

Synthesis of an N₂S-Cyclodecane Macrocyclic and its Nickel(II) Complex†

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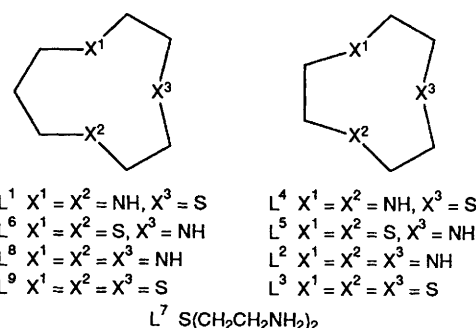
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The ligand 1-thia-4,8-diazacyclodecane ([10]aneN₂S, L¹) and its nickel(II) complex have been synthesised and characterised. The complex [Ni([10]aneN₂S)₂]Br₂ crystallised in the space group *P*2₁/*n* (no. 14) with *a* = 11.419(3), *b* = 9.439(2), *c* = 10.288(3) Å and β = 96.66(3)°. Refinement converged with *R* = 0.0411 (*R*' = 0.0472) for 115 parameters using 1559 reflections with *I* > 3σ(*I*). The metal-ion complex is nominally octahedral with mean Ni–N and Ni–S bond lengths of 2.142(5) and 2.395(1) Å respectively. Oxidation of the nickel(II) complex results in the formation of a nickel(III) species which exhibits a tetragonally elongated geometry according to the ESR spectrum obtained. Spectroscopic and redox properties of the complex are compared with those of other ligands in the ten-membered series and with the nine-membered ring analogues.

Transition-metal complexes of small macrocyclic ligands, especially the nine- and ten-membered triaza- and trithia-systems [9]aneX₃ [X = NH(L²) or S(L³)] have been studied extensively^{1–14} in recent years. In most instances there is a regularity of geometry in the octahedral ions (Co^{III}, Co^{II}, Fe^{III}, Fe^{II}), while in others (e.g., Pd^{II}, Pt^{II}) the triaza systems display square planarity.^{7,15} In contrast, the latter metal ions with trithia donors^{13,16,17} show weak axial co-ordination. Oxidised forms of the complexes are invariably six-co-ordinate. More recently, interest has been stimulated in mixed N,S donor sets where there is an asymmetry in the co-ordination environment. The nickel(II) complex of [9]aneN₂S (L⁴) is octahedral¹⁸ as a result of the facial disposition of the donor atoms. Complexes of the late transition metals give rise to a variety of species of contrasting geometries.¹⁹ In the case of the corresponding [9]aneNS₂ ligand, L^{5,20,21} oxidation of the complex [Ni(L⁵)₂]²⁺ led to formation of an octahedrally elongated d⁷ ion. In contrast, the nickel(III) ion prepared from the corresponding ten-membered ring [10]aneNS₂ (L⁶) exhibited compressed geometry.²² Interest in the ten-membered ring systems also stems from the fact that, with greater conformational freedom, they may be better suited to encapsulate the metal ion.^{13,14,22a} The lower symmetry associated with the ten-membered rings also imparts stereochemical characteristics and in some instances differing isomeric forms.^{13,22b} Investigation of the effects of incorporation of a soft sulfur donor into a ligand framework containing harder N atoms is also of interest. The possible occurrence of such a mixed-donor environment has been reported recently around the central nickel(II) ion in methanogenic bacterium.²³

Experimental

All chemicals were of reagent grade except where otherwise indicated. Infrared spectra were obtained as KBr discs or as neat samples on NaCl plates with a Perkin Elmer 283 grating spectrometer. Proton NMR spectra were measured on a 90 MHz Perkin Elmer R32 spectrometer. High-field ¹H and ¹³C NMR spectra were obtained with either a Bruker WM250 or a Bruker 360 instrument. All chemical shifts are reported relative to tetramethylsilane. Electronic spectra were recorded on a Philips PU 8740 or a Cary-5 spectrophotometer. The EPR

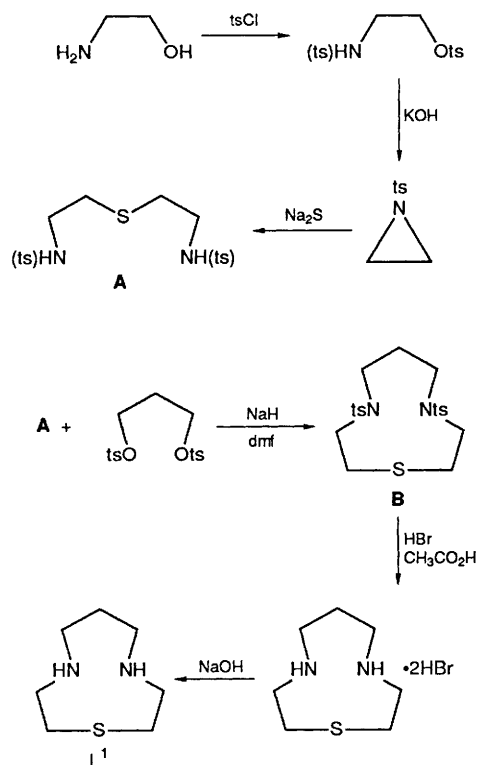


spectra were obtained with a Varian E6S spectrometer. Diphenylpicrylhydrazyl (dpph) radical was used as a field marker (*g* = 2.0037). Mass spectra were recorded with a Finnegan 330GC-MS instrument by electron impact, methane or isobutane chemical ionization (CI). Elemental analyses were performed by Microanalytical Services, Vancouver, B.C., Canada. Electrochemical measurements were recorded with a Princeton Applied Research model 273 potentiostat-galvanostat, interfaced with an IBM/PC using the 'Headstart' program. An electrochemical cell employed the standard three-electrode configuration with platinum working and auxiliary electrodes and a reference electrode [Ag–AgNO₃ (0.1 mol dm^{–3}) was used in non-aqueous systems containing 0.1 mol dm^{–3} NEt₄BF₄]. Blank electrolyte solutions were scanned before each experiment and in each instance the ferrocenium–ferrocene couple (*E*_{1/2} = 0.15 V vs. Ag⁺–Ag) was used as an external standard to calibrate the reference electrode. Acetonitrile was distilled over CaH₂ prior to use for electrochemical purposes.

Synthesis of 1-thia-4,8-diazacyclodecane [10]aneN₂S.—The ligand [10]aneN₂S was synthesised by using a form of the Richman and Atkins method²⁴ (Scheme 1).

2-(Toluene-*p*-sulfonylamino)ethyl toluene-*p*-sulfonate was synthesised by a modification²⁵ of the procedure of Hope and Horncastle.²⁶ To a stirred suspension of toluene-*p*-sulfonyl chloride, tsCl (802.6 g, 4.2 mol) in pyridine (500 cm³), cooled to –40 °C, was added dropwise a solution of 2-aminoethanol (122.2 g, 2 mol) in pyridine (200 cm³) (cooled to 0 °C). After the addition was complete, the temperature was maintained at –10 °C for 2 h and then at 0 °C for 24 h. After crushed ice was

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 1 Synthetic route to ligand **L**¹

added, the solid formed was filtered off, washed with water and dissolved in CHCl₃ (1 l). This solution was washed thrice with water, and the non-aqueous layer treated with anhydrous Na₂SO₄ and taken to dryness. The resulting solid was dissolved in a minimum of boiling CCl₄ and the compound crystallised upon cooling. Yield: 517 g (70%), m.p. 87 °C. ¹H NMR (CDCl₃): δ 7.6 (dd, 8 H), 5.3 (t, 1 H), 4.0 (t, 2 H), 3.2 (m, 2 H) and 2.4 (s, 6 H).

N-Toluene-*p*-sulfonylaziridine was synthesised according to published procedures.²⁷

N,N'-Di(toluene-*p*-sulfonyl)bis(2-aminoethyl) Sulfide A.—*N*-Tosylaziridine (53 g, 0.3 mol) was added in small portions to an aqueous ethanolic solution [EtOH (500 cm³)–water (150 cm³)] of Na₂S·9H₂O (33.3 g, 0.14 mol). The mixture was refluxed for 3 h. The solution was then evaporated to a small volume (75 cm³) and made acidic (pH ≈ 1) with aqueous HCl. Following extraction thrice with CH₂Cl₂ (200 cm³) and drying over anhydrous Na₂SO₄, the CH₂Cl₂ layer was evaporated to dryness to yield the crude product as a solid. After boiling in ethanol, crystals were obtained upon cooling. Yield: 40.3 g (70%), m.p. 111 °C (Found: C, 50.25; H, 5.60; N, 6.40. Calc. for C₁₈H₂₄N₂O₄S₃: C, 50.45; H, 5.65; N, 6.55%). NMR (CDCl₃): ¹H, δ 2.39 (s, 6 H, CH₃), 2.51 (t, *J* 6, 4 H, CH₂S), 3.03 (q, *J* 6, 4 H, CH₂N), 5.27 (t, *J* 6 Hz, 2 H, NH) and 7.2–7.7 (m, 8 H, aromatic); ¹³C, δ 21.5 (2 C, CH₃), 31.7 (2 C, CH₂S), 42.2 (2 C, CH₂N), 127.0 and 129.8 (4 C + 4 C, aromatic), 136.8 and 143.6 (2 C + 2 C, quaternary aromatic). Mass spectrum (CI): *m/z* 429 (*M* + 1), 457 (*M* + 29) and 469 (*M* + 41).

4,8-Di(toluene-*p*-sulfonyl)-1-thia-4,8-diazacyclodecane, B.—Sodium hydride (0.2 mmol, 8.3 g of a 60% dispersion in oil) was added to a vigorously stirred solution of **A** (35.5 g, 0.08 mol) in dimethylformamide (dmf) (600 cm³) to form the disodium salt. After effervescence was complete, the solution was slowly heated to 70 °C, and stirring was continued for 3 h. The temperature was raised to 105 °C and a solution of TsOCH₂CH₂CH₂Ots²⁸ (31.87 g, 0.083 mol), in dmf (500 cm³) was added over 2 h. The yellow solution formed was stirred at 105 °C for a further 2 h. The dmf solution was concentrated to a small volume (≈ 200

cm³) and added dropwise to a stirred mixture of ice–water (2 l). The colourless precipitate obtained was filtered off, washed with water, cold ethanol and diethyl ether and dried under vacuum. The material was recrystallised from boiling ethanol. Yield: 27.5 g (70%), m.p. 286 °C (Found: C, 54.05; H, 5.90; N, 5.95. Calc. for C₂₁H₂₈N₂O₄S₃: C, 53.80; H, 6.00; N, 5.95%). NMR (CDCl₃): ¹H, δ 2.37 (q, 2 H, CH₂), 2.39 (s, 6 H, CH₃), 3.03 (m, 4 H, CH₂S), 3.07 (t, 4 H, NCH₂CH₂CH₂N), 3.29 (m, 4 H, CH₂N) and 7.28–7.65 (m, 8 H, aromatic); ¹³C, δ 21.4 (2 C, CH₃), 28.6 (1 C, –CH₂CH₂CH₂–), 31.0 (2 C, CH₂S), 47.4 (2 C, NCH₂CH₂CH₂N), 54.1 (2 C, CH₂N), 127.6 and 129.7 (4 C + 4 C, aromatic), 133.1 and 143.7 (2 C + 2 C, quaternary aromatic). Mass spectrum (CI): *m/z* 469 (*M* + 1) and 497 (*M* + 29).

1-Thia-4,8-diazacyclodecane Dihydrobromide, L¹·2HBr.—After addition of the cyclised tosylate, **B** (7 g, 0.015 mol) to a solution of 30% HBr in acetic acid (250 cm³) and phenol (10 g), the solution was heated under reflux for 3 d after which it was cooled to room temperature. The resulting solution was added dropwise to a vigorously stirred solution of diethyl ether and ethanol (350 cm³; 6:1 v/v). A white-brown solid was obtained which was further purified using an EtOH–HBr mixture. Yield: 2.21 g (46%). NMR (D₂O): ¹H, δ 2.19 (q, 2 H, CCH₂C), 3.06 (m, 4 H, CH₂S), 3.30 (m, 4 H, CH₂CCH₂), 3.47 (t, 4 H, CH₂N); ¹³C, δ 21.8 (1 C, CCC), 29.2 (2 C, CH₂S), 42.6 (2 C, NCCCCN) and 44.6 (2 C, CH₂N).

The free ligand, **L**¹, was obtained by dissolving the hydrobromide salt (2.21 g) in water (50 cm³) which was made basic (pH ≈ 13) with aqueous NaOH. After continuous extraction with CHCl₃ for 24 h, the CHCl₃ layer was treated with anhydrous Na₂SO₄ and evaporated to dryness leaving a pale yellow oil. Yield: 1.3 g (85%). NMR (CDCl₃): ¹H, δ 1.6 (m, 2 H, CCH₂C), 2.6–2.8 (m, 12 H) and 3.4 (s, 1 H, NH); ¹³C, δ 26.4 (1 C, CCC), 34.3 (2 C, CH₂S), 47.6 (2 C, CCC) and 49.4 (2 C, CH₂N). Mass spectrum (CI): *m/z* 161 (*M* + 1), 189 (*M* + 29) and 201 (*M* + 41).

[Ni([10]aneN₂S)₂]Br₂·2H₂O.—The free ligand, **L**¹ (0.5 g, 3.1 mmol) was dissolved in EtOH (50 cm³) and heated to 50 °C while stirring. A solution containing Ni(ClO₄)₂·6H₂O (0.366 g, 1 mmol) (**CAUTION**) dissolved in EtOH (10 cm³) was added dropwise to the ethanolic solution of the ligand and the mixture was refluxed for 1 h. The brown-purple solid obtained was filtered off and recrystallised from ethanol–water (10 cm³, 9:1, v/v) containing NaBr. Upon cooling, purple crystals were obtained which were filtered off, washed with small amounts of ethanol and diethyl ether and dried under vacuum. Yield: 324 mg (60%) (Found: C, 29.30; H, 6.05; Br, 28.00; N, 9.65. Calc. for C₁₄H₃₂Br₂N₄NiS₂·2H₂O: C, 29.20; H, 6.30; Br, 27.80; N, 9.75%).

Crystal Structure of [Ni([10]aneN₂S)₂]Br₂·2H₂O.—Pink crystals of the nickel(II) complex were obtained by slow evaporation of solutions of the complex in aqueous ethanol (95:5 v/v). The crystal was mounted along the *c* axis in a Lindemann tube. Both Weissenberg and precession photography were used to establish the symmetry and unit-cell dimensions. The crystallographic data are presented in Table 1. After photography, the crystal was transferred to a Picker four-circle diffractometer automated with a PDP11/10 computer. The final lattice parameters were obtained from a least-squares refinement of 24 accurately centred, high-angle reflections.

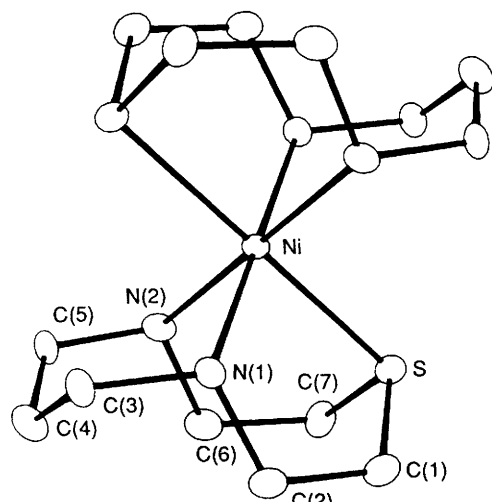
The data collection was carried out in the θ–2θ mode using 200 steps of 0.01° in 2θ and counting for 0.25 s per step. The background was counted for 25 s at each end of the scan. A set of three standard reflections preceded each batch of 50 measurements. A total of 1943 reflections were measured of which 1559 [*I* > 3σ(*I*)] were used in the final data set.

After correction for absorption effects, Ni and Br atoms were located by MULTAN.²⁹ The atomic scattering factors

Table 1 Experimental crystallographic data for $[\text{Ni}([\text{10}] \text{aneN}_2\text{S}_2)_2] \cdot \text{Br}_2 \cdot 2\text{H}_2\text{O}$

Formula	$\text{C}_{14}\text{H}_{36}\text{Br}_2\text{N}_4\text{NiO}_2\text{S}_2$
M	575.1
Crystal colour	Pink
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
Cell dimensions	
$a/\text{\AA}$	11.419(3)
$b/\text{\AA}$	9.439(2)
$c/\text{\AA}$	10.288(3)
$\alpha/^\circ$	90
$\beta/^\circ$	96.66(3)
$\gamma/^\circ$	90
$U/\text{\AA}^3$	1101.46
Z	2
$F(000)$	1150
$D_c/\text{g cm}^{-3}$	1.734
$D_m/\text{g cm}^{-3}$	1.727
Crystal dimensions/mm	$0.62 \times 0.12 \times 0.16$
Diffractometer	Picker
Radiation ($\lambda/\text{\AA}$)	Mo-K α (0.710 69)
Filter	Zirconium
2θ range/ $^\circ$	2–50
Octants collected	$\pm h, k, l$
Standard reflections	3: 040, 004, 600
No. reflections collected	1943
No. observed reflections [$I > 3\sigma(I)$]	1559 ($n = 3$)
No. parameters	115
Linear absorption coefficient/ cm^{-1}	49.56
R^a	0.0411
R'^b	0.0472

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}$ where $w = 1.41 / (\sigma^2 F + 0.001 F^2)$.

**Fig. 1** An ORTEP³² diagram of the $[\text{Ni}([\text{10}] \text{aneN}_2\text{S}_2)_2]^{2+}$ ion with 25% thermal ellipsoids

together with the nickel f curves were taken from ref. 30. Completion and refinement of the structure was achieved by difference electron density maps and by least-squares minimizing using SHELX 76.³¹ The asymmetric unit consisted of half a molecule of the complex cation, one bromide ion and one molecule of water of crystallisation. Hydrogen atoms were not included in the calculations. All non-hydrogen atoms were refined anisotropically. Refinement converged to $R = 0.0411$ and $R' = 0.0472$, with a maximum shift/estimated standard deviation of 0.009 on the final cycle. The final difference map had a maximum peak of $0.77 \text{ e } \text{\AA}^{-3}$.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Table 2 Fractional atomic coordinates ($\times 10^5$ for Br, Ni and S; $\times 10^4$ for others) with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Br	47 518(6)	23 928(7)	87 721(7)
Ni	50 000(0)	50 000(0)	50 000(0)
S	68 833(12)	60 867(15)	55 821(15)
O	1 640(6)	–5(7)	4 605(7)
N(1)	5 818(4)	3 104(5)	5 805(4)
N(2)	5 665(4)	4 452(5)	3 202(4)
C(1)	7 570(5)	4 658(7)	6 555(6)
C(2)	7 130(5)	3 190(7)	6 133(6)
C(3)	5 482(5)	1 797(6)	5 029(6)
C(4)	5 836(6)	1 801(7)	3 632(6)
C(5)	5 350(5)	2 993(7)	2 729(6)
C(6)	6 960(5)	4 684(7)	3 184(6)
C(7)	7 423(5)	5 985(7)	3 992(6)

Table 3 Selected interatomic distances ($\text{\AA}$) and bond angles ($^\circ$) with e.s.d.s in parentheses

S–Ni	2.395(1)	N(1)–Ni–S	85.5(1)
N(1)–Ni	2.141(5)	N(2)–Ni–S	85.5(1)
N(2)–Ni	2.143(4)	N(2)–Ni–N(1)	87.1(2)

Results and Discussion

The structure of the nickel complex is shown in Fig. 1. The fractional atomic coordinates are given in Table 2. Pertinent bond lengths and angles are listed in Table 3. The Ni atom is co-ordinated to two N atoms and one S atom from each ligand in a facial manner, to form a distorted octahedral complex. Two geometrical isomers are possible for the $[\text{Ni}([\text{10}] \text{aneN}_2\text{S}_2)]^{2+}$ ion, the *cis* and *trans* forms based on ring conformation. In the present case both the S atoms and the trimethylene linkages are *trans* to one another.

The average five-membered intraligand angle, S–Ni–N is $85.5(1)^\circ$ (mean of two values) similar to those found in $[\text{Ni}([\text{9}] \text{aneN}_2\text{S}_2)]^{2+}$ [$85.1(3)^\circ$].¹⁸ In the open-chain complex ion, $[\text{Ni}(\text{L}^7)_2]^{2+}$ [$\text{L}^7 = \text{S}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$]³³ the average S–Ni–N angle is 85.0° . The six-membered intraligand angle, N(2)–Ni–N(1), is comparable [$87.1(2)^\circ$] to the corresponding N–Ni–N angle [$86.6(6)^\circ$]^{1b} in $[\text{Ni}(\text{L}^8)_2]^{2+}$ ($\text{L}^8 = [\text{10}] \text{aneN}_3$).

The average Ni–N bond length is $2.142(5) \text{ \AA}$ and is comparable to that of $2.134(30) \text{ \AA}$ in $[\text{Ni}([\text{10}] \text{aneN}_3)_2]^{2+}$ which also contains the propyl linkage. However, it is longer than those in the open-chain complex $[\text{Ni}(\text{L}^7)_2]^{2+}$ ($2.11 \text{ \AA}$)³² and in $[\text{Ni}([\text{9}] \text{aneN}_2\text{S}_2)]^{2+}$ [$2.115(7) \text{ \AA}$].¹⁸ The Ni–S bond length [$2.395(1) \text{ \AA}$] is shorter than that in the $[\text{Ni}(\text{L}^7)_2]^{2+}$ ion ($2.455 \text{ \AA}$) and in $[\text{Ni}([\text{9}] \text{aneN}_2\text{S}_2)]^{2+}$ [$2.418(1) \text{ \AA}$]. This may reflect the ability of the ten-membered ring to expand and for the S atom to reach over and encapsulate the Ni atom better than in the nine-membered ring. The trigonal twist angle ϕ of 58° is similar to that in $[\text{Ni}([\text{10}] \text{aneN}_3)_2]^{2+}$,^{1b} deviating by only two degrees from the octahedral value of 60° .

Spectroscopic Studies and Electrochemistry.—The electronic spectrum of $[\text{Ni}([\text{10}] \text{aneN}_2\text{S}_2)_2][\text{ClO}_4]_2$ shows transitions due to $^1\text{E}_g \leftarrow ^3\text{A}_{2g}$ at 964 nm (sh), $^3\text{T}_{2g} \leftarrow ^3\text{A}_{2g}$ at 863 nm (ν_1 , $\epsilon = 14 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), $^3\text{T}_{1g}(\text{F}) \leftarrow ^3\text{A}_{2g}$ at 531 nm (ν_2 , $\epsilon = 14$), and $^3\text{T}_{1g}(\text{P}) \leftarrow ^3\text{A}_{2g}$ at 343 nm (ν_3 , $\epsilon = 27$). It is of interest that in the present case the bands are well separated permitting direct evaluation of the ligand-field strength ($10Dq = 11\,588 \text{ cm}^{-1}$). This is not so for the corresponding $[\text{Ni}([\text{9}] \text{aneN}_2\text{S}_2)]^{2+}$ ion, where the transitions to the spin-forbidden and spin-allowed $^1\text{E}_g$ and $^3\text{T}_{2g}$ states approach each other in energy, requiring calculation of the energies³² leading to $\nu_1 = 11\,844 \text{ cm}^{-1}$. (It is noteworthy that the ligand-field strengths of the nine- and ten-membered ring systems are very similar when the same donor set is involved.) The Racah parameter B for the free Ni^{2+} ion is 1038 cm^{-1} and with

Table 4 Ligand-field parameters and redox potentials ($\text{Ni}^{3+/2+}$) for nickel(II) complexes of ten-membered macrocycles

Ligand	$10Dq/\text{cm}^{-1}$	B_{35}/cm^{-1}	β_{35}	E_1/V	$\Delta E/\text{mV}$	Ref.
[10]aneN ₃	12 500	937	0.90	0.997 ^a	78	1b
[10]aneN ₂ S	11 588	882	0.85	1.21 ^a	150	c
[10]aneNS ₂	11 862	—	—	1.26 ^b	114	22
[10]aneS ₃	12 136	736	0.71	1.30 ^b	78	14

^a Aqueous media. ^b In MeCN. ^c This work.

$B_{35} = 882 \text{ cm}^{-1}$ a value of 0.85 has been evaluated for the nephelauxetic ratio (β_{35}). The ligand-field parameters for the ten-membered series may be compared in Table 4. The band due to the ${}^3\text{T}_{1g} \leftarrow {}^3\text{A}_{2g}$ transition is clearly discernible in the present complex, while in the case of the nine-membered ring analogue it is obscured by charge transfer bands. The origin of the difference may lie in the asymmetry of the ten-membered ring. The value of $10Dq$ is lower than those for the homoleptic complexes of aza and thia ligands consistent with the greater symmetry of such systems.

Oxidation of the nickel(II) complex in aqueous solutions with Co^{3+} yielded a nickel(III) complex cation. The ESR spectrum of frozen solutions of the nickel(III) species at 77 K was anisotropic with $g_{\parallel} = 2.046$ and $g_{\perp} = 2.236$, owing to the presence of a Jahn-Teller distorted low-spin octahedral complex. The sequence $g_{\perp} > g_{\parallel} > g_e$ is consistent with the presence of a low-spin d^7 ion. No hyperfine structure was observed in the $g_{\parallel}$ feature. Thus, for the nickel(III) species the four N atoms occupy the equatorial plane with the two S donors in the apical positions. The corresponding nickel(III) complex of [10]aneNS₂²² showed an inverted spectrum characteristic of a compressed octahedral complex. It appears that by changing the nature of the ligating atoms, axial compression or elongation can be achieved preferentially.

Cyclic voltammetry of the nickel(II) complex, in aqueous solutions containing $1 \text{ mol dm}^{-3} \text{ NaNO}_3$, showed a wave with $E_1 = +0.97 \text{ V}$ vs. saturated calomel electrode [1.21 V vs. normal hydrogen electrode (NHE), $\Delta E = 150 \text{ mV}$] which is attributed to the $[\text{Ni}(\text{L}^1)_2]^{3+/2+}$ couple. The E_1 values for the nickel(III)–nickel(II) couple of complexes of ten-membered macrocycles are given in Table 4. The redox potentials increase as the harder N atoms are substituted by the softer S atoms. This is consistent with the ability of the trithia ligand to stabilize Ni^{II} relative to Ni^{III} and the triaza ligand to accommodate the nickel(III) state more readily. It should be noted that the potentials observed in the present study are much higher than those encountered in the methanobacterial systems, suggesting other factors are responsible for stabilisation of Ni^{III} relative to the lower oxidation states.

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