained from an *in-situ* ligand synthesis.

Bis-[o-aminobenzaldehyde-(2'-pyridyl)hydrazone nickel(II)] perchlorate

2 mmol of nickel(II) perchlorate in water (10 ml) was added to 4 mmol of (IV) in refluxing ethanol (50 ml). Green-brown crystals deposited over several days. These were filtered off, washed with cold ethanol and air-dried. Yields 75–85%. *Analysis.* Found: C, 42.44; H, 3.64; N, 16.5. Calc. for $C_{24}H_{24}N_8Cl_2NiO_8$: C, 42.25; H, 3.52; N, 16.4%.

Bis-[o-aminobenzaldehyde-(2'-pyridyl)hydrazone]-copper(II) perchlorate

This brown compound was prepared in a manner similar to the foregoing nickel complex. *Analysis.* Found: C, 41.72; H, 3.41; N, 16.2. Calc. for $C_{24}H_{24}N_8Cl_2CuO_8$: C, 41.95; H, 3.50; N, 16.3%.

Results and Discussion

Ligands

The three tridentate ligands derived from glyoxal are easily prepared in good yield by direct reaction of glyoxalmonophenylhydrazone with the corresponding amine or hydrazine in a reaction analogous to that used for the preparation of the bidentate anil-hydrazones. Best yields were obtained when the amines *o*-phenylenediamine or *o*-aminophenol had been freshly recrystallised or freshly sublimed respectively. The ligands readily recrystallise from methanol or ethanol.

Attempts to further condense glyoxal-(2-aminophenyl)-anil-(1)-phenylhydrazone-(2) with another molecule of a different carbonyl compound to characterise the anil-hydrazone and possible generate quadridentate systems, brought about rearrangements in the anil-hydrazone. For example, with salicylaldehyde, condensation and a carbonyl exchange took place, the reaction product being the bis-salicylaldehyde derivative of *o*-phenylenediamine [M.Pt. 156 (lit. = 163 °C); Found (calc. for $C_{20}H_{16}N_2O_2$), C = 75.69 (75.95); H = 5.33 (5.06); N = 8.97 (8.87)%] rather than the mixed anil. Benzaldehyde with glyoxal-(2-aminophenyl)-anil-(1)-phenylhydrazone-(2) produced the bis-glyoxalmonophenylhydrazone derivative of *o*-phenylenediamine [M.Pt. 183; Found (calc. for $C_{22}H_{20}N_6$), C = 71.17 (71.74); H = 5.54 (5.43); N = 22.92 (22.82)] rather than a mixed anil or the bis-benzaldehyde derivative of *o*-phenylenediamine. This would suggest an affinity order towards *o*-phenylenediamine for the carbonyls considered as salCHO > glyoxalmonophenylhydrazone > PhCHO.

The preparation of a benzoylhydrazine derivative of glyoxalmonophenylhydrazone indicates the preparation of mixed arylaroyl hydrazone derivatives of glyoxal is possible. These arylaroyl hydrazones would be potential tridentates capable of behaving as either monobasic or dibasic ligands with behaviour towards metal ions being expected to be similar to that of the aroylhydrazones of salicylaldehyde and acetylacetone as reported by Iskander and coworkers [5]. This ligand system was not subject to any further investigation.

o-aminobenzaldehyde-(2′-pyridyl)hydrazone was readily obtained in high yield, although attempts to prepare the similar tridentate by condensation of *o*-aminobenzaldehyde and 2-aminomethyl pyridine were not successful. Only an intractable green yellow oil could be obtained. The mass spectrum of the tridentate (IV) showed a parent peak at 212 a.m.u. consistent with the expected value.

The infrared spectrum of (IV) exhibits two bands in the region 3200–3400 cm^{-1}, one sharp and intense at 3360 cm^{-1} and a weaker one at 3260 cm^{-1}. Both bands are absent from the spectrum of the salicylaldehyde derivative of (IV), and thus they are assigned to primary amine N–H stretches. A relatively intense band at 3190 cm^{-1} in the spectrum of (IV), is assigned to the amine stretch of the hydrazone residue, on the basis that no band exists in this region for the metal complexes where it is proposed, on the basis of ^1H n.m.r. evidence principally, that deprotonation of this group occurs upon complexation. By similar reasoning a band at 1629 cm^{-1} in the spectrum of (IV) and absent in the spectrum of its salicylaldehyde derivative is assigned to the amine group. The 1600 cm^{-1} region however, is far more complicated than that above 3200 cm^{-1}, being overlapped by ring vibrations and C=C vibrations, making band assignment tentative. An intense sharp band at 1600 cm^{-1} in the spectrum of (IV) is tentatively assigned to azomethine vibration.

The ^1H n.m.r. spectra of (IV) and its salicyaldehyde derivate (IV-sal) were recorded in $(CD_3)_2SO$, and D_2O. The principal peaks of interest are tabulated in Table I.

Due to the complexity of the aromatic region (δ 8–6), no band assignments have been made for the aromatic protons. The signals at δ 10.60 and δ 6.62 in the spectrum of (IV) are assigned to the –NH– and $-NH_2$ groups, on the observation of rapid loss of these signals when D_2O is added to the solution. In particular, the signal at δ 10.60 is assigned to the –NH– group, on the observation of a similar signal at δ 10.84 in the spectrum of (IV-sal) being lost upon addition of D_2O to the solution. The only group common to both (IV), and (IV-sal) expected to show such behaviour is the –NH– group. Higson and MacKenzie [6] in a study of ligands of similar type have reported the azomethine resonance (–CH=N–) in the region δ 7–9.

TABLE I. ^1H N.m.r. of Ligands (IV) and (IV-sal)[a].

Solvent	–CH=N–	$-NH_2$[b]	–NH–	–OH
$(CD_3)_2SO$	8.22(SI)	6.62(S)	10.60(SI)	–
$(CD_3)_2SO$	8.22(S)			–
$(CD_3)_2SO$	8.22(SI)	–	10.84(SI)	12.24(SI)
$+D_2O$	8.44(SI)			
$(CD_3)_2SO$	8.44(SI)	–		
$+D_2O$	8.84(SI)			

[a] TMS internal reference [δ values]. The figure given in parentheses after the multiplicity is the relative intensity of the resonance. [b] Due to the proximity of this resonance to the aromatic region (δ 8–6) no reliable integrated intensity data is available.

A singlet at δ 8.22 in the spectrum of (IV) is assigned to the azomethine resonance. The spectrum of (IV-sal) shows two singlets at δ 8.44 and δ 8.84 which is expected, since this compound contains two non-equivalent azomethine groups.

Due to the similarity in the chemical shifts of signals at δ 8.22 in the spectrum of (IV) and at δ 8.44 in the spectrum of (IV-sal), the signal at δ 8.44 is further assigned to the azomethine resonance of the hydrazone residue, whereas the signal at δ 8.84 is assigned to the azomethine resonance of the salicylaldehyde residue. On the observation of rapid loss of the signal at δ 12.24 in the spectrum of (IV-sal), upon addition of D_2O to the solution, this signal is assigned to the –OH group.

Metal Complexes

Metal complexes from the four quadridentate ligands were not exhaustively studied. Glyoxal-(2-hydroxyphenyl)-anil-(1)-phenylhydrazone-(2) either as the ligand or prepared *in-situ* in methanol or ethanol, reacts readily with an aqueous methanolic solution of copper(II) acetate to yield a brown solid for which analytical data is compatible with an empirical stoichiometry of the complex of one doubly deprotonated ligand per metal atom. Considering the nature of the ligand, this complex could be considered as being dimeric and formulated as $[Cu(L-2H)]_2$ suggesting the presence in the complex of Cu_2O_2 bridging system. This would be compatible with the observed magnetic moment of 1.05 per copper atom, the low moment arising from an antiferromagnetic exchange interaction of the bridged copper(II) atoms. The visible spectrum of the complex in pyridine differs little from the spectrum in dichloromethane and apart from an intense band in the 21 kK region, the visible spectrum is featureless in the range measured.

Glyoxal-(2-aminophenyl)-anil-(1)-phenylhydrazone-(2) in methanol or ethanol reacted with aqueous methanolic copper(II) acetate to yield a product of varying purity which was not further studied. However, reaction of the anil-hydrazone in methanol or ethanol with nickel(II) acetate in methanol or ethanol produced an intensely coloured, crystalline complex which analytically corresponded to the nickel complex of the doubly deprotonated bis-glyoxalmonophenylhydrazone derivative of *o*-phenylenediamine [found (calc. for $[(C_{22}H_{18}N_6)Ni]$), C = 61.80 (62.16); H = 4.43 (4.24); N = 20.10 (19.78); Ni = 13.82)], a symmetrical quadridentate ligand, rather than being a derivative of the tridentate anil-hydrazone.

No further metal complexes of the two anil-hydrazones or the mixed aryl-aroyl hydrazone were investigated.

Bis-tridentate complexes of the general formula $[M(lig)_2](ClO_4)_2$ have been prepared, where M = Cu(II), Ni(II) and lig is (IV). The complexes formed readily upon the addition of metal perchlorate to the ligand in hot ethanol. Empirical stoichiometry was determined by analytical data. No further physical measurements were recorded for these complexes.

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