Novel Ligational Behaviour of Thiosalicylohydrazide and its Derivatives with Cobalt(II), Nickel(II), Copper(II), and Palladium(II)

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The metal (Co^{II}, Co^{III}, Ni^{II}, Cu^{II}, and Pd^{II}) complexes of thiosalicylohydrazide, H_2L^1 [o-$HOC_6H_4C(=S)N^1$-$R^1N^2R^2R^3$, $R^1 = R^2 = R^3 = H$], and its derivatives H_2L^2 ($R^1 = H$, $R^2 = R^3 = Me$), HL^3 ($R^1 = Me$, $R^2 = R^3 = H$), H_2L^4 ($R^1 = R^2 = H$, $R^2 = Ph$), and HL^5 ($R^1 = Ph$, $R^2 = R^3 = H$) have been prepared and characterised. The compounds H_2L^1, H_2L^2, and H_2L^4 act as monobasic bidentate ligands {except in [$Pd(HL^4)_2$] where one ligand is bidentate and the other one is tridentate to form a five-co-ordinate neutral chelate} to form neutral chelates. Compounds HL^3 and HL^5 behave as both bi- and tri-dentate species and form four-co-ordinate cationic aquocobalt(II), aquo- and halogeno-copper(II), Zwitterionic palladium(II) chelates, and five-co-ordinate cationic halogenonickel(II) chelates. The chelating ligands show four types of co-ordination, *i.e.* N^1O, N^2S, OS, and N^2OS. The structural relationships of the complexes are discussed.

THE compounds $S=C(R)N^1H(N^2H_2)$ have long been of interest [1,2] as potential donor ligands towards transition metal ions. Both the organic ligands and their complexes with metals show a wide range of biological activity.[3-6] Jensen and Miquel [7] demonstrated the similarity of thiosemicarbazide to thiobenzohydrazide [8] with respect to complex chemistry and a large range of thiohydrazides including substituted thiohydrazides have been characterised.[9] However, examples of aliphatic thiohydrazides having α hydrogen atoms and the corresponding metal complexes are scanty [10-13] since these hydrazides undergo ring-closure reactions. Considerable research has been carried out on *NOO′* tridentate ligands but little is known about metal complexes of tridentate ligands which have oxygen, nitrogen, and sulphur donors.[14,15] Metal complexes of salicylohydrazide have been investigated extensively [16-18] but the complexes of analogous systems, *e.g.* thiosalicylohydrazide and its derivatives, are yet to be studied. Shome and co-workers [19,20] have, however, investigated the analytical behaviour of some selected thiohydrazides.

With the aim of exploring systematically the thiohydrazides, with respect to their potential donor sites, we now report on metal complexes of thiosalicylohydrazide (H_2L^1), N^2N^2-dimethylthiosalicylohydrazide (H_2L^2), N^1-methylthiosalicylohydrazide (HL^3), N^2-phenylthiosalicylohydrazide (H_2L^4), and N^1-phenylthiosalicylohydrazide (HL^5) and discuss their binding sites and structures on the basis of some of their physical properties.

EXPERIMENTAL

All chemicals were AnalaR grade. Elemental analyses (C, H, N, and halogen) were determined by the Microanalytical Section of the Australian Mineral Development Laboratories and by the microanalytical laboratory of this institute.

Infrared (KBr disc, 490—4 000 cm^{-1}), far-i.r. (Polythene discs, 100—400 cm^{-1}), and electronic (solution and Nujol mull) spectra were recorded using Beckman IR 20A, IR-720M, and Cary 17D spectrophotometers respectively. Hydrogen-1 n.m.r. spectra ($SiMe_4$ as calibrant) were obtained using a Varian EM-390 90-MHz instrument. Magnetic susceptibilities were determined at room temperature by the Gouy technique using $Hg[Co(SCN)_4]$ as standard. Diamagnetic correction was made using literature data.[21] Conductivity data were obtained using a Philips conductivity meter.

Preparation of Ligands.—Thiosalicylohydrazide (H_2L^1) *and* N^2N^2-*dimethylthiosalicylohydrazide* (H_2L^2). These were prepared following the method described by Jensen and Pedersen [9] starting from carboxymethyl *o*-hydroxydithiobenzoate.

N^1-*Methylthiosalicylohydrazide* (HL^3). This was prepared following the method for N^1-methylthiobenzohydrazide.[9]

N^2-*Phenylthiosalicylohydrazide* (H_2L^4). Carboxymethyl *o*-hydroxydithiobenzoate (1 mmol) dissolved in the minimum volume of sodium hydroxide (1 mol dm^{-3}) was added dropwise with stirring to freshly distilled phenylhydrazine (1 mmol). The resulting mixture was cooled and neutralised with hydrochloric acid (1 mol dm^{-3}). The product was extracted with chloroform. On addition of light petroleum (b.p. 60—80 °C) to a concentrated chloroform extract, the transparent crystals separated slowly.

N^1-*Phenylthiosalicylohydrazide* (HL^5). Carboxymethyl *o*-hydroxydithiobenzoate (1 mmol) was dissolved in Na[OH] (2 cm^3, 1 mol dm^{-3}) and excess of alkali was neutralised by HCl (1 mol dm^{-3}). This solution was added dropwise with stirring to the cooled phenylhydrazine hydrochloride (1 mmol) dissolved in the minimum volume of alkali (1 mol dm^{-3}). The resulting mixture was neutralised with HCl (1 mol dm^{-3}) and cooled. The product was extracted with chloroform. Light petroleum was added to the chloroform extract and the mixture kept on a water-bath. Fine transparent crystals separated out on cooling the concentrated solution.

Recrystallisation of Ligands.—The ligands are slightly soluble in hot water but very soluble in common organic solvents. The ligand H_2L^1 was recrystallised from benzene–light petroleum (1 : 1); H_2L^2 from ethanol; HL^3 from water–ethanol; and H_2L^4 and HL^5 from a mixture of chloroform and light petroleum (1 : 1).

Preparation of Complexes.—[$Co^{III}(HL^1)_3$], [$M(HL^1)_2$] (M = Ni^{II} *or* Cu^{II}), [$Co^{III}(HL^4)_3$], [$Ni(HL^4)_2$], *and* [$Cu^{II}(HL^4)_2(OH_2)$]. An ethanolic solution of metal(II) chloride (1 mmol) was added dropwise with stirring to an ethanolic solution of the ligand (3 mmol). The complex slowly crystallised and was filtered off, washed with ethanol, and dried. Complexes $[Co^{III}(HL^1)_3]$, $[Co^{III}(HL^4)_3]$, and $[Cu^{II}(HL^1)_2]$ were recrystallised from acetone, $[Ni^{II}(HL^1)_2]$ and $[Ni(HL^4)_2]$ from dimethylformamide–water (1 : 1), and $[Cu^{II}(HL^4)_2(OH_2)]$ from ethanol.

$[Pd(HL^1)_2]$, $[Pd(HL^3)_2]Cl_2$, *and* $[Pd(HL^4)_2]$. Ethanolic solutions of sodium tetrachloropalladate(II) (1 mmol) and ligand (2 mmol) were mixed. Fine yellow crystals separated out slowly while stirring the mixture. These were filtered off, washed several times with a small quantity of water to remove sodium chloride, and dried. The complexes were recrystallised from acetone, $[Pd(HL^1)_2]$; dimethylformamide–water (1 : 1), $[Pd(HL^4)_2]$; and water–ethanol (1 : 1), $[Pd(HL^3)_2]Cl_2$.

$[Pd(HL^2)_2]$ *and* $[Pd(HL^5)_2]Cl_2$. These were prepared in the same way as $[Pd(HL^1)_2]$. On occasions it was necessary to reflux the reaction mixture on a water-bath for 1 h instead of stirring. In order to isolate $[Pd(HL^5)_2]Cl_2$, light petroleum was necessary. Complex $[Pd(HL^2)_2]$ was recrystallised from chloroform and $[Pd(HL^5)_2]Cl_2$ from water–ethanol(1 : 1).

$[Co^{II}(HL^2)_2]$. An ammoniacal solution of cobalt(II) chloride (1 mmol) was mixed with an ethanolic solution of H_2L^2 (2 mmol). The fine brown crystals which separated out were filtered off, washed with ethanol, and dried. The complex was recrystallised from chloroform.

$[Ni^{II}(HL^2)_2]$, $[Cu^{II}(HL^2)_2]$, $[Ni^{II}(HL^3)_2Cl]Cl$, *and* $[Ni^{II}(HL^5)_2Cl]Cl$. Ethanolic solutions of metal(II) chloride (1 mmol) and ligand (2 mmol) were mixed. Shiny crystals separated while refluxing the mixture on a water-bath for *ca.* 1 h. These were filtered off, washed with ethanol, and dried. Complexes were recrystallised from chloroform, $[Ni^{II}(HL^2)_2]$ and $[Cu^{II}(HL^2)_2]$, and from water–ethanol (1 : 1), $[Ni^{II}(HL^3)_2Cl]Cl$ and $[Ni^{II}(HL^5)_2Cl]Cl$.

$[M^{II}L^3(OH_2)]Cl$ ($M = Co^{II}$ *or* Cu^{II}), $[Co^{II}L^5(OH_2)]Cl$, *and* $[Cu^{II}(HL^5)Cl]Cl$. Ethanolic solutions of metal(II) chloride (1 mmol) and ligand (1 mmol) were mixed and stirred for 1 h. Crystals of product separated out slowly while adding light petroleum dropwise to the mixture. These were filtered off, washed with chloroform, and dried. The complexes were recrystallised from water–ethanol (1 : 1).

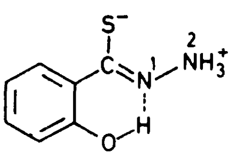
Preparation of Deuteriated H_2L^2, HL^3, HL^5, *and* $[Cu(HL^5)Cl]Cl$.—The compounds were refluxed for 30 min on a water-bath with D_2O (99.9%) and then the mixture was filtered. The solvent (D_2O) was evaporated off in a vacuum desiccator using a strong desiccating agent.

RESULTS AND DISCUSSION

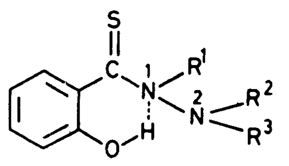
The analytical, magnetic, and conductance data are given in Table 1; ^1H n.m.r. data in Table 2; i.r. data in Table 3; and electronic spectral (solution and mull) data in Table 4.

Assignments of bands which signify metal–ligand bond formation were initially made from a comparison of the spectra with those of some known S,N-containing ligands and their metal complexes.[22-25] Confirmation of these assignments was obtained from a comparison of the vibrational spectra of the free ligands with those of the deuteriated ligands H_2L^2 and HL^5. The most significant differences to emerge were: (*i*) disappearance or weakening of $\nu(NH_2/NH)$, $\nu(OH)$, $\beta(NH_2/NH)$, $\delta(OH)$,[16,24] and $\rho_w(NH_2)$[24] vibrations as a consequence of the respective deuteriated vibrations which appear at wavenumbers of *ca.* 0.75 times those of the non-deuteriated bands and (*ii*) lowering[26] of $\nu(CS)$ by *ca.* 30 cm^{-1}.

A comparison of the vibrational spectra of the free ligand with those of their complexes leads to the following important observations: (*i*) lowering of $\nu(NH_2)$ accompanied by either disappearance[24] or weakening[24] of $\rho_w(NH_2)$ due to the co-ordination of the N^2 nitrogen; (*ii*) splitting[23] of the $\beta(NH_2/NH)$ band corresponding to involvement of the N^1 nitrogen in bonding; (*iii*) disappearance of $\nu(OH)$ and $\delta(OH)$, indicating the bonding of the *o*-hydroxy-oxygen and deprotonation; (*iv*) shift of the $\nu(CS)$ band towards lower frequency due to the presence of an M–S bond; and (*v*) the appearance of new bands in the far-i.r. region, which seem to be due to the vibrations of the M–Y (Y = S, N, O, or Cl) bond (Table 3).



(1) (H_2L^1)



(2; $R^1 = H$, $R^2=R^3=Me$) (H_2L^2)
(3; $R^1 = Me$, $R^2=R^3=H$) (HL^3)
(4; $R^1 = R^2=H$, $R^3=Ph$) (H_2L^4)
(5; $R^1 = Ph$, $R^2=R^3=H$) (HL^5)

The Ligands.—H_2L^1. The peak at δ 3.5 p.p.m. (N^2H_2) (in $[^2H_6]$dimethyl sulphoxide) is not observed in the ^1H n.m.r. spectrum in $[^2H_6]$chloroform at room temperature, although a signal at 4.4 p.p.m. $(N^2H_3^+)$, consistent with Zwitterionic[12] form (1), is observed. Structure (1) is identified by the absence of $\nu(SH)$ (*ca.* 2 600 cm^{-1}) and the presence of a broad i.r. band in the ranges 2 720—2 880 and 660—680 cm^{-1} in potassium bromide as well as in chloroform. The i.r. band (broad shoulder) at *ca.* 3 500 cm^{-1} and the ^1H n.m.r. signal at δ 11.16 p.p.m. (OH) indicate that the *o*-hydroxy-group is hydrogen bonded.

H_2L^2. The thionic form of the ligand is illustrated by the absence of $\nu(SH)$ in KBr and in chloroform. Absence of $\nu(OH)$ at *ca.* 3 500 cm^{-1} may be due to strong hydrogen bonding which probably shifts $\nu(OH)$ to lower frequency. Lowering of $\nu(N^1H)$ in the i.r. and the presence of the peak at δ 11.5 p.p.m. (N^1H) in the ^1H n.m.r. spectrum suggests structure (2) with intermolecular hydrogen bonding of N^1H.

HL^3. The spectral (i.r. and ^1H n.m.r.) data suggest structure (3) for this ligand with *o*-hydroxy-hydrogen in the shielded zone.

H_2L^4 *and* HL^5. Elemental analyses, melting points, ^1H n.m.r. and i.r. spectral data (see Tables 1—3) clearly indicate that these two ligands are positional isomers. The downfield shift of the signal δ 7.3 p.p.m. $(\gt N^1Ph)$ compared to that of δ 7.0 p.p.m. $(\gt N^2Ph)$ is due to the increased ring current arising from the greater extent of π delocalisation in HL^5 rings than in those of H_2L^4.

The analogous behaviour of the complexes of HL^3 and HL^5 with silver nitrate solution and the other similarities (see below) between these complexes clearly show that HL^5 has structure (5). Therefore, H_2L^4 has structure (4).

Table 1

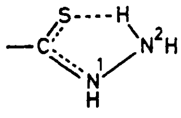
Conductance, magnetic, and analytical data

Compound	Colour	M.p. (θ_c/°C)	Λ [a]/ S cm^2 mol^{-1}		$\mu_{eff.}$/ B.M.	Analysis (%) [b] C	H	N	Cl	Metal
H_2L^1	White	101.3 [c]				49.75 (50.0)	4.60 (4.75)	16.45 (16.65)		
$[Co(HL^1)_3]$	Brown	203	7.0 [d]		*e*	45.3 (45.0)	3.85 (3.75)	14.9 (15.0)		10.6 (10.55)
$[Ni(HL^1)_2]$	Pale yellow	*f*	3.5 [d]		*e*	42.05 (42.8)	3.7 (3.55)	14.3 (14.25)		15.0 (14.95)
$[Cu(HL^1)_2]$	Brown	162	2.5 [d]		1.65	42.15 (42.25)	3.40 (3.50)	14.2 (14.1)		15.55 (16.0)
$[Pd(HL^1)_2]$	Yellow	*f*	2.8 [d]		*e*	38.25 (38.4)	3.20 (3.20)	12.5 (12.7)		24.5 (24.2)
H_2L^2	White	165.0 [c]				55.0 (55.1)	6.20 (6.15)	14.2 (14.3)		
$[Co(HL^2)_2]$	Brown	*f*	1.7 [g]		2.20	47.1 (48.1)	4.80 (4.90)	12.3 (12.45)		13.25 (13.15)
$[Ni(HL^2)_2]$	Pale yellow	*f*	4.0 [g]		*e*	48.2 (48.15)	4.75 (4.90)	12.35 (12.5)		13.1 (13.1)
$[Cu(HL^2)_2]$	Brown	*f*	2.5 [g]		1.68	47.2 (47.6)	4.90 (4.85)	12.5 (12.35)		13.9 (14.0)
$[Pd(HL^2)_2]$	Yellow	*f*	0.5 [g]		*e*	43.8 (43.5)	4.55 (4.45)	11.1 (11.25)		21.85 (21.5)
HL^3	White	112.9 [c]				51.95 (52.75)	5.30 (5.50)	15.6 (15.4)		
$[CoL^3(OH_2)]Cl$	Green	205	125.0 [h]	104.0 [i]	2.05	32.65 (32.7)	3.80 (3.75)	9.30 (9.55)	12.3 (12.1)	19.95 (20.1)
$[Ni(HL^3)_2Cl]Cl$	Green	*f*	140.0 [h]	105.0 [i]	3.20	38.65 (38.9)	4.00 (4.05)	11.15 (11.35)	14.15 (14.35)	11.75 (11.9)
$[CuL^3(OH_2)]Cl$	Green	150	119.0 [h]	80.0 [i]	1.65	32.5 (32.2)	3.75 (3.70)	9.50 (9.40)	11.75 (11.9)	21.5 (21.3)
$[Pd(HL^3)_2]Cl_2$	Yellow	*f*	245.0 [h]	76.0 [i]	*e*	36.0 (35.45)	4.05 (3.70)	10.2 (10.35)	12.8 (13.1)	19.2 (19.65)
H_2L^4	White	71.8 [c]				62.55 (63.95)	5.20 (4.90)	11.4 (11.45)		
$[Co(HL^4)_3]$	Black	187	0.7 [j]		*e*	58.2 (59.4)	3.95 (4.20)	10.2 (10.65)		7.60 (7.50)
$[Ni(HL^4)_2]$	Grey	165	0.3 [j]		*e*	57.1 (57.3)	4.05 (4.05)	9.95 (10.3)		10.4 (10.8)
$[Cu(HL^4)_2(OH_2)]$	Green	144	0.5 [j]		1.69	54.4 (55.0)	4.10 (4.25)	9.75 (9.85)		11.35 (11.2)
$[Pd(HL^4)_2]$	Brown	200	0.2 [j]		*e*	52.85 (52.65)	4.05 (3.70)	9.05 (9.45)		17.7 (17.95)
HL^5	White	117.6 [c]				64.75 (63.95)	5.05 (4.90)	11.15 (11.45)		
$[CoL^5(OH_2)]Cl$	Green	172	130.0 [h]	93.0 [i]	2.10	43.25 (43.9)	3.80 (3.65)	7.60 (7.90)	10.05 (10.0)	16.4 (16.6)
$[Ni(HL^5)_2Cl]Cl$	Pale yellow	190	139.0 [h]	109.0 [i]	3.35	50.2 (50.5)	3.80 (3.90)	8.65 (9.05)	11.15 (11.5)	9.45 (9.50)
$[Cu(HL^5)Cl]Cl$	Green	138	132.0 [h]	97.0 [l]	1.60	41.3 (41.2)	3.30 (3.15)	7.05 (7.40)	17.1 (18.75)	16.5 (16.8)
$[Pd(HL^5)_2]Cl_2$	Yellow	240.0	240.0 [h]	89.0 [i]	*e*	47.35 (46.9)	3.55 (3.60)	7.60 (8.40)	11.05 (10.65)	16.1 (16.0)

[a] *ca.* 10^{-3} mol dm^{-3} solution. [b] Calculated values are given in parentheses. [c] Melts without decomposition. [d] In dimethylformamide. [e] Diamagnetic. [f] Decomposes above 225 °C. [g] In acetone. [h] In water. [i] In methanol. [j] In nitrobenzene.

Complexes of H_2L^1.—On treatment of H_2L^1 with a cobalt(II) salt in ethanolic solution a brown crystalline compound is formed. Elemental analyses and magnetic data clearly show that Co^{II} is oxidised during complexation [27-29] forming $[Co^{III}(HL^1)_3]$. Hydrogen-1 n.m.r. and i.r. spectral data suggest bonding through N and O. Structure (1a) is supported by the presence of the spin-allowed transition ($^1A_{1g} \rightarrow {}^1T_{1g}$) in the range 17 500—23 000 cm^{-1} of the absorption spectra (in solution and in mull) for the CoN_3O_3 [30] chromophore. The doublet at 760 and 740 cm^{-1} of H_2L^1 assigned [22] to ν(CS) collapses to a singlet in the complex due to delocalisation, while the weakening of $\rho_w(NH_2)$ is probably due to the hydrogen bonding of N^2H_2. The above observations suggest that the thiohydrazide unit in (1a) exists in the form (I).

Treatment of the ligand with nickel(II) and copper(II) salts in ethanol affords crystalline pale yellow and brown compounds respectively, whose elemental analyses correspond to the formulation $[M^{II}(HL^1)_2]$ (M = Ni or Cu). The spectral (i.r. and ^1H n.m.r.) properties of



(I)

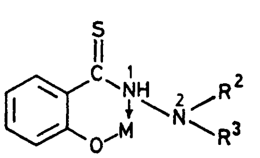
TABLE 2

Proton n.m.r. spectral data (δ/p.p.m.)[a]

Compound	Ring protons	CH_3	N^2H_2	N^1H	OH
H_2L^1 [b]	7.2 (m, 4)		4.4 (br s, 3)[c]		11.16 (br s, 1)[c]
H_2L^1 [d]	7.1 (m, 3), 8.3 (d, 1)		3.5 (br s, 2)[c]	10.65 (br s, 1)[c]	11.23 (br s, 1)[c]
$[Co(HL^1)_3]$ [e]	6.9 (m), 7.3 (m), 8.3 (m) (12)		6.0— 9.0 (br, 9)[c]		
$[Ni(HL^1)_2]$ [f]	7.0 (m), 7.3 (m), (6); 8.6 (d, 2)		7.90— 10.66 (vbr, 4)[c]	11.16— 13.16 (vbr, 2)[c]	
$[Pd(HL^1)_2]$ [g]	7.0 (m, 4), 7.4 (m, 2), 8.2 (d, 2)		9.0 (s, 2)[c]	12.0 (s, 2)[c]	12.3 (s, 2)[c]
H_2L^2 [d]	6.8 (m), 7.1 (m), (3); 8.2 (d, 1)	3.1 (s, 6)		11.6— 12.1 (vbr, 2)[c]	
H_2L^2 [b]	6.8 (m), 6.98 (m), (3); 8.4 (d, 1)	3.1 (s, 6)		11.5 (br s, 1)[c]	12.4 (br s, 1)[c]
$[Ni(HL^2)_2]$ [b]	7.02 (m, 4), 7.32 (m, 2), 8.20 (d, 2)	3.0 (s, 12)		11.26 (2)	
$[Pd(HL^2)_2]$ [b]	7.0 (m, 4), 7.3 (m, 2), 8.25 (d, 2)	3.27 (s, 12)			7.8— 8.5 (br, 2)[c] 7.8 (br s, 1)[c]
HL^3 [b]	7.1 (m, 3), 7.3 (m, 1)	3.5 (s, 3)	6.03 (br s, 2)[c]		
$[Pd(HL^3)_2]Cl_2$ [h]	7.1 (m), 7.3 (m) (8)	3.5 (m, 6)[i]	4.85 (br s, 6)[c]		
H_2L^4 [b]	7.0 (m, 5), 7.3 (m, 3), 7.56 (d, 1)		6.60 (br s, 2)[c]		8.5 (br s, 1)[c]
$[Ni(HL^4)_2]$ [f]	7.3 (br s), 7.6 (br s), 8.8 (br s) [j]			9.1— 11.6 (vbr)[c]	
$[Pd(HL^4)_2]$ [f]	7.13 (s, 10), 7.30 (s, 6), 8.56 (br s, 2) [j]		8.1— 9.8 (vbr, 3)[c]		10.26 (br s, 1)[c]
HL^5 [b]	6.60 (m, 2), 7.03 (m, 2), 7.30 (s, 5)		6.33 (br s, 2)[c]		8.3 (br s, 1)[c]
$[Pd(HL^5)_2]Cl_2$ [f]	6.22 (s, 10), 7.16 (m, 6), 7.60 (m, 2)		6.22 (s, 6)[c,k]		

[a] Relative to $SiMe_4$, solvent as stated. [b] In $[^2H_1]$chloroform. [c] Signal disappears on shaking with deuteriated water. [d] In $[^2H_6]$dimethyl sulphoxide. [e] In $[^2H_6]$acetone. [f] In $[^2H_5]$pyridine. [g] In $[^2H_6]$dimethyl sulphoxide–$[^2H_6]$acetone. [h] In $[^2H_6]$-dimethyl sulphoxide–$[^2H_5]$pyridine. [i] Persistence of multiplet (m) of methyl protons on shaking with deuteriated water. [j] Signals of the solvent broaden due to co-ordination of solvent to the metal ion. [k] Signal at 6.22 p.p.m. shifts to 5.83 p.p.m. on deuteriation.

$[Ni(HL^1)_2]$ suggest that the bonding is analogous to that in $[Co(HL^1)_3]$, (1a). The diamagnetic character and the mull spectrum support square-planar geometry whilst the

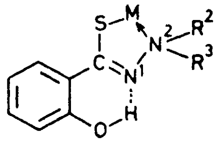


(1a; $M = \frac{1}{3}Co^{III}$ or $\frac{1}{2}Ni^{II}, R^2 = R^3 = H$)

(2a; $M = \frac{1}{2}Co^{II}$ or $\frac{1}{2}Ni^{II}, R^2 = R^3 = Me$)

presence of an absorption band (in solution) above 12 500 cm^{-1} indicates the formation of six-co-ordinate species.[31] The bands of the solution absorption spectrum are tentatively assigned[32,33] as $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$, $^3A_{2g} \rightarrow {}^1T_{1g}$ (P), and charge transfer + $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) on the basis of O_h symmetry.

The i.r. spectrum of $[Cu(HL^1)_2]$ suggests bonding through N and S, (1b), with delocalisation, consistent with the *d–d* interaction of a sulphur donor atom with copper(II) ion.[34,35] The low magnetic moment found for the copper complex is likely to arise from Cu–Cu interaction in the solid.* The absorption band at *ca.* 12 000 cm^{-1} (in solution and mull) is probably due to considerable distortion of tetrahedral towards square-planar geometry.[36,37]



(1b; $M = \frac{1}{2}Cu^{II}$ or $\frac{1}{2}Pd^{II}, R^2 = R^3 = H$)

(2b; $M = \frac{1}{2}Cu^{II}$ or $\frac{1}{2}Pd^{II}, R^2 = R^3 = Me$)

(4a; $M = \frac{1}{3}Co^{III}$ or $\frac{1}{2}Ni^{II}, R^2 = H, R^3 = Ph$)

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* As pointed out by one of the referees.

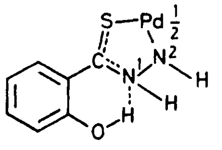
TABLE 3

Infrared spectral data [a] (cm^{-1})

Compound	$\nu(OH)$	$\nu(NH_2)$ and/or $\nu(NH)$	$\beta(NH_2)$/ (NH) + $\nu(CN)$	$\delta(OH)$	$\rho_w(NH_2)$	$\nu(CS)$ + $\nu(NH)$ + $\nu(CN)$	$\nu(MN)$	$\nu(MS)$	$\nu(MO)$
H_2L^1	3 520w,br (sh)	3 240s, 2 880— 2 720m,br [b]	1 462s	1 350m	935s	760vs, 740vs			
$[Co(HL^1)_3]$		3 100s,br	1 480vs, 1 440m		935w	748s	500m		300m
$[Ni(HL^1)_2]$		3 200s	1 482vs, 1 445m		935w	750s	412s		292s
$[Cu(HL^1)_2]$	3 440m,br	2 900m,br	1 475s	1 360m	935w	742s	585m	350m	
$[Pd(HL^1)_2]$	3 440m,br	3 140s,br, 2 900m,br	1 480s	1 360m	935w	740s	495m	370m	
H_2L^2		2 875m,br	1 470s,br	1 368s		765vs,br, 710vs			
H_2L^2 [c]		2 190m,br	1 470s, 1 140s	1 035m (sh)		765vs, 712vs, 708s (sh)			
$[Co(HL^2)_2]$			1 542s, 1 480s			755vs, 740vs	520m		290m
$[Ni(HL^2)_2]$			1 535s, 1 480s			750vs, 730vs	540m		302s
$[Cu(HL^2)_2]$			1 507s, 1 472s	1 375s		740s, 710vs	555m, 515m	370m	
$[Pd(HL^2)_2]$			1 540s, 1 450s, 1 470m	1 375s		758vs, 740vs, 730s	520m	380m	
HL^3	3 500br (sh)	3 260s, 3 200s	1 550s	1 370m (sh)	890s	765s (sh), 735s			
HL^3 [c]	2 700br	2 435s, 2 390s	1 148s	1 030m (sh)	895w	740s (sh), 745s			
$[CoL^3(OH_2)]Cl$ [d]	3 400s,br	3 100s,br	1 600s,br			750s	500 (sh)		306vbr
$[Ni(HL^3)_2Cl]Cl$ [e]	3 350s	3 180s	1 570s	1 360m	890w	745vs	454m	412m	
$[CuL^3(OH_2)]Cl$ [f]	3 400s,br	3 100s,br	1 610s,br			750s	470m	390 (sh)	370w,br
$[Pd(HL^3)_2]Cl_2$		3 240s, 2 850— 2 700s,br [b]	1 630vs [g]			742s	600m		475m
H_2L^4		3 240 (sh), 3 170s,br, 3 050 (sh), 2 920m	1 510s, 1 470s	1 350m		765s, 705m			
$[Co(HL^4)_3]$	3 420s,br	3 190m,br, 3 150 (sh)	1 475s,br	1 350s		730s, 680m	490m	350m	
$[Ni(HL^4)_2]$		3 040s	1 522m, 1 485s, 1 470s	1 350m		760s, 690m	424s	365s, 236s	
$[Cu(HL^4)_2(OH_2)]$ [h]	3 450s,br	3 060m, 2 930m,br	1 485s, 1 470s			745s, 685m	440m (sh)		335m, 310m
$[Pd(HL^4)_2]$	3 440m,br	3 160s	1 522m, 1 485s, 1 470s	1 347m		762vs, 720m, 690s	520s	384vs	412m
HL^5	3 450m,br	3 300vs, 3 170m,br	1 580s	1 380m	900vs	800s, 763s, 750s			
HL^5 [c]		2 480s, 2 350br	1 580m, 1 175m	1 020m	900m	773s, 760vs			
$[CoL^5(OH_2)]Cl$ [i]	3 360s,br	3 250— 2 900s,br	1 600s			745s	510m (sh)	350m,br	470m,br
$[Ni(HL^5)_2Cl]Cl$ [j]	3 400s,br	3 250— 3 000s,br	1 605vs			768s	470m	410m	
$[Cu(HL^5)Cl]Cl$ [k]	3 600 (sh), 3 540 (sh), 3 500m, 3 420s,br	3 200— 3 000s,br	1 605s			750s	470m (sh)	370m	350w
$[Pd(HL^5)_2]Cl_2$		3 250— 2 700s,br [b]	1 605s,br [f]			758s	500m (sh)		485m

[a] s = Strong, m = medium, br = broad, sh = shoulder, w = weak. [b] $\nu(NH_3^+)$. [c] Deuteriated. [d] $\delta(HOH)$, $\rho_w(HOH)$, and $\rho_r(HOH)$ at 1 620m (sh), 580vbr, and 450w,br cm^{-1} respectively. [e] $\nu(NiCl)$ at 318vs, 304s, 250s, and 220s cm^{-1}. [f] $\delta(HOH)$, $\rho_w(HOH)$ and $\rho_r(HOH)$ at 1 620m (sh), 618m, and 460 cm^{-1} respectively. [g] $\delta_d(NH_3^+)$. [h] $\delta(HOH)$, $\rho_w(HOH)$, and $\rho_r(HOH)$ at 1 635m, 600m,br, and 410m, br cm^{-1} respectively. [i] $\delta(HOH)$ at 1 615m cm^{-1}. [j] $\nu(NiCl)$ at 350 m cm^{-1}. [k] $\delta(MOH)$ at 1 190m shifts to 935m cm^{-1} on deuteriation. $\nu(CuCl)$ at 320m,br cm^{-1}.

Addition of $Na_2[PdCl_4]$ to H_2L^1 in ethanol immediately produces yellow crystalline $[Pd(HL^1)_2]$. The ν(CS), $\beta(NH_2)$, $\rho_w(NH_2)$, ν(Pd–S), and ν(Pd–N) bands in the i.r. spectrum suggest bonding through N^2 and S. The presence of a broad ν(OH) band indicates the hydrogen-bonded *o*-hydroxy-group. Hydrogen-1 n.m.r. data indicate two tautomeric forms, (1b) and (1c), as suggested in bis(thioacetohydrazidato)nickel(II).[10] However, (1c) is the preferred form since the assignments (Table 2) of the *N*-bound protons are consistent with the electron density around the N^1 nitrogen being less than that around N^2 in the five-membered chelate ring, resulting in the N^1-bound proton being more deshielded. A band in the absorption spectrum at *ca.* 23 000 cm⁻¹ assigned as $^1A_g \rightarrow {}^1B_{1g}$ is probably due to the square-planar geometry of the complex.



(1c)

TABLE 4

Electronic spectral data (cm⁻¹)

Compound	Solution spectra		Mull spectra (Nujol)
	Medium *	Absorbance (ε/dm³ mol⁻¹ cm⁻¹)	Arbitrary absorbance
$[Co(HL^1)_3]$	dmso	9 259(41), 12 345(64), 19 048 (sh) (2 400), 23 923 (4 100)	9 615 (sh), 17 241 (sh), 21 739
$[Ni(HL^1)_2]$	dmso	10 638(200), 12 820(400), 18 182 (sh) (110), 20 080 (sh) (150), 22 727 (sh) (260)	16 260 (sh), 23 810 (sh)
$[Cu(HL^1)_2]$	dmso	12 195 (sh) (70), 25 000(360)	12 121 (sh), 24 390 (sh)
$[Pd(HL^1)_2]$	dmso	22 727(360)	
$[Co(HL^2)_2]$	Acetone	15 873(74), 20 618 (sh) (265), 24 390 (sh) (950)	8 403s, 12 121 (sh), 18 519 (sh), 27 027 (sh)
$[Ni(HL^2)_2]$	Chloroform	16 393(36), 21 978(103)	
$[Cu(HL^2)_2]$	Chloroform	14 286br(140), 18 868 (sh) (70), 25 000 (sh) (700), 26 316(680)	
$[Pd(HL^2)_2]$	Chloroform	22 988(90)	
$[CoL^3(OH_2)]Cl$	Methanol	15 873(1 200), 19 231 (sh) (990), 25 000 (sh) (3 000)	8 264 (sh), 10 000 (sh), 11 905 (sh), 14 285 (sh), 16 393 (sh), 27 778 (sh)
$[Ni(HL^3)Cl]Cl$	Methanol	9 901 (sh) (23), 10 869(27), 12 195 (sh) (23), 16 667(32), 24 390 (sh) (480)	10 204, 16 000br, 22 727 (sh)
$[CuL^3(OH_2)]Cl$	Methanol	9 091br (78), 20 833(1 200), 26 216 (sh)(3 200)	11 765, 20 833
$[Pd(HL^3)_2]Cl_2$	H_2O	22 222 (sh) (190)	
$[Co(HL^4)_3]$	dmf	10 000 (sh) (680), 12 658(1 820), 17 544 (sh) (3 400), 22 222 (sh) (9 300)	9 523 (sh), 12 500 (sh), 16 667, 27 397
$[Ni(HL^4)_2]$	dmf	15 385 (sh) (1 400), 17 857 (sh) (2 200), 22 988 (11 500)	12 500 (sh), 16 949 (sh), 21 739 (sh), 27 397 (sh)
$[Cu(HL^4)_2(OH_2)]$	dmf	10 101 (sh) (365), 12 048 (sh) (990), 14 706 (sh) (1 400), 23 256 (sh) (8 600), 27 397 (sh) (13 000)	8 928 (sh), 10 000 (sh), 13 514 (sh), 22 222 (sh)
$[Pd(HL^4)_2]$	dmf	7 353(2 400), 12 821(100), 16 667 (sh) (1 100), 18 182 (sh) (1 800), 19 608 (sh) (3 600), 21 739(5 000), 27 778(27 300)	7 380, 11 364, 18 519br (sh), 25 000 (sh)
$[CoL^5(OH_2)]Cl$	Methanol	16 393(770), 20 202 (sh) (1 100), 24 096 (sh) (4 700)	8 474, 11 111 (sh), 22 727 (sh), 27 397
$[Ni(HL^5)_2Cl]Cl$	Methanol	10 204 (sh) (32), 13 423(210), 15 625 (sh) (170), 21 739 (sh) (980), 27 027 (sh) (5 300)	9 524 (sh), 11 765, 16 667 (sh), 21 277 (sh), 27 778 (sh)
$[Cu(HL^5)Cl]Cl$	Methanol	9 524 (sh) (65), 13 889(180), 19 608 (sh) (1 700),	10 000 (sh), 14 285, 22 222
$[Pd(HL^5)_2]Cl_2$	Methanol	20 408 (sh) (250)	

* dmso = Dimethyl sulphoxide, dmf = dimethylformamide.

Complexes of H_2L^2.—Treatment of an ammoniacal solution of cobalt(II) chloride with an ethanolic solution of H_2L^2 afforded a brown crystalline compound of formula $[Co^{II}(HL^2)_2]$. Infrared data suggest bonding through N^1 and O, (2a). The absorption band (in mull) of $[Co(HL^2)_2]$ near 20 000 cm⁻¹ is similar to that exhibited by other cobalt(II) square-planar complexes.[38-41] The weak absorption band (in mull) at 8 403 cm⁻¹ is characteristic of a square-planar cobalt(II) species[42-44] which is further supported by the magnetic moment (2.20 B.M.*).[45] On the other hand, the ligand-field spectrum in solution displays O_h symmetry due to co-ordination of two solvent molecules, with a band near 16 000 cm⁻¹ attributed[36,42,46] to $^4T_{1g}\ (F) \rightarrow {}^4T_{1g}\ (P)$ in admixture with a spin-forbidden transition to the doublet state.

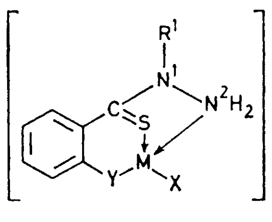
The addition of H_2L^2 to metal(II) (Ni, Cu, or Pd) salts in ethanol gave $[M^{II}(HL^2)_2]$. The very low upfield shift of two Me protons and absence of OH signal in $[Ni(HL^2)_2]$ are presumably attributable to the bonding through oxygen and N^1 nitrogen, where the bound proton is less deshielded than that in H_2L^2. The positive shift of the band at 1 470 cm⁻¹ [β(NH) + ν(CN)] and the absence of the band at *ca.* 1 370 cm⁻¹ [δ(OH)[16,24] + other mode of vibration[12]] in the i.r. spectrum also support N^1O bonding, (2a). The diamagnetism suggests a square-planar geometry which is also retained in solution, as is evident from absorption spectra (Table 4) where the bands are tentatively assigned as $^1A_g \rightarrow {}^1B_{1g}$ and $^1A_g \rightarrow {}^1B_{3g}$, based on D_{2h} microsymmetry (local symmetry about Ni).[47]

The bonding sites in $[Cu(HL^2)_2]$, (2b), appear to be similar to those in $[Cu(HL^1)_2]$ on the basis of i.r. spectral

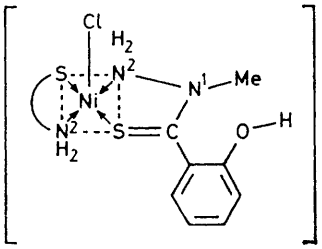
* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m².

data. However, comparison of the i.r. spectra of H_2L^1, H_2L^2, and the respective copper(II) complexes indicates that the delocalisation in $[Cu(HL^1)_2]$ is absent in $[Cu(HL^2)_2]$. Other physical properties correspond well to those of $[Cu(HL^1)_2]$.

In the case of $[Pd(HL^2)_2]$, (2b), Pd–N^2 bonding is inferred from the downfield shift of Me protons on complex formation. The Pd–S bond is indicated by the negative shift of ν(CS) in the i.r. spectrum. The upfield shift of the OH signal compared to that of the free ligand in ^1H n.m.r. and the absence of ν(OH) at *ca.* 3 500 cm^{-1} in the i.r. spectra seem to be due to the existence of a hydrogen-bonded OH group in the shielded zone. A similar absorption spectrum to that of $[Pd(HL^1)_2]$ suggests that a similar geometry exists in $[Pd(HL^2)_2]$.



(3a; M = Co^{II} or Cu^{II}, R^1 = Me, X = H$_2$O, Y = O)
(5a; M = Co^{II}, R^1 = Ph, X = H$_2$O, Y = O)
(5c; M = Cu^{II}, R^1 = Ph, X = Cl, Y = OH)

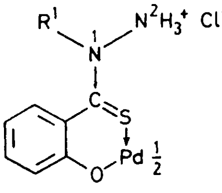


(3b)

Complexes of HL^3.—Treatment of HL^3 with cobalt(II) or copper(II) salts in ethanol, followed by light petroleum, produced green compounds which on the basis of elemental analyses and conductance data (1 : 1 electrolyte) can be formulated as $[ML^3(OH_2)]Cl$, (3a), with tridentate monobasic character of the ligand. The magnetic moments of these compounds are very close to the values of $[M^{II}(HL^2)_2]$ (M = Co or Cu). The δ(OH), $\rho_w(NH_2)$, and ν(CS) bands (Table 3) suggest *O*, N^2, and *S* bonding, while the very broad band at 3 400 cm^{-1} and shoulder at *ca.* 1 620 cm^{-1} support the presence of a water molecule which probably takes part in co-ordination as suggested [48,49] by the ρ_w(HOH) and ρ_r(HOH) bands in the far-i.r. region (Table 3). The geometry of $[Cu^{II}L^3(OH_2)]Cl$ in the solid state is similar to that of $[Cu^{II}(HL^1)_2]$, as evident from the similar absorption bands in the mull spectra, whilst less distorted tetrahedral geometry [36,50] is suggested to prevail in solution because of the absence of any absorption band in the range 10 000—20 000 cm^{-1}. The vibrational spectral properties of $[Co^{II}L^3(OH_2)]Cl$ are analogous to those of $[Co^{II}(HL^2)_2]$, inferring the existence of similar geometries in both systems.

Refluxing a mixture of nickel(II) chloride and HL^3 in ethanol on a water-bath produces a green compound. The elemental analyses and conductance data (1 : 1 electrolyte in water as well as in methanol) correspond to the formulation $[Ni(HL^3)_2Cl]Cl$. The electronic spectral data (Table 4) fit well to C_{4v} symmetry,[51] (3b) ,which is also corroborated by the magnetic moment.[52] The $\nu(NH_2)$, $\beta(NH_2)$, $\rho_w(NH_2)$, and ν(CS) bands in the i.r. spectrum suggest bonding through N^2 and S sites of the ligand, while the presence of sharp ν(OH) (3 350 cm^{-1}) and δ(OH) (1 360 cm^{-1}) bands indicates the free (not hydrogen-bonded) OH group. Bands in the region 220—320 cm^{-1} of the far-i.r. spectrum support Ni–Cl bonding, resulting in the vibration ν(Ni–Cl) (*ca.* 230br cm^{-1}).[53]

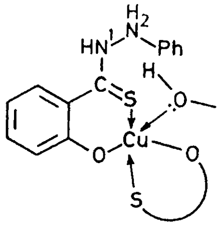
On prolonged stirring of a mixture of ethanolic solutions of $Na_2[PdCl_4]$ and HL^3, yellow crystals were formed of $[Pd(HL^3)_2]Cl_2$. The conductance data in methanol and in water show the complex to be a 1 : 1 and 1 : 2 electrolyte in the respective solvents. This is probably due to the formation of an ion pair (in non-aqueous media) which is separated in a high dielectric solvent such as water. The geometry of the complex is similar to that of $[Pd(HL^1)_2]$ as evident from the identical absorption spectrum in solution. The ^1H n.m.r. spectrum accounts for 20 protons, representing two ligands without deprotonation. The absence of Pd–N bonding is inferred from the non-shift of the signal for Me protons on complex formation. On the other hand, the splitting of the Me signal and the persistence of splitting even on deuteriation reveal that coupling between Me and ring protons is occurring, which is possible if Me protons lie environmentally and stereospecifically in the region of the ring protons. The occurrence of exchangeable protons at δ 4.8 p.p.m. reveals the existence of protons in the same environment, *e.g.* $N^2H_3^+$ as observed in thioacetohydrazide.[12] The $\nu(NH_3^+)$ and $\delta_d(NH_3^+)$ bands in the i.r. spectrum also support the Zwitterionic form [54,55] with intermolecular hydrogen bonding. The negative shift of ν(CS) by 23 cm^{-1} and the absence of ν(OH) and δ(OH) are consistent with *OS* bonding, (3c).



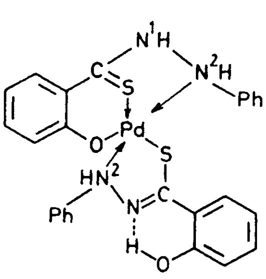
(3c; R^1 = Me)
(5d; R^1 = Ph)

Complexes of H_2L^4.—Treatment of a cobalt(II) salt with H_2L^4 in ethanol resulted in $[Co^{III}(HL^4)_3]$ which is similar to $[Co^{III}(HL^1)_3]$, (1a), except for the bonding sites (S, N^2), (4a), as evident from the negative shift of ν(NH) and ν(CS) in the i.r. spectrum, and by the presence of a spin-allowed transition in the range 17 500—18 500 cm^{-1} due to the $Co^{III}N_3S_3$ chromophore.[56] The non-splitting of the β(NH) band is probably due to more delocalisation along $C \cdots N^1 \cdots N^2$.

Diamagnetic pale yellow $[Ni(HL^4)_2]$ was synthesised by the method adopted for $[Ni(HL^1)_2]$. The bonding sites (N^2,S) appear to be similar to those in $[Co^{III}(HL^4)_3]$, (4a), on the basis of spectral evidence (i.r. and ^1H n.m.r.). The broadness of the solvent ([$^2H_5$]pyridine) signals is possibly due to the axial co-ordination of solvent.[57] In contrast, the absence of an absorption band (in dimethylformamide) above 14 285 cm^{-1} is indicative of the non-existence of six-co-ordinate species. The two low-energy bands with high intensity are due to overlapping of the *d→d* transitions in square-planar geometry with the charge-transfer bands. The similar absorption band positions in the solid (mull) support the proposed geometry.



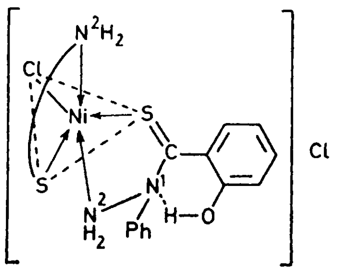
(4b)



(4c)

The addition of H_2L^4 to copper(II) chloride in ethanol afforded green $[Cu(HL^4)_2(OH_2)]$. The negative shift of ν(CS), the existence of ν(OH) as well as δ(HOH), and the absence of δ(OH) in the i.r. spectrum suggest *OS* bonding, (4b). The bands at 600 and 410 cm^{-1} are probably due to the vibrations of a co-ordinated water molecule.[48,49] The lowest-energy band at *ca.* 10 000 cm^{-1} (in solution and in mull) is probably due to the strong field strength of a S,N-ligand. The spectra support trigonal bipyramidal geometry [27,36] although it is difficult to identify a five-co-ordinate copper(II) complex from the absorption spectrum alone.

The addition of two equivalents of H_2L^4 to an ethanolic solution of $Na_2[PdCl_4]$ gave a brown precipitate of $[Pd(HL^4)_2]$, (4c), containing one tridentate ligand and one bidentate ligand as evident from the neutral chelating character and from the absorption spectra (in solution and in mull) which accord with a five-co-ordinate geometry by comparison with the spectra of five-co-ordinate nickel(II) [52] and palladium(II) [58] complexes. The ^1H n.m.r. spectrum reveals that deprotonation occurs from the SH group (one ligand) and from the OH group (another ligand). The Pd–N^2 bonding is inferred from the downfield shift (0.13 p.p.m.) of N^2–phenyl ring protons. The involvement of sulphur atoms in two different environments [23] in the complex is further supported by the splitting of the ν(CS) band in the i.r. spectrum. The broad ν(OH) and δ(OH) bands imply the presence of a hydrogen-bonded hydroxy-group.



(5b)

Complexes of HL^5.—Complexes of HL^5 with Co^{II} and Cu^{II} were prepared by the method employed for the synthesis of $[Co^{II}L^3(OH_2)]Cl$, (3a). The physical properties of the complex $[Co^{II}L^5(OH_2)]Cl$, (5a), are very similar to those of (3a), whereas the copper(II) complex corresponds to the formulation $[Cu(HL^5)Cl]Cl$, on the basis of elemental analysis and conductance data (1 : 1 electrolyte in methanol and water). The splitting of ν(OH), the presence of δ(MOH) at 1 190 cm^{-1} which shifts to 935 cm^{-1} on deuteriation,[59] and the absence of δ(OH) at *ca.* 1 380 cm^{-1} are attributed to the involvement of *o*-hydroxy-oxygen in bond formation without deprotonation.[15,60] The ν(NH_2), ρ_w(NH_2), and ν(CS) bands suggest *N^2S* bonding, (5c), where Cu–Cl bonding is recognised by a band at *ca.* 340 cm^{-1} for ν(Cu–Cl).[53] The absorption band at *ca.* 13 500 cm^{-1} in the electronic spectra (in solution and in mull) seems to be due to the chlorine-bonded copper(II) complex, which is distorted towards the square-planar configuration.[61]

The complex formed between HL^5 and nickel(II) chloride, which was synthesised in the same way as $[Ni(HL^3)_2Cl]Cl$, (3b), corresponds to the formulation $[Ni(HL^5)_2Cl]Cl$, (5b), with identical bonding sites to (3b). The complex (5b), unlike (3b), is suggested to possess C_{3v} symmetry [51] based on the electronic spectral (in solution and in mull) data and the value of the magnetic moment.[62] The occurrence of hydrogen bonding of the OH group in (5b) is supported by the broadness of the ν(OH) band in the i.r. spectrum.

The addition of HL^5 to an ethanolic solution of Na_2-$[PdCl_4]$, followed by refluxing on a water-bath and treatment with light petroleum, afforded a yellow crystalline compound having the formula $[Pd(HL^5)_2]Cl_2$, (5d). The spectral and other physical properties of this complex are very similar to those of $[Pd(HL^3)_2]Cl_2$, (3c). The absence of Pd–N^1 bonding is inferred from the upfield shift of the N^1 phenyl-ring protons on complex formation as shown by a sharp singlet where $N^2H_3^+$ protons merge.

Conclusions.—Steric factors as well as the $+I$ effect of the two methyl groups in H_2L^2 inhibit the formation of octahedral geometry for cobalt(II) with H_2L^2.

The different spectral features of the two nickel(II) five-co-ordinate complexes suggest the existence of $N^2{}_2S_2$ donor sites on the same plane in $[Ni(HL^3)_2Cl]Cl$, (3b), but on different planes in (5b). This is due to the steric hindrance of the bulky phenyl group bound to N^1 in HL^5 which results in placement of the halogen in an equatorial position in (5b). However, one cannot predict exact stereochemistry on the basis of only spectral data since geometrical distortions and different strengths of the axial and equatorial ligands also influence the splitting of energy levels. Furthermore, the spectra of high-spin five-co-ordinate nickel(II) complexes with either square-pyramidal or trigonal-bipyramidal stereochemistry closely resemble one another.[63] Therefore, exact positions of the donor sites await crystal-structure determinations, although tentative structures (3b) and (5b) are proposed on the basis of electronic spectra,[51] hydrogen bonding, steric hindrance in the compounds, and the magnetic moments.[52,62]

The presence of a water molecule in the HL^3–copper(II) complex seems to be due to the $+I$ effect of the methyl group. On the other hand, the absence of water in the HL^5–copper(II) complex is probably due to the fact that the phenyl group bound to N^1 in HL^5 acts as an electron-withdrawing group * which diminishes the electron density of copper(II), thus, making Cu^{II} prefer halide ion to a water molecule.

Co-ordination of water molecules to HL^3– and HL^5–cobalt(II) complexes is probably due to the $+I$ effect of methyl as well as phenyl groups bound to N^1.

The zwitterionic form of palladium(II) complexes with HL^3 and HL^5 ligands arises from the presence of the free amino-group whose basicity is increased by the methyl or phenyl group bound to N^1, which here acts as an electron-releasing group, resulting in deprotonation of the *o*-hydroxy-group of the ligand.

The complexes $[Co(HL^1)_3]$ and $[Co(HL^4)_3]$ are similar in structure but have different bonding sites. This is probably due to the fact that the phenyl group bound to N^2 augments the liberation of the proton from N^1H rather than from the *o*-hydroxy-group. A similar argument is also applicable to $[Ni(HL^1)_2]$ and $[Ni(HL^4)_2]$.

The anomalous behaviour of $[Pd(HL^4)_2]$, (5c), compared to other palladium(II) complexes cannot be unequivocally explained. The phenyl ring attached to N^2 in H_2L^4 may stimulate the ligand to behave as a soft base, like arsine ligands [58] in palladium(II) five-co-ordinate complexes. Moreover, the feasibility of the ligand being tridentate as well as the apparent steric hindrance in the complex also facilitate five-co-ordination.

To support the exact structures of the complexes studied so far we believe more physical data are necessary. We are continuing our studies on related species as well as investigating the reactions of the complexes in order to extend our knowledge of the chemistry of metal complexes of thiohydrazides.

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* The phenyl group can act either as an electron-releasing ($+I$) or an electron-withdrawing group ($-I$) depending on the electrophilicity or nucleophilicity of the substituent attached to it.

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