Pergamon

Polyhedron Vol. 14, No. 7, pp. 919–926, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277–5387/95 $9.50+0.00

0277–5387(94)00313–0

A HEXADENTATE NICKEL(II) COMPLEX WITH A TRIPODAL LIGAND BEARING S_3N_3 DONORS: SYNTHESIS, SPECTROSCOPIC AND X-RAY CRYSTAL STRUCTURAL INVESTIGATION

SUBRATA MANDAL and PARIMAL K. BHARADWAJ*

Department of Chemistry, Indian Institute of Technology, Kanpur, 208016, India

and

ZHONG-YUAN ZHOU and THOMAS C. W. MAK*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

(*Received* 29 *March* 1994; *accepted* 4 *August* 1994)

Abstract—A tripodal ligand, tris[2-(2-aminoethyl)thio]ethane (L^1), bearing three thioether sulphurs and three primary amino nitrogens has been synthesized in high yield. Reaction with nickel(II) perchlorate hexahydrate yielded the complex $[Ni(L^1)](ClO_4)_2$, which has been characterized by X-ray crystallography. The structure consists of two independent hexacoordinate cage cations and four independent perchlorate anions. The Ni^{II} ion is bound equatorially to two nitrogen and two sulphur atoms, while the other two donor atoms occupy the axial positions. Both the independent cage cations are disordered, with thioether sulphurs occupying two alternative sets of ligand sites. One of the four perchlorate anions is also disordered. IR, conductivity, RT magnetic susceptibility and electronic absorption spectral data are consistent with the solid state structure. The corresponding aromatic analogue, tris[2-(2-aminophenyl)thio]ethane (L^2), forms the complex $[Ni(L^2)](ClO_4)_2$, which has been characterized spectroscopically.

Tripodal ligands are capable of forming complexes with metal ions which can exhibit unusual coordination, high thermodynamic stability and kinetic inertness.[1] The coordination geometry of these complexes depends upon factors like: (i) the electronic configuration and size of the metal ion, (ii) repulsions between non-bonded atoms in different ligand arms, (iii) inherent rigidity due to the presence of aromatic rings, etc. Two idealized symmetries are trigonal antiprismatic (TAP) and trigonal prismatic (TP) with D_{3d} and D_{3h} microsymmetries, respectively. The energy difference between these two arrangements depends not only on the metal ion but also on the ligand superstructure.[1] In the present paper, we report the synthesis of two ligands of different inherent rigidity that contain both hard and soft donors in order to study their coordination modes upon complexation. The choice of Ni^{II} as the metal ion was influenced by the recent findings of the presence of distorted octahedral nickel complexed with sulphur and nitrogen donors at the active sites of several dehydrogenases[2] and carbon monoxide dehydrogenases.[3] There has been an unprecedented interest in nickel chemistry with mixed sulphur and nitrogen donor ligands.[4–6] A new approach in modelling these sites might be the use of tripodal ligands bearing sulphur and nitrogen donors. Another important aspect of these two ligands is that, once coordinated to a metal ion, the three amino groups will describe an open face. This open face can be

---

*Authors to whom correspondence should be addressed.

capped[7] by suitable reagents, thus providing a convenient route to the synthesis of macrobicyclic compounds.

EXPERIMENTAL

Materials

Reagent grade chemicals, toluene-4-sulphonyl chloride, 1,1,1-tris(hydroxymethyl)ethane, cysteamine hydrochloride, 2-mercaptoaniline and nickel(II) diperchlorate hexahydrate were obtained from Aldrich and used as received. All the solvents were from Glaxo Labs and were purified prior to use following standard methods.[8]

Synthesis of the ligands

A synthetic scheme for the ligands is shown in Fig. 1.

Tritosylate of 1,1,1-*tris*(*hydroxymethyl*)*ethane*. Toluene-4-sulphonyl chloride (5.8 g; 0.03 mol) was dissolved in pyridine (10 dm^3) and cooled to -10°C in an ice-salt bath. An ice-cold solution of 1,1,1-tris(hydroxymethyl)ethane (1.2 g; 0.01 mol) in pyridine (5 dm^3) was added slowly through a syringe over a period of 30 min while maintaining the temperature around -10°C with continuous stirring. After the addition was complete, the mixture was stirred for another 15 min and then left in a refrigerator (5°C) overnight. A white solid settled which was collected by filtration, washed thoroughly with water and finally dried *in vacuo*. Yield 85%, m.p. 101°C. δ_H (80 MHz; CDCl$_3$; ppm): 1.0 (s, 3H, CH$_3$); 2.5 [s, 9H, CH$_3$(tosyl)]; 3.8 (s, 6H, CH$_2$) and 7.5 (m, 12H, aromatic).

Tris[2-(2-*aminoethyl*)*thio*]*ethane* (L^1). Sodium metal (0.8 g; 35 mmol) was added to n-BuOH (15 dm^3) in a three-necked round-bottomed flask. A vigorous reaction started immediately and all the metal reacted in about 20 min. To this hot reaction mixture (50°C) was added cysteamine hydrochloride (2 g; 17.6 mmol) under argon with constant stirring. After the addition was complete, the

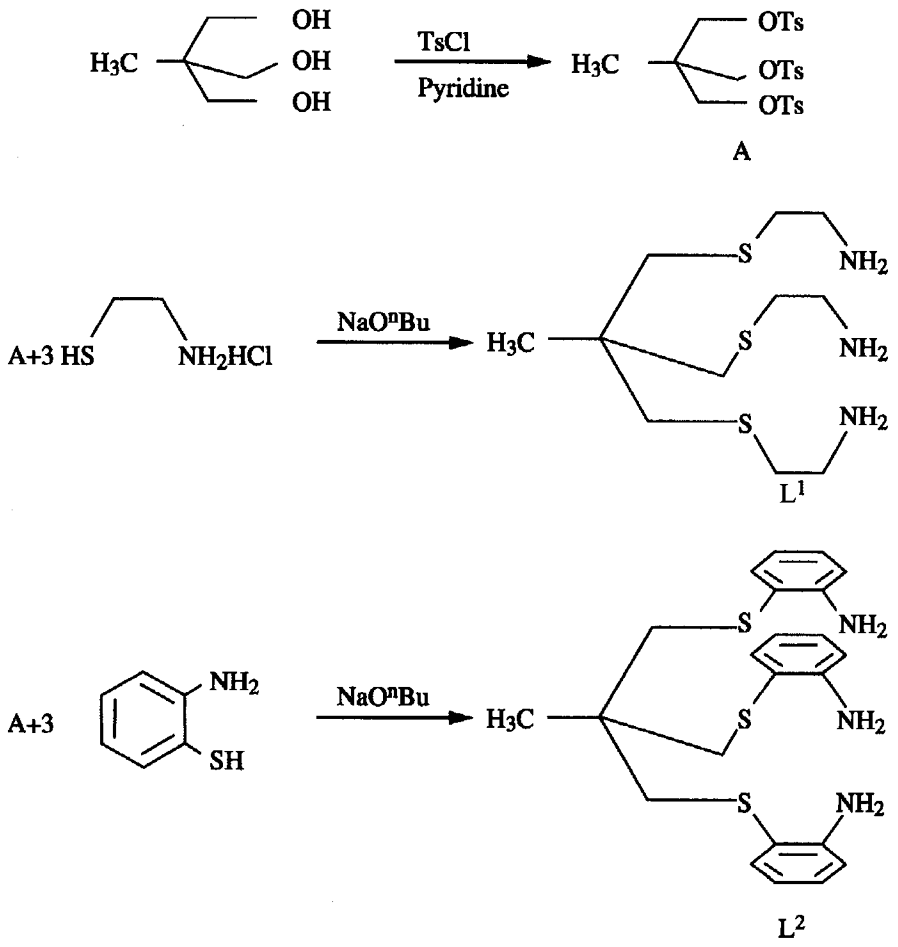

Fig. 1. Synthetic scheme for the ligands.

mixture was refluxed for 10 min. Solid 1,1,1-tris (hydroxymethyl)ethane tritosylate (3.4 g; 5.8 mmol) was then added to the hot reaction mixture in portions over a period of 20 min. A small amount of white solid began to appear immediately. For completion of the reaction, the mixture was refluxed for 2 h and then cooled to room temperature. White sodium tosylate was removed by filtration, and the light brown filtrate treated with activated charcoal and filtered to afford a light yellow solution. n-BuOH was evaporated off under reduced pressure to obtain a light yellow oily mass. The product was dissolved in chloroform, washed several times with water and the ligand L^1 was isolated as a light yellow oil after removal of chloroform in about 70% yield. δ_H (80 MHz; $CDCl_3$; ppm): 1.0 (s, 3H, CH_3); 3.0 (m, 18H, all CH_2) and 3.5 (s br, 6H, NH_2). The ligand L^1 has been reported recently.[9]

The ligand L^2 was synthesized in about 65% yield as a yellow oil following the above procedure, except that 2-mercaptoaniline was used instead of cysteamine hydrochloride. δ_H (80 MHz; $CDCl_3$; ppm): 1.0 (s, 3H, CH_3); 3.0 (s, 6H, CH_2); 4.2 (s br, 6H, NH_2) and 7.2 (m, 12H, aromatic).

Synthesis of $[Ni(L^1)](ClO_4)_2$ (1)

To a warm (50°C) stirred solution of the ligand, L^1 (0.5 g; 1.7 mmol) in methanol (25 dm^3) was added dropwise a methanolic solution (15 dm^3) of nickel(II) perchlorate hexahydrate (0.6 g; 1.7 mmol). The solution was refluxed for 45 min after the addition was complete to obtain a dark green solution. It was then concentrated to about 5 dm^3 and left in a refrigerator at 5°C for 2 h. A dark green solid settled at the bottom, which was collected by filtration and air-dried. Yield 80%. Found: C, 23.8; H, 4.8; N, 7.5; S, 17.4. $C_{11}H_{27}N_3O_8S_3Cl_2Ni$ requires: C, 23.8; H, 4.9; N, 7.6; S, 17.3%. This complex can be crystallized as well-formed dark green crystals by slow evaporation of an acetonitrile solution.

Synthesis of $[Ni(L^2)](ClO_4)_2$ (2)

This complex was isolated as a dark green solid in 75% yield following the above procedure. Found: C, 39.4; H, 3.8; N, 5.9; S, 13.9. $C_{23}H_{27}N_3O_8S_3Cl_2Ni$ requires: C, 39.5; H, 3.9; N, 6.0; S, 13.7%. Attempts to recrystallize this complex for X-ray crystallography were unsuccessful.

CAUTION: Care must be taken when treating organic compounds with metal perchlorates as potentially explosive mixtures may be formed.

Physical measurements

The physical data were collected as follows: IR (KBr disc, 4000–400 cm^{-1}), Perkin–Elmer model 1320; electronic absorption spectra (298 K, MeOH, MeCN and DMF solvents), Perkin–Elmer model Lambda-2; ^1H NMR (80 MHz, $CDCl_3$, standard $SiMe_4$), Bruker WP80 FT instrument; magnetic susceptibility (300 K, $[CoHg(SCN)_4]$ standard), Cahn Faraday Magnetic Balance; solution electrical conductivity (298 K, *ca* 1×10^{-3} mol dm^{-3} in MeCN and MeOH), Elico model CM-82T conductivity bridge; cyclic voltammetry (298 K, MeCN solvent, complex: supporting electrolyte (n-Bu_4ClO_4) ratio 1 : 100, glassy carbon working electrode and saturated calomel reference electrode), PAR model 370-4 electrochemistry system. Under our experimental conditions, the reversible[10] ferrocenium–ferrocene couple ($E_f = 0.40$ V vs SCE in MeCN) had ΔE_p of 80 mV [$E_f = 0.5(E_{pa}+E_{pc})$]. Elemental analyses were done at the Central Drug Research Institute, Lucknow, India.

X-ray crystallographic analysis of **1**

Crystal data, data collection, structure solution and refinement details are given in Table 1. All diffraction measurements were made at room temperature (21°C) with a Siemens P4 diffractometer system using graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for decay and Lorentz polarization effects; empirical absorption corrections were applied by fitting[11] a pseudo-ellipsoid to the ω-scan data of selected strong reflections over a range of 2θ angles. The structure was solved by the heavy atom method and refined with the SHELXTL-PC program package.[12] Analytic expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections[13] were incorporated. Two-fold disorder was found for the sulphur atoms of the tripod in each cation and the three oxygen atoms in one of the perchlorate anions. The sulphur atoms in each cage cation were represented by six "half sulphur atoms" and likewise the three disordered oxygen atoms in one perchlorate group were constrained to an occupancy factor of 1/2. The oxygen atoms of the disordered perchlorate group were refined isotropically, while all other non-hydrogen atoms were refined anisotropically. Some of the hydrogen atoms could be located in the difference Fourier maps, while the rest were generated geometrically (C—H 0.96 Å, N—H 0.87 Å), assigned a common isotropic thermal factor ($U = 0.08$ Å^2), allowed to ride on their corresponding parent atoms and included in the structure factor calculations.

Table 1. Data collection and processing parameters for complex **1**

Molecular formula	$C_{11}H_{27}N_3S_3Ni.2ClO_4$
Molecular weight	555.15
Colour and habit	black–green prism
Unit cell parameters	$a = 12.760(5)$ Å $\alpha = 90°$ $b = 17.932(6)$ Å $\beta = 92.70(2)°$ $c = 19.333(4)$ Å $\gamma = 90°$ $V = 4418.7$ Å^3 $Z = 8$ $F(000) = 2304$
D_{calc}	1.84 g cm^{-3}
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Crystal size	0.22 × 0.18 × 0.32 mm^3
Radiation	graphite-monochromatized Mo-$K\alpha$, $\lambda = 0.71073$ Å
Standard reflections	(1,0,7); (0,−3,−3)
Intensity variation	±1.2%
R_{int} (from merging of eqiv. reflections)	0.0193
Absorption coefficient	14.5 cm^{-1}
Mean μr	0.17
Transmission factors	0.647–0.779
Scan type and rate	ω-scan; 4.0° min^{-1}
Scan range	0.80° below $K\alpha_1$ to 0.80° above $K\alpha_2$
Background counting	stationary counts for one-fifth of scan time at each end of scan range
Collection range	$h, k, \pm l$; $2\theta_{max} = 47°$
Unique data measured	5817
Obs. data with $\lvert F_o\rvert \geqslant 3\sigma(\lvert F_o\rvert)$, n	3187
No. of variables, P	554
Weighting scheme	$w = [\sigma^2\lvert F_o\rvert + 0.00015\lvert F_o\rvert^2]$
$R_F = \Sigma\lvert\lvert F_o - \lvert F_o\rvert\rvert/\Sigma\lvert F_o\rvert$	0.076
$R_w = [\Sigma w^2(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w^2\lvert F_o\rvert^2]^{1/2}$	0.088
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert^2/(n-p)]^{1/2}$	1.63
Residual extrema in final difference map	+0.94 to −0.62 e Å^{-3}

The highest peak (0.94 e Å^{-3}) was located near the metal ion. Selected bond lengths and bond angles are given in Tables 2 and 3, respectively.

Supplementary material

Tables of coordinates, anisotropic thermal parameters, bond lengths and bond angles and a list of observed and calculated structure factors have been deposited with the Editor.

RESULTS AND DISCUSSION

Perspective views of the complex cations of **1** are shown in Figs 2 and 3. The asymmetric unit consists of two independent formula units. Each cation is formed through coordination to Ni^{II} of all three pairs of sulphurs and nitrogens from the tripod.

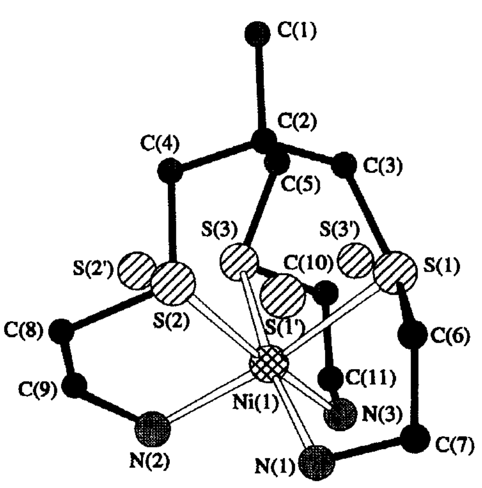

Fig. 2. A perspective view of the cation **1** showing the atom numbering scheme without the hydrogen atoms.

Table 2. Selected bond lengths (Å) for the cations in **1**

Cation 1			
Ni(1)—S(1)	2.428(5)	Ni(1)—S(1′)	2.49(5)
Ni(1)—S(2)	2.409(5)	Ni(1)—S(2′)	2.54(5)
Ni(1)—S(3)	2.403(5)	Ni(1)—S(3′)	2.33(4)
Ni(1)—N(1)	2.10(1)		
Ni(1)—N(2)	2.11(2)		
Ni(1)—N(3)	2.10(1)		
S(1)—C(3)	1.86(2)	S(1′)—C(3)	2.34(6)
S(2)—C(4)	1.83(2)	S(2′)—C(4)	2.09(5)
S(3)—C(5)	1.86(2)	S(3′)—C(5)	2.05(5)
S(1)—C(6)	1.88(2)	S(1′)—C(6)	1.82(5)
S(2)—C(8)	1.82(2)	S(2′)—C(8)	2.10(6)
S(3)—C(10)	1.85(2)	S(3′)—C(10)	1.96(5)
Cation 2			
Ni(2)—S(4)	2.336(6)	Ni(2)—S(4′)	2.37(2)
Ni(2)—S(5)	2.469(7)	Ni(2)—S(5′)	2.37(2)
Ni(2)—S(6)	2.374(7)	Ni(2)—S(6′)	2.72(2)
Ni(2)—N(4)	2.18(2)		
Ni(2)—N(5)	2.13(2)		
Ni(2)—N(6)	2.07(2)		
S(4)—C(14)	1.91(2)	S(4′)—C(14)	1.95(2)
S(5)—C(15)	1.91(2)	S(5′)—C(15)	2.01(3)
S(6)—C(16)	1.96(2)	S(6′)—C(16)	2.07(3)
S(4)—C(17)	1.83(2)	S(4′)—C(17)	1.76(3)
S(5)—C(19)	1.77(2)	S(5′)—C(19)	2.09(3)
S(6)—C(21)	1.91(2)	S(6′)—C(21)	1.97(3)

The perchlorate anions remain uncoordinated. As both the independent cage cations exhibit the same kind of statistical disorder for their set of donor sulphur atoms, there is a definite equilibrium between the trigonal antiprismatic (TAP) and trigonal prismatic (TP) arrangements[1] of the six donors around Ni^{II}. The twist angle (as defined in Fig. 4) will be 60° for the TAP arrangement, while for the TP geometry it should be 0°. When the positions of the sulphur atoms are as shown by S(1), S(2) and S(3), the twist angle is 52.1°. However, for the set S(1′), S(2′) and S(3′), the value is 13.2°. For the second independent cation, the corresponding values of the twist angles are 49.2 and 9.6°. An occupancy factor of 0.5 (which remained almost unchanged when treated as a variable) for each sulphur atom indicates that both structures exist in a 1 : 1 ratio at room temperature. The observed Ni—S bond lengths (range 2.403–2.428 Å) in the TAP conformation are shorter compared to those (2.461–2.490 Å) found in a tripodal complex of Ni^{II} with the same chromophore.[14] In the TP arrangement, the bond lengths vary widely and lie in the range 2.33–2.54 Å. The Ni—N bond lengths are similar to those found in similar complexes.[14, 15] For the ligand moiety, the bond lengths and angles are normal within statistical errors, except the S–C lengths in the TP arrangement, which are appreciably longer[16] than normal values (Table 2). The bond lengths and angles of the second cation are found to vary in a similar fashion, although the magnitudes are different (Tables 2 and 3). Of the four perchlorate anions in the asymmetric unit, one is disordered.

Conductivity data for the complexes in acetonitrile are given in Table 4. As the data indicate, both **1** and **2** behave as 1 : 2 electrolytes. We have carried out conductance measurements in methanol and DMF. In both these solvents, the complexes behave as 1 : 2 electrolytes.[17]

In the IR spectra of the complexes, a strong and broad absorption occurs at 1100 cm^{-1} which is attributable[18] to the anionic perchlorates.

Electronic absorption bands observed for the complexes in acetonitrile solutions are collected in Table 4 with assignments. No appreciable changes in the band positions occur on changing the solvent,

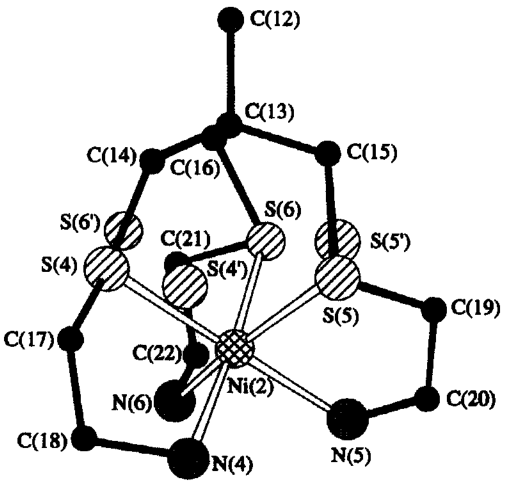

Fig. 3. A perspective view of the cation **2** showing the atom numbering scheme without the hydrogen atoms.

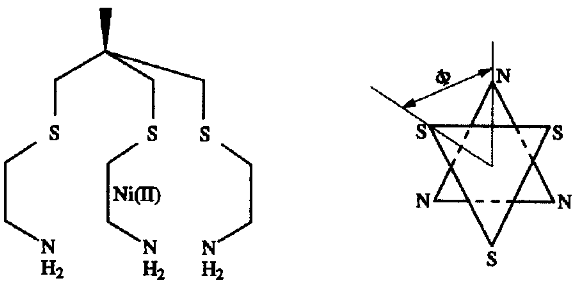

Fig. 4. Schematic drawing of the Ni^{II} complex **1** and the definition of the twist angle ϕ. For TAP, $\phi = 60$; for TP, $\phi = 0$.

Table 3. Selected bond angles (°) for the cations in **1**

Cation 1			
S(1)—Ni(1)—S(2)	86.6(2)	S(1′)—Ni(1)—S(2′)	89.4(15)
S(1)—Ni(1)—S(3)	89.9(2)	S(1′)—Ni(1)—S(3′)	92.0(16)
S(1)—Ni(1)—N(1)	85.4(4)	S(2′)—Ni(1)—S(3′)	90.8(16)
S(1)—Ni(1)—N(2)	170.1(5)		
S(1)—Ni(1)—N(3)	92.9(4)		
S(2)—Ni(1)—S(3)	91.3(2)		
S(2)—Ni(1)—N(1)	94.5(4)		
S(2)—Ni(1)—N(2)	83.6(5)		
S(2)—Ni(1)—N(3)	174.4(4)		
S(3)—Ni(1)—N(1)	172.4(4)		
S(3)—Ni(1)—N(2)	92.0(5)		
S(3)—Ni(1)—N(3)	83.1(4)		
N(1)—Ni(1)—N(2)	93.6(6)		
N(1)—Ni(1)—N(3)	91.1(6)		
N(2)—Ni(1)—N(3)	97.0(6)		
Cation 2			
S(4)—Ni(2)—S(5)	91.3(2)	S(4′)—Ni(2)—S(5′)	93.05(12)
S(4)—Ni(2)—S(6)	90.6(2)	S(4′)—Ni(2)—S(6′)	84.00(14)
S(4)—Ni(2)—N(4)	86.0(5)	S(5′)—Ni(2)—S(6′)	82.32(15)
S(4)—Ni(2)—N(5)			
S(4)—Ni(2)—N(6)	97.9(5)		
S(5)—Ni(2)—S(6)	89.3(2)		
S(5)—Ni(2)—N(4)	91.4(5)		
S(5)—Ni(2)—N(6)	169.1(5)		
S(6)—Ni(2)—N(4)	176.5(5)		
S(6)—Ni(2)—N(6)	84.9(5)		
N(4)—Ni(2)—N(5)	87.7(7)		
N(4)—Ni(2)—N(6)	95.0(7)		
N(5)—Ni(2)—N(6)	90.7(7)		

Table 4. Molar conductance and electronic spectral data for the complexes

Complex	λ_M (Ω^{-1} cm^{-1})	λ_{max}, nm (ε_{max}, dm^3 mol^{-1} cm^{-1})	Assignment
1	246	975 (28)	$^3A_{2g} \rightarrow {}^3T_{2g}$
		850 (53)	$^3A_{2g} \rightarrow {}^3T_{1g}$
		540 (51)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
		335 (1420)	LMCT[a]
		282 (3125)	LMCT + ligand absorption
2	249	935,br[b] (20)	$^3A_{2g} \rightarrow {}^3T_{2g} + {}^3A_{2g} \rightarrow {}^3T_{1g}$
		577 (15)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
		305 (11,680)	LMCT + ligand absorption
		260 (17,720)	LMCT + ligand absorption

[a] LMCT, ligand-to-metal charge transfer.
[b] br, broad absorption.

indicating that the solvent molecules do not coordinate to the metal ion. Octahedral or TAP Ni^{II} complexes exhibit[19] three spin-allowed ligand field bands, corresponding to the transitions from the $^3A_{2g}$ ground state to the $^3T_{2g}$, $^3T_{1g}$ and $^3T_{1g}(P)$ excited states. For complexes with usual octahedral or TAP (D_{3d}) symmetries, the extinction coefficients for these bands lie[19,20] below 30 dm^3 mol^{-1} cm^{-1}. As the geometry distorts from the ideal octahedral or TAP, the intensities increase and sometimes may result in splitting of the bands as well. Intensities are two to three times larger in complexes of TP with effective D_{3h} microsymmetry than in TAP complexes.[20,21] Thus, intensities of the three ligand field bands obtained in case of the complex **1** are consistent with its solid state structure, which is an equilibrium mixture of TAP and TP microsymmetry. For **2**, however, the intensities are significantly lower and are well within the usual octahedral limit. This is suggestive of the fact that for **2**, TAP geometry predominates over TP geometry, which is a result of extra rigidity in the ligand superstructure due to the presence of the three aromatic rings.

Room temperature magnetic moment ($\mu_{\text{eff}}/\mu_{\text{B}}$) values for **1** and **2** after diamagnetic corrections are found to be 3.06 and 3.01, respectively, showing non-zero orbital contribution. The values are within normal ranges found for TAP and TP complexes of Ni^{II} with mixed sulphur/nitrogen donor ligands.[14,20,22]

Both complexes show only ill-defined peaks in their cyclic voltammograms which disappear upon scan reversals, indicating rapid decomposition of the oxidized or reduced species formed. The overall picture does not change upon variation of the scan rate from 50 to 500 mV s^{-1}.

CONCLUSION

Two new hexadentate tripodal ligands have been synthesized that form 1 : 1 complexes with nickel(II) perchlorate hexahydrate. The structure of one shows there is an equilibrium between the TAP and TP arrangements of donor atoms around Ni^{II}, which is the first known occurrence of such a structure. The possible influence of the metal ion to enforce one of these arrangements can be probed by substituting other metal ions for Ni^{II}. Also, X-ray structural studies at low temperature might be able to indicate whether one of the conformations of the complex **1** is preferred at low temperature. Work in these directions is in progress.

Acknowledgements—Financial support from the Department of Science and Technology, New Delhi, India and the Hong Kong Research Grants Council (CUHK 22/91) is gratefully acknowledged.

REFERENCES

1. (a) R. M. Kirchner, C. Mealli, M. Bailey, M. Howe, L. P. Torre, L. J. Wilson, L. C. Andrews, N. J. Rose and E. C. Lingafelter, *Coord. Chem. Rev.* 1987, **77**, 89; (b) C. Orvig, D. J. Berg and S. J. Rettig, *J. Am. Chem. Soc.* 1991, **113**, 2528; S. Liu, L. Gelmini, S. J. Retig, R. C. Thompson and C. Orvig, *J. Am. Chem. Soc.* 1992, **114**, 6081.
2. R. Cammack, in *The Bioinorganic Chemistry of Nickel* (edited by J. R. Lancaster Jr.), Ch. 8. VCH, New York (1988).
3. S. W. Ragsdale, H. G. Wood, J. A. Morton, L. G. Ljungdahl and D. V. DerVartanian, in *The Bioinorganic Chemistry of Nickel* (edited by J. R. Lancaster Jr.), Ch. 14. VCH, New York (1988).
4. H. J. Krugar and R. H. Holm, *J. Am. Chem. Soc.* 1990, **112**, 2955; P. Starropoulos, M. Carrie, M. C. Muetterties and R. H. Holm, *J. Am. Chem. Soc.* 1990, **112**, 5385; S. Fox, Y. Wang, A. Silver and M. Millar, *J. Am. Chem. Soc.* 1990, **112**, 3218; S. B. Choudhury, D. Ray and A. Chakravorty, *Inorg. Chem.* 1990, **29**, 4603 and references cited therein.
5. H. J. Krugar, G. Peng and R. H. Holm, *Inorg. Chem.* 1991, **30**, 734; M. Zimmer, G. Schulte, X. L. Luo and R. H. Crabtree, *Angew. Chem., Int. Edn Engl.* 1991, **30**, 193.
6. N. Baidya, M. M. Olmstead and P. K. Mascharak, *J. Am. Chem. Soc.* 1992, **114**, 9666.
7. L. R. Gahan, T. M. Donlevy and T. W. Hambley, *Inorg. Chem.* 1990, **29**, 1451.
8. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 1st edn. Pergamon Press, Oxford (1966).
9. J. I. Bruce, L. R. Gahan, T. W. Hambley and R. Stranger, *Inorg. Chem.* 1993, **32**, 5997.
10. S. K. Mandal and P. K. Bharadwaj, *Polyhedron* 1992, **11**, 1037.
11. G. Kopfmann and R. Huber, *Acta Cryst.* 1968, **24A**, 348.
12. G. M. Sheldrick, SHELXTL-PC 92, Structure Determination Software Programs. Siemens AG, Karlsruhe, Germany (1992).
13. *International Tables for X-ray Crystallography*, Vol. 4, pp. 55, 99, 149. Kynoch Press, Birmingham, Kluwer Academic Publishers, Dordrecht (1974).
14. K. G. Ragunathan and P. K. Bharadwaj, *J. Chem. Soc., Dalton Trans.* 1992, 2417.
15. G. J. Colpas, M. Kumar, R. O. Day and M. J. Maroney, *Inorg. Chem.* 1990, **29**, 4779.
16. H. J. Prochaska, W. F. Schwindinger, M. Schwartz, M. J. Burk, E. E. Barnarducci, R. A. Lalancette, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc.* 1981, **103**, 3446 and references cited therein.
17. W. J. Grey, *Coord. Chem. Rev.* 1971, **7**, 81.

18. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn, p. 251. John Wiley, New York (1987).
19. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, p. 507. Elsevier, New York (1984).
20. E. Larsen, G. N. La Mar, B. E. Wagner, J. E. Parks and R. H. Holm, *Inorg. Chem.* 1972, **11**, 2652 and references cited therein.
21. E. I. Baucom and R. S. Drago, *J. Am. Chem. Soc.* 1971, **93**, 6469.
22. M. Ciampolini, J. Gelsomini and N. Nardi, *Inorg. Chim. Acta* 1968, **2**, 343.