Stability, Electronic Spectra, and Structure of Transition-metal Ion Complexes of a Novel Mixed-donor (Nitrogen–Sulphur) Macrocycle, 1-Thia-4,7-diazacyclononane †

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The synthesis of the novel ligand 1-thia-4,7-diazacyclononane (L^1) is described. A potentiometric study yields pK_1 as 9.67, and pK_2 as 3.98 in 0.1 mol dm^{-3} $NaNO_3$ at 25 °C; complex-formation constants logK_1 and logK_2 are found to be 10.45 and 9.6 for Ni^{II} and 12.42 and 9.87 for Cu^{II} in 0.1 mol dm^{-3} $NaNO_3$ at 25 °C. Comparison of these constants shows a stabilisation relative to the complexes of the open-chain analogue 3-thiapentane-1,5-diamine (L^2) which is similar to that found for comparable cyclononane macrocycles such as those with N_3 and N_2O donors. The electronic spectra of $[NiL^1{}_2]^{2+}$ and $[NiL^2{}_2]^{2+}$ are discussed, and it is shown that, if correction is made for spin–orbit coupling effects, 10*Dq* is larger in the former complex. The crystal structure of $[NiL^1{}_2][NO_3]_2$ has been determined and refined to a conventional *R* factor of 0.0398. Average bond lengths of Ni–N 2.115 ± 0.007 Å and Ni–S 2.418 ± 0.001 Å are found, which are very similar to those in the open-chain analogue. The structure has the sulphur donor atoms placed *trans* to each other, in contrast to that of the L^2 complex where they are *cis*. The structures of the complexes are discussed in relation to possible origins of the high ligand-field strengths of the macrocycles.

A striking feature of macrocyclic chemistry is that oxygen-donor macrocycles form their most stable complexes with metal ions which have very ionic metal to ligand bonding, such as the alkali- and alkaline-earth-metal ions, while nitrogen donors prefer metal ions capable of more covalent metal to ligand bonding, such as the transition-metal ions. The effect of substituting oxygen-donor atoms with nitrogen and sulphur donors has been well documented for the alkali- and alkaline-earth-metal ions, where it is seen to lower the stability.[1] A study of the effect of substituting an oxygen donor into an N-donor macrocycle has recently been reported.[2] Some work has already been done on mixed-donor macrocycles with both nitrogen and sulphur donor atoms,[3] but the presence of a benzo-group in the ring makes difficult comparison with the results on other macrocycles and there is no study on a linear analogue for comparison. The bonds from metal ions to sulphur appear to be far more covalent than those to oxygen, and if covalence is of any importance in the macrocyclic effect,[4] such sulphur–nitrogen mixed-donor macrocycles should prove to have extremely interesting properties.

We report here the synthesis of the novel ligand 1-thia-4,7-diazacyclononane (L^1), the formation constants of its complexes with copper(II) and nickel(II), the electronic spectra of these complexes, and the crystal structure of the complex $[NiL^1{}_2][NO_3]_2$. This ligand is directly comparable with the linear analogue 3-thiapentane-1,5-diamine (L^2) and also the macrocyclic ligands L^3 and L^4. Important features of the macrocyclic effect in L^1 would be:[4] (1) the increase in 10*Dq* relative to the L^2 complex; (2) the increase in formation constants relative to the L^2 complexes; and (3) the rate of complex formation relative to other macrocycles considered here. The crystal structure of $[NiL^1{}_2]^{2+}$ may be compared with that recently reported[5] for $[NiL^2{}_2]^{2+}$. This would allow evaluation of the idea that compression[6] or trigonal distortion[7] is responsible for the high 10*Dq* values associated with complexes of N-donor macrocycles.

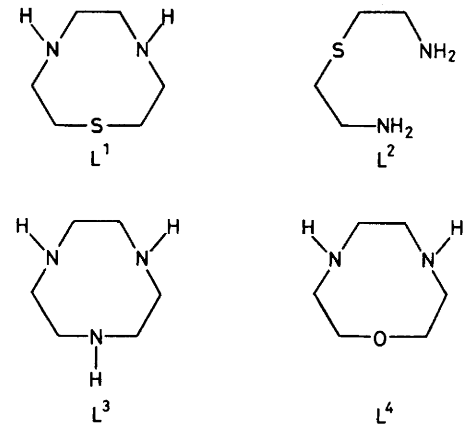

Figure 1. Structures of macrocyclic ligands and their open-chain analogues

Experimental

Synthesis of the Ligand.—From the cost aspect, the synthesis of L^1 from the ditosylate of thiodiglycol (2,2′-thiodiethanol), route (*a*) below, is more attractive. However, the ditosylate of thiodiglycol proved to be very unstable to hydrolysis, so that the alternative route (*b*), starting with the ditosylate of L^2, had to be followed.

NN′-*Di*(*toluene*-p-*sulphonyl*)*bis*(2-*aminoethyl*) *sulphide*. Toluene-*p*-sulphonyl (tosyl) chloride (34.0 g, 0.18 mol) in diethyl ether (200 cm^3) was added to a stirred solution containing NaOH (7.0 g, (0.18 mol) and L^2 (8.5 g, (0.07 mol) (K & K Chemicals) in water, and stirred for 24 h. After separating off the ether layer, the water was extracted with two 200-cm^3 portions of chloroform. Evaporation of the solvent yielded 29.5 g of crude product. Recrystallisation of a portion of this from $CHCl_3$ gave a product with m.p. 109—111 °C (Found: C, 50.2; H, 5.80; N, 6.65. $C_{18}H_{24}N_2S_3$ requires C, 50.45; H, 5.65; N, 6.55%). N.m.r.: δ (in $CDCl_3$, relative to $SiMe_4$) 2.43 (s, 6 H, Me), 2.52 (t, 4 H, CH_2S), 2.98 (t, 4 H, CH_2N), 5.20 (s, 2 H, NH), and 7.50 (q, 8 H, Ph).

NN′-*Di*(*toluene*-p-*sulphonyl*)-1-*thia*-4,7-*diazacyclononane*.

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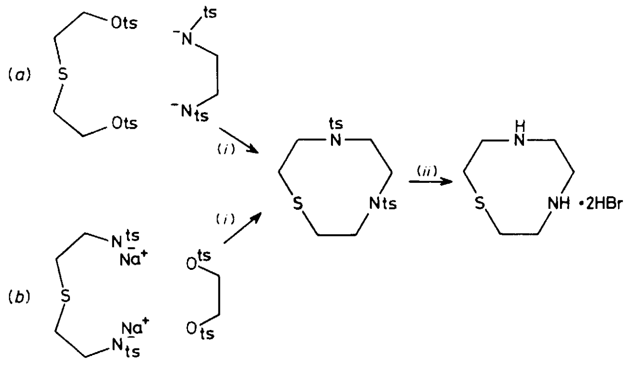
† *Supplementary data available* (No. SUP 23594, 13 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme. Synthetic route followed in synthesis of $L^1 \cdot 2HBr$. Route (*a*) was abandoned because of the instability of the tosylate of thiodiglycol (ts = toluene-*p*-sulphonyl, dmf = dimethylformamide). (*i*) dmf, 110 °C; (*ii*) HBr, glacial acetic acid, reflux

Sodium metal (1.2 g, 0.052 mol) was placed in dimethylformamide (220 cm^3) and stirred. *NN′*-Di(toluene-*p*-sulphonyl)bis-(2-aminoethyl) sulphide (10.7 g, 0.025 mol) was added and the reaction stirred for a total of 24 h; the sodium had reacted completely after 7 h forming the disodium salt of the ditosylate. The mixture was heated to 110 °C, and 1,2-dibromoethane (5.0 g, 0.027 mol) in dimethylformamide (100 cm^3) was added dropwise over 75 min. Heating and stirring was continued for another 5 h. The solution was concentrated to 30 cm^3, water was added until a solid precipitated and then the mixture was extracted with hot benzene. The benzene extract was dried over anhydrous Na_2SO_4 and evaporated to a yellow oil which partially crystallised. This was dissolved in hot ethanol and allowed to cool. After standing, 1.18 g (2.6 mmol; 10.4% yield) of the required product were collected as white crystals, m.p. 276—279 °C (Found: C, 52.65; H, 6.00; N, 6.35. $C_{20}H_{26}N_2O_4S_3$ requires C, 52.85; H, 5.75; N, 6.15%). N.m.r.: δ (in $CDCl_3$, relative to $SiMe_4$) 2.44 (s, 6 H, Me), 3.13 (m, 4 H, CH_2S), 3.38 (s, 4 H, NCH_2CH_2N), 3.48 (m, 4 H, CH_2N), and 7.45 (q, 8 H, Ph).

1-*Thia*-4,7-*diazacyclononane dihydrobromide*. The procedure of Koyama and Yoshino [8] was used to hydrolyse the cyclic tosylate. A solution of it (1.83 g, 0.004 mol) in 30% hydrobromic acid–glacial acetic acid (140 cm^3) was refluxed for 48 h. The solution was filtered whilst hot and concentrated to one tenth of its original volume. Addition of diethyl ether–absolute ethanol (1 : 3) gave yellow-white crystals which decomposed on heating between 220 and 230 °C (Found: C, 23.05; H, 5.40; N, 8.90. $C_6H_{16}Br_2N_2S$ requires C, 23.4; H, 5.25; N, 9.10%). N.m.r.: δ (in D_2O, relative to sodium 2,2-dimethyl-2-silapentanesulphonate) 3.10 (m, 4 H, CH_2S), 3.50 (m, 4 H, CH_2N), and 3.75 (s, 4 H, NCH_2CH_2N).

$[NiL^1{}_2][NO_3]_2$.—A solution of the dihydrobromide was neutralised with NaOH, extracted into chloroform, and evaporated down to obtain a few mg of the free ligand. This was dissolved in a little ethanol and water, a little $Ni(NO_3)_2 \cdot 6H_2O$ was added, and the solution allowed to stand. One of the few purple crystals obtained was suitable for an *X*-ray structural study.

Stability-constant Studies.—These were carried out in 0.1 mol dm^{-3} $NaNO_3$ at 25 °C by techniques described previously.[9] It was found that copper(II) solutions equilibrated rapidly with the ligand during the course of titration, within 20 min of each addition. Nickel(II) reacted far more slowly, requiring up to 24 h for equilibration. To overcome sources of inaccuracy such as drifting potentials over this time span, the nickel(II) system was studied by an ‘ out-of-cell ’ technique.[10] A number of solutions with different amounts of metal, ligand, and acid were made up, and left in tightly stoppered flasks to equilibrate for 1 week. After this time the pH of each solution was measured with a Radiometer PHM 84 pH meter, and $\bar{n}$ (the average number of ligands bound to the metal ion) calculated. Values of $\log K_1$ and $\log K_2$ for the system were calculated using a computer program described previously.[11]

Structure Determination.—Diffraction quality crystals were selected by standard oscillation and Weissenberg techniques using Cu-K_α radiation. The space group and approximate cell constants were obtained at the same time. Intensity data and accurate cell dimensions were obtained with a Philips PW 1 100 diffractometer using Mo-K_α *X*-rays (λ = 0.710 70 Å).

Crystal data. $C_{12}H_{28}N_6NiO_6S_2$, $M = 475.23$, Monoclinic, $P2_1/c$, $a = 8.128(4)$, $b = 14.197(7)$, $c = 9.573(5)$ Å, $\beta = 112.51(3)°$, $U = 1\,020.47$ Å^3, $F(000) = 496.00$, $D_m = D_c = 1.55$ g cm^{-3}, $Z = 2$, μ(Mo-K_α) = 11.24 cm^{-1}.

A scan rate of 0.04° s^{-1} and a scan width of 1.2° were used, with a background counting time of 30 s. The structure was determined by Patterson and Fourier techniques, using the SHELX program.[12] The hydrogen atoms were found after the penultimate least-squares cycle, and were refined with a common isotropic thermal parameter. The other atoms were refined with anisotropic thermal parameters. The final atomic co-ordinates are listed in Table 1, Table 2 gives the more important interatomic distances and angles, and Table 3 the endocyclic torsion angles. At the end of refinement the conventional *R* factor was 0.0398 for the total of 1 959 observed reflections.

Spectra.—Ultraviolet-visible spectra were recorded on a Cary 17 spectrophotometer, and n.m.r. spectra on a Varian EM 360.

Results and Discussion

Formation Constants.—In Table 4 are shown the pK_a values and complex-formation constants with Cu^{II} and Ni^{II} of the N_2X-donor macrocycles, where X = S, O, or N, together with the log*K* values for their open-chain analogues. Also listed are the values for log*K*(mac), which are log*K* for the macrocycle minus log*K* for the open-chain analogue. The pK_a values form a most interesting series. We see that for all the open-chain ligands pK_1 and pK_2 do not vary much as we change the central donor atom from nitrogen to sulphur or oxygen. This suggests that the different central donor atoms do not exert any electronic effects which markedly change the basicity of the neighbouring nitrogen-donor atoms. One must therefore conclude that the marked differences in pK_a in the macrocycles as we change X from nitrogen to sulphur or oxygen do not reflect electronic, *i.e.* inductive, effects, but are probably due to differences in the hydrogen-bonding ability of X. Thus when X = N, the pK_1 and pK_2 values are at their highest, and become progressively lower as we exchange N for O and then S. This is exactly as would be expected if the donor atoms in the macrocycle were involved in a co-operative stabilisation of the attached proton by hydrogen bonding to the proton or its accompanying waters of solvation, since the expected hydrogen-bonding ability of the different groups would be N > O > S. If reduction in solvation by steric hindrance is the predominant factor in producing the macrocyclic effect,[13] we might, from the pK_a values of the macrocycles, expect that the size of log*K*(mac) would decrease in the order X = N > O > S for the cyclononane N_2X-donor macrocycles.

We see in Table 4 that this order is not realised for Ni^{II},

Table 1. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ni[a]	0.0	0.5	0.5	C(4)	0.240 8(5)	0.328 9(3)	0.528 7(5)
S	0.011 4(1)	0.340 2(1)	0.416 7(1)	C(5)	0.180 1(5)	0.477 6(3)	0.820 1(5)
N(1)	−0.122 0(3)	0.439 0(2)	0.638 7(3)	C(6)	0.009 0(5)	0.425 6(3)	0.795 8(4)
N(2)	0.229 8(3)	0.463 5(2)	0.689 0(3)	N(3)	0.624 8(3)	0.594 0(2)	0.781 2(3)
C(1)	−0.214 3(4)	0.350 5(2)	0.570 4(4)	O(1)	0.575 2(2)	0.530 0(2)	0.683 4(3)
C(2)	−0.095 3(5)	0.283 1(2)	0.530 8(4)	O(2)	0.782 6(3)	0.619 0(2)	0.831 4(3)
C(3)	0.301 0(5)	0.367 3(3)	0.686 3(5)	O(3)	0.513 5(3)	0.630 7(2)	0.822 8(3)
H1C1[b]	−0.162(5)	0.233(3)	0.477(4)	H1C4	0.160(5)	0.552(3)	0.827(4)
H2C1	−0.005(5)	0.253(3)	0.627(4)	H2C4	0.270(5)	0.456(3)	0.909(4)
H1C2	−0.325(5)	0.360(3)	0.476(4)	H(N2)	0.313(5)	0.498(3)	0.702(4)
H2C2	−0.260(5)	0.321(3)	0.634(4)	H1C5	0.251(5)	0.328(3)	0.745(4)
H(N1)	−0.199(5)	0.476(3)	0.644(4)	H2C5	0.424(5)	0.371(3)	0.725(4)
H1C3	0.027(5)	0.359(3)	0.807(4)	H1C6	0.286(5)	0.261(3)	0.535(4)
H2C3	−0.039(5)	0.451(3)	0.859(4)	H2C6	0.308(5)	0.357(3)	0.458(4)

[a] Nickel atom situated on centre of symmetry; transpose *x*,*y*,*z* to −*x*,1 − *y*,1 − *z* to obtain co-ordinates of other ligand. [b] To obtain the co-ordinates for the hydrogen atoms on the other ligand transpose *x*,*y*,*z* to −*x*,1 − *y*,1 − *z*. All atoms refined with a common isotropic thermal parameter $U = 0.056(3)$ Å^2. H1C1 means H(1) attached to C(1).

Table 2. Important bond lengths (Å) and angles (°)

Ni−S	2.418(1)	S−C(1)	1.824(3)	N(1)−C(3)	1.485(4)	C(1)−C(2)	1.509(5)
Ni−N(1)	2.122(2)	S−C(6)	1.815(4)	N(2)−C(4)	1.471(4)	C(3)−C(4)	1.511(5)
Ni−N(2)	2.108(2)	N(1)−C(2)	1.481(4)	N(2)−C(5)	1.488(4)	C(5)−C(6)	1.503(6)

N(1)−Ni−S	84.8(1)	C(6)−S−Ni	93.1(1)	C(4)−N(2)−C(5)	112.0(3)
N(2)−Ni−S	85.4(1)	C(1)−S−C(6)	104.2(2)	C(2)−C(1)−S	111.5(2)
N(1)−Ni−N(2)	80.5(1)	C(2)−N(1)−Ni	110.4(2)	C(5)−C(6)−S	113.1(2)
N(1)−Ni−S′*	95.2(1)	C(3)−N(1)−Ni	111.1(2)	C(1)−C(2)−N(1)	112.6(3)
N(2)−Ni−S′*	94.8(1)	C(4)−N(2)−Ni	104.8(2)	C(4)−C(3)−N(1)	110.8(3)
N(1)−Ni−N(2′)	99.7(1)	C(5)−N(2)−Ni	115.7(2)	C(3)−C(4)−N(2)	109.9(3)
C(1)−S−Ni	97.6(1)	C(2)−N(1)−C(3)	112.6(2)	C(6)−C(5)−N(2)	112.7(3)

* Primes indicate atom of second ligand attached to nickel (see footnote *a* of Table 1).

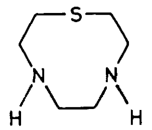
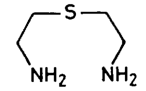
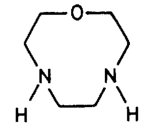
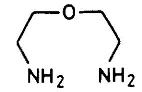
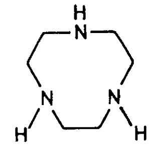
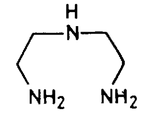
Table 3. Endocyclic torsion angles (°)

Ni−S−C(1)−C(2)	25.0(4)	S−C(1)−C(2)−N(1)	−51.9(5)
Ni−S−C(6)−C(5)	44.1(4)	S−C(6)−C(5)−N(2)	−49.3(5)
Ni−N(1)−C(2)−C(1)	52.2(5)	N(1)−Ni−S−C(1)	0.7(2)
Ni−N(1)−C(3)−C(4)	12.0(6)	N(1)−Ni−N(2)−C(4)	−34.9(3)
Ni−N(2)−C(4)−C(3)	52.0(5)	N(2)−Ni−N(1)−C(3)	12.8(3)
Ni−N(2)−C(5)−C(6)	24.1(6)	N(2)−Ni−S−C(6)	−23.2(2)
S−Ni−N(1)−C(2)	−26.8(3)	N(1)−C(3)−C(4)−N(2)	−43.1(5)
S−Ni−N(2)−C(5)	3.6(3)		

rather N $\gg$ S $>$ O with the macrocyclic effect slightly greater for L^1 than L^4 for both Cu^{II} and Ni^{II}. The position of L^3 in the series with Ni^{II}, where it produces the greatest macrocyclic effect, appears to support the arguments of Hinz and Margerum[13] concerning the role of solvation in producing the macrocyclic effect. This must be considered with some caution, however, since logK_2 for L^3 has not been determined with either Cu^{II} or Ni^{II} because of slow kinetics and problems with hydrolysis of the 1 : 1 complex.[10] If we look at the Cu^{II} systems with L^1 and L^4, we see that logK_1 is greater than logK_2 by *ca.* 2.4 log units in both cases. A reasonable value for logK_2 for the L^3 system with Cu^{II} would therefore be about 13.1, which would give logK_2(mac) = 8.1. This would give log β_2(mac) values for the copper(II) systems with cyclononane-N$_2$X donors of 8.14 (X = S), 7.7 (N), and 6.4 (O), in complete contradiction of what would be expected from solvation arguments. In support of our estimate of logK_2 for Cu^{II} with L^3, it should be noted that logK_2 for Cu^{II} with 1,4,7-triazacyclodecane, which should be somewhat lower, has been reported[14] as 10.26. As it seems to be of paramount importance to establish the values of logK_2 for L^3 systems, in spite of the difficulties, we have undertaken such a study with both Cu^{II} and Ni^{II}.

For Cu^{II} we see that logK_1(mac) is greatest for L^1, and least for L^3, which probably reflects the fact that the S and O donor atoms occupy the axial co-ordination site. One sees that for Ni^{II} logK_1(mac) is rather similar to logK_2(mac) for both L^4 and L^1. For Cu^{II}, however, logK_2(mac) is considerably larger than logK_1(mac) for both L^1 and L^4, and probably also L^3. This facilitation of the addition of subsequent ligands is also seen in non-macrocyclic ligands where square-planar co-ordination is prevented. The best example of this is 2,2′-bipyridyl (bipy), where steric repulsion between the *ortho*-hydrogens of two bipy ligands prevents square-planar co-ordination geometry. logK_3, where the third bipy is being added to complete the octahedron, is[15] uncharacteristically large for Cu^{II} at 3.3, which may be compared with −1.0 for the ethylenediamine (en) system where there are no constraints against planar co-ordination. Thus, the enforcing of facial octahedral co-ordination with Cu^{II} in the complexes containing one cyclononane N$_2$X ligand destabilises the complex relative to the open-chain analogue where meridional co-

Table 4. pK_1 and pK_2 for a variety of cyclononane N_2X macrocycles, and their open-chain analogues, together with $\log K_1$ and $\log K_2$ for complex formation with Cu^{II} and Ni^{II} [a]

Ligand	Ref.	pK_1	pK_2	Cu^{II}		Ni^{II}	
				$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
	*b*	9.67(2)	3.98(2)	12.42(2)	9.87(2)	10.45(2)	9.60(2)
	*c*	9.50	8.7	9.07	5.08	7.16 [b]	5.93 [b]
				$\log K$(mac) [d]: 3.35	4.79	3.29	3.67
	2	9.59	5.32	10.85	8.64	8.59	7.27
	*c*	9.75	8.90	8.70	4.4	5.62	3.39
				$\log K$(mac): 2.15	4.24	2.97	3.88
	10	10.42	6.82	15.52		16.24	
	*c*	9.70	8.98	15.9	5.0	10.5	8.1
				$\log K$(mac): −0.4		5.74	

[a] At 25 °C and $I = 0.1$ mol dm^{-3}. [b] This work, 0.1 mol dm^{-3} $NaNO_3$. [c] R. M. Smith and A. E. Martell, ' Critical Stability Constants,' vol. 2, ' Amines,' Plenum, New York, 1975. [d] $\log K$(mac) is the magnitude of the macrocyclic effect, *i.e.* $\log K$ for the macrocyclic complex minus $\log K$ for the analogous open-chain complex.

ordination is possible. For addition of the second cyclononane N_2X ligand, or of the open-chain analogue, full octahedral co-ordination is enforced, so that whether a ligand can accommodate square-planar co-ordination or not now becomes irrelevant. We thus find that log β_2(mac) for Cu^{II} is very close to log β_2(mac) for Ni^{II} for both L^1 and L^4, even though $\log K_1$(mac) and $\log K_2$(mac) for Cu^{II} are rather different.

Electronic Spectra.—In Table 5 are shown the electronic transitions for the $[NiL_2]^{2+}$ complexes, where L is L^2 or L^1. One of the more important features of the chemistry of N-donor macrocycles[4] is that, provided the metal ion binds to the macrocycle without causing a large amount of distortion, and hence a large amount of steric strain, $10D_q$ (the ligand-field splitting parameter) is much larger than that in the complex of the linear analogue. This has been interpreted[4] as being due to the presence of more secondary nitrogen-donor atoms in the macrocycle than in the linear analogue, coupled with less strain than is normally induced when primary nitrogens are turned into secondary in open-chain ligands by alkylation. We thus expect to see a larger $10Dq$ for $[NiL^1{}_2]^{2+}$ than $[NiL^2{}_2]^{2+}$. At first sight it would seem that this expectation has not been realised, in that the most intense band in the low-energy region, which would be assigned to $^3A_2 \longrightarrow {}^3T_2$ and hence be of the energy $10Dq$, is at almost the same energy in both complexes. However, as seen in Figure 2, the spin-forbidden transition $^3A_2 \longrightarrow {}^1E$ is much less intense in the complex with the macrocycle than with L^2, which suggests different amounts of spin–orbit coupling. The problem of spin–orbit coupling has already been briefly discussed[16] in relation to calculating $10Dq$ in complexes of high-spin octahedral Ni^{II}, where it was pointed out that the ' true ' position (*i.e.* that which would be observed in the absence of spin–orbit coupling, and which is the energy relevant to ligand-field theory) was neither of those observed in the spectrum. We have recently[5] devised a method whereby the ' true ' position of the band may be calculated from the relative intensities of the spin-allowed and spin-forbidden bands. Briefly, the ' true ' position of the band would be exactly halfway between the two bands if these are of equal intensity, and moves towards the more intense of the two bands as the

Table 5. Electronic spectra (cm^{-1}) in water of L^1 and L^2 complexes of Ni^{II}: sh = shoulder

$[NiL^1_2]^{2+}$	10 500 (sh), 11 770, 19 230
$[NiL^2_2]^{2+}$	10 750 (sh), 11 700, 18 250, 28 500
$[NiL^2(H_2O)_3]^{2+}$	9 804, 12 740 (sh), 17 400
$[NiL^1(H_2O)_3]^{2+}$	10 100, 18 000, 27 400

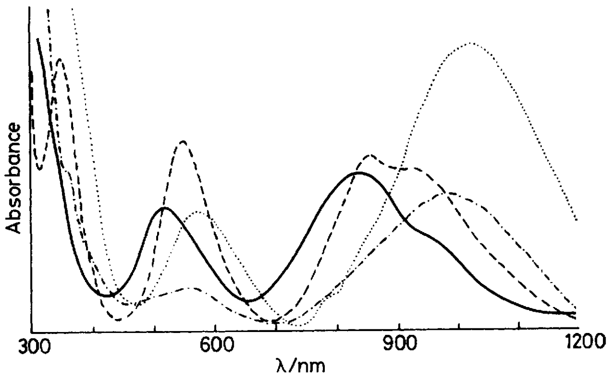


Figure 2. Ultraviolet-visible spectra of solutions of complexes of Ni^{II} in water: (——), $[NiL^1_2]^{2+}$; (– – – –), $[NiL^2_2]^{2+}$; (— · — · —), $[NiL^1(H_2O)_3]^{2+}$; and (· · ·), $[NiL^2(H_2O)_3]^{2+}$

difference in intensity grows. One thus takes the ratio of the absorption coefficients of the two bands at their band maxima, $\varepsilon_1/\varepsilon_2$, and uses this in expression (1), where ν_1 is the ' true '

$$\nu_1 = \nu_M + 1.142\delta_M[\varepsilon_1/\varepsilon_2 - 1] \qquad (1)$$

position of the band $^3A_2 \longrightarrow {}^3T_2$, and ν_M is the midpoint in energy of the two bands. The factor 1.142 was obtained from an analysis of the spectra of a large number of complexes of high-spin octahedral Ni^{II}; δ_M is the separation in energy of the $^3A_2 \longrightarrow {}^1E$ and $^3A_2 \longrightarrow {}^3T_2$ transitions as observed, ε_1 is the absorption coefficient at the band maximum of the band at higher energy and ε_2 is that for the band at lower energy. Applying this expression, we see that the ' true ' position of $^3A_2 \longrightarrow {}^2T_2$ in $[NiL^1_2]^{2+}$ is at 11 560 cm^{-1} and in $[NiL^2_2]^{2+}$ is at 11 180 cm^{-1}. If we assume that the energy of this band is $10Dq$, then we see that the usual difference in ligand-field strength between macrocyclic ligands and their open-chain analogues is found for L^1. In support of the above indication that L^1 provides a more intense ligand field than L^2, we see that $^3A_2 \longrightarrow {}^3T_2$ in the complexes $[NiL^1(H_2O)_3]^{2+}$ and $[NiL^2(H_2O)_3]^{2+}$, which is now too far away energetically to be coupled with $^2A_2 \longrightarrow {}^1E$, occurs at 10 100 and 9 800 cm^{-1} respectively (Table 5).

For $[NiL^2_2]^{2+}$ a good fit to the observed spectrum can be obtained with B = 820 cm^{-1} as compared with 880 cm^{-1} for [5] $[Ni(en)_3]^{2+}$. The lower value of B for the L^2 complex would be expected from the lower position of S than N donors in the nephelauxetic series. For $[NiL^1_2]^{2+}$ which has *trans* positioning of the sulphur donors, the $^3A_2 \longrightarrow {}^3T_1$ (P) transition is obscured by charge-transfer bands. This makes the calculation of B rather too sensitive to the position of the $^3A_2 \longrightarrow {}^3T_1$ (F) transition, and we would calculate a very high value of B of over 1 100 cm^{-1}. This high apparent value is probably caused by several factors, one of which must be that the $^3A_2 \longrightarrow {}^3T_1$ (F) transition appears to be split into two components because of the *trans* positioning of the sulphur donors, and we are simply using the more intense of these in our calculation.

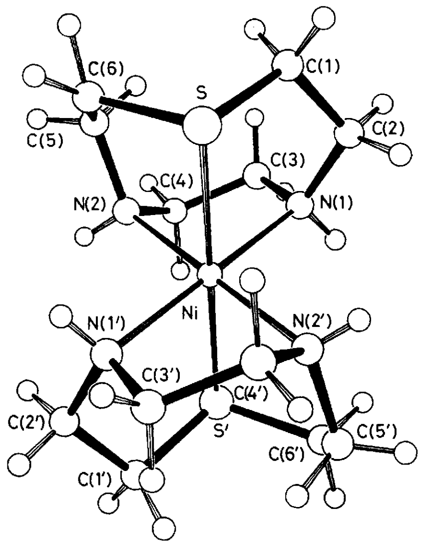


Figure 3. ORTEP [20] drawing of the cation $[NiL^1_2]^{2+}$ showing the numbering scheme

One could attempt to resolve the components of the observed transitions, and analyse the spectrum as that of a tetragonal rather than octahedral complex, but the added complication of spin–orbit coupling makes this seem an unreliable procedure. We simply note that the energies of the $^3A_2 \longrightarrow {}^1E$ transitions in the two complexes are rather similar, and since these transitions are the most sensitive to the Racah parameters B and C, that B in $[NiL^1_2]^{2+}$ is probably also about 820 cm^{-1}.

Reaction Rates.—Both L^1 and L^4 equilibrate with Ni^{2+} much more rapidly than does L^3. This is probably not related to the third donor atom X in the cyclononane N$_2$X being non-protonatable when X = S or O, but rather is due the fact that the pK_1 and pK_2 values are lowered when X = S or O relative to X = N. The pK_3 for L^3 is [10] very low, so that at the pH values at which we carried out our potentiometric studies the ligand would behave as though the third donor atom were non-protonatable as is the case for L^1 and L^4. The low values of pK_1 and pK_2 for L^1 and L^4 mean that, at the same pH, the concentration of the free ligand, through which reaction probably occurs, will be much higher than for L^3, with a corresponding increase in the reaction rate.

Structural Studies.—The complex $[NiL^1_2]^{2+}$ has a centre of symmetry with the sulphurs placed *trans* to each other (Figure 3). This means that it is not easy to compare the co-ordination geometry directly with that of the open-chain analogue, in which the sulphurs are placed *cis* to each other.[5] We may note, however, that the average Ni–N bond length in both the macrocyclic and open-chain complexes is 2.11 Å, which indicates no compression of the bonds in the complex of the macrocycle relative to that of the open-chain analogue. These Ni–N lengths are also very close to the strain-free bond length [17] (2.10 Å). The Ni–S bond length in the macrocyclic complex at 2.418(1) Å is slightly shorter than that (2.455 Å) in the open-chain one. This slight shortening probably does reflect the steric effects of the more constrained macrocyclic ligand, but is hardly likely to produce the differences in $10Dq$, especially in the light of the very normal, and if anything slightly long, Ni–N distances.

The co-ordination geometry around the Ni in both the L^1 and L^2 complex is considerably distorted away from octahedral, in that the N–Ni–N, S–Ni–S, and N–Ni–S bond angles are all considerably different from 90°. Thus, in the L^1 complex the N–Ni–N angle is 80.5(1)° and the N–Ni–S angles average 85.1°. One must consider what possible role such distortions might play in producing the high ligand-field strengths of macrocycles. It is most instructive here to consider the structure of $[NiL^3{}_2]^{2+}$ reported recently,[18] and compare it with that of $[Ni(en)_3]^{2+}$.[19] The contention that the large $10Dq$ in $[NiL^3{}_2]^{2+}$ as compared with, say $[Ni(en)_3]^{2+}$, is due to trigonal distortion[7] does not seem correct in that the trigonal distortion in $[Ni(en)_3]^{2+}$ is *larger* than in $[NiL^3{}_2]^{2+}$. Thus, the twist angle, which is the projection of the N–Ni–N′ angles onto a plane at right angles to the C_3 axis, where N is above the plane and N′ is the adjacent nitrogen below the plane, is 60° in a regular octahedron. Rotation of the three nitrogens above the plane relative to the three below it causes the angles to become more or less than 60°. In $[NiL^3{}_2]^{2+}$ this amount of distortion away from 60° is only 3.8 ± 0.8,[18] but in $[Ni(en)_3]^{2+}$ it is 9.3 ± 1.5°.[19] Consideration of the literature shows that the amount of distortion in the $[NiL^3{}_2]^{2+}$ complex is rather small for a nickel(II) complex. Conformational analysis calculations which we are carrying out indicate that the small amount of trigonal distortion actually present in $[NiL^3{}_2]^{2+}$ is caused by the 'meshing' of the hydrogen atoms on the two L^3 ligands where they make contact with each other.

The bond angles, although distorted for the co-ordination polyhedron around Ni^{2+} in $[NiL^1{}_2]^{2+}$, are normal for Ni^{2+}. Thus, the N–Ni–N bond angle of 80.5(1)° may be compared with that of 80.8° in $[Ni(en)_3]^{2+}$,[20] and the N–Ni–S bond angles which average 85.1° can be compared with the corresponding average of 85.0° in $[NiL^2{}_2]^{2+}$.[5] It is our feeling that since the phenomenon of increased ligand-field strength is so common in N-donor macrocycles a general explanation must be sought for it, rather than a multitude of explanations which apply only to the example under consideration. In this regard, we feel that the general explanation offered by us[4] in terms of the increased donor power of the secondary nitrogens present in macrocycles, coupled with a smaller amount of steric strain than would normally be associated with turning primary into secondary nitrogens in a complex, gives a satisfactory general explanation.

After completion of this work, Graham *et al.*[21] reported the synthesis of 1-thia-4,7-diazacyclononane but no details or any metal binding properties were given.

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