The Chemistry of Sulphur–Nitrogen Ligands. Part II.[1] Nickel(II) Complexes of the *cis*-N_2S_2 Macrocycle 14,14,16-Trimethyl-2,6-dithia-13,17-diazatricyclo[16.4.0.0^{7,12}]-docosa-1(18),7(12),8,10,16,19,21-heptene

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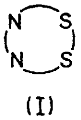
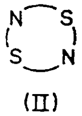
The reaction of acetone with the nickel(II) complex of 1,5-bis(2-aminophenylthio)pentane in methanol solution gives the nickel complex of the new macrocyclic title ligand, L^1. The complexes [$NiI_2(L^1)$], [$Ni(L^1)(NCS)_2$], and [$NiBr(ClO_4)(L^1)$] have been prepared by metathesis reactions of [$NiBr_2(L^1)$] with an appropriate salt in methanol solution. In the solid state, the electronic spectra and magnetic-susceptibility measurements are consistent with distorted octahedral structures for the various complexes. Axial co-ordination is relatively weak; thus [$NiBr_2(L^1)$] behaves as a 2 : 1 electrolyte in methanol solution.

THERE has been continuing interest in the chemistry of quadridentate macrocyclic ligands containing the N_2S_2 donor system. Such macrocycles can be of the *cis*-N_2S_2 type, (I), or of the *trans*-N_2S_2 type, (II). Macrocycles of the *trans*-N_2S_2 type have been prepared by conventional organic routes.[2] The *cis*-N_2S_2 type can be synthesised by reactions of co-ordinated ligands involving either the nitrogen or sulphur donors. Macrocyclic complexes containing both imine and thioether donors have been prepared by reaction of two co-ordinated thiol groups with a difunctional alkylating reagent [3,4] and by the reaction of acetone [5] with two primary amine functions.



(I)



(II)

Curtis and House [6] first showed that two molecules of acetone will condense with two primary amine functions to give a six-membered chelate ring and this reaction has

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[1] Part I, R. W. Hay, A. L. Galyer, and G. A. Lawrance, preceding paper.

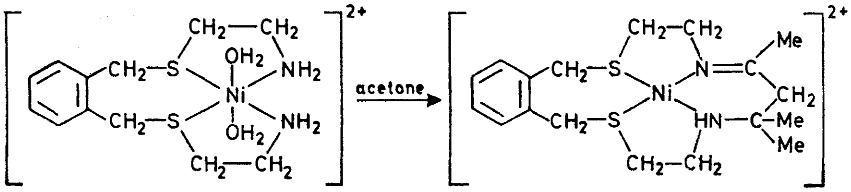
[2] F. Vogtle and L. Schunder, *Chem. Ber.*, 1969, **102**, 2677.

[3] M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.*, 1964, **86**, 3651.

[4] M. S. Elder, G. M. Prinz, P. Thornton, and D. H. Busch, *Inorg. Chem.*, 1968, **7**, 2426.

[5] F. L. Urbach and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 408.

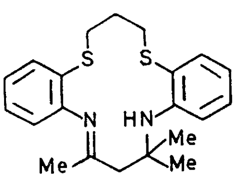
[6] N. F. Curtis and D. A. House, *Chem. and Ind.*, 1961, 1708.



(III) (IV)

been used to prepare a large variety of macrocyclic tetra-amines.[7] Urbach and Busch[5] prepared the nickel(II) complexes, (IV), by the reaction of acetone with (III). The macrocyclic ligand in (IV) gives four-, five-, and six-co-ordinate complexes of Ni^{II} with a variety of anions, *e.g.* $[ClO_4]^-$, $[NCS]^-$, Cl^-, Br^-, and I^-.

The present paper discusses the preparation and co-ordination chemistry with Ni^{II} of the macrocyclic ligand 14,14,16-trimethyl-2,6-dithia-13,17-diazatricyclo-$[16.4.0.0^{7,12}]$docosa-1(18),7(12),8,10,16,19,21-heptene (L^1).



L^1

EXPERIMENTAL

1,5-Bis(2-aminophenylthio)pentane dihydrobromide (L^2·2HBr) was prepared as follows. Sodium (9.3 g) was dissolved in methanol (300 cm³). 2-Aminobenzenethiol (50 g, 0.37 mol) was added and the mixture stirred under an atmosphere of nitrogen for 10 min. 1,3-Dibromopropane (39 g, 0.19 mol) dissolved in methanol was then added slowly dropwise. The mixture was stirred overnight under nitrogen, then heated under reflux for 6 h and allowed to cool. Hydrobromic acid (40 cm³, 48%) was added to precipitate the dihydrobromide salt, which was filtered off and washed with cold methanol. The salt was recrystallised from methanol (a few drops of 48% HBr being added to prevent hydrolysis) and dried *in vacuo*, m.p. 225—230 °C (decomp.) (Found: C, 39.5; H, 4.45; N, 6.3. Calc. for $C_{15}H_{20}Br_2N_2S_2$: C, 39.8; H, 4.45; N, 6.2%).

Metal Complexes.—$[NiBr_2(L^1)]$. Nickel(II) acetate tetrahydrate (2.49 g, 0.1 mol) and 1,5-bis(2-aminophenylthio)-dithiapentane (4.52 g, 0.1 mol) were dissolved in the minimum volume of methanol and the solution stirred for *ca.* 0.5 h. Acetone dried over $Na_2[SO_4]$ (30 cm³) was then added and the pale green solution stirred overnight in a stoppered flask. As the reaction occurred the solution darkened. The pale blue *complex* obtained was filtered off, washed with a little cold methanol then diethyl ether, and dried *in vacuo*. More stirring of the filtrate gave additional quantities of the *product*, total yield *ca.* 80% prior to recrystallisation from methanol. The complex is moderately soluble in methanol and the volume of methanol used as the solvent in the reaction should be kept to a minimum (Found: C, 42.6; H, 4.6; N, 4.6. $C_{21}H_{26}Br_2N_2NiS_2$ requires C, 42.8; H, 4.5; N, 4.8%).

The thiocyanate, perchlorate, and iodide salts were prepared from the bromide by metathesis with a methanol solution of an appropriate salt (K[NCS], $Na[ClO_4]$, NaI): $[NiI_2(L^1)]$, bright green crystals, dried *in vacuo* (Found: C, 37.1; H, 4.0; N, 4.0. $C_{21}H_{26}I_2N_2NiS_2$ requires C, 36.9; H, 3.8; N, 4.1%); $[NiBr(ClO_4)(L^1)]$, blue crystals using an excess of $Na[ClO_4]$ in methanol, dried *in vacuo* (Found: C, 41.8; H, 4.5; N, 4.5. $C_{21}H_{26}BrClN_2NiO_4S_2$ requires C, 41.4, H, 4.3; N, 4.6%); and $[Ni(NCS)_2(L^1)]$, violet crystals, dried *in vacuo* (Found: C, 50.9; H, 4.5; N, 10.1. $C_{23}H_{26}N_4NiS_4$ requires C, 50.6; H, 4.8; N, 10.3%).

On standing in air all the complexes appeared to form hydrates as strong bands due to ν(OH) were observed in the infrared spectra.

[1,5-*Bis*(2-*aminophenylthio*)*pentane*]*dibromonickel*(II), $[NiBr_2(L^2)]$. To 1,5-bis(2-aminophenylthio)pentane dihydrobromide (1.5 g, 0.0033 mol) in anhydrous ethanol was added triethylamine (0.68 g, 0.0066 mol) and the solution was stirred then filtered. To the filtrate was added anhydrous nickel(II) chloride (0.50 g, 0.0033 mol) in anhydrous ethanol. The mixture was stirred for 2 d and the resulting pale green *complex* was washed with dry ethanol and then with sodium-dried diethyl ether (Found: C, 35.8; H, 3.9; Ni, 11.5. $C_{15}H_{18}Br_2N_2NiS_2$ requires C, 35.4; H, 3.6; Ni, 11.5%).

1,4-Bis(2-aminophenylthio)butane dihydrobromide (L^3·2HBr) was prepared essentially as described for 1,5-bis(2-aminophenylthio)pentane dihydrobromide by replacing 1,3-dibromopropane with 1,2-dibromoethane (Found: C, 38.6; H, 4.1; N, 36.4. Calc. for $C_{14}H_{18}Br_2N_2S_2$: C, 38.4; H, 4.1; N, 36.5%).

[1,4-*Bis*(2-*aminophenylthio*)*butane*]*dibromonickel*(II), $[NiBr_2(L^3)]$. Nickel(II) acetate tetrahydrate (1.25 g) was dissolved in hot methanol (20 cm³) and the solution filtered. To this solution 1,4-bis(2-aminophenylthio)butane dihydrobromide (2.16 g) was added with stirring. A pale blue *complex* separated immediately and was filtered off, washed with methanol, and dried *in vacuo* (Found: C, 34.3; H, 3.4; N, 5.8. $C_{14}H_{16}Br_2N_2NiS_2$ requires C, 34.1; H, 3.25; N, 5.7%).

Infrared spectra were recorded on Perkin-Elmer 457 and 577 grating instruments using KBr discs. The KBr was dried at 110 °C for 3 h before use. Visible and u.v. spectra were obtained on a Perkin-Elmer 402 spectrophotometer using 1 cm cells and the appropriate solvent as blank. Solid-state visible spectra were recorded on a Unicam SP 700A instrument with $Mg[CO_3]$ as reference. Conductivity measurements (at 25 °C) were made on 10^{-3} mol dm^{-3} solutions in absolute methanol using a Portland conductivity meter. Magnetic susceptibilities were determined by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant.

RESULTS AND DISCUSSION

The reaction of nickel(II) chloride with 1,5-bis(2-aminophenylthio)pentane dihydrobromide (L^2·2HBr) in dry ethanol in the presence of a non-co-ordinating base (triethylamine) gave [1,5-bis(2-aminophenylthio)-pentane]dibromonickel(II), $[NiBr_2(L^2)]$, which is pale green and paramagnetic ($\mu_{eff.}$ 3.20 ± 0.10 B.M. at

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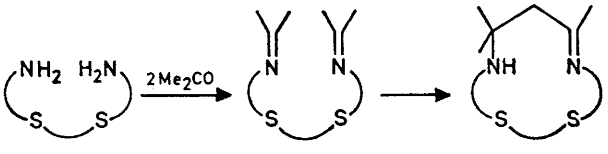
[7] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.

25 °C).* The reflectance spectrum had bands at 10 000 (ν_1), 15 400 (ν_2), and 29 000 cm^{-1} (ν_3) typical of six-co-ordinate Ni^{II}. The i.r. spectrum had strong sharp bands at 3 333, 3 265, and 3 172 cm^{-1} [$\nu(NH_2)$] and 1 556 cm^{-1} [$\delta(NH_2)$].

The complex [NiBr$_2$(L^1)], obtained by the reaction of nickel(II) acetate with 1,5-bis(2-aminophenylthio)pentane and acetone in methanol, analyses for the presence of two acetone residues. Acetone could give a simple bis-imine (V) with the two primary amino-groups; however, the i.r. evidence supports the view that cyclisation has occurred (VI). The primary amine N–H stretching and deformation bands present in [NiBr$_2$(L^2)] have disappeared to be replaced by bands at 3 280, 1 620, and 1 377 cm^{-1} which can be assigned to the secondary N–H stretching frequency, the C=N stretching frequency, and the deformation mode of the *gem*-dimethyl groups, respectively. These i.r. data (Table 1) agree well with values reported in the literature for the i.r. absorptions of similar macrocyclic complexes,[5,7] and are consistent with the structure given for the ligand L^1.



(V) (VI)

TABLE 1

Infrared spectra (cm^{-1})

Complex	ν(C=N)	ν(NH)	*gem*-Me$_2$	*o*-substituted aromatic δ(CH)	Other
[NiBr$_2$(L^1)]	1 620	3 160	1 370	755	
[NiI$_2$(L^1)]	1 618	3 160	1 370	755	
[NiBr(ClO$_4$)(L^1)]	1 620	3 235	1 370	755	ClO$_4$ 1 100br, 935w, 625s
[Ni(L^1)(NCS)$_2$]	1 625	3 260	1 370	755	NCS 2 090, 820, 467

The reaction conditions are quite mild and significantly milder than those reported by Curtis for the analogous reactions of tetra-amine compounds with acetone. The conditions are similar to those used by Urbach and Busch [5] for the preparation of the macrocyclic complex (IV). The complexes of the general formulation [NiX$_2$(L^1)] [X = NCS, Br(ClO$_4$), or I] were readily prepared by metathesis reactions with the appropriate salt in methanol solution.

The electronic spectra of the various complexes are listed in Table 2. Octahedral nickel(II) complexes display three bands: $^3T_{2g}\leftarrow{}^3A_{2g}$ (ν_1); $^3T_{1g}\leftarrow{}^3A_{2g}$ (ν_2); and $^3T_{1g}(P)\leftarrow{}^3A_{2g}$ (ν_3). The ν_3 band in the present complexes is obscured by charge-transfer bands. There is pronounced splitting of the low-energy band (ν_1) which can be attributed to axial distortion. All the complexes exhibited similar electronic spectra which are very comparable to that of [Ni(L^4)(NCS)$_2$] (L^4 = 7,9,9-trimethyl-3,13-dithia-6,10-diazabicyclo[13.4.0]nonadeca-1(15),6,16,-18-tetraene) to which Urbach and Busch [5] have assigned an octahedral structure with a *trans* arrangement of the [NCS]$^-$ ligands on the basis of its ligand-field spectrum and magnetic moment ($\mu_{eff.}$ 3.10 B.M.).

TABLE 1

Electronic spectra (10^3 cm^{-1}) of the complexes

Complex	Solid state ν_1	Solid state ν_2	In dmf [a]
[NiBr$_2$(L^1)]	11.5	17.5	17.15 (7.0)
[NiI$_2$(L^1)]	11.3	17.5	17.24 (12.6)
[NiBr(ClO$_4$)(L^1)]	11.5	17.5	16.67 (11.3)
[Ni(L^1)(NCS)$_2$]	10.8, 11.5	17.5	17.54 (9.8)
[Ni(L^4)(NCS)$_2$] [b]	10.58, 11.54	17.9	

[a] Values of ε (dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] Ref. 5.

The location and number of the ν(CN), ν(CS), and δ(NCS) bands in the i.r. spectra of metal thiocyanate complexes are generally diagnostic of the mode of co-ordination of the NCS group and the stereochemistry of the complexes.[8] When the NCS groups are in a *trans* position to one another a single band corresponding to ν(CN) is observed. For [Ni(NCS)$_2$(L^1)], ν(CN) occurs at 2 090 cm^{-1}, ν(CS) at 820 cm^{-1}, and δ(NCS) at 467 cm^{-1}, consistent with *trans* *N*-bonded thiocyanate groups.

The reaction of [NiBr$_2$(L^1)] with excess of Na[ClO$_4$] in methanol gives the bromide perchlorate [NiBr(ClO$_4$)(L^1)]. For complexes containing unidentate perchlorate it has been reported [8] that strong well defined bands are displayed at 1 120, 1 063, 935, and 622 cm^{-1}. The present complex has a relatively sharp perchlorate band at *ca.* 1 100 cm^{-1} which shows signs of splitting, a weak band at 932 cm^{-1} (absent in the dibromo-derivative), and a strong sharp band at 625 cm^{-1}. Conclusive evidence for unidentate perchlorate must await crystallographic work.

Axial co-ordination is apparently quite weak. The complex [NiBr$_2$(L^1)] is sufficiently soluble in methanol for conductivity measurements to be carried out. The value of Λ = 141 S cm^2 mol^{-1} at 25 °C compared with NaI for which Λ = 89 S cm^2 mol^{-1} is consistent with the view that the complex is a 2 : 1 electrolyte in this solvent. The magnetic moment of solid [NiBr$_2$(L^1)] ($\mu_{eff.}$ 3.02 B.M. at 18 °C) is consistent with the electronic spectra and indicates six-co-ordinate Ni^{II}.

The ligand L^1 has a 14-membered ring which on complex formation gives the favourable 5,6,5,6 arrangement of the chelate rings. Attempts were made to prepare the analogous 13-membered ring compound by the reaction of acetone with nickel(II) acetate and 1,4-bis(2-aminophenylthio)butane dihydrobromide (L^3·2HBr). A pale blue complex separated immediately on mixing the reagents and the analytical data confirmed that this was [NiBr$_2$(L^3)]. This complex is essentially insoluble in methanol–acetone mixtures and no further attempts were made to bring about cyclisation.

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* 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

[8] R. C. Paul, R. S. Chopra, R. K. Bhambri, and G. Singh, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3703.