Synthesis, structure and electrochemistry of isomeric nickel(II) complexes of a [9]ane fused cyclam macrotricycle: evidence for a stable *trans*-IV and a redox induced rearrangement in a *trans*-I conformation†
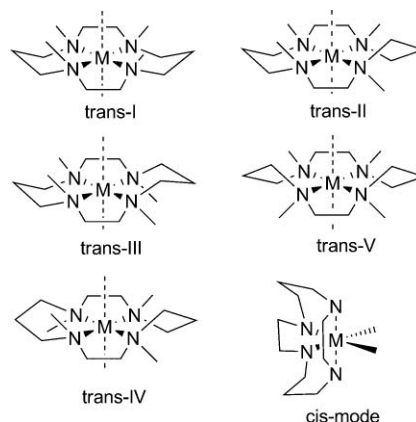
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The macrotricyclic ligand, 1,11-dithia-4,8,14,18-tetraaza-[5,2,2,5]-eicosane, L3 has been synthesized from cyclam. Both the *cis*- and the *trans*- isomers of the Ni(II) complexes have been prepared and characterized by single crystal X-ray crystallography. In the *cis*-[Ni(*trans*-I, *syn*-L3)](Cl$_2$)·4H$_2$O, the *syn*-isomer of L3 is present in which the cyclam ring adopts a *trans*-I stereochemistry. Crystal structure data ($Pna2_1$, tetragonal, $a = 17.450(3)$, $b = 12.188(2)$, $c = 11.897(2)$ Å, $V = 2530.2(8)$ Å^3, $R_1 = 0.032$ and $wR_2 = 0.078$) indicate that two of the Ni–N distances, Ni–N(4) = 2.164(3) Å and Ni–N(2) = 2.179(3) Å are longer than Ni–N(1) = 2.100(3) Å and Ni–N(3) = 2.101(3) Å. The Ni–S distances, 2.4265(11) Å and 2.4512(11) Å, are similar to lengths observed in many thioether complexes. The cyclic voltammogram for the Ni$^{2+/3+}$ redox couple of the *cis*-complex is scan rate dependent. Although quasi-reversible at a scan rate of 1000 mV s^{-1}, when the scan rate is lowered below 100 mV s^{-1} the redox couple shows chemical irreversibility. There is evidence for rearrangement of the inner coordination sphere and adsorption of the oxidized species onto the Pt electrode. However, there is no evidence to suggest that isomerization of the *cis*- to the *trans*-complex occurs. Consistent with this electrochemical behavior, a time-dependent change in the ESR spectrum for the Ni(III) species was also observed. A mechanism is proposed where through dissociation of a thioether donor and subsequent substitution of a solvent CH$_3$CN, the *trans*-I conformation changes from a *cis*-type coordination to a *trans*-mode. In the *trans*-[Ni(*trans*-IV, *anti*-L3)](ClO$_4$)$_2$ complex, the *anti*-form of L3 is present where the cyclam moiety adopts the rare *trans*-IV stereochemistry. The *trans*-complex ($C_2/_c$, monoclinic, $a = 22.382(9)$, $b = 10.118(2)$, $c = 14.300(3)$ Å^3, $V = 2493.3(13)$ Å^3, $R_1 = 0.051$ and $wR_2 = 0.142$) is a minor product with all Ni–N distances at 2.124(4) Å and Ni–S distances at 2.5321(13) Å. The *trans*-complex shows a reversible cyclic voltammogram for the Ni$^{2+/3+}$ couple and an axial ESR spectrum for the Ni(III) species that is expected for such a symmetrical system. That there are no changes in the ESR spectroscopic features following redox cycles is consistent with the structural rigidity expected in an encapsulated system.

Introduction

Over the past several decades, many strategies have been designed to encapsulate metal ions.[1] The most widely studied examples are of complexes of sepulchrate[2] and diamsar.[3] Cyclam is a versatile structural entity[4] that can adopt either a *cis*-mode of coordination with C_2 symmetry or a *trans*-mode of coordination with D_{4h} symmetry in which the nitrogen donors can adopt a variety of stereochemistries (Scheme 1). Studies pursued in this laboratory have tried to exploit these stereochemical aspects to devise synthetic strategies that produce ligands for encapsulation

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† Electronic supplementary information (ESI) available: Table S1, crystallographic data, Table S2, important bond lengths and angles and Fig. S1, scan rate dependent cyclic voltammogram of *cis*-[Ni(*trans*-I, *syn*-L3] cation. CCDC reference numbers 772067 for *cis*-[Ni(L3)]Cl$_2$·4H$_2$O and 772068 for the *trans*-[Ni(L3)](ClO$_4$)$_2$. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00550a

Scheme 1 Various stereochemical conformations of coordinated cyclam derivatives.

of metal ions. In an earlier communication, we described the crystal structures of [H$_2$(*anti*-L3)](ClO$_4$)$_2$ and [HLi(*anti*-L3)](ClO$_4$)$_2$.[5] Here, we describe details of further studies and isolation of the *cis*- and the *trans*-Ni(II) complexes with the *syn*- and the *anti*-forms of L3, respectively (Scheme 2).
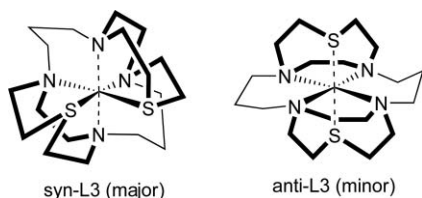
Scheme 2 Coordination conformation modes of *syn*-L3 in *trans*-I complexes and of *anti*-L3 in *trans*-IV complexes. The [9]ane rings are shown in bold.

In order to include the description of both the ligand geometry and the coordination geometry in our notation, we denote the *cis*-Ni(II) complex ion as *cis*-[Ni(*trans*-I, *syn*-L3)]$^{2+}$ and the *trans*-complex ion as *trans*-[Ni(*trans*-IV, *anti*-L3)]$^{2+}$. It is interesting to note that in the *trans*-complex, the cyclam moiety adopts the relatively rare *trans*-IV conformation.[6] The crystal structures of these complexes and their electrochemical behaviour are also described.

Experimental

Chemicals for syntheses were purchased from Aldrich-Sigma and used without further purification. Solvents were purified as follows: chloroform was distilled over calcium hydride to remove ethanol used as a preservative and acetonitrile was also distilled over calcium hydride and passed through a column of activated alumina before being used for electrochemical and ESR studies.

X-Ray quality crystals were obtained by slow diffusion of alcohol into a solution of the chloride salt for the *cis*-complex in aqueous media and for the *trans*-complex by diffusing ether into a perchlorate salt solution in acetonitrile. Single crystals were mounted on a fiber glass with silicon glue and X-ray data were collected on a Smart 1000 diffractometer with graphite monochromated Mo K$_\alpha$ radiation (0.71073 Å) using the Omega Scan method at a temperature of 293 K over a 2θ range of 4–50°. Absorption corrections were carried out using SADABS[7] and the solutions and the final refinement were obtained with SHELXL-97.[8] All non-hydrogen atoms were refined using anisotropic parameters and H-atoms were treated by the riding method.

Electrochemical analyses were carried out using a PAR-273 instrument. A three-electrode configuration with Pt working and counter electrodes and an Ag wire as the reference electrode were used. A solution of 0.1 M tetrabutylammonium perchlorate in anhydrous acetonitrile was used as the electrolyte with Fc$^{0/+}$ as the internal standard. ESR spectra were recorded on a Bruker EMX 300 X-band instrument in acetonitrile glass at liquid nitrogen temperatures. Mass spectroscopic data were obtained using LSIMS on a Kratos Concept instrument for complexes and intermediates.

Safety

Perchlorate salts are potentially explosive and should be handled carefully and in small quantities only.

N,*N*′,*N*″,*N*‴-Tetrakis(chloroacetyl)-1,4,8,11-tetraazacyclo tetradecane, L1

A solution of cyclam (2.5 g, 12.48 mmol) in 400 mL of CHCl$_3$ was prepared in a 3-necked 1.0 L round bottomed flask, cooled to −5 °C in an ice–salt bath and stirred vigorously using an overhead stirrer. To this, portions of a solution of chloroacetyl chloride (9.67 g, 85.6 mmol) in 200 mL of CHCl$_3$ were added dropwise over a period of 20 min while maintaining the temperature well below 0 °C. After addition of a quarter of the acid chloride, 5 mL of a solution of Me$_4$NOH·5H$_2$O (9.0 g, 49.7 mmol) in 20 mL of water was added in one lot. In a similar manner, the second, third and fourth aliquots were added sequentially. The Cl–H$_2$CO group is known to undergo photo-hydrolysis in the presence of aqueous base. Therefore, the reaction was carried out with minimum exposure to light by covering the flask with aluminium foil. The reaction mixture was allowed to warm to room temperature and the aqueous layer was separated using a separating funnel. The CHCl$_3$ solution was washed with two 25 mL portions of water. The CHCl$_3$ layer was separated, dried over anhydrous Na$_2$SO$_4$ and concentrated to about 100 mL and diluted with hexanes until the solution turned just cloudy.

Upon standing in a refrigerator, this solution deposited 3.9 g of a white crystalline solid. Concentration of the mother liquor to 25 mL yielded a further 0.7 g of pure material. Upon acidification of the aqueous layer, an additional 0.2 g was deposited. Total yield: 4.8 g (77%, 9.48 mmol). M.p. 185–186 °C. NMR data (ppm): ^{1}H: 1.92 (4H, m, C–CH$_2$–C); 3.38 (8H, m, CH$_2$–N in propylene); 3.52 (8H, s, CH$_2$–N in ethylene) and 4.43 (8H, m, CO–CH$_2$–Cl). ^{13}C: 13.9 (C–CH$_2$–C); 25.8, 26.3, 27.0 and 28.0 (N–CH$_2$); 61.6 (CH$_2$–Cl); 168.6 (C═O). In addition to the major carbonyl peak, several closely spaced signals were also observed in the carbonyl and the methylene regions suggesting the existence of various conformational isomers. LSIMS: $m/e = 506.09$ ($M + 1$, 100%).

1,7,11,17-Tetraoxo-2,6,12,16-tetraaza-9,19-dithia-[5,2,2,5]-eicosane, L2

The tetraamide, L1 (2.4 g, 4.74 mmol) was suspended in 800 mL of water under vigorous stirring. To this, 5 g of anhydrous K$_2$CO$_3$ was added and dissolved by heating to 70 °C. At this point, the solution (pH of about 9) was not completely clear. The sodium salt Na$_2$S·9H$_2$O (98%) (2.41 g, 9.8 mmol) dissolved in 200 mL of water was added all in one batch. The solution clarified and the pH stabilized at 11. The reaction mixture was maintained at 70 °C for 10 h. At the end of reaction, the pH of the solution was neutral. The reaction mixture was concentrated to about 100 mL and the white curdy precipitate that formed was filtered off under suction and dried in vacuum.

The mother liquor was made strongly acidic with hydrochloric acid and concentrated to yield a further quantity of L2. The total mass of the cream colored solid was 2.20 g (5.13 mmol). Yield: 108.6%. NMR data: (ppm) ^{1}H: 1.85 (4H, multiplet, C–CH$_2$–C); 3.40 (16H, broad multiplet, CH$_2$–N–CH$_2$) and 4.25 (8H, m, CO–CH$_2$–S) ^{13}C: 25.6 (C–CH$_2$–C); 47.0, 48.5, 52.9, 589 (–CH$_2$–); 168.6 (C═O). FAB MS: the solids isolated showed peaks corresponding to a mixture of free ligand and its alkali metal complexes of Na$^+$

and K$^+$ in various ratios depending upon the fraction. A typical MS showed the following: m/e: 429 ($M + 1$, 50%), 451 ($M + Na^+$, 25%) and 467 ($M + K^+$, 25%).

1,11-Dithia-4,8,14,18-tetraaza-[5,2,2,5]-eicosane, (L3)

Vacuum oven dried L2 (2.20 g, 5.10 mmol) was ground into a fine powder and added to 500 mL of 1 M BH$_3$/THF solution and the mixture was refluxed in an oil bath for 48 h. The reaction mixture was cooled and added slowly under vigorous stirring into a 2 L beaker containing 50 mL of 3 M HCl to decompose unreacted diborane. THF was distilled off using a rotary evaporator and the resulting acidic aqueous solution was refluxed for 30 min and concentrated to dryness. The resulting solid was suspended in 100 mL of water and made strongly basic (pH = 13) using solid NaOH and extracted with 3 aliquots of 30 mL of CHCl$_3$ using a separating funnel. The combined CHCl$_3$ extracts were dried over anhydrous Na$_2$SO$_4$ and concentrated to dryness. The nearly colorless oil solidified into a creamy solid (1.00 g, 2.68 mmol) upon evacuation on a vacuum line. Yield: 52%. ^{1}H NMR: 1.48 (4H, quintuplet, C–CH_2–C), 2.60–2.62 (16H, broad multiplet, N–CH_2), 2.75 (8H, m, CH_2–S). ^{13}C nmr: 27.5 (CH$_2$–C–CH$_2$), 34.2 (C–S–C), 54.7 (N–C–CH$_2$), 55.4, 58.5 (N–C–C–S and N–C–C–N). FAB MS: m/e = 373 ($M + 1$, 100%).

### Preparation and separation of isomers of [Ni(L3)]$^{2+}$ salts

In 25 mL benzonitrile, nickel nitrate hexahydrate (0.5 g, 1.72 mmol) was dissolved under reflux. To this solution, the ligand L3 (0.5 g, 1.34 mmol) dissolved in 10 ml of benzonitrile was added and the mixture was refluxed at 140 °C for 18 h under a N$_2$ atmosphere. The solvent was removed and the residue was dissolved in 25 ml of water and filtered to remove the cloudiness. This solution was charged onto a Sephadex C-25 cation exchange column (100 cm high × 3 cm diameter) and eluted with 0.1 M NaCl solution. A very pale pink band that eluted first was collected (about 150 mL). The pink band was concentrated and the NaCl removed by extracting the complex with 95% ethanol. Concentration of this ethanol extract provided two different types of crystals. Yield: 88% (0.76 g 1.51 mmol).

This mixture of complexes was further separated as follows. The chloride salts (200 mg, 0.4 mmol) were dissolved in water and loaded onto a long column of Sephadex C-25. Elution with 0.08 M NaClO$_4$ showed no clear cut separation of the isomers. However, the initial portions were collected from a long stretched band of very light reddish pink (about 150 mL) and concentrated to isolate the minor *trans*-[Ni(L3)](ClO$_4$)$_2$ complex. A small middle cut (150 mL) was collected separately. Following this, a major concentrated dark purplish pink band that was eluted very slowly (about 1.0 mL per min) with 0.08 M NaClO$_4$ solution (about 250 mL) provided pure *cis*-complex. In all cases, the eluants were concentrated to dryness and the complexes were extracted with 95% ethanol. Further purification was carried out by precipitating them as perchlorate salts by the addition of sodium perchlorate and recrystallising from acetonitrile. HRMS data: Calcd. for *cis*-[C$_{18}$H$_{36}$N$_4$S$_2$NiCl]$^+$ 465.14233. Found, 465.1427. Calcd. for *trans*-[C$_{18}$H$_{36}$N$_4$S$_2$Ni]$^{2+}$ = 215.0867. Found: 215.1102.

Results and discussion

Synthesis

The synthetic route is presented in Scheme 3. Several factors influence the relative ratio of *syn*- to *anti*-L3. In all investigations, this ratio was elucidated from the yields of isolated Ni(II) complexes only. It might be expected that the intermediate, L1 adopts the *trans*-I stereochemistry leading to the formation of predominantly *syn*-L3.[9] This is supported by the observation that the major product (up to 90%) was invariably the *cis*-[Ni(*trans*-I, *syn*-L3)]$^{2+}$ complex ion. In order to minimize such complications, Me$_4$NOH was used during the preparation of L1. This did improve the yields and purity of L1. However, it was observed that in the absence of Li$^+$ the yields of *anti*-L3 decreased considerably and also neither the Na$^+$ nor the K$^+$ salts of L3 were isolated possibly owing to the lack of encapsulation. Although the relative ratio of *anti*- to *syn*- L3 is low, (<10%) that the yield of the former is influenced by the presence and nature of alkali metal ions is clearly noticeable during separation and isolation of the Ni(II) complexes.
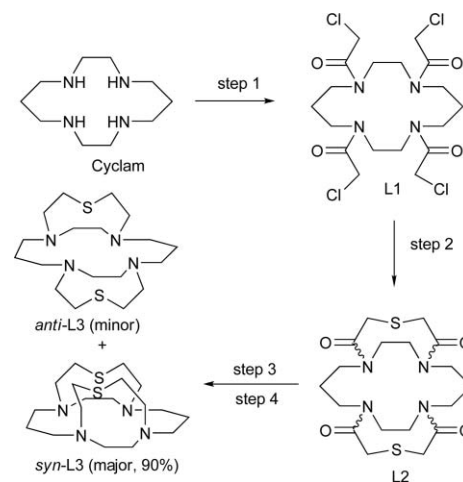

Scheme 3 Step 1: CHCl$_3$/ClCH$_2$COCl/base in H$_2$O, temp. 5 °C; step 2: Na$_2$S·9H$_2$O/CH$_3$COCH$_3$: H$_2$O (1 : 1), temp. 70 °C, 10 h reflux; step 3: THF/BH$_3$, reflux, 12 h; step 4: HCl, reflux, 30 min, NaOH/CHCl$_3$, extraction.

That complex formation with alkali metal ions occurs is shown by the fact that the yields of L2 always appeared to be in excess of 100%. This is due to the fact that separation of pure L2 from its complex from residual salt mixture after cyclization was very difficult. Only a partial separation may be achieved by continuous Soxhlet extraction of the well dried reaction mixture using ethanol. The complexes of [Na(L2)]$^+$ and [K(L2)]$^+$ were found in mass spectroscopic studies when these metal ions were present during cyclization. The formation of a small amount of the pentacyclic ligand L4 complexes of Na$^+$ ($m/e = 879$) was observed when the reaction was carried out at concentrations higher than 0.1 M.

The isomeric [Ni(L3)]$^{2+}$ complexes were formed by reaction of nickel nitrate hexahydrate with ligand L3 in benzonitrile under reflux at 140 °C under a N$_2$ atmosphere. Following removal of
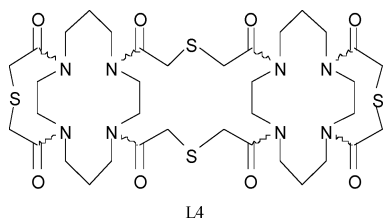
L4

solvent the mixture was dissolved in water and the isomers resolved chromatographically as described.

Crystal structures

The ORTEP diagrams of the cations *cis*-[Ni(*trans*-I, *syn*-L3)]$^{2+}$ and the *trans*-[Ni(*trans*-IV, *anti*-L3)]$^{2+}$ are shown in Fig. 1. The experimental parameters for the structures and important bond lengths and angles are listed in Tables S1 and S2, ESI.† In the *cis*-[Ni(*trans*-I, *syn*-L3)]$^{2+}$ ion, two N-donors and two S-donors define the equatorial plane and the other two N-donors occupy the axial positions. The equatorial Ni–N distances, Ni–N(1) and Ni–N(3) are 2.164(3) and 2.179(3) Å, respectively. These are slightly longer than the average apical Ni–N(2) and Ni–N(4) distances of (2.100(3) Å) commonly observed in octahedral Ni(II) complexes.[10] The Ni–S distances are 2.4265(11) and 2.4512(11) Å, respectively, and are in the normal range. The geometry around the nickel(II) centre is distorted, as has been observed in most Ni(II) complexes in which the cyclam ring is coordinated in a *cis*-fashion.[11] The geometrical parameters clearly place the nickel in an anisotropic environment. However, this cannot be construed to be a compression along the shorter Ni–N bonds and an elongation

along the longer Ni–N bonds that usually affect the electronic states of the metal ion.[12]

In the *trans*-[Ni(*trans*-IV, *anti*-L3)]$^{2+}$ ion, the nickel sits at an inversion center and the Ni–N and Ni–S distances are symmetry generated. All the N-donors lie in the equatorial plane with an average Ni–N distances of 2.125(4) Å and the two S-donors occupy the axial sites with Ni–S distances of 2.5321(11) Å. The Ni–S distances are slightly longer than those observed in the *cis*-complex cation and in many octahedral nickel(II) examples.[12] Clearly, this cation exhibits D_{4h} symmetry, typically observed for most Ni(II) cyclam complexes. Again, the notable feature is the stereochemistry of the cyclam ring where the *trans*-IV configuration[6a,13] is adopted in the ion. Though this stereochemistry is imposed by the *anti*-orientation of the [9]ane rings, it is relatively unknown. The strain energy reported[6a,14] for the *trans*-IV configuration has been found to be the highest and it has been suggested to be the least favored among the various possible stereochemical arrangements that the cyclam ring can adopt.

Electronic Spectroscopy

The spectroscopic data for the Ni(II) complexes reflects the differences in the geometry imposed by the *syn*- and the *anti*-L3. The *cis*-[Ni(*syn*, *trans*-I, L3)]$^{2+}$ ion shows absorptions at 998 nm (26 M^{-1} cm^{-1}) and 538 (16 M^{-1} cm^{-1}) nm and the *trans*-[Ni(*anti*, *trans*-IV, L3)]$^{2+}$ ion at 996 (10 M^{-1} cm^{-1}) and 522 (11 M^{-1} cm^{-1}). These absorptions are normally assigned to the spin-allowed $^3T_{2g} \leftarrow {}^3A_{2g}$ and the spin-forbidden $^1E_g \leftarrow {}^3A_{2g}$ transitions, respectively. However, the values obtained from experiments for the $^3T_{2g} \leftarrow {}^3A_{2g}$ has often been disputed due to the effects of spin–orbit coupling.

Hancock and co-workers[12a] have suggested a method to calculate the "true" positions of the $^3T_{2g} \leftarrow {}^3A_{2g}$ transitions if the spin–orbit coupling were absent. Use of this treatment to calculate the 10 Dq for these complexes yielded a value of 953 nm (10 Dq = 10 485 cm^{-1}) for the for the *cis*-[Ni(*trans*-I, *syn*-L3)]$^{2+}$ ion, but the value for the *trans*-[Ni(*trans*-IV *anti*-L3)]$^{2+}$ ion was abnormally high (599 nm, 16,690 cm^{-1}). As has been suggested,[12a] this might be due to use of the wrong absorption band for the calculation as several bands are observed between 1000 and 600 nm and are often superimposed by low energy charge transfer bands. The extinction coefficients observed for the spin-forbidden transitions in the case of *trans*-[Ni(*trans*-IV, *anti*-L3)]$^{2+}$ ion are much smaller, consistent with the more symmetrical nature of the *anti*-L3 and the D_{4h} symmetry of the *trans*-complex. The *trans*-[Ni(*trans*-IV, *anti*-L3)](ClO$_4$)$_2$ crystals were very pale violet-red in color compared to that of the *cis*-[Ni(*trans*-I, *syn*-L3)]Cl$_2$ crystals which were very intensely purple in color. This distinction in color and its intensity aided in the separation of these complexes that elute very closely on the chromatographic column.

Electrochemical and ESR spectroscopy

The redox process for both Ni$^{2+/3+}$ couples was investigated using cyclic voltammetry. The *trans*-[Ni(*trans-IV*, *anti*-L3)]$^{2+}$ ion showed a reversible wave ($E_{1/2}$ = 0.91 V (ΔE_p = 60 mV, $i_{p,a}/i_{p,c}$ = 0.98). This value is comparable to redox potentials observed in other [NiN$_4$S$_2$]$^{2+/3+}$ couples in similar environments.[11,12] The *trans*-[Ni(*trans*-IV, *anti*-L3)]$^{3+}$ species also showed an axial ESR

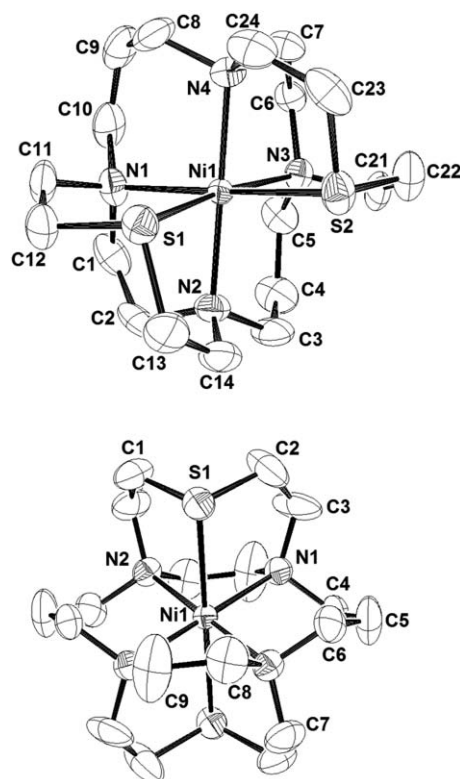**Fig. 1** ORTEP diagrams (50% ellipsoid) for the cations, *cis*-[Ni(*trans*-I, *syn*-L3)]$^{2+}$ and the *trans*-[Ni(*trans*-IV, *anti*-L3)]$^{2+}$.

spectrum with $g_\perp = 2.18$ and $g_\parallel = 2.01$, consistent with D_{4h} symmetry.[15] Despite the high strain energies that have been reported for the *trans*-IV stereochemistry of cyclam in complexes,[6a,14] this observation confirms that both the Ni(II) and Ni(III) oxidation states are stable, a finding confirmed by the relatively low redox potential. In this case, there is a strong charge transfer interaction between S-donors and the nickel centers that would facilitate such a stability.[16]

However, the *cis*-complex (see Fig. 2) showed a much more complicated electrochemical behavior with a scan rate dependent wave. At a rate of 1000 mV s^{-1}, the redox cycle for the Ni$^{2+/3+}$ couple showed a quasi-reversible wave with $E_{p,c} = 1.35$ V, $E_{p,a} = 1.45$ V, $\Delta E_p = 100$ mV and $i_{p,a}/i_{p,c} = 0.8$. However, as the rate was lowered to less than 100 mV s^{-1} the cyclic voltammogram showed oxidation and reduction peaks separated by 260 mV. At scan rates below 50 mV s^{-1}, the reduction wave was more symmetrical ($E_{p,c} = 1.25$ V, $E_{p,a} = 1.42$ V, $\Delta E_p = 170$ mV and $i_{p,a}/i_{p,c} = 1.2$), the wave shape being characteristic of a species adsorbed onto the electrode surface.[16c,17]
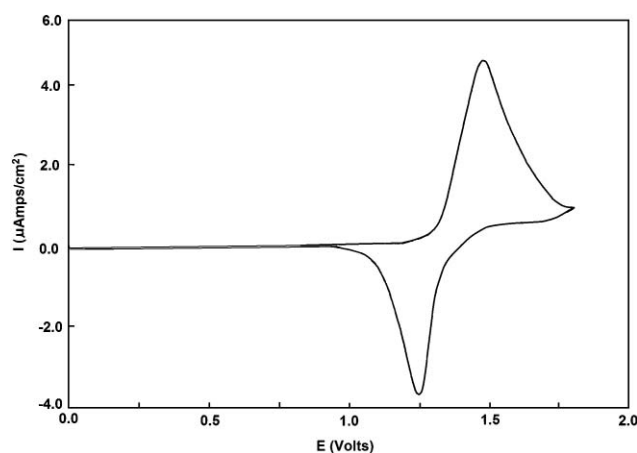
Fig. 2 Cyclic voltammogram of *cis*-[Ni(*trans*-I, *syn*-L3)]$^{2+}$ cation in CH$_3$CN at a scan rate of 10 mV s^{-1}.

Redox induced substitution in square planar Ni(II) systems by anions and solvents is well known both in open chain and macrocyclic systems. However, such rearrangements in 1,4,8,11-tetra substituted and 1,8-disubstituted cyclams have been documented only recently and mostly involve low-valent couples[6] such as Cu$^{+/2+}$, Cu$^{0/2+}$ and Ni$^{+/2+}$. However, rearrangements in high-valent macrotricycles are less well characterized as these ligands are designed with the expectation that inner coordination sphere will withstand redox changes. The observations presented here for the *cis*-complex are consistent with the rearrangement of the inner coordination sphere upon oxidation of the metal center. The very high oxidation potential indicates that the *cis*-[Ni(*trans*-I, *syn*-L3)]$^{3+}$ is not a stable species. In the absence of other pathways for decomposition, it undergoes rearrangement as indicated by the ESR spectra monitored at various time intervals. The Ni(III) species obtained soon after oxidation showed (Fig. 3a) three distinctive features ($g_{xx} = 2.135$, $g_{yy} = 2.103$ and $g_{yy} = 2.033$) indicative of an anisotropic environment at the Ni(III) center consistent with the structural features of the Ni(II) species. However, as seen in Fig. 3b, this structure did not persist. Within 18 min an axial type spectrum with $g_\perp = 2.11$ and $g_\parallel = 2.03$ was
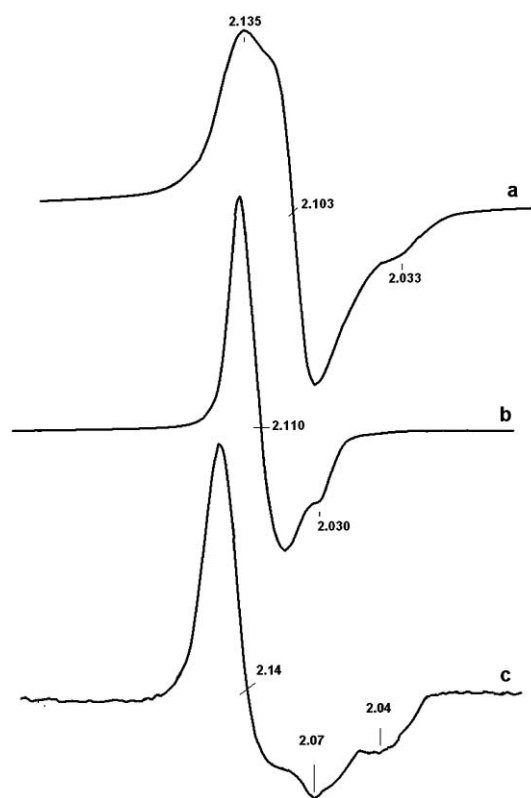
Fig. 3 ESR spectra of [Ni(L3)]$^{3+}$ species at various time intervals. (a) Immediately after oxidation. (b) after 18 min. (c) after 18 h.

observed. This Ni(III) species was also not stable resulting in a much slower change over time to a different spectrum ($g_{xx} = 2.14$, $g_{yy} = 2.07$ and $g_{zz} = 2.04$). This transformation might be envisaged as an isomerization of the *cis*-[Ni(*trans*-I, *syn*-L3)]$^{3+}$ to a species of *trans*-[Ni(*trans*-IV, *anti*-L3)]$^{3+}$ configuration. However, experimental evidence does not support such a process.

A plausible scenario, consistent with these observations is shown in Scheme 4. This involves the rearrangement of the coordination mode of the cyclam framework from a *cis*-mode (A) in *cis*-[Ni(*trans*-I, *syn*-L3)]$^{3+}$ to a *trans*-type intermediate (B) in which all of the four N-donors occupy the equatorial plane, thereby releasing the strain on the N$_4$S$_2$ donor set. Inevitably, this could occur only with the concurrent release of one of the S-donor atoms which also provides a suitable point of attachment on a surface like the Pt electrode. Adsorption of coordinated thioethers to a Pt like metal electrode surface is known[16c,17] and the electrochemical behavior observed here at slow scan rates is consistent with such a behaviour. Also, this releases one of the axial sites at the Ni(III) center for substitution by either solvent or an anion in a secondary reaction to again form a six-coordinate Ni(III) species (C). This substitution process is too slow to be detected during the electrochemistry experiment but is observed
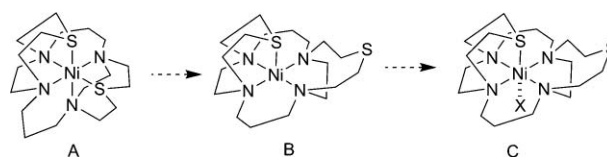
Scheme 4

in the ESR spectrum. Species C, has an asymmetric geometry and can be denoted by *trans*-[Ni(X)(*trans*-I, *syn*-L3)-S]$^{3+}$, "-S" denoting the free thioether moiety and the "X", the sixth ligand.

Thermal isomerization of the *cis*-[Fe(cyclam)Cl$_2$]Cl to the *trans*-species has been investigated by DSC/TG techniques.[18] This transformation occurs with the aid of a solvent or anion substitution and does not involve changes in the oxidation state of the metal ion. The possibilities of thermal transformation of *syn*-L3 to *anti*-L3 were investigated in order to improve the yield of the free *anti*-L3. However, attempts to induce such a process were unsuccessful. Also, the *cis*-[Ni(II)(*trans*-I, *syn*-L3)]$^{2+}$ complex cation did not convert to the symmetrical *trans*-[Ni(*trans*-IV,*anti*-L3)]$^{2+}$ even after refluxing at the boiling point of benzonitrile for several days. These observations preclude a thermal process for the inter-conversion at both the ligand as well as at the Ni(II) complex level. Therefore, we attribute the observed changes to a redox induced process only.

Summary

This paper describes the synthesis of the hexadentate ligand L3 and the various factors that influence the formation of the *syn*- and *anti*-forms of the ligand. The preparation and the chromatographic separation of the *cis*- and the *trans*-Ni(II) complexes is reported. Confirmation of the identity of these isomeric complexes has been established by single crystal X-ray crystallographic studies. In the *cis*-Ni(II) complex, the *syn*-form of L3 is present with the cyclam moiety coordinating in a *cis*-fashion. In the *trans*-Ni(II) complex, the *anti*-form of L3 is present displaying the less common *trans*-IV conformation. This symmetrical *trans*-complex is stable both in the Ni(II) and the Ni(III) states. A reversible cyclic voltammogram for the Ni$^{2+/3+}$ couple ($E_{1/2}$ = 0.91 V) and an axial ESR spectrum were observed for the *trans*-Ni(III) species. However, the *cis*-[Ni(L3)]$^{3+}$ ion showed a high oxidation potential ($E_{p,a}$ = 1.45 V). A scan rate dependent cyclic voltammogram and a time-dependent ESR spectrum were observed. Evidence is presented for a redox induced rearrangement where configuration of the cyclam ring changed from a *cis*- to a planar coordination mode while retaining its *trans*-I stereochemistry. The displacement of one of the thioether donors from the inner coordination sphere by a substitution reaction is consistent with changes observed in the ESR spectrum and also adsorption onto the Pt electrode. Neither the free ligand nor the complexes undergo thermal isomerization and there is no evidence for the inter-conversion between the *syn* and the *anti*-forms of L3.

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