Synthesis and Structural Studies of Copper(II), Nickel(II) and Cobalt(II) Complexes of a 14-Membered *trans*-N_2S_2 Dibenzo Macrocycle with two Pendant Pyridylmethyl Groups†

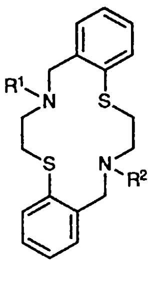
Dieter Funkemeier and Rainer Mattes*
Anorganisch-Chemisches Institut der Westfälischen Wilhelms-Universität Münster, Wilhelm-Klemm-Strasse 8, 4400 Münster, Germany

The 8,17-bis(2-pyridylmethyl)-functionalised derivative (L^2) of a 14-membered *trans*-N_2S_2 dibenzo macrocycle 6,7,8,9,15,16,17,18-octahydrodibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine has been prepared and its crystal structure determined. The ligand L^2 forms stable complexes with nickel(II) **1**, copper(II) **2** and cobalt(II) **3**. The complexes have been isolated in the solid state and characterised by standard methods and single-crystal X-ray diffraction. Crystal data for L^2: space group $P2_1/c$, $a = 945.6(1)$, $b = 1467.9(2)$, $c = 1041.1(2)$ pm, $\beta = 115.67(1)°$, $Z = 2$, $R(R') = 0.035(0.040)$ for 2183 observed reflections. Complex **1**: space group $P2_1/n$, $a = 1418.8(3)$, $b = 1288.8(3)$, $c = 1867.0(4)$ pm, $\beta = 109.20(3)°$, $Z = 4$, $R(R') = 0.067(0.068)$ for 4124 observed reflections. The nickel atom lies outside the macrocyclic cavity and is in a distorted octahedral *cis*-N_4S_2 environment. Complex **2**: space group $P\bar{1}$, $a = 787.8(2)$, $b = 1137.5(2)$, $c = 1800.5(4)$ pm, $\alpha = 98.84(3)$, $\beta = 99.43(3)$, $\gamma = 94.74(3)°$, $Z = 2$, $R(R') = 0.082(0.075)$ for 2165 observed reflections. The copper atom exhibits a highly distorted trigonal-prismatic co-ordination geometry with the following distances: Cu–S, 242.7(4) and 269.8(4), Cu–N(amine) 225.8(11) and 255.2(10) and Cu–N(pyridine) 198.4(11) and 200.2(12) pm, respectively. Complex **3**: space group $P\bar{1}$, $a = 789.3(2)$, $b = 1165.8(2)$, $c = 1806.2(3)$ pm, $\alpha = 98.90(1)$, $\beta = 98.86(2)$, $\gamma = 94.24(2)°$, $Z = 2$, $R(R') = 0.066(0.063)$ for 3039 observed reflections. The geometry about high-spin cobalt(II) is trigonal prismatic with average Co–S, Co–N(amine) and Co–N(pyridine) bond lengths of 252.5, 229.0 and 213.7 pm, respectively. The stereochemistry of the free and complexed ligand is discussed with respect to these structures.

The design and synthesis of macrocycles bearing pendant arms which provide additional co-ordination sites have attracted increasing interest in recent years because of their general co-ordination chemistry. These compounds may also have relevance as model ligands for metal enzymes, as metal-ion selective ligands and as metal-chelating agents for medical application.[1] Among them a number of pyridylmethyl functionalised macrocycles attached to nitrogen donor atoms have been prepared and their co-ordination chemistry studied.[2–7] Pendant pyridylmethyl groups are flexible and their nitrogen donor atoms are sterically efficient.[2] All these ligands reported contain only one kind of donor atom, *i.e.* nitrogen.

Recently we started a program to study the ligating properties of functionalised macrocycles with N- and S-donor atoms, *e.g.* of 1-thia-4,7-diazacyclononane[8] and of 6,7,8,9,15,16,17,18-octahydrodibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine (L^1). The combination of different donor atoms may influence the selectivity of the ligands and the stability of the complexes, and may have stereochemical consequences. We have already reported on the synthesis and complex chemistry of the N-functionalised derivatives of L^1, bearing one (L^3) or two (L^4) pendant carboxylic acid groups.[9] Further work on hydroxybenzyl derivatives is in progress. To our knowledge no functionalised derivatives of other N_xS_y-macrocyclic ligands have been described so far. The properties of saturated macrocyclic polyamino polythioether ligands have recently been surveyed under several aspects.[10–12]

In this work we report on the synthesis and the co-ordination properties of the hexadentate ligand 6,7,8,9,15,16,17,18-octahydro-8,17-bis(2-pyridylmethyl)-dibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine (L^2) towards copper(II), nickel(II) and cobalt(II). X-Ray structure determinations were carried out for the respective complexes and the free ligand itself.



L^1: $R^1 = R^2 = H$

L^2: $R^1 = R^2 = CH_2C_5H_4N\text{-}2$

L^3: $R^1 = H$; $R^2 = CH_2CO_2H$

L^4: $R^1 = R^2 = CH_2CO_2H$

Results and Discussion

The hexadentate ligand L^2 was prepared in good yields by a one-step reaction of the preformed macrocycle L^1 and the appropriate pyridine derivative. The reaction of L^2 with metal(II) perchlorates in equimolar ratios gave compounds with the general formula $[ML^2][ClO_4]_2$ (M = Ni **1**, Cu **2** or Co **3**). All the complexes are readily soluble in acetonitrile, water or methanol.

The electronic spectra of the compounds were registered in water–acetonitrile (4:1) solution. Absorption maxima and assignments are reported in Table 1. The high absorption maxima in the region 225–255 nm are due to $\pi \longrightarrow \pi^*$ transitions within the aromatic rings. Metal-to-ligand charge

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Electronic spectral data of the complexes†

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Assignment
1 [CuL^2][ClO$_4$]$_2$	225 (20 000)	$\pi \longrightarrow \pi^*$ (ligand)
	257 (22 000)	l.m.c.t. (N $\longrightarrow$ Cu)
	330 (sh) (1800)	l.m.c.t. (S $\longrightarrow$ Cu)
	460 (2200)	d–d
	680 (300)	
2 [NiL^2][ClO$_4$]$_2$	230 (2800)	$\pi \longrightarrow \pi^*$ (ligand)
	255 (sh) (16 000)	l.m.c.t. (S $\longrightarrow$ Ni)
	305 (8000)	
	540 (35)	
	900 (52)	
	1000 (sh) (40)	
3 [CoL^2][ClO$_4$]$_2$	250 (br) (100 000)	$\pi \longrightarrow \pi^*$ (ligand)
	460 (50)	
	510 (50)	
	540 (sh) (42)	
	580 (sh) (26)	

† sh = Shoulder, br = broad.

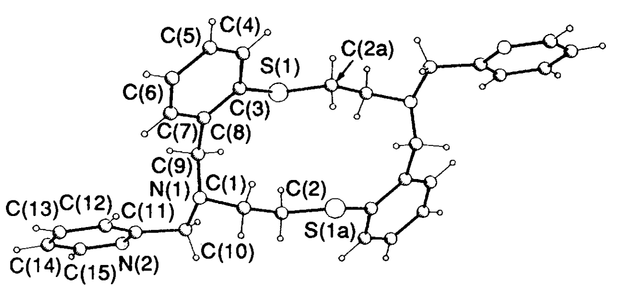

Fig. 1 Structure of the ligand L^2

transfer bands were observed for **1** and **2** in the range 300–460 nm and may be obscured in **3** by the very intense $\pi \longrightarrow \pi^*$ transitions. The electronic spectrum of **1** is typical of octahedral nickel(II) species with N$_x$S$_y$-donor ligands.[13,14] The $^3A_{2g} \longrightarrow {}^3T_{1g}$(F) transition at 540 nm is broad and unsymmetrical, the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition is clearly split, indicating that a significant distortion from octahedral symmetry is present. The $^3A_{2g} \longrightarrow {}^3T_{1g}$(P) transition is obscured by an intense charge transfer band. The d–d transition at 680 nm in **2** corresponds to a weak ligand field; surprisingly it is shifted to lower energies by 50 nm compared to [Cu(HL^4)]ClO$_4$·1.5H$_2$O.[9]

The UV/VIS spectrum of **3** shows two bands with two shoulders on the low-energy band. Their origin remains unclear. No comparisons with similar ligand fields can be made so far.

In order to investigate a possible pH-dependent behaviour of the ligand in its complexes due to a possible protonation of the pendant groups, we recorded the spectra of **1**–**3** in the range pH 6–2. All complexes proved to be stable in this range with no spectral changes occurring. At even lower pH the spectra of the respective hexaquo species were observed and the ligand precipitated as hydrochloride.

The magnetic moment of the cobalt(II) complex **3** is 4.8 ± 0.1 indicating a high-spin configuration. The value is larger than the spin-only value (3.87) for $S = \frac{3}{2}$ and falls approximately in the middle of the range of μ_{eff} values (4.2–5.2) observed for octahedral cobalt(II) complexes.[15]

Structure of L^2.—Fig. 1 shows the molecular structure of L^2 in the solid state. The molecule is situated on a crystallographic inversion centre. Selected bond distances and angles are provided in Table 2. Bond lengths and angles are normal. The non-bonding distances between the donor atoms in the ring are N(1)···N(1a) 706.7(3) and S(1)···S(1a) 420.0(2) pm. The macrocycle displays a rectangular [2525] conformation with N(1) and C(8) at the corners (for the nomenclature, see below), with the pendant groups folded outwardly. No donor function is oriented towards the ring cavity. The interplanar angles between the plane through the donor atoms N(1), N(1a), S(1), S(1a) and the phenyl and pyridyl groups are 73.9 and 92.6°, respectively.

Table 2 Selected bond distances (in pm) and angles (°) for L^2

S(1)–C(3)	177.6(2)	S(1)–C(2a)	180.5(2)
N(1)–C(1)	146.2(2)	N(2)–C(11)	133.6(3)
N(1)–C(9)	146.8(2)	N(2)–C(15)	133.6(2)
N(1)–C(10)	145.8(2)		
C(1)–C(2)	153.3(3)	C(7)–C(8)	139.4(2)
C(2)–S(1a)	180.5(2)	C(8)–C(9)	150.7(2)
C(3)–C(4)	139.7(3)	C(10)–C(11)	151.1(2)
C(3)–C(8)	140.3(2)	C(11)–C(12)	138.2(2)
C(4)–C(5)	137.5(3)	C(12)–C(13)	138.4(2)
C(5)–C(6)	138.6(2)	C(13)–C(14)	137.5(3)
C(6)–C(7)	137.4(3)	C(14)–C(15)	136.9(3)
C(3)–S(1)–C(2a)	102.3(1)	C(1)–C(2)–S(1a)	108.3(1)
C(1)–N(1)–C(9)	113.5(1)	S(1)–C(3)–C(8)	120.8(1)
C(1)–N(1)–C(10)	113.5(1)	C(3)–C(8)–C(9)	123.5(1)
C(9)–N(1)–C(10)	110.9(1)	N(1)–C(9)–C(8)	111.7(1)
N(1)–C(1)–C(2)	115.9(2)		

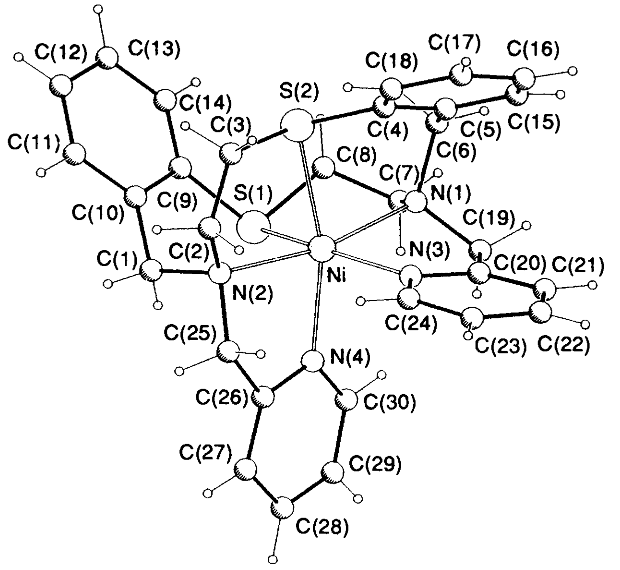

Fig. 2 Structure of the [NiL^2]$^{2+}$ ion in complex **1**

Structure of [NiL^2][ClO$_4$]$_2$ **1**.—The molecular structure of **1** with the atomic labelling scheme is shown in Fig. 2, the co-ordination polyhedron in Fig. 3. Table 3 contains selected structural parameters. The nickel atom is six-co-ordinate and the complex cation exhibits a distorted octahedral geometry comprising all six donor atoms of the N$_4$S$_2$-donor ligand. As in the nickel(II), copper(II) and cobalt(III) complexes of the bis(acetato)-functionalised macrocyclic ligand L^3 the metal centre is not incorporated into the macrocyclic cavity.[9,16] The 14-membered *trans*-N$_2$S$_2$ ring of L^2 is folded such that the N-donor atoms occupy *trans* positions, and the S-donor atoms mutual *cis* positions opposite to the two N(pyridyl) groups. In the nickel(II) complex of the unfunctionalised ligand, *cis*-[NiL^{1}Cl$_2$], the S-donor atoms occupy *trans* positions.[17]

The main angular distortions from regular octahedral geometry result from the steric requirements for the pendant groups. The *cis* angles at the metal centre range from 79.5

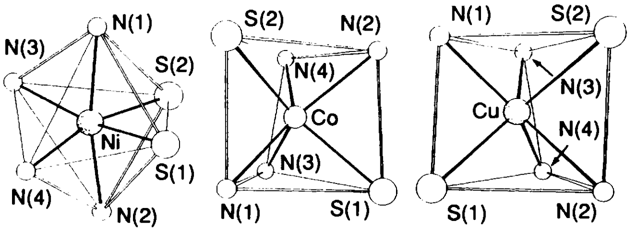

Fig. 3 Co-ordination polyhedra of the metal centres in the structures of complexes **1**, **2** and **3**

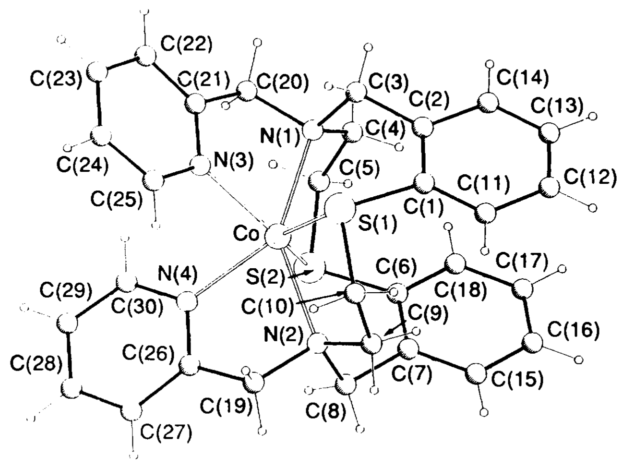

Fig. 4 Structure of the $[CoL^2]^{2+}$ ion in complex **3**

[N(1)–Ni–N(3)] to 109.9° [N(1)–Ni–N(4)] and the *trans* angles from 159.6 to 168.7°. The two longest bonds to the metal atom are from the sulfur donors with Ni–S 241.7(2) and 243.9(2) pm. Slightly shorter values (by 3–4 pm) have been found in the homoleptic complexes $[NiL^5]^{2+}$ (L^5 = 1,4,7-trithiacyclononane)[18] and $[NiL^6{}_2]^{2+}$ (L^6 = 1,4,7-trithiacyclodecane),[19] and in $[NiL^7(H_2O)]^{2+}$ (L^7 = 5,6,7,8,10,11,12,13,19,20-decahydrodibenzo[*f*,*l*][1,8,11,4,15]oxadithiadiazacycloheptadecine[14] and *cis*-$[NiL^1Cl_2]$.[17] The Ni–N(amine) distances, mean at 213.8 pm, are significantly longer than the Ni–N(pyridine) distances with a mean value of 209.5(3) pm. Similar relations, but with slightly shorter distances, hold in $[NiL^8]^{2+}$ [L^8 = 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane].[2] The N(pyridine) donors are not co-ordinated optimally. The C–N–Ni angles within the five-membered chelate rings are much smaller [mean at 113.4(4)°] than the angles outside [mean at 129.4(4)°]. One five-membered chelate ring with $-CH_2-CH_2-$ segments shows disorder [at C(3)], having λ- and δ-configuration in the crystal; the other one displays λ- or δ-configuration.

Structure of $[CoL^2][ClO_4]_2$ **3**.—The molecular structure of **3** is shown in Fig. 4 and the co-ordination polyhedron is depicted in Fig. 3. Table 3 contains selected bond distances and angles. The cobalt atom is six-co-ordinate; the co-ordination polyhedron exhibits, surprisingly, a trigonal-prismatic geometry which is rather scarce for macrocyclic cobalt(II) complexes. The arrangement of the donor centres and the aromatic rings has nearly C_2 symmetry. The Co–S bond lengths in **3**, 250.7(2) and 253.7(2) pm, are considerably longer than in Jahn–Teller-distorted low-spin octahedral cobalt(II) hexathia complexes, such as $[CoL^5{}_2]^{2+}$, $[CoL^9]^{2+}$ (L^9 = 1,4,7,10,13,16-hexathiacyclooctadecane)[18] and $[CoL^6{}_2]^{2+}$ (ref. 19) where the bond distances (for the undistorted bonds) range from 225 to 232 pm. The difference in ionic radius between high- and low-spin cobalt(II) is estimated to be 10 pm.[20] The Co–N(amine) and Co–N(pyridine) bond lengths differ to a larger extent than in the nickel(II) complex **1**. The short Co–N(pyridine) bond lengths at 212.8(8) and 214.7(7) pm are consistent with a better fit of the donor groups to the metal centre. The bond angles Co–N(pyridine)–C inside and outside the chelate ring differ only by 4–6°. The Co–N(amine) distances, at 228.2(7) and 229.7(7) are slightly larger than usual.[6,21] The metal atom is again not centred in the macrocyclic cavity but is situated 81 pm above the mean plane through the donor atoms of the ring system.

Table 3 Selected distances (in pm) and angles (°) for the perchlorate salts of $[NiL^2]^{2+}$ **1**, $[CuL^2]^{2+}$ **2** and $[CoL^2]^{2+}$ **3**

	1	**2**	**3**
M–S(1)	241.7(2)	242.7(4)	250.7(2)
M–S(2)	243.9(2)	269.8(4)	253.7(2)
M–N(1)	215.1(4)	225.8(11)	229.7(7)
M–N(2)	212.4(4)	255.2(10)	228.2(7)
M–N(3)	209.2(5)	198.4(11)	212.8(8)
M–N(4)	209.8(6)	200.2(12)	214.7(7)
S(1)–M–S(2)	94.7(1)	128.8(1)	138.3(1)
S(1)–M–N(1)	84.4(1)	81.3(3)	88.5(2)
S(1)–M–N(2)	91.3(2)	84.0(2)	79.6(2)
S(1)–M–N(3)	159.6(1)	138.0(3)	84.9(2)
S(1)–M–N(4)	86.2(2)	88.5(3)	126.1(2)
S(2)–M–N(1)	87.7(1)	84.8(2)	79.3(2)
S(2)–M–N(2)	82.2(2)	72.3(2)	87.1(2)
S(2)–M–N(3)	97.1(2)	86.5(3)	128.4(2)
S(2)–M–N(4)	162.3(1)	122.7(3)	87.4(2)
N(1)–M–N(2)	168.7(2)	135.3(4)	143.7(3)
N(1)–M–N(3)	79.5(2)	80.2(4)	74.8(3)
N(1)–M–N(4)	109.9(2)	150.0(4)	136.0(3)
N(2)–M–N(3)	106.7(2)	133.9(4)	136.9(2)
N(2)–M–N(4)	80.2(2)	70.7(4)	75.9(3)
N(4)–M–N(4)	87.5(2)	89.0(5)	81.7(3)

Structure of $[CuL^2][ClO_4]_2$ **2**.—Since it became established that the copper binding site in blue copper proteins consists of a N_2S_2 donor set, intense interest has arisen in the structures of copper complexes involving N_xS_y ligands. The present copper(II) complex **2** is green, so that no direct relationship can be expected. Nevertheless, the structure of **2** is interesting with respect to its highly distorted trigonal-prismatic co-ordination geometry, which is depicted in Figs. 3 and 5 (together with the atom labelling scheme). All six donors co-ordinate to the metal centre. The shortest bonds are those to N(pyridine) of 198.4(11) and 200.2(12) pm. Similar values have been found for Cu–N(pyridine) in complexes of 4,7-bis(2-pyridylmethyl)-1-thia-4,7-diazacyclononane[22] and 1,4,8,11-tetraazacyclotetradecane.[4] The two Cu–N(amine) distances at 225.8(11) and 255.2(10) pm differ greatly, as do the Cu–S distances at 242.7(4) and 269.8(4) pm. In the equatorial sites of square-pyramidally and octahedrally co-ordinated macrocyclic copper(II) complexes Cu–N(amine) distances usually range from 200 to 210 pm and Cu–S distances from 230 to 240 pm.[4,9,18,22–25] In this complex copper(II) also lies outside the macrocyclic cavity being situated 100 pm above the mean plane through the donor atoms of the folded macrocycle. The thermal parameters for the copper atom are relatively high and anisotropic. This may indicate some mobility of the copper centre within the polyhedron of the donor groups. No such behaviour is observed for the cobalt(II) atom in **3**, probably due to its larger ionic radius.

Finally some remarks are made to the overall conformation of the ligand L^2 in the present compounds. The nitrogen and sulfur donor groups are effectively chiral in the crystals. The configurations at the donor groups N(1), N(2), S(1) and S(2) are *RRSR* (or *SSRS*) in **1** and *RRSS* (or *SSRR*) in **2** and **3**. This means that in complexes **2** and **3** chemically identical sections

Table 4 Summary of cell data, data collection and refinement details

Compound	L^2	$[NiL^2][ClO_4]_2$	$[CuL^2][ClO_4]_2$	$[CoL^2][ClO_4]_2$
Formula	$C_{30}H_{32}N_4S_2$	$C_{30}H_{32}Cl_2N_4NiO_8S_2$	$C_{30}H_{32}Cl_2CuN_4O_8S_2$	$C_{30}H_{32}Cl_2CoN_4O_8S_2$
M	512.7	770.3	775.2	770.5
Colour, habit	Colourless, block	Blue-violet, block	Green, plate	Purple, block
Crystal size/mm	0.3 × 0.4 × 0.5	0.2 × 0.2 × 0.35	0.1 × 0.25 × 0.45	0.3 × 0.4 × 0.35
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
a/pm	945.6(1)	1418.8(3)	787.8(2)	789.3(2)
b/pm	1467.9(2)	1288.8(3)	1137.5(2)	1165.8(2)
c/pm	1041.1(2)	1867.0(4)	1800.5(4)	1806.2(3)
α/°	—	—	98.84(3)	98.90(1)
β/°	115.67(1)	109.20(3)	99.43(3)	98.86(2)
γ/°	—	—	94.74(3)	94.24(2)
10^{-6} U/pm^3	1302.5(3)	3224(3)	1563.1(6)	1614(1)
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	2	4	2	2
$F(000)$	544	1592	798	794
D_c/g cm^{-3}	1.31	1.59	1.65	1.59
Diffractometer	CAD4	CAD4	Siemens R3/V	CAD4
Radiation, mode	Mo-Kα, ω–2θ	Mo-Kα, ω–2θ	Mo-Kα, ω–2θ	Mo-Kα, ω–2θ
Absorption correction	None	Empirical	Empirical	Empirical
Lattice segment	$\pm h, -k, \pm l$	$\pm h, +k, \pm l$	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$
μ/cm^{-1}	2.3	9.6	10.6	8.8
2θ range/°	4–54	4–54	4–48	4–48
Reflections measured	5323	7642	5455	5465
Unique reflections	2711	5987	3897	4387
Reflections with $I \geqslant 2\sigma(I)$	2183	4124	2165	3039
No. variables in least squares	171	424	274	424
R, R'	0.035, 0.040	0.067, 0.068	0.082, 0.075	0.066, 0.063
Maximum residual electron density in final difference map/e Å^{-3}	0.25	0.86	0.74	0.87

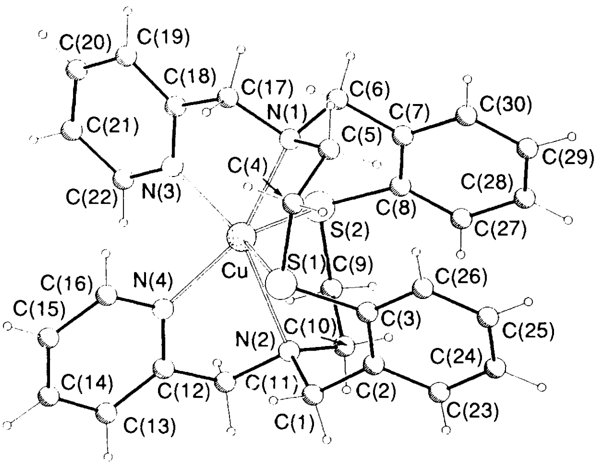

Fig. 5 Structure of the $[CuL^2]^{2+}$ ion in complex **2**

Table 5 Positional parameters (× 10^4) for L^2 with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
S(1)	6886(1)	4493(1)	1827(1)
N(1)	3770(1)	2776(1)	−1304(1)
N(2)	1645(2)	893(1)	−707(1)
C(1)	3475(2)	3682(1)	−1952(2)
C(2)	2808(2)	4387(1)	−1275(2)
C(3)	7502(2)	3769(1)	799(1)
C(4)	8917(2)	3946(1)	725(2)
C(5)	9433(2)	3381(1)	−38(2)
C(6)	8566(2)	2623(1)	−732(2)
C(7)	7173(2)	2449(1)	−665(2)
C(8)	6610(2)	3006(1)	95(1)
C(9)	5081(2)	2752(1)	126(2)
C(10)	2377(2)	2349(1)	−1306(2)
C(11)	2432(2)	1320(1)	−1328(2)
C(12)	3166(2)	861(1)	−2031(2)
C(13)	3057(2)	−79(1)	−2115(2)
C(14)	2233(2)	−524(1)	−1492(2)
C(15)	1566(2)	−15(1)	−797(2)

of the ligand have identical chirality and, as was calculated, have nearly identical torsional angles. If one applies the nomenclature of Dale,[26] Boeyens and Dobson,[27] which was developed to describe saturated macrocycles, to the present structures, the 14-membered macrocycle of L^2 exhibits in the unco-ordinated state a [2525] conformation while **2** and **3** adopt a [133133] conformation. The octahedral co-ordination mode in the nickel(II) complex is linked to a very unsymmetrical [111434] configuration with *gauche* conformations at seven saturated bonds.

Despite the lack of molecular mechanics calculations, it can be concluded that the ligand highly prefers to co-ordinate in a trigonal-pyramidal manner. In the high-spin cobalt(II) and in the copper(II) complex octahedral geometry would lead to lower total d-electron energy and higher ligand-field stabilisation energy than in the observed trigonal prismatic geometry.[15] However the adopted conformation of the ligand, giving trigonal-prismatic geometry at the metal centre, is energetically favoured to such a degree that the loss in stabilisation energy is outweighed. For the high-spin d^8 configuration the total d-electron and the ligand-field stabilisation energy are even more in favour of octahedral geometry. Therefore nickel(II) adopts this geometry, despite an unfavourable macrocyclic ligand conformation. A similar difference in co-ordination geometry has been observed in the nickel(II) and copper(II) complexes of 1,4,7-tris(acetato)- and 1,4,7-tris(2-methylpyridyl)-1,4,7-triazacyclononane.[28]

In contrast to L^2, both the nickel(II) and copper(II) complexes of L^4 exhibit octahedral co-ordination, since the pendant acetato groups of L^4 are clearly less space-demanding than the pyridylmethyl arms of L^2. Recently we studied the structures of copper(II) and nickel(II) complexes of the *cis*-N_2S_2 analogue of L^2. Nickel(II) again exhibits octahedral geometry, but copper(II) is five-co-ordinate with trigonal-bipyramidal geometry and one S-donor atom remaining unco-ordinated.[29]

Table 6 Positional parameters (× 10^4) for $[NiL^2][ClO_4]_2$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	2490(1)	1848(1)	369(1)	C(8)	2742(5)	−428(5)	1061(4)
S(1)	1634(1)	316(1)	579(1)	C(9)	1162(5)	−204(6)	−344(4)
S(2)	2998(1)	1073(2)	−638(1)	C(10)	558(5)	483(7)	−894(4)
N(1)	3785(3)	1142(4)	1169(3)	C(11)	125(7)	93(9)	−1617(5)
N(2)	1229(4)	2298(5)	−562(3)	C(12)	317(9)	−899(11)	−1795(6)
N(3)	3485(3)	3099(4)	601(3)	C(13)	934(8)	−1543(8)	−1254(6)
N(4)	1680(4)	2660(4)	949(3)	C(14)	1333(6)	−1197(7)	−530(5)
Cl(1)	2175(1)	6226(2)	1373(1)	C(15)	5810(6)	1740(7)	502(5)
O(1)	1812(6)	5706(8)	688(4)	C(16)	6101(7)	2356(7)	−20(7)
O(2)	2570(13)	7079(9)	1270(9)	C(17)	5444(8)	2520(7)	−724(7)
O(3)	1462(5)	6424(8)	1705(4)	C(18)	4497(7)	2160(6)	−939(5)
O(4)	2898(8)	5710(12)	1847(5)	C(19)	4281(4)	1997(5)	1679(3)
Cl(2)	3025(2)	218(2)	−2956(1)	C(20)	4260(4)	2980(5)	1245(3)
O(5)	2905(9)	196(9)	−3696(5)	C(21)	4999(5)	3722(6)	1497(4)
O(6)	2332(9)	−260(14)	−2811(9)	C(22)	4923(6)	4616(6)	1098(4)
O(7)	3076(18)	1155(11)	−2748(9)	C(23)	4133(5)	4769(5)	458(4)
O(8)	3863(8)	−130(16)	−2586(7)	C(24)	3440(5)	3989(5)	223(4)
C(1)	362(5)	1572(6)	−700(4)	C(25)	905(5)	3300(6)	−322(4)
C(2)	1476(6)	2472(7)	−1256(4)	C(26)	951(5)	3254(5)	495(4)
C(3)	2153(8)	1788(11)	−1403(5)	C(27)	303(5)	3798(6)	766(5)
C(4)	4197(5)	1578(5)	−423(4)	C(28)	431(6)	3767(7)	1516(6)
C(5)	4836(5)	1361(5)	290(4)	C(29)	1162(6)	3169(6)	1985(5)
C(6)	4528(5)	665(6)	833(4)	C(30)	1771(5)	2625(6)	1683(4)
C(7)	3472(5)	306(5)	−1592(4)				

Table 7 Positional parameters (× 10^4) for $[CuL^2][ClO_4]_2$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	4 642(1)	7 765(1)	2 415(1)	C(8)	1 837(10)	8 091(7)	3 508(5)
S(1)	7 185(3)	7 527(2)	3 378(1)	C(9)	4 717(10)	8 207(8)	4 216(5)
S(2)	1 599(3)	6 809(2)	1 929(1)	C(10)	6 645(10)	8 348(7)	4 215(5)
N(1)	5 183(9)	6 086(6)	1 678(4)	C(11)	6 536(11)	5 717(8)	4 160(5)
N(2)	3 700(8)	8 476(5)	3 513(4)	C(12)	6 214(12)	4 523(8)	4 188(6)
N(3)	6 519(9)	8 307(6)	1 778(4)	C(13)	6 037(12)	3 715(8)	3 547(6)
N(4)	3 695(9)	9 387(6)	2 211(4)	C(14)	6 165(12)	4 037(8)	2 862(6)
Cl(1)	819(3)	8 627(2)	6 007(2)	C(15)	1 218(10)	6 248(7)	4 032(5)
Cl(2)	1 860(5)	7 261(3)	9 330(2)	C(16)	853(11)	5 053(8)	3 937(6)
O(11)	2 235(9)	8 621(6)	5 623(5)	C(17)	690(11)	4 377(8)	3 245(6)
O(12)	−461(9)	7 721(7)	5 634(4)	C(18)	937(11)	4 875(7)	2 615(5)
O(13)	210(12)	9 723(7)	6 086(7)	C(19)	3 830(11)	9 783(7)	3 562(5)
O(14)	1 382(12)	8 379(7)	6 750(4)	C(20)	5 637(12)	6 449(8)	979(5)
O(21)	8 039(14)	3 930(8)	567(5)	C(21)	6 763(11)	7 589(8)	1 161(5)
O(22)	7 809(19)	2 015(11)	21(7)	C(22)	7 922(12)	7 881(10)	711(6)
O(23)	7 347(33)	2 564(12)	1 224(12)	C(23)	8 828(13)	8 954(11)	881(6)
O(24)	9 734(25)	2 715(12)	972(11)	C(24)	8 589(13)	9 714(10)	1 516(7)
C(1)	6 633(10)	6 033(7)	3 467(5)	C(25)	7 436(12)	9 359(9)	1 947(6)
C(2)	6 472(11)	5 223(8)	2 804(5)	C(26)	3 375(10)	10 127(7)	2 805(5)
C(3)	6 697(11)	5 570(8)	2 062(5)	C(27)	2 822(12)	11 223(8)	2 734(6)
C(4)	3 709(12)	5 167(8)	1 458(5)	C(28)	2 615(14)	11 521(9)	2 035(7)
C(5)	2 034(11)	5 667(8)	1 207(5)	C(29)	2 944(13)	10 787(10)	1 422(7)
C(6)	1 372(10)	6 090(7)	2 709(5)	C(30)	3 445(12)	9 714(9)	1 526(5)
C(7)	1 486(10)	6 771(7)	3 416(5)				

Experimental

Materials and Regents.—All chemicals used were of reagent grade. Solvents were dried according to standard procedures.

Macrocycle and Complex Synthesis.—The ligand L^1 was synthesised as described previously.[30]

6,7,8,9,15,16,17,18-*Octahydro*-8,17-*bis*(2-*pyridylmethyl*)-*dibenzo*[f,m][1,8,4,11]*dithiadiazacyclotetradecine*] (L^2). Solutions of L^1 (1.0 g, 3 mmol) in CH_2Cl_2 (10 cm^3) and of NaOH (0.5 g) in water (20 cm^3) were combined. The two-phase mixture was stirred and a solution of 2-(chloromethyl)pyridine hydrochloride (1.0 g, 6 mmol) in CH_2Cl_2 (15 cm^3) was added over a period of 2–3 h. Stirring was continued for 2 d at 50 °C. The aqueous phase was separated and eluted three times with CH_2Cl_2 (30 cm^3). The solvent was dried with Na_2SO_4 and removed with a rotary evaporator to leave the product L^2, which was recrystallised from EtOH. Yield 1.1 g (71%), m.p. 180 °C (Found: C, 69.7; H, 6.3; N, 10.8. $C_{30}H_{32}N_4S_2$ requires C, 70.3; H, 6.3; N, 10.9%); ν_{max} 1580vs, 1560s, 1460s, 1350vs, 755vs and 745vs cm^{-1} (KBr); δ_H 2.70 (4 H, t, *J* 7.3, CH_2N), 3.00 (4 H, t, *J* 7.3, CH_2S), 3.79 (4 H, s, CH_2Ph), 3.90 (4 H, s, CH_2-pyridyl), 7.05–7.65 (14 H, m, aryl H, pyridyl H) and 8.50 (2 H, d, *J* 4.8 Hz, pyridyl H); *m*/*z* 512 (M^+, 63%), isotopic distribution: 512 (found 61.5, requires 63.3%), 513 (25.3, 23.5), 514 (10.4, 9.9), 515 (2.8, 2.5); λ_{max}(EtOH) 263 and 208 nm (ε 15 000 and 24 000 dm^3 mol^{-1} cm^{-1}).

$[NiL^2][ClO_4]_2$ **1**. Solutions of L^2 (200 mg, 0.4 mmol) in MeOH (5 cm^3) and of $Ni(ClO_4)_2 \cdot 6H_2O$ (150 mg, 0.4 mmol) in MeOH (5 cm^3) were combined and refluxed for 14 h. The precipitate was filtered off and washed with MeOH and CH_2Cl_2. Crystallisation from MeCN–MeOH (1:1) afforded blue prismatic crystals of **1** (190 mg, 62%) (Found: C, 47.0; H,

Table 8 Positional parameters (× 10^4) for $[CuL^2][ClO_4]_2$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu(1)	226(2)	2052(2)	2553(1)
S(1)	−2125(4)	2546(3)	1644(2)
S(2)	3383(5)	3270(3)	3095(2)
N(1)	1290(12)	1534(8)	1473(6)
N(2)	−195(13)	4022(9)	3359(6)
N(3)	1299(13)	605(9)	2790(6)
N(4)	−1484(13)	1737(9)	3228(6)
Cl(1)	4136(5)	1326(3)	8997(3)
O(1)	2780(16)	1298(10)	9423(8)
O(2)	4786(18)	245(10)	8927(10)
O(3)	5419(14)	2247(10)	9346(7)
O(4)	3474(19)	1569(11)	8253(7)
Cl(2)	3098(8)	2600(5)	5661(3)
O(5)	3038(25)	3764(16)	5539(9)
O(6)	2760(34)	1866(24)	5067(13)
O(7)	2400(48)	2425(17)	6239(20)
O(8)	4661(40)	2614(22)	5952(17)
C(1)	−1715(17)	4499(12)	2951(8)
C(2)	−1453(16)	4830(11)	2220(8)
C(3)	−1602(16)	3999(11)	1538(7)
C(4)	−1654(16)	1719(12)	787(8)
C(5)	286(16)	1853(12)	785(8)
C(6)	3168(16)	1965(11)	1523(8)
C(7)	3533(15)	3267(11)	1599(7)
C(8)	3643(16)	3948(11)	2322(8)
C(9)	2982(18)	4423(12)	3813(8)
C(10)	1301(17)	4919(12)	3572(8)
C(11)	−640(18)	3616(12)	4042(8)
C(12)	−1733(17)	2499(12)	3853(8)
C(13)	−2928(18)	2186(13)	4278(9)
C(14)	−3806(20)	1104(14)	4127(9)
C(15)	−3589(20)	353(14)	3498(9)
C(16)	−2438(18)	703(13)	3068(9)
C(17)	1162(16)	258(11)	1419(7)
C(18)	1599(16)	−107(11)	2161(8)
C(19)	2205(18)	−1170(13)	2259(9)
C(20)	2415(19)	−1484(14)	2933(9)
C(21)	2057(20)	−804(14)	3549(10)
C(22)	1533(17)	277(13)	3456(9)
C(23)	−1196(16)	5982(12)	2138(8)
C(24)	−1029(17)	6317(13)	1471(8)
C(25)	−1175(17)	5508(12)	820(9)
C(26)	−1465(16)	4338(12)	866(8)
C(27)	4049(16)	5168(12)	2402(8)
C(28)	4310(15)	5648(11)	1764(7)
C(29)	4172(17)	4967(12)	1051(8)
C(30)	3810(16)	3775(11)	987(8)

4.2; N, 7.3. $C_{30}H_{32}Cl_2N_4NiO_8S_2$ requires C, 46.8; H, 4.2; N, 7.3%); ν_{max} 1600s, 1570s, 1460s, 1080vs (br) (ClO_4), 750s and 620s cm^{-1} (ClO_4).

$[CuL^2][ClO_4]_2$ **2**. The compound was prepared in the form of green crystals as described for **1** by using $Cu(ClO_4)_2 \cdot 6H_2O$. Yield 220 mg (71%) (Found: C, 46.3; H, 4.2; N, 7.2. $C_{30}H_{32}Cl_2CuN_4O_8S_2$ requires C, 46.5; H, 4.2; N, 7.2%); ν_{max} 1600vs, 1440vs, 1080vs (br) (ClO_4), 760s, 745s and 620s cm^{-1} (ClO_4).

$[CoL^2][ClO_4]_2$ **3**. This compound was prepared as described for **1**. The reaction of L^2 and $Co(ClO_4)_2 \cdot 6H_2O$ yielded red crystals of **3** (260 mg, 84%) (Found: C, 46.5; H, 4.2; N, 7.2. $C_{30}H_{32}Cl_2CoN_4O_8S_2$ requires C, 46.8; H, 4.2; N, 7.3%); ν_{max} 1600s, 1440s, 1080vs (br) (ClO_4), 760s, 740s and 620s cm^{-1} (ClO_4).

Physical Measurements.—Infrared spectra were recorded using a Perkin Elmer 683 spectrometer and the KBr technique. VIS/near-IR spectra in the range 190–1400 nm were recorded on a Shimadzu 3100 instrument. Magnetic susceptibilities were measured at three temperatures and several field strengths using a Gouy balance. Proton NMR spectra were recorded at 300 MHz on a Bruker WM 300 instrument. Chemical shifts are given in ppm relative to $SiMe_4$. Mass spectra, using electron impact mode, were recorded on a CH5 Varian instrument.

Structural Analyses and Refinements.—Details of X-ray experimental conditions, all data, data collection and refinement parameters are summarised in Table 4. Direct methods were followed by standard full-matrix least-squares procedures {program system SHELXTL-PLUS[31] using the weighting scheme $w = 1/[\sigma^2(F_o) + gF_o^2]$ with $g = 0.000\,25$ for L^2 and 0.0004 for **1**–**3**}. Hydrogen atoms were included in calculated positions with overall $U_{iso} = 80$ pm^2. Atomic coordinates are given in Tables 5–8.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

The work was supported by the Fonds der Chemischen Industrie im Verband der Chemischen Industrie e.V. der Bundesrepublik Deutschland.

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Received 21*st December* 1992; *Paper* 2/06744G