Nickel(II) Complexes with Tripodal Ligands: Synthesis, X-Ray Structural and Spectroscopic Studies†

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The synthesis, X-ray crystal structures and electronic spectra of two nickel complexes with tripodal ligands are reported. The nickel(II) complex, $[NiL^1(ClO_4)]ClO_4$, with the ligand, tris{[2-(2-aminophenyl)thio]ethyl}amine L^1 crystallizes as purple rectangular parallelopipeds in the monoclinic space group $P2_1/a$ with a = 9.542(7), b = 28.231(13), c = 11.136(7) Å, β = 91.50(6)°, Z = 4, R = 0.058 and R' = 0.067 for 2782 reflections. The Ni atom is bound equatorially to two S and two N atoms from two arms of the tripod while the two axial positions are occupied by the bridgehead nitrogen and an oxygen from a perchlorate. The complex $[NiL^2][ClO_4]_2$ with the ligand tris{[2-(2-aminoethyl)thio]ethyl}amine L^2 crystallizes as blue prisms in the monoclinic space group $P2_1/n$ with a = 11.7923(9), b = 16.813(2), c = 12.716(1) Å, β = 109.567(7)°, Z = 4, R = 0.039 and R' = 0.060 for 3354 reflections. All the three arms of the ligand are bound to the Ni^{II} providing a distorted-octahedral S_3N_3 donor set. Solution electronic spectra (in acetonitrile, dimethylformamide or dimethyl sulfoxide) of $[NiL^2][ClO_4]_2$ indicate retention of the solid-state structure, whereas for $[NiL^1(ClO_4)]ClO_4$ bound perchlorate is released in acetonitrile and replaced by solvent.

The synthesis of tripodal ligands and their complexation properties are of considerable current interest.[1] These ligands are capable of forming complexes with metal ions which can exhibit unusual co-ordination, high thermodynamic stability and kinetic inertness. In addition, these ligands can serve as precursors to the synthesis of interesting macrobicyclic[2,3] compounds which usually require high-dilution techniques[4] or the use of metal ions as templates[5–7] for their formation. We have concentrated on the synthesis of tripodal ligands containing six donors (excluding the bridgehead) following methods that do not require high-dilution conditions. These tripodal ligands can form octahedral complexes by wrapping around the metal ion leaving an open face with three groups positioned such that it may be capped by suitable reagents. One of the advantages in this approach is that the donor atoms, as well as the substituents in the tripodal arms, may be varied. It is therefore possible to tune the shape of the metal-ion containing cavity described by the resulting macrobicyclic ligands. We have initiated a research programme to investigate the co-ordination behaviour of tripodal ligands containing sulfur and nitrogen donor atoms with the ultimate goal of synthesising macrobicyclic compounds. In this paper the synthesis and complexing modes of two such ligands towards nickel(II) are presented. The recent findings of the presence of nickel–sulfur and –nitrogen bonds at the active sites of several hydrogenases[8] and carbon-monoxide dehydrogenases[9] has stimulated interest in nickel chemistry with mixed sulfur and nitrogen donor ligands.[10–15] Thus it is worthwhile to study nickel complexes with mixed N,S ligands to probe the electrochemical as well as their chemical properties. We are not aware of prior studies of nickel(II) complexes with such tripodal ligands.

Experimental

Triethanolamine, thionyl chloride and solvents were purchased from SD Fine Chemicals, India while 2-mercaptoaniline and 2-mercaptoethylamine were acquired from Aldrich Chemicals, USA. Solvents and thionyl chloride were purified using established methods.[16] All other reagents were used as received.

Infrared spectra were recorded on a Perkin Elmer model 580 grating spectrophotometer with polystyrene as an external reference. Proton NMR spectra were taken in $CDCl_3$ on a Bruker WP-80 Fourier-transform instrument using $SiMe_4$ as internal reference. Electronic spectral data were measured on a Perkin Elmer Lamda-2 UV/VIS spectrophotometer in freshly distilled solvents. Room-temperature magnetic susceptibility measurements were made on a Cahn Faraday magnetic balance using $[CoHg(SCN)_4]$ as a calibrant. Cyclic voltammograms were recorded at room temperature in acetonitrile for *ca.* 1×10^{-3} mol dm^{-3} solutions of the complexes on a PAR model 370–4 electrochemistry system as described earlier[16] with tetrabutylammonium perchlorate as the supporting electrolyte and a glassy carbon working electrode. Molar conductivity values for 1×10^{-3} mol dm^{-3} acetonitrile solutions of the complexes were determined using an Elico model CM-82T conductivity bridge. Microanalyses were done at the Central Drug Research Institute, Lucknow, India. Reported melting points were uncorrected.

Preparations.—Tris{[2-(2-*aminophenyl*)*thio*]*ethyl*}*amine* L^1. The synthesis of L^1 is depicted in Scheme 1. Tris(2-chloroethyl)amine hydrochloride was prepared[17] from triethanolamine and thionyl chloride in dry $CHCl_3$ in 92% yield; m.p. 128 °C (lit. 127–130 °C). To a solution of sodium *n*-butoxide [4 mmol, generated by dissolving Na metal (0.9 g) in *n*-butanol (5 cm^3)] was added 2-mercaptoaniline (0.38 g, 3 mmol) and the reaction mixture allowed to reflux to obtain a light brown solution. After an interval of 15 min, solid tris(2-chloroethylamine) hydrochloride (0.24 g, 1 mmol) was added in small portions to the refluxing solution over a period of 5 min. A white solid began to appear immediately. After further refluxing for 2 h the reaction mixture was allowed to cool to room temperature and the solid NaCl filtered off. Treatment of the brown filtrate with decolourizing charcoal afforded a light yellow solution. After evaporation of the BuOH the residue was extracted with $CHCl_3$ (100 cm^3). Evaporation of the solvent afforded the crude ligand L^1 in 70% yield. The ligand was purified by conversion to its hydrochloride salt followed by

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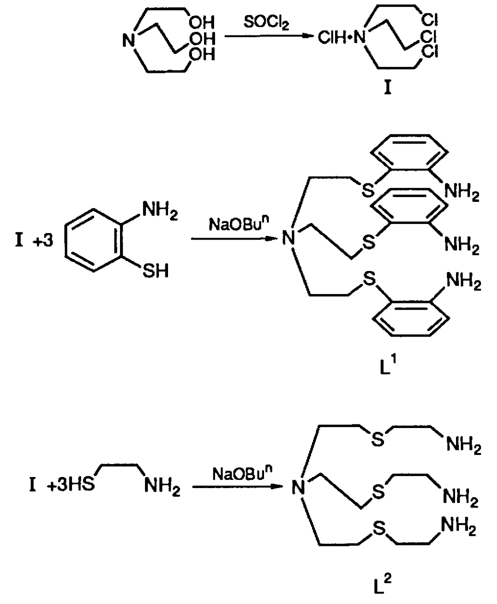
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Crystal and refinement data

Complex	1	2
Formula	$C_{24}H_{30}Cl_2N_4NiO_8S_3$	$C_{12}H_{30}Cl_2N_4NiO_8S_3$
M	728.3	584.20
Space group	$P2_1/a$	$P2_1/n$
a/Å	9.542(7)	11.7923(9)
b/Å	28.231(13)	16.813(2)
c/Å	11.136(7)	12.716(1)
β/°	91.50(6)	109.567(7)
U/Å^3	2999(3)	2376.0(4)
D_c/g cm^{-3}	1.613	1.633
D_m/g cm^{-3}	1.62	1.63
μ/cm^{-1}	10.81	13.4
Crystal dimensions (mm)	0.32 × 0.38 × 0.40	0.70 × 0.50 × 0.27
Relative transmission factor range	0.4762–0.5105	0.91–1.00
Scan type	ω	θ–2θ
Scan range/°	1.80 (ω)	0.60 + 0.35 tanθ
2θ range/°	2–50	4–50
Index ranges	$0 < h < 11, 0 < k < 33, -13 < l < 13$	$0 < h < 14, 0 < k < 20, -15 < l < 15$
Variation in standard intensity (%)	0.4	0.3
Standard reflections	2 Measured every 98	3 Measured every 97
Independent reflections	5268 (R_{int} = 0.0556)	3858
No. of reflections used	2782	3354
Data: parameter ratio	7.8	12.4
Hydrogen atoms	Riding model, fixed isotropic U	fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F)$	$w = 4(F_o)^2/[\sigma(F_o)^2]^2$
Final goodness of fit	1.01	2.20
Final R, R' (obs. data)	0.057, 0.064	0.039, 0.060
Final R, R' (all data)	0.058, 0.067	—
Largest and mean shift/e.s.d.	0.0048, 0.0000	0.01, 0.0004
Highest peak in final difference map/e Å^{-3}	0.79	0.60

Details in common: crystal system, monoclinic; $Z = 4$; $\lambda = 0.710\,73$ Å; variable scan rate.



Scheme 1 Synthesis of the tripodal ligands

treatment with an aqueous NaOH solution and extraction with $CHCl_3$. Purified L^1 was isolated as a pale yellow liquid in 64% yield. $\delta(^1H)$ (80 MHz; $CDCl_3$) 2.8 (12 H, br s, SCH_2CH_2N), 4.3 (6 H, br s, NH_2) and 7.1 (12 H, m, aromatic).

The corresponding aliphatic analogue L^2 was prepared in 75% yield as a light yellow liquid following the above procedure but using 2-mercaptoethylamine in place of 2-mercaptoaniline. The purified product was isolated as a colourless liquid in 68% overall yield. $\delta(^1H)$ (80 MHz, $CDCl_3$) 2.9 (24 H, m, all CH_2), 3.5 (6 H, br s, NH_2).

$[NiL^1(ClO_4)][ClO_4]$ **1**. To a warm (50 °C) stirred solution of ligand L^1 (0.47 g, 0.1 mmol) in methanol (25 cm^3) was added dropwise a methanol solution (20 cm^3) of $Ni(ClO_4)_2\cdot 6H_2O$ (0.37 g, 0.1 mmol). The solution turned purple and a small amount of purple solid appeared by the end of the addition. The mixture was allowed to cool to room temperature and the purple solid was filtered off and air-dried. Yield 80% (Found: C, 38.95; H, 4.30; N, 7.80; S, 13.40. $C_{24}H_{30}Cl_2N_4NiO_8S_3$ requires C, 39.60; H, 4.15; N, 7.70; S, 13.20%). Purple crystals of the complex suitable for X-ray diffraction studies were grown by slow evaporation of an acetonitrile solution at room temperature.

$[NiL^2][ClO_4]_2$ **2**. A similar procedure to the above afforded the nickel(II) complex with ligand L^2 in 88% yield (Found: C, 24.55; H, 5.25; N, 9.50; S, 16.50. $C_{12}H_{30}Cl_2N_4NiO_8S_3$ requires C, 24.65; H, 5.20; N, 9.60; S, 16.45%). Blue crystals of **2** were grown from acetonitrile solution by slow evaporation at room temperature. **CAUTION**: Care must be taken upon treating organic compounds with nickel(II) perchlorate as potentially explosive mixtures may be formed.

X-Ray Crystallography.—Cell parameters and reflection intensities were measured at room temperature on Nicolet R3m/V (for **1**) and Nonius CAD-4 (for **2**) diffractometers with graphite-monochromated Mo-Kα radiation. A summary of crystal data, intensity measurements and structure solution and refinements is given in Table 1. Intensity data were corrected for decay, Lorentz-polarization and absorption effects. The structures were solved by direct methods and refined on F by full-matrix least-squares calculations. For **1**, the SHELXTL-PLUS program package[18] and a microVAX II computer, and for **2**, the Nonius SDP/PDP package[19] and a PDP 11/73 computer were used for calculations. In each case, a few hydrogen atoms could be located in successive Fourier difference maps while others were added at calculated positions. Anisotropic refinement of non-hydrogen atoms and isotropic refinement of hydrogen atoms were carried out. For **1**, difficulty was encountered in locating perchlorate atoms O(2), O(3), O(5) and O(8) owing to

Table 2 Coordinates of non-hydrogen atoms for complex **1**

Atom	*x*	*y*	*z*
Ni	8 209(1)	3 809(1)	2 275(1)
S(2)	6 895(2)	4 101(1)	3 919(2)
S(1)	7 484(2)	3 012(1)	2 453(2)
S(3)	6 202(3)	4 375(1)	−2 357(2)
N(4)	6 328(6)	3 931(2)	1 187(5)
N(1)	9 453(7)	3 554(2)	910(6)
N(2)	9 057(7)	4 488(2)	2 214(6)
N(3)	3 922(14)	3 715(6)	−3 306(11)
C(8)	8 713(9)	4 798(3)	3 197(7)
C(22)	5 560(9)	4 327(3)	1 754(7)
C(1)	8 083(9)	2 820(3)	1 026(7)
C(2)	9 006(8)	3 106(3)	394(7)
C(9)	9 387(10)	5 236(3)	3 335(8)
C(6)	7 681(10)	2 382(3)	558(9)
C(21)	5 304(9)	4 245(3)	3 068(8)
C(11)	8 013(11)	5 399(3)	5 046(9)
C(3)	9 455(10)	2 955(3)	−710(8)
C(7)	7 693(9)	4 665(3)	4 003(7)
C(5)	8 151(11)	2 242(3)	−537(10)
C(12)	7 360(11)	4 977(3)	4 924(8)
C(10)	9 025(12)	5 530(3)	4 261(9)
C(4)	9 041(12)	2 524(4)	−1 171(9)
C(20)	5 449(9)	3 493(3)	1 093(8)
C(19)	5 667(9)	3 139(3)	2 093(9)
C(16)	6 856(31)	2 986(6)	−4 232(13)
C(15)	5 510(24)	3 133(6)	−4 078(11)
C(14)	5 227(15)	3 559(5)	−3 463(10)
C(13)	6 381(11)	3 803(3)	−3 004(7)
C(18)	7 730(15)	3 632(5)	−3 155(9)
C(17)	7 916(21)	3 221(6)	−3 773(13)
C(23)	5 575(10)	4 244(3)	−880(7)
C(24)	6 752(9)	4 077(3)	−47(7)
Cl(1)	11 058(3)	3 341(1)	3 677(2)
Cl(2)	1 712(2)	4 393(1)	−147(3)
O(1)	9 988(7)	3 698(2)	3 609(6)
O(6)	264(7)	4 441(2)	−381(6)
O(2)	11 531(10)	3 298(3)	4 862(8)
O(7)	2 465(8)	4 761(3)	−650(7)
O(8)	1 929(20)	4 524(8)	1 259(17)
O(4)	12 137(13)	3 494(4)	2 879(11)
O(5)	1 997(21)	3 980(7)	−1 044(20)
O(3)	10 484(11)	2 903(4)	3 312(9)
O(5A)	2 296(15)	3 955(5)	−239(15)
O(8A)	1 965(21)	4 247(8)	947(19)
O(2A)	12 444(59)	3 471(18)	4 042(49)
O(3A)	11 042(38)	3 050(13)	2 689(32)

Table 3 Coordinates of non-hydrogen atoms for complex **2**

Atom	*x*	*y*	*z*
Ni	0.954 71(3)	0.138 04(3)	0.232 05(3)
Cl(1)	0.553 27(8)	0.051 55(6)	0.268 68(9)
Cl(2)	0.988 51(9)	0.152 17(6)	0.628 49(7)
S(1)	1.053 78(7)	0.268 62(6)	0.275 02(6)
S(2)	1.103 60(7)	0.075 29(6)	0.157 74(7)
S(3)	0.809 51(8)	0.176 51(6)	0.048 06(7)
N(1)	0.834 5(2)	0.188 8(2)	0.306 9(2)
N(2)	1.075 5(3)	0.096 1(2)	0.386 1(2)
N(3)	0.857 7(3)	0.030 8(2)	0.200 5(3)
N(4)	1.052 2(3)	0.237 9(2)	0.034 2(2)
C(1)	0.963 1(3)	0.306 0(2)	0.354 4(3)
C(2)	0.836 3(3)	0.276 4(3)	0.308 1(3)
C(3)	1.192 5(3)	0.028 8(3)	0.287 2(3)
C(4)	1.198 9(3)	0.077 4(3)	0.386 9(3)
C(5)	0.716 7(4)	0.088 9(3)	0.032 3(4)
C(6)	0.787 7(4)	0.016 2(3)	0.082 8(4)
C(7)	1.016 1(4)	0.337 3(2)	0.159 2(3)
C(8)	1.087 0(4)	0.316 3(2)	0.082 9(3)
C(9)	1.212 2(3)	0.145 0(2)	0.135 9(3)
C(10)	1.152 2(3)	0.189 4(2)	0.027 2(3)
C(11)	0.869 9(4)	0.165 8(3)	−0.065 8(3)
C(12)	0.949 0(4)	0.236 9(3)	−0.065 4(3)
O(1)	0.658 6(3)	0.006 7(3)	0.302 4(4)
O(2)	0.468 2(4)	0.015 3(3)	0.179 3(4)
O(3)	0.577 3(4)	0.129 2(2)	0.246 3(5)
O(4)	0.496 9(3)	0.049 6(3)	0.349 2(3)
O(5)	1.027 8(4)	0.133 3(2)	0.741 7(3)
O(6)	1.077 2(3)	0.192 5(3)	0.598 4(3)
O(7)	0.949 5(4)	0.085 2(2)	0.562 1(3)
O(8)	0.895 2(4)	0.203 9(4)	0.609 0(6)

disorder and they were refined isotropically. Difference electron-density maps showed multiple peaks and a model involving partially occupied sites was used for the refinement. The highest peak (0.79 e Å^{-3}) in the final Fourier difference map for **1** was located near the Cl atom of the bound perchlorate. For **2**, the highest peak (0.60 e Å^{-3}) was located near the Ni atom. Atomic coordinates for the non-hydrogen atoms are listed in Tables 2 and 3. Selected bond lengths and angles for both complexes are reported in Table 4.

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

Results and Discussion

A perspective view of complex **1** is shown in Fig. 1. The Ni^{II} is co-ordinated equatorially to two arms of the ligand with the bridgehead nitrogen and a perchlorate oxygen occupying the two axial sites to complete six-co-ordination. The third arm as well as the second perchlorate are not co-ordinated. The co-ordination geometry around the Ni^{II} is slightly distorted from octahedral as revealed by the bond angles and distances. The ligand tris(2-aminoethyl)amine (tren) which has four potential donor sites has been found[12] to bind nickel(II) in a similar fashion (*i.e.* with only two arms of the ligand co-ordinated while the third arm remains free) in the complex, [Ni(tren)$_2$][Ni(mnt)$_2$] (mnt = maleonitriledithiolate). The Ni–N (bridgehead) bond length is considerably longer than those involving the aromatic amines despite the higher basicity of the bridgehead nitrogen. This, however, is expected since in order to reduce the Ni–N(bridgehead) bond length, the two co-ordinating arms must move out further and the C(22)–N(4)–C(20) angle must increase considerably from the present value of 111.7°. This would then lead to appreciably elongated Ni–N and Ni–S bond distances. The observed Ni–S bond length (2.378 Å) is appreciably shorter compared to that[20] (2.459 Å) found in the complex [NiL$_2$][ClO$_4$]$_2$ (L = 3-azapentane-1,5-diamine) which shows an unsymmetrical facial co-ordination of the two ligands. The Ni–S distance in **1** is however comparable to the average values in the homoleptic thioether complexes [Ni([9]aneS$_3$)$_2$]$^{2+}$ (2.386 Å)[21] and [Ni([18]aneS$_6$)]$^{2+}$ (2.386 Å)[22] ([9]aneS$_3$ = 1,4,7-trithiacyclononane, [18]aneS$_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane). The Ni–O bond length is slightly longer compared[23] to those found in [Ni(3,5Me$_2$-py)$_4$(ClO$_4$)$_2$] (3,5Me$_2$-py = 3,5-dimethylpyridine) which has two monodentate perchlorates. However, in the nickel complex with the ligand 15-thia-1,5,8,12-tetraazabicyclo[10.5.2]nonadecane,[24] which has one perchlorate bound in a monodentate fashion to the nickel(II) centre, the Ni–O length (2.563 Å) is quite long. For the ligand moiety the interatomic distances and angles are normal within statistical errors. Both the perchlorates are, however, disordered.

For complex **2**, all three pairs of sulfurs and nitrogens from the tripod are co-ordinated to the nickel in a slightly distorted octahedral fashion (Fig. 2). The bridgehead nitrogen lies 3.5 Å from the Ni^{II} and is unco-ordinated. While the Ni–N bond lengths are comparable with those in **1**, the Ni–S distances are longer and compare[20] well with those found for [NiL$_2$-

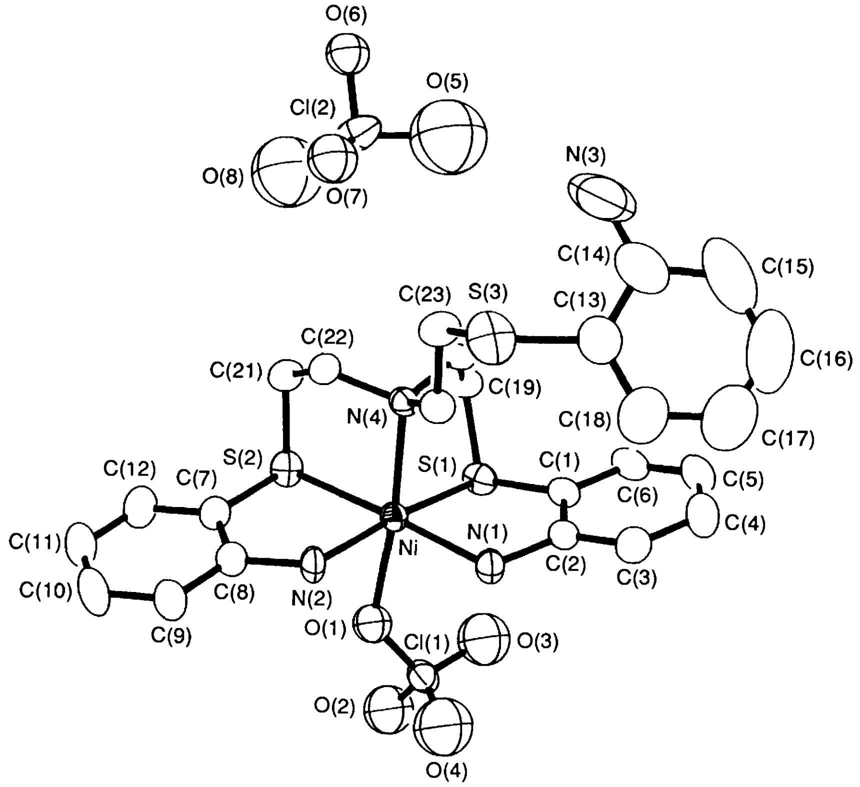


Fig. 1 Perspective view of complex **1**. Hydrogen atoms are omitted for clarity

Table 4 Selected bond lengths (Å) and angles (°)

Complex **1**					
Ni–S(1)	2.363(3)	Ni–S(2)	2.393(3)	Ni–N(1)	2.081(7)
Ni–N(2)	2.081(6)	Ni–N(4)	2.167(6)	Ni–O(1)	2.249(7)
S(2)–Ni–S(1)	95.9(1)	S(1)–Ni–N(1)	84.7(2)		
S(1)–Ni–N(4)	87.6(2)	S(2)–Ni–N(1)	176.7(2)		
S(2)–Ni–N(4)	86.0(2)	S(2)–Ni–N(2)	85.4(2)		
S(1)–Ni–N(2)	173.6(2)	N(1)–Ni–N(2)	93.7(3)		
N(1)–Ni–N(4)	97.3(2)	N(2)–Ni–N(4)	98.8(2)		
S(1)–Ni–O(1)	91.7(2)	S(2)–Ni–O(1)	86.8(2)		
N(1)–Ni–O(1)	90.0(2)	N(2)–Ni–O(1)	82.1(2)		
N(4)–Ni–O(1)	172.6(2)				
Complex **2**					
Ni–S(1)	2.461(1)	Ni–S(2)	2.490(9)	Ni–S(3)	2.478(1)
Ni–N(1)	2.132(3)	Ni–N(2)	2.120(3)	Ni–N(3)	2.102(3)
S(1)–Ni–S(2)	96.88(3)	S(1)–Ni–S(3)	95.92(4)		
S(1)–Ni–N(1)	83.17(9)	S(1)–Ni–N(2)	88.27(9)		
S(2)–Ni–S(3)	95.99(3)	S(2)–Ni–N(2)	82.47(9)		
S(2)–Ni–N(3)	88.36(9)	S(3)–Ni–N(1)	87.97(9)		
S(3)–Ni–N(3)	83.30(1)	N(1)–Ni–N(2)	93.50(1)		
N(1)–Ni–N(3)	91.60(1)	N(2)–Ni–N(3)	92.60(1)		
S(1)–Ni–N(3)	174.76(9)	S(2)–Ni–N(1)	176.01(9)		
S(3)–Ni–N(2)	175.7(1)				

$(ClO_4)_2$]. Unlike **1**, the perchlorates are not disordered. All the interatomic distances and angles of the ligand moiety are within normal ranges.

Conductivity data for the complexes are collected in Table 5. In acetonitrile solution complex **1** behaves[25] as a 1:2 electrolyte indicating that at *ca.* 1×10^{-3} mol dm^{-3} concentration a perchlorate ion is no longer bound to the nickel. As might be expected, complex **2** behaves as a 1:2 electrolyte under similar conditions.

The strongest peak in the IR spectrum of **1** appears at 1100 cm^{-1} and is quite broad. This is attributed[26] to ionic perchlorate. Additionally a strong peak at 1030 cm^{-1} and a medium peak at 915 cm^{-1} are attributable[27] to monodentate perchlorate. For complex **2** only a strong broad peak centred at 1103 cm^{-1} is observed which is attributed to ionic perchlorate.

Electronic absorption bands observed for acetonitrile solutions of **1** and **2** at 298 K are listed in Table 5 along with suggested assignments. Octahedral nickel(II) complexes exhibit three spin-allowed ligand-field bands[28] corresponding to transitions from the $^3A_{2g}$ ground state to the $^3T_{2g}$, $^3T_{1g}$ and $^3T_{1g}(P)$ excited states. The extent of distortion from ideal octahedral geometry is reflected in the intensities and sometimes splitting of these bands. For complexes which are octahedral or only slightly distorted from octahedral, molar absorption coefficients lie below 30 dm^3 mol^{-1} cm^{-1}. The intensities of the three ligand-field bands obtained for complex **2** are consistent with its near-octahedral structure. For complex **1** the case is not so clear since conductivity data indicate breakdown of the solid-state structure. However, both the energies and intensities of the ligand-field bands suggest that an acetonitrile molecule might occupy the sixth co-ordination site (at *ca.* 1×10^{-3} mol dm^{-3} concentration) so preserving pseudo-octahedral co-ordination at nickel. To probe solvent effects upon the electronic spectral transitions, solutions of the complexes in dimethylformamide (dmf) and dimethyl sulfoxide (dmso) were also investigated.

While complex **1** decomposes readily in either dmf or dmso, complex **2** remains intact in these solvents and the spectral transitions are found to be unchanged relative to acetonitrile. For complex **2**, in contrast to **1**, the Ni^{II} ion is encapsulated by six donors from the three arms of the ligand so leaving no vacant site to enable solvent to attack the metal ion.

Room-temperature magnetic moment values μ_B for complexes **1** and **2** are 3.10 and 3.09 respectively after diamagnetic corrections are applied. These values lie within the normal range found for octahedral nickel(II) complexes with mixed S,N-donor ligands.[29]

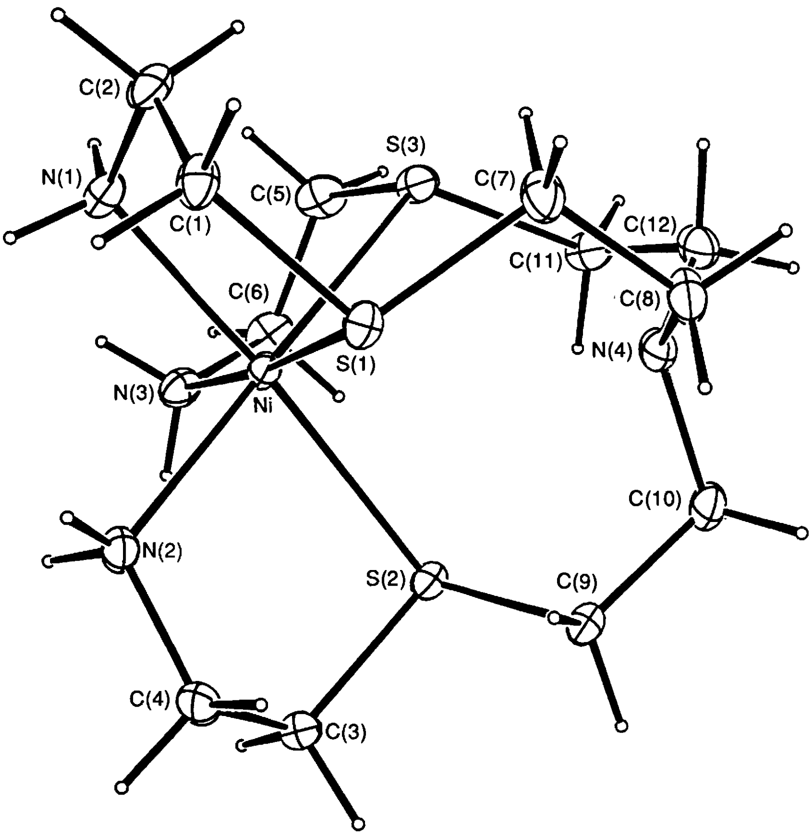


Fig. 2 Perspective view of complex **2**

Table 5 Molar conductance and UV/VIS data for the complexes

Complex	Λ_M/ohm^{-1} cm^2 mol^{-1}	λ_{max}/nm(ε_{max}/dm^3 mol^{-1} cm^{-1})	Assignment *
1	243	960(25)	$^3A_{2g} \longrightarrow {}^3T_{2g}$
		870(20)	$^3A_{2g} \longrightarrow {}^3T_{1g}$
		560(35)	$^3A_{2g} \longrightarrow {}^3T_{1g}$(P)
		305(7 580)	l.m.c.t. + ligand absorption
		230(34 320)	l.m.c.t. + ligand absorption
2	249	965(15)	$^3A_{2g} \longrightarrow {}^3T_{2g}$
		885(20)	$^3A_{2g} \longrightarrow {}^3T_{1g}$
		580(25)	$^3A_{2g} \longrightarrow {}^3T_{1g}$(P)
		280(4 480)	l.m.c.t. + ligand absorption
		240(4 670)	l.m.c.t. + ligand absorption

* l.m.c.t. = Ligand-to-metal charge transfer.

In acetonitrile at room temperature, cyclic voltammetry shows both complexes to undergo irreversible oxidation and reduction processes. For complex **1**, a broad anodic peak appears at about +0.9 V *vs.* saturated calomel electrode with no peak observed on scan reversal. Two broad cathodic peaks at −0.7 and −1.3 V are also observed which do not have any counterparts in the reverse scan. Likewise, for complex **2**, an anodic peak at +0.95 V and a cathodic peak at −0.8 V are found. On scan reversal, no return peaks are observed. Upon variation of the scan rate (from 50 to 500 mV s^{-1}) the overall picture does not change. These results indicate that both the oxidized and the reduced species undergo rapid chemical decomposition once they are generated electrochemically.

Conclusion

The present study reports the characterization of nickel(II) complexes with two new potentially heptadentate tripodal ligands. Since the thioether sites act as weak donors, the mode of binding to Ni^{II} depends upon the nature of the amino groups. The ligating behaviour of these two ligands towards different metal ions is currently being investigated.

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