Complexes of the Pyridine-based, Tridentate, Sulphur-containing Ligands 2,6-Bis(ethylthiomethyl)pyridine, 2,6-Bis(methoxycarbonylethylthiomethyl)-pyridine, and 2,6-Bis(benzylthiomethyl)pyridine. Crystal Structure of [2,6-Bis(ethylthiomethyl)pyridine]dichlorocadmium(II) Hydrate†

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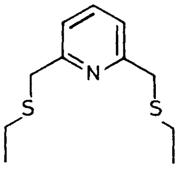
New pyridine-based, tridentate, sulphur-containing ligands, 2,6-bis(ethylthiomethyl)pyridine, 2,6-bis(methoxycarbonylethylthiomethyl)pyridine, and 2,6-bis(benzylthiomethyl)pyridine, and their complexes with Zn, Cd, Cu, Co, and Ni are reported. The molecular structure of [2,6-bis(ethylthiomethyl)pyridine]dichlorocadmium(II) hydrate is also described. This compound is binuclear with bridging chlorine atoms, being triclinic, space group $P\bar{1}$ with a = 8.267(2), b = 10.444(2), c = 11.825(3) Å, α = 64.98(2), β = 79.66(3), γ = 64.52(3)°, and Z = 1. For the complexes of Zn and Cu a mononuclear, five-co-ordinate structure is proposed, while for Cd, Co, and Ni binuclear structures with the metal ion in an octahedral arrangement and with bridging chlorine atoms are suggested.

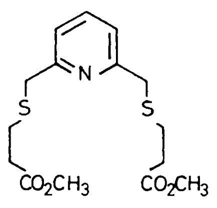
The chemistry of transition-metals with tridentate ligands containing N and/or O, or quadridentate ligands containing N and S as donor atoms is well known and documented, as indicated by the extensive studies on 2,2′:6′,2″-terpyridine (terpy),[1] pyridyldi-imines,[2] N_2S_2 macrocycles,[3] or N_2S_2 open-chain ligands.[4] On the other hand, little information, particularly structural, is available on tridentate NS_2 (S = thioether) ligands. Two of our recent papers, one giving structural information about [2,6-bis(ethylthiomethyl)pyridine]dibromozinc(II),[5] and the other about [2,6-bis(ethylthiomethyl)pyridine]-dichlorocopper(II) and dichloro{3,10-dithia-16-azabicyclo-[10.3.1]hexadeca-1(16),12,14-triene}copper(II)[6] are, we believe, the only examples of this type of NS_2 complex yet characterized by *X*-ray diffraction methods. Parker *et al.*[7] gave structural information about rhodium and palladium NS_2 complexes only on the basis of n.m.r. data.

The distorted trigonal bipyramidal geometry observed in all these compounds lead us to believe that ligands of this type would preferentially force the formation of a monomeric trigonal bipyramidal or square pyramidal geometry.

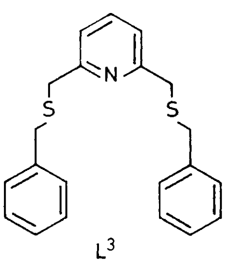
In order to become better acquainted with the stereochemical problems we decided to solve the crystal structures of two metal complexes of these types of NS_2 ligands where the metal atoms did not show a strong tendency to become five-co-ordinate. Here we describe the synthesis of two new ligands, 2,6-bis-(methoxycarbonylethylthiomethyl)pyridine (L^2) and 2,6-bis-(benzylthiomethyl)pyridine (L^3), and of their metal complexes. For comparison we also present new complexes of the previously described[5] ligand 2,6-bis(ethylthiomethyl)pyridine (L^1). Furthermore, the crystal structure of the complex [2,6-bis(ethylthiomethyl)pyridine]dichlorocadmium(II) hydrate, $[\{Cd(L^1)Cl_2{\cdot}H_2O\}_2]$, is reported. This compound is binuclear, each nucleus having a pseudo-octahedral stereochemistry. The six positions are filled by the nitrogen, two sulphurs, one terminal chlorine, and two bridging chlorines. Magnetic data concerning nickel complexes of these ligands are also presented.



L^1



L^2



L^3

Experimental

All ligands were synthesized under a nitrogen atmosphere unless otherwise stated. Dehydrated and deoxygenated solvents were used in the ligand syntheses. Methanol was dehydrated using Mg, and benzene with sodium–benzophenone. Solvents were placed under vacuum to eliminate dissolved oxygen. In all cases this treatment was sufficient to perform the reaction. Sodium methoxide was prepared from sodium metal and dehydrated MeOH. 2,6-Bis(bromomethyl)pyridine[8] and methyl 3-mercaptopropanoate[9] were prepared according to reported procedures. 2,6-Dimethylpyridine and ethanethiol (Fluka) were commercially available and used as received.

Microanalyses (C, H, N) were performed in our analytical laboratory on a Perkin-Elmer 240-B instrument. Proton n.m.r. spectra were recorded on a Bruker WP 80SY spectrometer in $CDCl_3$ solution, electronic spectra on a Kontron UVIKON-860 spectrophotometer in CH_2Cl_2 or methanolic solution.

Syntheses.—2,6-*Bis*(*ethylthiomethyl*)*pyridine* (L^1). This ligand was prepared as previously reported.[5]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical and physical data for the complexes

Compound	Analysis (%)*			Yield (%)	Colour
	C	H	N		
L^3	71.5	3.7	3.7	61	Colourless
	(71.80)	(4.00)	(4.00)		
L^2	52.7	6.3	3.9	27	Colourless
	(52.50)	(6.10)	(4.10)		
$[Zn(L^3)Br_2]$	43.4	3.9	2.6	53	Colourless
	(43.75)	(3.65)	(2.45)		
$[Cu(L^3)Cl_2]$	51.4	4.2	2.6	39	Green
	(51.90)	(4.35)	(2.90)		
$[Co(L^3)Cl_2]$	52.3	4.6	2.9	45	Deep blue
	(52.40)	(4.35)	(2.90)		
$[Ni(L^3)Cl_2]$	52.2	4.3	2.6	50	Green
	(52.45)	(4.35)	(2.90)		
$[Cu(L^2)Cl_2]$	37.5	4.2	3.1	37	Green
	(37.70)	(4.40)	(2.95)		
$[Co(L^2)Cl_2]$	38.4	4.6	3.0	63	Blue
	(38.05)	(4.45)	(2.95)		
$[Ni(L^2)Cl_2]$	37.8	4.6	2.9	57	Green
	(38.10)	(4.45)	(2.95)		
$[Co(L^1)Cl_2(H_2O)]$	36.6	5.0	3.8	16	Deep blue
	(36.45)	(4.75)	(3.90)		
$[Cd(L^1)Cl_2(H_2O)]$	30.6	4.5	3.4	40	Colourless
	(30.85)	(4.45)	(3.25)		

* Calculated values in parentheses.

2,6-*Bis(methoxycarbonylethylthiomethyl)pyridine* (L^2). In a three-necked flask, NaH (0.988 g, 0.033 mol, 80% emulsion in white oil) was washed three times with benzene (10 cm^3 each), and methyl 3-mercaptopropanoate (3.95 g, 0.033 mol) in benzene (20 cm^3) was added slowly. The mixture was stirred for 10 min and 2,6-bis(bromomethyl)pyridine (4.36 g, 0.0165 mol) in benzene (20 cm^3) was added. Stirring was continued for 2 h at room temperature. The resulting suspension was filtered. The filtrate was washed twice with aqueous molar NaOH (50 cm^3) and twice with water (50 cm^3). The organic layer was separated, dried (using $MgSO_4$), and evaporated (using a Rotavapor) to 10 cm^3. Chromatography on alumina using benzene as the eluant, and evaporation of the solvent yielded a solid. This was stirred at room temperature with hexane (50 cm^3). Upon filtration, a white solid was obtained. Yield: 27% (1.53 g). ^{1}H N.m.r.: δ 7.7—6.7 (py), 3.8 (py–CH_2S), 3.7 (OCH_3), and 3.0—2.5 (SCH_2CH_2–CO).

2,6-*Bis(benzylthiomethyl)pyridine* (L^3). Sodium methoxide (30 mmol) in methanol was stirred for 15 min with phenylmethanethiol (30 mmol) (total volume of methanol *ca.* 20 cm^3). The solution was then added to a solution of 2,6-bis(bromomethyl)pyridine (4 g, 15 mmol) in methanol (30 cm^3). After 3 h under reflux, the solvent was eliminated under reduced pressure. The resulting residue was extracted twice with diethyl ether (150 cm^3) and the combined organic layers washed twice with aqueous molar NaOH and twice with water (50 cm^3), dried ($MgSO_4$), and evaporated under vacuum. Yield 61% (3.2 g). ^{1}H N.m.r.: δ 7.6—6.8 (py,Ph) and 3.7 (py–CH_2S).

$[M(L^1)X_2]$ (M = Zn, X = Br; M = Cd, Cu, Co, *or* Ni, X = Cl). The synthesis of $[Zn(L^1)Br_2]$,[5] $[Ni(L^1)Cl_2]$,[5] and $[Cu(L^1)Cl_2]$[6] has been reported previously. The salt $CoCl_2{\cdot}6H_2O$ (1.7 mmol) in methanol (5 cm^3), or $CdCl_2{\cdot}2.5H_2O$ (1.7 mmol) in methanol–water (4:1, 5 cm^3), was added to a solution of L^1 (1.7 mmol) in ethyl acetate (10 cm^3, M = Co) or methanol (5 cm^3, M = Cd). The mixture was allowed to stand at room temperature for a few hours. A deep blue (M = Co), or colourless (M = Cd), solid was obtained in crystalline form, which was filtered off, washed with (10 cm^3) ethyl acetate (M = Co) or methanol (M = Cd), and vacuum dried. Yield: 16% (M = Co), 40% (M = Cd).

$[M(L^3)X_2]$ (M = Zn, X = Br; M = Cu, Co, *or* Ni, X = Cl). The salt $MX_2{\cdot}yH_2O$ (0.19 mmol) in alcohol [M = Zn or Co, methanol (2 cm^3); M = Ni, ethanol (1 cm^3); M = Cu, isopropyl alcohol (1 cm^3)] was added to a solution of L^3 in methanol (2 cm^3, M = Zn or Cu) or Pr^{i}OH (2 cm^3, M = Ni or Co). After standing at room temperature for a few hours, coloured solids were obtained in crystalline form, which were filtered off and vacuum dried. Yields varying between 40 (Cu) and 50% (Co) were obtained.

$[M(L^2)X_2]$ (M = Cu, Co, *or* Ni, X = Cl). The reactions were carried out as above using L^2 instead of L^3. Yields varying between 40 (Cu) and 55% (Ni) were obtained.

Analytical data for all the above compounds are reported in Table 1.

X-Ray Structure Determination of [2,6-*Bis(ethylthiomethyl)pyridine*]*dichlorocadmium*(II) *Hydrate*.—Crystals of this stoicheiometry were obtained by slow evaporation of a methanol–water solution (2:1 v/v).

Crystal data. Colourless, single prismatic crystal, 0.15 × 0.05 × 0.2 mm, $C_{22}H_{34}Cd_2Cl_4N_2S_4{\cdot}2H_2O$ triclinic, M = 428.0, space group $P\bar{1}$, a = 8.267(2), b = 10.444(2), c = 11.825(3) Å, α = 64.98(2), β = 79.66(3), γ = 64.52(3)°, U = 835.2 Å^3, Z = 1, D_c = 1.70 g cm^{-3}, μ(Mo-K_α) = 18.5 cm^{-1}, $F(000)$ = 428.

X-Ray diffraction data were collected at 294 K with an Enraf-Nonius CAD-4 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). Using the ω-2θ scan technique, 3 123 reflections with $2\theta < 50°$ ($-9 \leqslant h \leqslant 9$, $-12 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 14$) were obtained. These non-unique data were averaged and the resulting 2 923 intensities were corrected for Lorentz and polarization effects; 2 619 reflections were considered observed with $F_o > 3\sigma(F_o)$.

The atomic co-ordinates of Cd, the two S, and the two Cl atoms were located by direct methods (MULTAN-11/84).[10] Subsequent Fourier difference synthesis combined with refinement of located atoms yielded the complete model of the structure. This model was refined with full least-squares methods (SHELX 76)[11] using anisotropic thermal parameters. The hydrogen atoms of the ethyl groups were introduced in calculated positions and the remaining hydrogen atoms were located by means of a Fourier difference synthesis and refined with a global isotropic thermal parameter. The final value of the R factor was 0.031 and R' = 0.037 with $w = 1/[\sigma^2(F) + 0.000\,854F^2]$ over 221 refined parameters. On a final Fourier difference synthesis, the maximum height was near the Cd atom (0.76 e Å^{-3}). The largest shift/estimated standard deviation (e.s.d.) in the final cycle was 0.41. Scattering factors were taken from ref. 12.

Magnetic Susceptibility Measurements.—Susceptibility measurements were made on polycrystalline samples at temperatures between 77 K and 300 K, with a Faraday-type balance. Diamagnetic corrections were calculated from Pascal's constants,[13] but no t.i.p (temperature independent paramagnetism) corrections were introduced in the experimental values.

Results and Discussion

General Results.—The synthetic route to these alkylthiopyridine ligands consists of the frequently employed preparation of sulphides by treatment of alkyl halides with salts of mercaptans.

Ligands L^3 and L^2 behave in a similar way towards first-row transition metals, and similarly to 2,6-bis(ethylthiomethyl)-

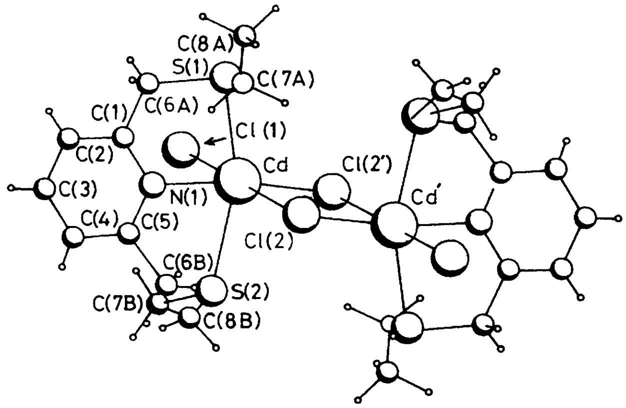

Figure. Perspective view of [2,6-bis(ethylthiomethyl)pyridine]dichlorocadmium(II)–hydrate with the atom numbering

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for [2,6-bis(ethylthiomethyl)pyridine]dichlorocadmium(II) hydrate

Atom	*X/a*	*Y/b*	*Z/c*
Cd	751(0)	5 137(0)	3 306(0)
Cl(2)	2 154(1)	3 618(1)	5 662(1)
Cl(1)	−602(1)	6 531(1)	1 133(1)
S(2)	2 410(1)	6 886(1)	3 278(1)
S(1)	1 017(1)	2 473(1)	3 248(1)
N	3 643(3)	4 099(3)	2 484(2)
C(5)	4 899(4)	4 618(3)	2 429(3)
C(4)	6 447(4)	4 270(4)	1 731(3)
C(3)	6 714(5)	3 343(4)	1 123(4)
C(2)	5 460(4)	2 772(4)	1 203(3)
C(1)	3 910(4)	3 184(3)	1 880(3)
C(6A)	2 443(4)	2 677(4)	1 890(4)
C(6B)	4 643(4)	5 491(4)	3 222(4)
C(7B)	2 162(5)	8 351(4)	1 705(4)
C(8B)	439(5)	9 701(4)	1 630(4)
C(7A)	2 560(5)	910(4)	4 494(5)
C(8A)	2 791(6)	−534(5)	4 745(6)
O	4 096(5)	719(4)	8 674(5)

Table 3. Bond lengths (Å) and angles (°) for [2,6-bis(ethylthiomethyl)pyridine]dichlorocadmium(II) hydrate

Cl(2)–Cd	2.731(1)	C(1)–N	1.346(4)
Cl(1)–Cd	2.538(1)	C(4)–C(5)	1.388(5)
S(2)–Cd	2.703(1)	C(6B)–C(5)	1.498(5)
S(1)–Cd	2.724(1)	C(3)–C(4)	1.360(6)
N–Cd	2.380(3)	C(2)–C(3)	1.374(6)
C(6B)–S(2)	1.805(4)	C(1)–C(2)	1.384(5)
C(7B)–S(2)	1.818(4)	C(6A)–C(1)	1.514(5)
C(6A)–S(1)	1.806(4)	C(8B)–C(7B)	1.495(5)
C(7A)–S(1)	1.819(4)	C(8A)–C(7A)	1.340(7)
C(5)–N	1.344(4)		
Cl(1)–Cd–Cl(2)	178.9(1)	C(5)–N–Cd	120.6(2)
S(2)–Cd–Cl(2)	78.8(1)	C(1)–N–Cd	118.9(2)
S(2)–Cd–Cl(1)	102.1(1)	C(1)–N–C(5)	119.5(3)
S(1)–Cd–Cl(2)	91.5(1)	C(4)–C(5)–N	121.5(3)
S(1)–Cd–Cl(1)	87.9(1)	C(6B)–C(5)–N	117.8(3)
S(1)–Cd–S(2)	148.5(1)	C(6B)–C(5)–C(4)	120.5(3)
N–Cd–Cl(2)	90.2(1)	C(3)–C(4)–C(5)	118.9(3)
N–Cd–Cl(1)	90.6(1)	C(2)–C(3)–C(4)	120.0(3)
N–Cd–S(2)	75.8(1)	C(1)–C(2)–C(3)	119.3(4)
N–Cd–S(1)	74.3(1)	C(2)–C(1)–N	120.8(3)
C(6B)–S(2)–Cd	94.8(1)	C(6A)–C(1)–N	119.0(3)
C(7B)–S(2)–Cd	106.6(1)	C(6A)–C(1)–C(2)	120.0(3)
C(7B)–S(2)–C(6B)	101.5(2)	C(1)–C(6A)–S(1)	116.7(3)
C(6A)–S(1)–Cd	92.2(1)	C(5)–C(6B)–S(2)	116.7(2)
C(7A)–S(1)–Cd	106.4(2)	C(8B)–C(7B)–S(2)	108.5(3)
C(7A)–S(1)–C(6A)	102.9(2)	C(8A)–C(7A)–S(1)	118.3(4)

pyridine (L^1). Some results obtained with this last ligand have already been reported.[5,6] Complexes with general formula [MLX_2] (M = Cu, Co, or Ni), where L represents L^3 or L^2, have been obtained. With L = L^3, the zinc complex has also been obtained. Zinc, cadmium, copper, cobalt, and nickel complexes with the ligand L^1 have been synthesized. The synthesis and co-ordinating properties of L^2 are interesting since this compound is a good precursor for the corresponding diacid compound and, in turn, the dichloride. This should permit the synthesis of ester, amide, *etc.*, macrocyclic compounds containing the pyridine group, which is our aim.[6] All attempts directly to synthesize the diacid from 2,6-bis(bromomethyl)pyridine and 3-mercaptopropanoic acid have failed, while the saponification of L^2 has been successful.

Structural Results.—The molecular structures of [$Zn(L^1)Br_2$] and [$Cu(L^1)Cl_2$] have been resolved by *X*-ray diffraction methods.[5,6] The metal environment in these mononuclear complexes corresponds to a distorted trigonal-bipyramidal geometry, the ligand acting as a tridentate molecule. The cobalt and cadmium complexes were obtained further to investigate the stereochemistry imposed by this ligand. For cadmium, good crystals were obtained with the ligand L^1 which permitted adequate solution of the structure. However, poor quality crystals, for *X*-ray diffraction analysis, were obtained for the cobalt complex with L^2. An *X*-ray structural study with a final *R* factor of 0.169 was obtained, indicating that both compounds have a similar binuclear structure.

As can be seen in the Figure, which shows the molecular structure of [$\{Cd(L^1)Cl_2{\cdot}H_2O\}_2$] and the atom labelling scheme, the co-ordination polyhedron about the cadmium atoms can be described as an octahedron. The six positions are filled by one nitrogen, two sulphurs, and three chlorine atoms (two of which are bridging and the other terminal). Each molecule contains two cadmium atoms sharing two bridged chlorines. The centre of symmetry is located at the midpoint of the two octahedra sharing one edge. The two cadmium and four chlorine atoms lie in the basal plane [root mean square deviation (r.m.s.d.) 0.001 Å] and the two nitrogen atoms are close to this plane (out of plane distances 0.22 and −0.22 Å). Table 2 gives the final positional parameters, Table 3 the bond lengths and angles.

It is interesting to compare the S–Cd distance in [$\{Cd(L^1)Cl_2{\cdot}H_2O\}_2$] with the observed S–Zn distance in [$Zn(L^1)Br_2$].[5] In this last case an average Zn–S distance of 2.69 Å was observed, which is comparable to the average Cd–S value of 2.71 Å. The similarity of these results poses a serious question about the nature of the S–Zn bond in [$Zn(L^1)Br_2$]. Usually a shortening of *ca.* 0.18 Å would have been expected due to the shorter radius of the Zn^{II} as compared to Cd^{II}, as is observed with the S–M distances in [$Cd(HL)_2$][ClO_4]$_2{\cdot}2H_2O$ (2.550 Å)[14a] and [$\{Zn(HL)Cl_2\}_2$]$\cdot H_2O$ (2.363 Å),[14b] where HL = 1-mercapto-4-methylpiperidine. The unusually long Zn–S distance in [$Zn(L^1)Br_2$] compared with [$\{Cd(L^1)Cl_2{\cdot}H_2O\}_2$] cannot be attributed to the different types of co-ordination polyhedra observed about the central metal atoms. For example, in [$Cu(L^1)Cl_2$],[6] which has a trigonal-bipyramidal geometry, as does [$Zn(L^1)Br_2$], a Cu–S distance of 2.351 Å is observed, 0.34 Å shorter than its equivalent in [$Zn(L^1)Br_2$]. However, both distances should have been comparable as observed in [MCl_4]$^{2-}$ compounds (M = Cu or Zn), where distances near 2.25 Å are found for *d*(Zn–Cl) or *d*(Cu–Cl),[15] indicative of comparable radii for Zn^{2+} and Cu^{2+}. According to these figures a distance of *ca.* 2.235 Å would have been expected for $[Zn(L^1)Cl_2]$ if the length of the M–S bond had been the same for $[Zn(L^1)Br_2]$ and $[Cu(L^1)Cl_2]$.

On the other hand, *d*(Zn–N) and *d*(Cu–N) are more comparable in these compounds, 2.08 *vs.* 2.02 Å, respectively, while *d*(Cd–N) is 2.38 Å, larger than *d*(Zn–N), as expected, due to the larger volume of Cd^{2+}, concomitant with the fact that Cd^{2+} has an octahedral environment. Consequently, it seems that the Zn atom in $[Zn(L^1)Br_2]$ could be better explained as trigonal by having a weak apical metal–thioether interaction, due to the lower affinity of this metal ion towards a thioether compared with, for instance, Cu^{2+}, Co^{2+}, or Cd^{2+}.

Spectroscopic Results.—We have reported[6] the molecular structure of the compound $[Cu(L^1)Cl_2]$. This is monomeric and the metal ion exhibits a distorted square-pyramidal co-ordination by the pyridinic nitrogen, the two sulphur atoms, and the two chlorine ions. On the basis of the electronic spectra it is possible to assign similar structures to the copper complexes of L^3 and L^2. All the complexes show a single band at 700—710 nm ($\varepsilon \simeq 300$ dm^3 mol^{-1} cm^{-1}) in methanolic solution, which is compatible with five-co-ordinated Cu^{II}.[16]

All three cobalt complexes presented here exhibit the same electronic spectra in CH_2Cl_2 or CH_3Cl solutions, consisting of one band split into two components at 574—578 and 610—612 nm. Our evidence suggests that the $[Co(L^2)Cl_2]$ complex is binuclear, like that of Cd^{II}, each Co^{II} being octahedrally co-ordinated and, on the basis of the electronic spectra,[17] a similar structure is proposed for the L^1 and L^3 cobalt complexes.

The electronic spectra of the nickel(II) complexes in methanolic solution are all similar. In the visible region there are two bands at 662—665 and 407—408 nm, which is typical of octahedral Ni^{II}.[18] As the spectra are similar, a common metal environment is proposed. In addition, based on magnetic measurements, binuclear structures like those for the cadmium(II) complexes are proposed.

Magnetic Susceptibility Results.—Magnetic measurements for both nickel complexes $[\{Ni(L^1)Cl_2\cdot H_2O\}_2]$ and $[\{Ni(L^2)Cl_2\}_2]$, are consistent with a binuclear structure with a ferromagnetic interaction between the metal ions.

The $\mu_{eff.}$ *versus* temperature curves for both nickel complexes are similar. At room temperature $\mu_{eff.}$ is in the range expected for octahedrally co-ordinated Ni^{II}, with a $^3A_{2g}$ ground state $[\{Ni(L^1)Cl_2\cdot H_2O\}_2]$, 3.0 $[\{Ni(L^2)Cl_2\}_2]$, 2.7). As the temperature is lowered, $\mu_{eff.}$ gradually increases, reaching a value of 3.4 for $[\{Ni(L^1)Cl_2\cdot H_2O\}_2]$ and 3.3 for $[\{Ni(L^2)Cl_2\}_2]$, as a consequence of the increasing population of the $S = 2$ binuclear ground state.

The behaviour is analogous to the well characterized and studied Ni^{II} binuclear complexes $[Ni_2(en)_4Cl_2]Cl_2$, $[Ni_2(en)_4Br_2]Br_2$, and $[Ni_2(en)_4(SCN)_2]I_2$[19] (en = ethylenediamine) where intramolecular ferromagnetic interaction was demonstrated and analysed by Ginsberg *et al.* ($7 < J < 14$ K).[19]

From the slope of the high-temperature interval of the Curie–Weiss curve *g* values of 2.1 $[\{Ni(L^1)Cl_2\cdot H_2O\}_2]$, and 2.0 $[\{Ni(L^2)Cl_2\}_2]$ were calculated, typical of octahedral Ni^{II} without significant interactions between the ions. This behaviour is expected for a low exchange-coupled binuclear compound at high temperatures. No attempt was made to fit the experimental data by a theoretical model, due to the restricted temperature interval studied.

It is concluded that these types of NS_2 pyridine-based ligands may show different stereochemistries as a result of the nature of the metal ion. Up to now the crystallographic results have indicated a trigonal-bipyramidal co-ordination for mononuclear complexes (Zn or Cu) and octahedral for binuclear complexes (Co or Cd). Probably we would find binuclear complexes for all strongly octahedrally oriented metal ions.

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