Template Preparation of a Nickel(II) Pyridinophane Complex; Crystal and Molecular Structure of *cis*-dichloro{2,11-dithia[3,3](2,6)pyridinophane}-nickel(II) †

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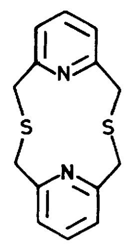
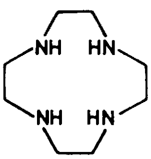
The crystal and molecular structure of the nickel(II) complex of a novel N_2S_2 pyridinophane macrocycle is reported. The complex is prepared by a template condensation about nickel(II) and possesses a distorted octahedral geometry.

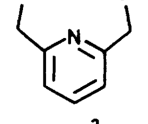
In the past two decades, numerous examples of macrocyclic ligands and their transition-metal complexes have been reported.[1] Macrocyclic ligands which incorporate heterocyclic moieties within their polydentate donor set have been particularly widely investigated.[2] Although a range of pyridinophanes of various types have been reported, their co-ordination chemistry has scarcely been investigated.[2,3] 2,11-Dithia[3,3]-(2,6)pyridinophane (L^1) is a potentially tetradentate N_2S_2 ligand, but although a number of conformational studies on the free pyridinophane have been reported,[4–9] no metal complexes have been described. This note reports the template synthesis of transition-metal complexes of 2,11-dithia[3,3](2,6)pyridinophane, and the crystal and molecular of the nickel(II) complex $[Ni(L^1)Cl_2]$.



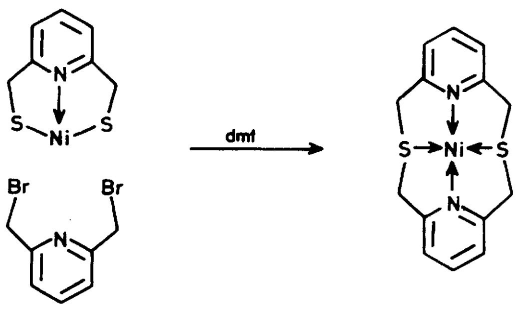
L^1



cyclen



H_2L^2



Scheme.

Results and Discussion

The ligand, 2,11-dithia[3,3](2,6)pyridinophane (L^1) possesses a 12-membered macrocyclic ring similar to that observed in cyclen (1,4,7,10-tetra-azacyclododecane). Molecular models, and a knowledge of the co-ordination chemistry of cyclen, suggested that the macrocyclic hole in L^1 is too small for the ligand to act as an N_2S_2 ligand occupying the equatorial plane of an octahedral transition-metal complex. Our current interests in the chemical consequences of metal ion–ligand mismatch[10–12] led us to consider the preparation of L^1 by template condensation about a transition-metal ion. The free ligand has been prepared by the reaction of 2,6-bis(halogenomethyl)pyridines with 2,6-bis(mercaptomethyl)pyridine (H_2L^2),[5] thiourea,[7] or sodium sulphide.[4,9] An extension of these syntheses led us to investigate the template reaction of 2,6-bis(bromomethyl)pyridine with the nickel(II) complex of 2,6-bis(mercaptomethyl)pyridine (Scheme). The possible consequences of the mismatch between the nickel(II) and the 2,11-dithia[3,3](2,6)pyridinophane are (*i*) that the metal ion is located above the N_2S_2 donor set in some form of square-based pyramidal five-co-ordinate environment; (*ii*) that the metal ion is labilised, such that the free ligand is obtained *via* a transient template effect;[11,12] (*iii*) that a [2 + 1] condensation occurs to give a larger, more flexible, macrocyclic ligand; (*iv*) that the ligand folds in such a way that an octahedral nickel(II) complex may form; *or* (*v*) that no reaction occurs.

2,6-Bis(mercaptomethyl)pyridine (H_2L^2) reacts rapidly with nickel(II) in the presence of aqueous ammonia to yield a very insoluble brown complex with a 1:1 stoicheiometry, $Ni(L^2)\cdot H_2O$. The mass spectrum of this material exhibited the highest mass peaks centred around *m/z* 456; this corresponds to a dimeric formulation $[Ni_2(L^2)_2]$, which has expected *m/z* 454, based on ^{58}Ni and ^{32}S. The precise structure of this complex is not known, but it is relevant to note that we have recently determined the crystal and molecular structure of the complex $[(H_2L^3)NiBr(\mu\text{-}Br)_2NiBr(H_2L^3)]$, which possesses a dimeric, bromo-bridged structure.[13]

The nickel(II) complex $[Ni_2(L^2)_2]\cdot 2H_2O$ reacted smoothly with 2,6-bis(bromomethyl)pyridine in warm dimethylformamide (dmf), to give a pale green solid, shown to possess the stoicheiometry $[Ni(L^1)Br_2]$. This complex readily underwent metathesis reactions upon treatment with aqueous solutions

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† *Supplementary data available* (No. SUP 56550, 3 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

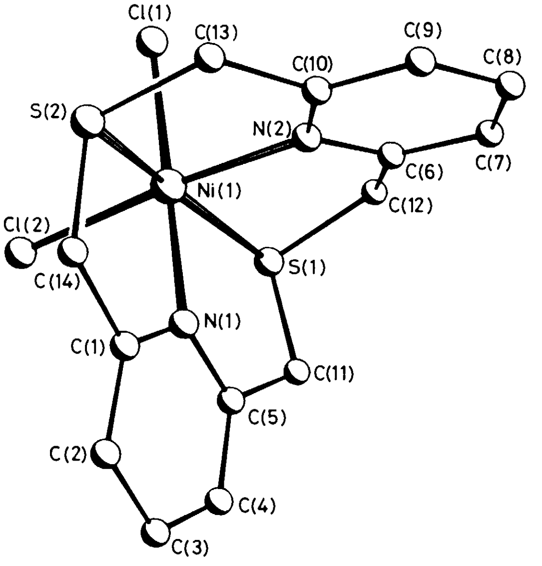
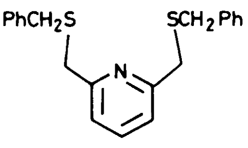


Figure. The molecular structure of $[Ni(L^1)Cl_2]$. Hydrogen atoms are omitted for clarity



H_2L^3

of NaX (X = Cl, I, SCN, or N_3), to yield the appropriate $[Ni(L^1)X_2]$ complexes. In no case could a satisfactory mass spectrum be obtained for these complexes, and in order to elucidate the structure of the products a crystal-structure determination was undertaken.

The molecular structure of the complex $[Ni(L^1)Cl_2]$ is shown in the Figure together with the atom-numbering scheme. Selected bond lengths and angles are presented in Table 1. The nickel(II) atom displays a slightly distorted octahedral co-ordination geometry. The two chlorine atoms occupy *cis* equatorial positions. The macrocyclic ligand, L^1, chelates the other four-co-ordination sites, bonding through the two nitrogen and two sulphur atoms. This ligand is folded in such a way that the sulphur atoms occupy mutually *trans* diaxial sites, while the pyridine nitrogen atoms occupy *cis* sites in the equatorial plane. This folding of the 12-membered macrocyclic ring is reminiscent of the conformation of the tetranitrogen donor, 12-membered cyclen rings in the complexes *cis*-$[Co(cyclen)(NO_2)_2]Cl$[14] and *cis*-$[Co(cyclen)(CO)_3]ClO_4 \cdot H_2O$.[15]

The *cis* conformation of two chlorine atoms in combination with a *trans* sulphur–sulphur arrangement, for a N_2S_2 donor set macrocycle, in a Ni^{II} octahedral complex has not been crystallographically characterised previously. In the related species dichloro(6,7,14,15,16,17,18,19-octahydro-13*H*-dibenzo-[*e*,*n*][1,4,8,12]dithiadiazapentadecine)nickel(II)[16] the chlorine atoms occupy *trans* axial sites and the sulphur donors take up *cis* equatorial positions. In the latter complex[16] the two Ni–Cl bond lengths (2.417 and 2.465 Å) differ by *ca.* 0.05 Å compared to a difference of *ca.* 0.08 Å in $[Ni(L^1)Cl_2]$, while the mean Ni–Cl distance for chlorine *trans* to chlorine is 2.441 Å compared to a mean value of 2.403 Å for chlorine *trans* to a nitrogen donor. In $[Ni(L^1)Cl_2]$ the two Ni–N bond lengths differ by *ca.* 0.02 Å, with the slightly shorter Ni–N bond *trans* to the longer Ni–Cl bond. The average of these two Ni–N distances (2.084 Å) is not significantly different from the value of 2.095 Å for the two Ni–N bonds in dichloro(6,7,14,15,16,17,18,19-octahydro-13*H*-dibenzo[*e*,*n*][1,4,8,12]dithiadiazapentadecine)nickel(II),[16] where the nitrogen atoms are *trans* to sulphur donor atoms. The two Ni–S bond lengths in $[Ni(L^1)Cl_2]$ differ by *ca.* 0.02 Å, and the average Ni–S distance is 2.396 Å. This average bond length is somewhat shorter than the distance of 2.418 Å in bis(1-thia-4,7-diazacyclononane-*S*,*N*,*N′*)nickel dinitrate[17] where the two sulphur donors are crystallographically constrained to occupy *trans* co-ordination sites. The bond parameters within L^1 itself do not deviate significantly from the expected values. A consequence of the folding of L^1 in $[Ni(L^1)Cl_2]$ is that the pyridine rings make an angle of 94.4° with each other. Although this near perpendicularity does not correspond to the equilibrium solution conformation of the free ligand, dithia[3,3]cyclophanes have been shown to be conformationally mobile in solution.[18] It is probably this flexibility in the ligand which allows the template synthesis about the Ni^{II} atom to proceed so readily.

Table 1. Bond lengths (Å) and interbond angles (°) for $[Ni(L^1)Cl_2]$

Cl(1)–Ni(1)	2.363(1)	Cl(2)–Ni(1)	2.443(1)
S(1)–Ni(1)	2.407(1)	S(2)–Ni(1)	2.385(1)
C(11)–S(1)	1.825(3)	C(12)–S(1)	1.814(3)
C(13)–S(2)	1.801(4)	C(14)–S(2)	1.812(3)
C(1)–N(1)	1.335(4)	C(5)–N(1)	1.366(4)
C(2)–C(1)	1.389(5)	C(14)–C(1)	1.507(5)
C(3)–C(2)	1.392(5)	C(4)–C(3)	1.378(5)
C(5)–C(4)	1.369(5)	C(11)–C(5)	1.500(4)
C(6)–N(2)	1.357(4)	C(10)–N(2)	1.334(4)
C(7)–C(6)	1.372(5)	C(12)–C(6)	1.496(4)
C(8)–C(7)	1.392(5)	C(9)–C(8)	1.387(5)
C(10)–C(9)	1.385(4)	C(13)–C(10)	1.527(4)
Cl(2)–Ni(1)–Cl(1)	93.7(1)	S(1)–Ni(1)–Cl(1)	97.4(1)
S(1)–Ni(1)–Cl(2)	94.6(1)	S(2)–Ni(1)–Cl(1)	94.6(1)
S(2)–Ni(1)–Cl(2)	95.6(1)	S(2)–Ni(1)–S(1)	163.7(1)
N(1)–Ni(1)–Cl(1)	178.3(1)	N(1)–Ni(1)–Cl(2)	87.0(1)
N(1)–Ni(1)–S(1)	84.1(1)	N(1)–Ni(1)–S(2)	83.8(1)
N(2)–Ni(1)–Cl(1)	91.1(1)	N(2)–Ni(1)–Cl(2)	175.1(1)
N(2)–Ni(1)–S(1)	84.1(1)	N(2)–Ni(1)–S(2)	84.8(1)
N(2)–Ni(1)–N(1)	88.2(1)	C(11)–S(1)–Ni(1)	97.5(1)
C(12)–S(1)–Ni(1)	94.9(1)	C(12)–S(1)–C(11)	101.3(2)
C(13)–S(2)–Ni(1)	97.9(1)	C(14)–S(2)–Ni(1)	98.1(1)
C(14)–S(2)–C(13)	103.4(2)	C(1)–N(1)–Ni(1)	119.5(2)
C(5)–N(1)–Ni(1)	120.1(2)	C(5)–N(1)–C(1)	118.7(3)
C(2)–C(1)–N(1)	122.2(3)	C(14)–C(1)–N(1)	119.3(3)
C(14)–C(1)–C(2)	118.5(3)	C(3)–C(2)–C(1)	118.4(3)
C(4)–C(3)–C(2)	119.3(3)	C(5)–C(4)–C(3)	119.5(3)
C(4)–C(5)–N(1)	121.7(3)	C(11)–C(5)–N(1)	117.6(3)
C(11)–C(5)–C(4)	120.6(3)	C(6)–N(2)–Ni(1)	120.1(2)
C(10)–N(2)–Ni(1)	120.9(2)	C(10)–N(2)–C(6)	118.9(3)
C(7)–C(6)–N(2)	121.9(3)	C(12)–C(6)–N(2)	117.7(3)
C(12)–C(6)–C(7)	120.4(3)	C(8)–C(7)–C(6)	119.1(3)
C(9)–C(8)–C(7)	119.1(3)	C(10)–C(9)–C(8)	118.6(3)
C(9)–C(10)–N(2)	122.5(3)	C(13)–C(10)–N(2)	119.0(3)
C(13)–C(10)–C(9)	118.5(3)	C(5)–C(11)–S(1)	115.6(2)
C(6)–C(12)–S(1)	114.9(2)	C(10)–C(13)–S(2)	115.8(2)
C(1)–C(14)–S(2)	116.0(2)		

Experimental

2,6-Bis(bromomethyl)pyridine[19] and 2,6-bis(mercaptomethyl)-pyridine[20,21] were prepared by the literature methods.

Table 2. Atomic fractional co-ordinates ($\times 10^4$) for [Ni(L^1)Cl$_2$]

Atom	X/b	Y/b	Z/c
Ni(1)	2 648(1)	2 766(1)	7 666(1)
Cl(1)	1 716(1)	2 027(1)	9 326(1)
Cl(2)	1 202(1)	1 097(1)	6 780(1)
S(1)	32(1)	5 643(1)	7 313(1)
S(2)	5 728(1)	382(1)	7 812(1)
N(1)	3 559(4)	3 376(3)	6 208(2)
C(1)	5 055(4)	2 131(4)	5 791(3)
C(2)	5 405(5)	2 221(5)	4 736(3)
C(3)	4 170(5)	3 686(5)	4 104(2)
C(4)	2 686(5)	5 020(4)	4 545(2)
C(5)	2 409(4)	4 848(4)	5 588(2)
N(2)	3 912(4)	4 269(3)	8 294(2)
C(6)	2 893(4)	6 043(4)	8 410(2)
C(7)	3 717(5)	7 129(4)	8 721(2)
C(8)	5 644(5)	6 375(4)	8 957(2)
C(9)	6 681(5)	4 553(5)	8 859(2)
C(10)	5 754(4)	3 547(4)	8 531(2)
C(11)	882(5)	6 333(4)	6 100(3)
C(12)	802(5)	6 775(4)	8 234(3)
C(13)	6 871(5)	1 519(4)	8 490(3)
C(14)	6 430(5)	583(4)	6 482(3)

Preparation of [Ni$_2$(L^2)$_2$].—Hexa-aquanickel(II) sulphate (6.0 g, 0.0226 mol) was dissolved in concentrated ammonia solution (d = 0.880 g cm^{-3}, 20 cm^3) and water (75 cm^3). To this solution was added, with stirring, 2,6-bis(mercaptomethyl)-pyridine (3.86 g, 0.0226 mol) in methanol (15 cm^3). A light brown precipitate was formed immediately. The solid was separated by filtration and dried *in vacuo* over sulphuric acid for 24 h. The product was powdered, washed with water, methanol, and diethyl ether, and dried again over sulphuric acid to yield the title complex as a dihydrate (4.6 g, 85%) (Found: C, 34.2; H, 3.0; N, 5.9. $C_{14}H_{18}N_2Ni_2O_2S_4$ requires C, 34.2; H, 3.4; N, 5.9%); m/z 454 (M − 2H$_2$O).

Preparation of [Ni(L^1)Br$_2$].—To a suspension of [Ni$_2$(L^2)$_2$]·2H$_2$O (0.492 g, 1 mmol) in dmf (10 cm^3) was added 2,6-bis(bromomethyl)pyridine (0.530 g, 2 mmol). The dark brown nickel(II) complex turned dark green upon the addition of the bromide. The mixture was heated to reflux and then stirred at 70 °C until all the dark green solid had vanished leaving a very light green material. This solid was collected by filtration, washed with cold absolute ethanol, and dried *in vacuo* over phosphorus pentoxide (0.42 g, 86%) (Found: C, 34.2; H, 3.0; Br, 30.5; N, 5.4; Ni, 12.0. $C_{14}H_{14}Br_2N_2NiS_2$ requires C, 34.1; H, 2.8; Br, 30.45; N, 5.4; Ni, 12.0%).

Crystal Structure Determination of [Ni(L^1)Cl$_2$].—Suitable single crystals were obtained as blue blocks by slow evaporation of a methanolic solution, and a crystal with dimensions *ca.* 0.36 × 0.31 × 0.20 mm was sealed in a 0.5-mm glass capillary. Space group and approximate cell parameters were determined *via* Weissenberg (Cu-K_α radiation) photography.

Crystal data. $C_{14}H_{14}Cl_2N_2NiS_2$, M = 404.0, triclinic, a = 7.754(1), b = 8.148(1), c = 12.945(2) Å, α = 85.08(1), β = 89.08(1), γ = 65.98(1)°, U = 744.1(2) Å^3 (by least-squares refinement for 15 automatically centred reflections in the range 50 < 2θ < 60°), space group $P\bar{1}$ (no. 2), D_m not measured, Z = 2, D_c = 1.803 g cm^{-3}, $F(000)$ = 412, Cu-K_α radiation, λ = 1.541 8 Å, μ(Cu-K_α) = 75.33 cm^{-1}.

Data collection and processing.[10] Syntex $P2_1$ diffractometer, 96-step ω—2θ scan mode with a scan range from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$, scan speed 3.0—29.3° min^{-1}, graphite-monochromated Cu-K_α radiation; 2 663 reflections measured (3.0 < 2θ < 125°, $+h$, $\pm k$, $\pm l$), 2 320 unique [merging R 0.008 after empirical absorption correction based on 444 ψ scans from 15 unique reflections (maximum and minimum transmission factors 0.391 and 0.208)], giving 2 275 with $F > 4\sigma(F)$. No significant variation in standard reflections during data collection.

Structure analysis and refinement. Nickel atom position from a Patterson synthesis, followed by Fourier difference techniques. Full-matrix least squares with all non-hydrogen atoms anisotropic. Hydrogen atoms placed in idealised positions and allowed to ride 1.08 Å from the relevant C atoms during refinement; each type of H assigned a common isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F) + 0.0008|F|^2]^{-1}$ gave satisfactory agreement analysis. Final R and R' values were 0.052 and 0.059. Complex neutral-atom scattering factors were employed,[22] and all computations were performed on the IBM 3081 computer at the University of Cambridge using SHELX 76.[23] The final atomic fractional co-ordinates are listed in Table 2.

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