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Syntheses and Complexes of Unsymmetrical Multidentate Ligands. Part I. Bidentate Glyoxalanil(1)-phenylhydrazone-(2) Ligands

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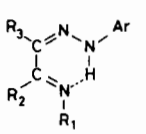
The synthesis of a series of new unsymmetrical bidentate ligands is described. They are obtained by stepwise condensation of the two carbonyl groups of glyoxal with firstly phenylhydrazine, and secondly a primary amine. The non-charged complexes of these ligands of the type $[M(L-H)_2]^\circ$ *(where L–H = a deprotonated ligand residue) for M = Cu(II), Ni(II) and Co(II) have been isolated and studied. A series of copper compounds of formula* $Cu_n ligX_{(n+1)}$ *(where n = 2, 3 or 4 and X = Cl or Br) have also been obtained, and are postulated as mixed Cu(I) and Cu(II) compounds.*

Introduction

The interaction of α-diketones with simple primary amines (or hydrazones) is usually carried out in the presence of enough of the amine to yield the bis-Schiff base compound, which can function as a symmetrical bidentate ligand. However, in a program of preparing unsymmetrical multidentate ligands, we have been able to readily condense, by stepwise reaction, two different primary amine containing groups to each of the carbonyls of various α-diketones. The ligands so obtained are unsymmetrical, and this paper reports upon the preparation and complex compounds of a series of new bidentate ligands of such type, *viz.* the glyoxalanil-(1)-phenylhydrazone (2) compounds (I, Ar = Phenyl; R_1 = various aryl groups, R_2 = R_3 = H). Later papers will extend the work to tri- and quadridentate ligands.



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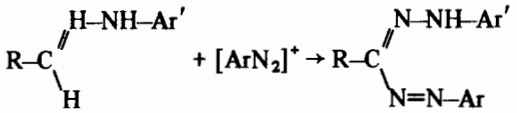
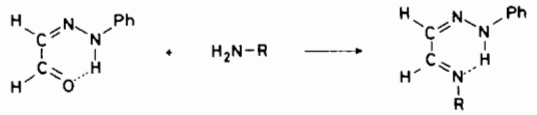
Although this synthetic approach is new, ligands of type I are not novel, and extensive series of substituted glyoxalanil-(1)-arylhydrazones(2) have been prepared by Hirsch and Coworkers [1, 2] by the action of a diazonium salt $[ArN_2]^+ X^-$ on anils containing an active methylene group. Such ligands have been shown to form metal complexes with cobalt(II), nickel(II) and copper(II) [1–4]. These metal complexes have been formulated as chelating through the nitrogen atoms attached to the aryl groups, and by analogy with formazans to which these anilhydrazones are closely related, resonance stabilisation of the six membered chelate ring would be expected.

Formazans and the anil-hydrazones are closely related as the replacement of the methine or substituted methine group (R_2–C) in (I) by a tertiary nitrogen (–N=) produces a formazan system. From this similarity in structure, it would be expected that the formazans and anilhydrazones would show analogous chemical behaviour and indeed, oxidation and metal ion complexation appear to be very closely related, while synthetic procedures used in the preparation of compounds from each class are also similar. Thus formazans have been prepared by the action of a diazonium salt $[ArN_2]^+ X^-$ upon an arylhydrazone Ar'NH·N:CHR in a reaction sequence as shown [5–7].



Formazans can function as ligands forming metal complexes characterised by the presence of a resonance stabilised, planar six-membered ring, in which the formazan has complexed in ionised form as the amide anion with complexes containing two bidentate ligands per metal(II) ion being assigned a planar structure on the basis of this resonance stabilisation [8, 9]. However, a recent X-ray crystal structure study [10] of bis-(1,5-diphenylformazan)-

TABLE I. Glyoxalanil-(1)-phenylhydrazone-(2) Ligands.



R	Ligand Designation	Decomposition Range °C	Molecular Formula	Analyses (%)				ν_{NH}[a] cm^{-1}	$\nu_{C=N}$ cm^{-1}
					C	H	N		
phenyl	GMPhA	148–149	$C_{14}H_{13}N_3$	Found	75.60	5.99	18.74	3130 w	1605 s
				Calc.	75.53	5.83	18.83	3200 w	
benzyl	GMPhBzA	127–128	$C_{15}H_{15}N_3$	Found	75.24	6.46	17.80	3220 br,w	1630 s
				Calc.	75.95	6.33	17.72		
p-tolyl	GMPhpTA	183–184	$C_{15}H_{15}N_3$	Found	75.10	6.37	17.49	3140 w	1612 s
				Calc.	75.95	6.33	17.72		
m-tolyl	GMPh*m*TA	124–125	$C_{15}H_{15}N_3$	Found	75.03	7.10	17.70	3120 w	1605 s
				Calc.	75.95	6.33	17.72	3200 w	
o-tolyl	GMPh*o*TA	105–106	$C_{15}H_{15}N_3$	Found	75.96	6.55	17.90	3140 w	1610 s
				Calc.	75.95	6.33	17.72	3200 w	
p-bromophenyl	GMPh*p*BA	174–175	$C_{14}H_{12}N_3Br$	Found	55.21	4.06	13.87	3120 vw	1600 s
				Calc.	55.6	3.97	13.90	3190 vw	
p-anisidyl	GMPh*p*An	155–156	$C_{15}H_{15}N_3O$	Found	71.23	6.14	16.50	3130 w	1605 s
				Calc.	71.15	5.93	16.60	3190 w	
o-anisidyl	GMPh*o*An	136–137	$C_{15}H_{15}N_3O$	Found	71.00	6.02	16.50	3120 w	1605 s
				Calc.	71.15	5.93	16.60	3180 w	
p-chlorophenyl	GMPh*p*CA	180–181	$C_{14}H_{12}N_3Cl$	Found	65.23	4.82	16.28	3120 w	1600 s
				Calc.	65.20	4.66	16.30	3180 w	
o-chlorophenyl	GMPh*o*CA	135–136	$C_{14}H_{12}N_3Cl$	Found	64.88	4.85	16.40	31.20 w	1603 s
				Calc.	65.20	4.66	16.30	31.80 w	
p-nitrophenyl	GMPh*p*NA	171–172	$C_{14}H_{12}N_4O_2$	Found	63.03	4.83	20.90	3190 vw	1600 s
				Calc.	62.69	4.48	20.90		
α-naphthyl	GMPhαNA	149–150	$C_{18}H_{15}N_3$	Found	79.21	5.70	15.10	3190 vw	1595 s
				Calc.	79.12	5.49	15.38		
β-naphthyl	GMPhβNA	180–181	$C_{18}H_{15}N_3$	Found	78.92	5.65	15.80	3125 w	
				Calc.	79.12	5.49	15.38	3195 w	1603 s

[a]s = strong; m = medium; w = weak; vw = very weak; br = broad.

copper(I) perchlorate has revealed that formazans can also complex in neutral form with five membered chelate rings being present in the complex which has a distorted tetrahedral structure. Price [11] in a study of metal formazan complexes has reported the preparation of a copper(I) complex of 1,2,5-triphenylformazan in which both neutral and anionic forms of the ligand are claimed to be present on the basis of stoichiometry and magnetic behaviour.

Experimental

Glyoxalmonophenylhydrazone

Glyoxalmonophenylhydrazone was prepared by an adaption of the method used by Pechmann [12] for the synthesis of diacetylmonophenylhydrazone. A slight excess of glyoxal hydrate dissolved in water was reacted at room temperature with a one mol portion of phenylhydrazine dissolved in dilute acetic acid. After standing overnight in a refrigerator, the precipitated glyoxalmonophenylhydrazone was isolated by filtration, washed free of acetic acid by cold water and air dried. The product, light brown in colour, was used without further purification for the preparation of the anil-hydrazone ligands.

Glyoxalanil-(1)-phenylhydrazone-(2) Ligands

These ligands were prepared by the reaction of the appropriate amine, dissolved in a minimum of warm ethanol if necessary, with the stoichiometric amount of glyoxalmonophenylhydrazone dissolved in a minimum volume of hot ethanol. Following an exothermic reaction, the dark reaction mixture deposited the crystalline anil-hydrazone on cooling. The anil-hydrazone product was filtered, washed with cold ethanol and recrystallised from a minimum volume of hot methanol or ethanol. The anil-hydrazones are listed in Table I.

Deprotonated Complexes

In general, these complexes were prepared by the reaction of the appropriate metal salt (acetate or per-

TABLE II. Deprotonated Complexes, $[M(L-H)_2]$.

Ligand	Metal	Analysis (%)					Preparation
			C	H	N	M	
GMPhA	Cu	Found	65.73	4.77	16.32	12.83	A
		Calc.	66.21	4.73	16.55	12.51	
GMPhpTA	Cu	Found	66.81	5.14	15.70	12.34	A
		Calc.	67.23	5.24	15.69	11.86	
GMPhBzA	Cu	Found	66.84	5.31	15.54	11.76	B
		Calc.	67.23	5.24	15.69	11.86	
GMPhθTA	Cu	Found	66.99	5.40	15.60	11.82	B
		Calc.	67.23	5.24	15.69	11.86	
GMPhmTA	Cu	Found	66.89	5.44	15.63	11.98	B
		Calc.	67.23	5.24	15.69	11.86	
GMPhpCA	Cu	Found	58.00	3.91	14.59	11.22	B
		Calc.	58.28	3.82	14.57	11.01	
GMPhθCA	Cu	Found	58.29	3.90	14.58	11.22	B
		Calc.	58.28	3.82	14.57	11.01	
GMPhpBA	Cu	Found	50.50	3.44	12.70	9.78	B
		Calc.	50.48	3.60	12.62	9.54	
GMPhβNA	Cu	Found	71.04	4.79	13.87	10.70	B
		Calc.	71.11	4.61	13.83	10.45	
GMPhθAn	Cu	Found	63.19	5.12	14.69	11.28	B
		Calc.	71.11	4.95	13.83	10.45	
GMPhpAn	Cu	Found	63.34	5.08	14.78	11.41	B
		Calc.	63.66	4.95	14.85	11.23	
GMphA	Co	Found	66.02	4.81	16.70	–	C
		Calc.	66.81	4.77	16.70	11.71	
GMPhBzA	Co	Found	67.41	5.42	15.81	–	C
		Calc.	67.80	5.27	15.82	11.09	
GMPhBzA	Ni	Found	67.06	5.48	15.80	11.17	D
		Calc.	67.83	5.28	15.83	11.06	

chlorate) dissolved in a minimum of hot solvent (ethanol or methanol for perchlorates and 30% aqueous methanol or ethanol for acetates) with the corresponding ligand dissolved in a minimum of hot ethanol or methanol. In the case of the cobalt and nickel complexes, a little triethylamine was added to the reaction mixture. The dark metal complex which precipitated was filtered, washed with solvent, cold 3% acetic acid, solvent and finally air dried. Metal complexes prepared and characterised are listed in Table II. The code for the methods of preparation refer to procedures described below.

A. 10 mmol glyoxalmonophenylhydrazone was dissolved in 15 cm^3 warm, absolute ethanol and 10 mmol of the appropriate amine, dissolved in a little warm absolute ethanol was added with thorough mixing, followed by 5 mmol of copper(II) acetate monohydrate in about 30 cm^3 of warm absolute ethanol. The dark precipitate which formed from the dark brown solution was filtered, washed with absolute ethanol, a little ether and finally air dried.

B. 5 mmol of the appropriate ligand was dissolved in a minimum of boiling methanol. 2.5 mmol of copper(II) acetate monohydrate dissolved in 10 cm^3 warm 70% aqueous methanol was added with mixing to the boiling ligand solution. The dark crytalline precipitate which separated from the dark brown solution was filtered, washed with methanol, 3% acetic acid, methanol and then air dried.

C. 5 mmol of the appropriate ligand was dissolved in a minimum of boiling methanol. 2.5 mmol of cobalt(II) acetate tetrahydrate dissolved in 15 cm^3 warm 70% aqueous methanol was added with mixing to the boiling ligand solution to which had been added a little (*ca.* 1.00 cm^3) triethylamine. The dark solution deposited black shining crystals which were washed with methanol, 3% acetic acid, methanol and then air dried.

D. 5 mmol of ligand was added directly to 2.5 mmol of nickel(II) perchlorate hexahydrate dissolved in 10 cm^3 of hot methanol and the mixture heated. The ligand dissolved, the resulting dark solution

TABLE III. Chloro Complexes, $Cu_n(Lig)Cl_{n+1}$.

Complex	Analysis %					
		C	H	N	Cl	Cu
$Cu_2(GMPhA)Cl_3$	Found	36.93	3.19	9.82	22.7	27.97
	Calc.	36.80	2.84	9.20	23.3	27.82
$Cu_3(GMPhpTA)Cl_4$	Found	31.30	2.92	7.10	24.3	34.00
	Calc.	31.72	2.64	7.40	24.67	33.56
$Cu_3(GMPhoTA)Cl_4$	Found	32.25	2.99	7.72	–	32.93
	Calc.	31.72	2.64	7.40	24.67	33.56
$Cu_3(GMPhpCA)Cl_4$	Found	28.50	2.36	6.79	29.0	32.26
	Calc.	28.57	2.04	7.12	29.9	32.40
$Cu_3(GMPhpBA)Cl_4$[a]	Found	26.14	2.13	6.72	21.1	30.40
	Calc.	26.48	1.89	6.62	22.4	30.12

[a]Br(found) = 12.61; Br(calc.) = 12.61.

TABLE IV. Bromo Complexes, $Cu_n(Lig)Br_{n+1}$.

Complex	Analysis %					
		C	H	N	Br	Cu
$Cu_2(GMPhA)Br_3$	Found	28.84	2.39	7.20	40.3	21.44
	Calc.	28.47	2.20	7.11	40.7	21.52
$Cu_2(GMPhpTA)Br_3$	Found	29.11	2.44	6.89	39.7	21.23
	Calc.	29.80	2.48	6.95	39.8	21.03
$Cu_4(GMPhoTA)Br_5$	Found	21.30	1.99	4.84	44.1	28.87
	Calc.	20.20	1.68	4.71	44.9	28.51
$Cu_2(GMPhmTA)Br_3$	Found	30.12	2.86	6.82	40.0	21.42
	Calc.	29.80	2.48	6.95	39.8	21.03
$Cu_3(GMPhoCA)Br_4$	Found	21.70	1.76	5.41	–	25.20
	Calc.	21.88	1.56	5.47	41.7	24.80
$Cu_3(GMPhpBA)Br_4$	Found	19.88	1.56	5.73	50.4	23.35
	Calc.	20.68	1.48	5.17	49.2	23.45
$Cu_3(GMPhoBA)Br_4$[a]	Found	20.22	1.62	4.99	–	24.35
	Calc.	20.68	1.48	5.17	49.2	23.45
$Cu_2(GMPhpCA)Br_3$[b]	Found	26.77	2.22	6.80	38.5	20.70
	Calc.	26.97	1.77	6.74	38.5	20.39
$Cu_3(GMPhoAN)Br_4$	Found	23.49	2.16	5.73	–	24.42
	Calc.	23.61	1.97	5.51	–	24.98

[a]The ligand prepared *in situ*. [b]Cl(found) = 5.45; Cl(calc.) = 5.70.

slowly depositing dark shining crystals which were filtered, washed with methanol and air dried.

Halo Complexes

These were prepared by both *in situ* and direct reaction procedures. In the *in situ* method, the appropriate amine in methanol or ethanol if necessary, was reacted with the requisite amount of glyoxalmonophenylhydrazone in hot methanol or ethanol followed by reaction with the corresponding copper halide dissolved in hot methanol or ethanol, the highly coloured precipitate which appeared immediately on mixing being filtered, washed with solvent and air dried. The chloro compounds, which showed some air sensitivity, were dried in a vacuum desiccator over phosphoric oxide.

In the direct reaction, the appropriate ligand dissolved in a minimum of hot methanol or ethanol was reacted with the corresponding copper halide dissolved in hot methanol or ethanol, the precipitated complex being recovered as above. The halo compounds are listed in Tables III and IV.

Other Reactions – Reduction

Two hydrazone-anils were catalytically reduced by hydrogen in the presence of Raney Nickel. On completion of reduction, the Raney Nickel was removed by filtration, the solvent ethanol was

TABLE V. Glyoxalanil-(1)-phenylhydrazone-(2) Reduction Products and Derivative Characteristics.

Anil-hydrazone	Reduction Products	Analysis			
			C	H	N
A. *Products*:					
GMPhA	Aniline + N-phenylethylenediamine	Found	71.73	8.98	19.2
	($C_8H_{12}N_2$)($b_{0.2}$ = 90 °C)	Calc.	70.59	8.82	20.59
GMPhoTA	Aniline + N-(*o*-tolyl)ethylenediamine	Found	72.03	9.43	18.19
	($C_9H_{14}N_2$)($b_{0.15}$ = 93 °C)	Calc.	72.00	9.33	18.67
Amine	Derivative	Analysis			
			C	H	N
B. Derivatives:					
N-phenylethylenediamine	picrate(mono)	Found	46.05	4.14	19.21
	($C_{14}H_{15}N_5O_7$) (MRa = 166–168 °C)	Calc.	46.02	4.11	19.18
	salicylaldehyde anil	Found	74.96	6.71	11.54
	($C_{15}H_{16}N_2O$ (MRa = 53–54 °C)	Calc.	75.00	6.67	11.67
N-(*o*-tolyl)ethylenediamine	salicylaldehyde anil	Found	75.39	7.29	11.00
	($C_{16}H_{18}N_2O$) (MRa = 46–47 °C)	Calc.	75.59	7.09	11.02

removed using a rotary evaporator with the residual oil being vacuum distilled and yielding two major fractions in each case, one fraction being aniline and the second fraction being an N-arylethylenediamine which was characterised by the preparation of a salicylaldehyde anil. The ligands reduced, their reduction products, characterising derivatives and analysis are listed in Table V.

Results and Discussion

Ligands

The direct reaction, under aqueous conditions, of an excess of glyoxal with a 1 mol portion of phenylhydrazine in the presence of a slight excess of the stoichiometric amount of acetic acid produced glyoxalmonophenylhydrazone in good yield (80–90%). This yield compares very favourably with the yield (50%) reported by Fischer and Taube [13] for the synthesis of glyoxalmonophenylhydrazone from glyoxal sulphate and phenylhydrazine in 50% acetic acid. The IR spectrum of the reaction product established the presence of both a carbonyl ($\nu_{C=O}$ = 1668 cm^{-1}) and an azomethine ($\nu_{C=N}$ = 1612 cm^{-1}) group while the broad, split band in the NH, OH region (ν = 3250, 3200, 3140 cm^{-1}) could be taken as an indication of hydrogen bonding. A PMR spectrum in dimethylsulphoxide showed an iminic proton resonance at 11.68 ppm which is in the same region as the iminic proton resonance in osazones from α-dicarbonyls [14].

Direct synthesis of glyoxalanil-(1)-phenylhydrazone-(2) ligands with no substituent groups attached to either glyoxal carbon, by reaction of glyoxalmonophenylhydrazone with the appropriate amine produced a good yield (60–90%) of ligand. Yields and the ease of preparation of these ligands contrast sharply with the apparently low yields obtained in the preparation, by an azoic coupling reaction, of glyoxalanil-(1)-arylhydrazones-(2) with substituents attached to one or both glyoxal carbons [1–4]. No glyoxalanil-(1)-phenylhydrazone-(2) ligands of the type prepared, appear to have been reported previously. The ligands are readily prepared from methanol, ethanol, isopropanol or ether in the absence of a catalyst by the typical Schiff condensation. The ligands readily recrystallise from methanol or ethanol. The ligands, together with their analytical and IR spectral characteristics are listed in Table I. The broad, split and generally weak band in the NH region could be taken as an indication of hydrogen bonding and the existence of the ligands in tautomeric form I. The strong absorption in the region of 1600 cm^{-1} is tentatively assigned to the azomethine group but as this lies close to a complex region which appears as a result of phenyl ring vibrations, the azomethine group absorption could be at lower frequency.

Reduction of the anil-hydrazone ligands was undertaken with a view to studying the effect of reduction of the azomethine groups on the coordination of the ligands. However under the conditions

TABLE VI. Spectral Properties of Deprotonated Complexes, $[M(L-H)_2]$.

Complex	IR Spectra $\nu_{C=N}$ cm^{-1}	Electronic Spectra ν_{max}, kK		
		CH_2Cl_2 (ϵ_{max})[a]	Py	Solid State
$(GMPhA-H)_2Cu$	1595	14.7 (2260)	20.2; 17.9(sh)	14.5
$(GMPhBzA-H)_2Cu$	1595	16.1 (2300)	20.8; 18.9(sh)	--
$(GMPhpTA-H)_2Cu$	1595	14.7(2180)	20.2; 17.9(sh)	13.5; 19.3
$(GMPhmTA-H)_2Cu$	1600	14.7 (2000)	20.2; 17.9(sh)	14.0
$(GMPhoTA-H)_2Cu$	1595	15.2 (1910)	20.4; 17.9(sh)	14.5
$(GMPhpCA-H)_2Cu$	1595	14.3 (2040)	19.9; 17.5(sh)	14.2
$(GMPhoCA-H)_2Cu$	1590	15.4 (1740)	20.6; 17.9(sh)	14.4
$(GMPhpBA-H)_2Cu$	1590	14.6 (2310)	19.9; 17.5(sh)	14.4
$(GMPh\beta NA-H)_2Cu$	1595	14.6 (2300)	19.6; 17.8(sh)	13.8
$(GMPhoAn-H)_2Cu$	1593	15.4 (1790)	--	15.3
$(GMPhpAn-H)_2Cu$	1610	14.5 (2190)	20.3; 17.8(sh)	14.0
$(GMPhBzA-H)_2Co$	1597	15.9 (1036)	15.9	15.3
$(GMPhBzA-H)_2Ni$	1597	14.8(sh)	14.8(sh)	15.5

[a] ϵ expressed in litres mol^{-1} cm^{-1}. sh = shoulder.

used, the anil-hydrazone system cleaved on reduction producing aniline and an N-arylethylenediamine. The general applicability of the reduction reaction was not investigated but it appears that this reaction could provide a route to highly substituted N-arylethylenediamine systems using the vast range of substituted anil-hydrazone systems available as starting materials. To retain the anil-hydrazone system intact, conditions much milder than Raney nickel-hydrogen would have to be employed.

Deprotonated Complexes

Deprotonated complexes of glyoxalanil-(1)-phenylhydrazone-(2) ligands of the type $[M(L-H)_2]$ form readily in the case of copper(II) and far less readily in the case of cobalt(II) and nickel(II). Complexes which have been prepared together with analytical, magnetic and spectral characteristics are listed in Tables II, VI and VII. Attempts to prepare cobalt(II) and nickel(II) complexes from the range of ligands reported using a variety of reaction conditions resulted in the ligands being recovered largely unreacted in the case of cobalt(II) while intensely coloured resinous material was obtained from nickel(II) reactions. Only the simple anil and benzylanil complexes were obtained with cobalt(II) while the only nickel(II) complex obtained was derived from glyoxalbenzylanil-(1)-phenylhydrazone-(2). Reaction yields in the preparation of copper(II) complexes were good while the cobalt(II) and nickel(II) complexes were obtained in poor yield. The complexes were soluble in a range of polar and non polar solvents.

Analytical data indicates an empirical stoichiometry compatible with two deprotonated ligands per metal atom. The absence of bands in the N–H region of the infrared spectra of the complexes has been taken as an indication of deprotonation [15], the iminic proton from the hydrazine residue in the ligands having been removed. The strong band at or just below 1600 cm^{-1} has been tentatively assigned to the azomethine group. Compared with the free ligands, the azomethine band has, in general, shifted only marginally to a lower wave number, this observation being compatible with the observation of Kovavic [16] in his study of the infrared spectra of a series of salicylaldehydeanil complexes. The magnitude of the shift is small and is considered to be of no

TABLE VII. Magnetic Properties of Deprotonated Complexes, $[M(L-H)_2]$.

Complex	T °K	10^6 χ	10^6 χ_m^{corr}	μ_{eff} (BM)
$(GMPhA-H)_2Cu$	298.6	2.054	1310	1.77
$(GMPhBzA-H)_2Cu$	292.7	2.226	1484	1.87
$(GMPhpTA-H)_2Cu$	299.2	1.975	1349	1.80
$(GMPhmTA-H)_2Cu$	294.7	2.149	1443	1.85
$(GMPhoTA-H)_2Cu$	294.4	2.104	1418	1.83
$(GMPhpCA-H)_2Cu$	300.7	2.011	1416	1.85
$(GMPhoCA-H)_2Cu$	295.5	2.134	1532	1.97
$(GMPhpBA-H)_2Cu$	295.2	1.835	1545	1.92
$(GMPh\beta NA-H)_2Cu$	295.5	1.968	1523	1.91
$(GMPhoAn-H)_2Cu$	294.2	2.015	1445	1.85
$(GMPhpAN-H)_2Cu$	292.7	2.139	1515	1.89
$(GMPhBzA-H)_2Co$	293.2	14.45	7969	4.34
$(GMPhBzA-H)_2Ni$	295.2	7.453	4248	3.18

TABLE VIII. X-ray Powder Diffraction Data for Deprotonated Complexes, $[M(L-H)_2]$.

Complex	'*d*' Spacings (nm)
$(GMPhA-H)_2Cu$	1.15m, 0.9s, 0.7s, 0.6vw, 0.54vw, 0.48m, 0.42m, 0.35m, 0.33m, 0.30w.
$(GMPh*p*Ta-H)_2Cu$	1.3m, 1.2m, 0.95s, 0.66s, 0.58w, 0.52vw, 0.46vw, 0.43w, 0.41s, 0.36vw, 0.35w, 0.33vw, 0.30w.
$(GMPhBzA-H)_2Cu$	1.05s, 0.83s, 0.64m, 0.56m, 0.51vw, 0.46w, 0.38vw, 0.34s, 0.32w.
$(GMPh*o*TA-H)_2Cu$	1.30s, 0.73s, 0.68m, 0.64m, 0.53m, 0.46s, 0.36w, 0.34w, 0.33w, 0.32vw, 0.30vw.
$(GMPh*m*TA-H)_2Cu$[a]	1.40s, 0.95s, 0.66s, 0.58w, 0.46m, 0.43vw, 0.42m, 0.38s, 0.36w, 0.34m, 0.32m, 0.31m.
$(GMPh*p*CA-H)_2Cu$[a]	1.40s, 0.95vw, 0.66s, 0.58w, 0.53vw, 0.43s, 0.41m, 0.36m, 0.34s, 0.32w, 0.31vw
$(GMPh*o*CA-H)_2Cu$	1.35s, 1.0vw, 0.90s, 0.85s, 0.68s, 0.45vw, 0.41w, 0.37m, 0.34w, 0.32vw.
$(GMPh*p*BA-H)_2Cu$[a]	1.40vw, 1.0vw, 0.70vw, 0.66s, 0.54m, 0.48vw, 0.43s, 0.37s, 0.35s, 0.32w, 0.31w.
$(GMPh\beta NA-H)_2Cu$	1.20s, 0.80s, 0.68s, 0.58s, 0.50m, 0.45w, 0.43w, 0.38s, 0.36vw, 0.34vw, 0.33s.
$(GMPh*p*An-H)_2Cu$[a]	1.40s, 0.95vw, 0.66s, 0.58w, 0.53vw, 0.44s, 0.42m, 0.36w, 0.34m, 0.32w, 0.31w.
$(GMPh*o*An-H)_2Cu$	1.20s, 0.73s, 0.66s, 0.62w, 0.54vw, 0.44w, 0.36vw, 0.34w, 0.32vw.

[a]Similar diffraction patterns. s = strong; m = medium; w = weak; vw = very weak.

real significance. The region 600–250 cm^{-1} shows considerable complexity for both the ligands and the complexes and no attempt has been made to assign M–N bands.

For the copper complexes, magnetic moments lie in a range generally considered normal for copper(II) complexes [17] while the magnetic moment of the cobalt(II) complex lies in a range considered by West and coworkers [18] to be normal for tetrahedral cobalt(II) and is comparable with the moment reported by Spacu and coworkers [3] for similar cobalt(II) complexes for which tetrahedral structures have been assigned. The nickel(II) complex, being high spin paramagnetic appears to be the only high spin nickel(II) complex from these types of ligands which has been reported. The nickel(II) complexes reported by Spacu and coworkers [3] are diamagnetic being assigned a planar structure. The nickel(II) complex reported here is provisionally assigned a tetrahedral structure. Crystals of this complex have been grown from hexane–toluene solvent for an X-ray structure study to elucidate stereochemistry.

The electronic spectra for the complexes generally differ little between the solid state and solution in a non donor solvent indicating similar species being present both in solution and the solid state. In dichloromethane, the copper(II) complexes possess a broad single band around the 15 kK region, the broad single band in this region being considered compatible with a square planar or distorted square planar structure for the complexes [19]. In pyridine, the spectra of the copper(II) complexes change significantly. The broad single band around 15 kK disappears, being replaced by a bands which appears as a shoulder in the 18 kK region on a more intense band at 20 kK. This change is compatible with the addition of donor pyridine molecules, the coordination number of the copper increasing to five and perhaps six.

The addition of pyridine was slowest with the glyoxal-(*o*-anisidyl)-anil-(1)-phenylhydrazone-(2) copper(II) complex. This was probably due to a shielding of the fifth and sixth coordination sites of the copper by the bulky *ortho*-methoxy group in the anil residue of the ligand molecules. Crystals of this complex have been grown from hexane–methanol for a crystal structure study to elucidate stereochemistry of this complex. No attempt was made to isolate and study the pyridine adducts. The cobalt(II) and nickel(II) complexes do not appear to add pyridine, the spectra in dichloromethane being the same as the spectra in pyridine.

X-ray powder diffraction patterns of the deprotonated copper(II) complexes were taken. The *d*-spacings of significant lines are recorded in Table VIII. Complexes with similar diffraction patterns and hence possibily similar structures are indicated at the foot of the table.

Halo Complexes

The reaction of anil-hydrazone ligands either directly or under *in situ* conditions with copper(II) chloride or bromide produced highly coloured halo complexes in good yield. The halo complexes which have been prepared together with their analytical data are listed in Tables III and IV. The purity of the reaction product was variable from preparation to preparation with the purest complexes being obtained from the direct reaction of metal salt and ligand. The sparing solubility of the complexes in most solvents hindered purification attempts. The complexes were of variable stability in air with the chloro complexes

in general being less stable than the corresponding bromo complexes. In some instances the chloro complex did not precipitate and in the case of the glyoxal-(*o*-chloro)-anil-(1)-phenylhydrazone-(2) and glyoxal-(*m*-tolyl)-anil-(1)-phenylhydrazone-(2) ligands, the chloro complex decomposed immediately after isolation. The reaction of glyoxal-(*o*-tolyl)-anil-(1)-phenylhydrazone-(2) with copper(II) chloride produced a highly crystalline reaction product from which the stereochemistry of the complexes can possibly be elucidated by X-ray studies.

The analytical data indicates an empirical stoichiometry of $Cu_n(Lig)X_{n+1}$ where n = 2, 3 or 4 and X is halogen. With the complexes prepared, no clear relationship appears to exist between the nature of ligand and stoichiometry of the complexes formed although with the bromo compounds, where relatively bulky groups are *ortho* positioned in the anil residue, complexes with n = 3 or 4 appear to be preferred while with the chloro complexes, the presence of either an *ortho* or *para* positioned substituent on the anil residue in the ligand increases n from 2 to 3.

The infrared spectra of some of the complexes showed the presence of a band in the NH region at 3220 cm^{-1} indicating the ligand present in the complex is not deprotonated. A strong band also appeared in the azomethine region at 1650 cm^{-1}. Considering the ligand not being deprotonated and on the basis of stoichiometry from analytical data, these complexes could be formulated on the basis of containing copper of both oxidation states I and II and the complexes represented as $[Cu^{II}LigX_2][Cu^{I}X]_n$ where n = 1, 2 or 3. This infers that in the reaction between the ligand and the copper(II) halide, chelation and a redox reaction are in competition. This would account for the variable purity of the reaction product from preparation to preparation. No attempt was made at this time to follow these reactions by the possible isolation and identification of other reaction products. Complexes of this type from anil-hydrazone ligands do not appear to have been reported previously, although the formation of mixed oxidation state copper complexes involving hydrazine ligands has previously been observed [20] with the crystal structure of the copper complex of benzoylhydrazine containing mixed oxidation state copper having been reported [21].

The electronic spectra of the few complexes investigated are featureless in the region 12–22 kK, the spectra being dominated by an intense band which reaches from the UV region far into the visible. Magnetic measurements carried out on some bromo complexes indicate these complexes are essentially diamagnetic at room temperature. This would suggest the presence of a structural feature in these compounds such that copper(II) centres experience a strong pairwise antiferromagnetic interaction. At this stage, the structure of these compounds remains unsolved and is one for much conjecture.

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