The synthesis and characterization of the pendant-armed ligand N,N'-bis(2'-pyridylmethyl)-1,7-dithia-4,11-diazacyclotetradecane (L₄) and crystal structures of L₄ and the copper(II) complex [Cu(L₄)](ClO₄)₂ — Crystal structure of the nickel(II) complex of N-(2'-pyridylmethyl)-1,4,7-trithia-11azacyclotetradecane (L₂), [Ni(L₂)(CH₃CN)](ClO₄)₂·CH₃CN¹

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Abstract: The synthesis and characterization of the mixed donor ligand N,N'-bis(2'-pyridylmethyl)-1,7-dithia-4,11diazacyclotetradecane (L_4) containing two pendant pyridine arms is described. The macrocycle formation involves reaction of *N*-tosylbis(2-bromoethyl)amine with *N*-tosylbis(3-mercaptopropyl)amine at high dilution followed by detosylation at the nitrogen atoms using LiAlH₄ in view of the presence of the thioether groups. An X-ray study of the ligand shows the sulphur atoms lie exo to the macrocyclic ring. The nickel(II) and copper(II) complexes of L_4 have been characterized and the X-ray structure of the Cu(II) ion exhibits a five-coordinate copper ion despite the presence of six available donor atoms. In the case of ligand *N*-(2-pyridylmethyl)-1,4,7-trithia-11-azacyclotetradecane (L_2), with a single pendant N donor, the Ni(II) complex is distorted octahedral with a molecule of acetonitrile in the sixth site. Details of UV-vis, ESR spectra, and electrochemical studies on the complexes are presented.

Key words: synthesis, pendant-armed, mixed donor S,N macrocycles, copper, nickel.

Résumé : On décrit la synthèse et la caractérisation du ligand donneur mixte N,N'-bis(2'-pyridylméthyl)-1,7-dithia-4,11diazacyclotétradécane (L_4) qui contient deux noyaux pyridines comme bras pendants. La formation du macrocycle implique la réaction du N-tosylbis(2-bromoéthyl)amine avec la N-tosylbis(3-mercaptopropyl)amine à dilution élevée, suivie d'une détosylation des atomes d'azote à l'aide de LiAlH₄ en raison de la présence de groupes thioéthers. Une étude par diffraction des rayons X du ligand montre que les atomes de soufre se trouvent en position exo par rapport au cycle macrocyclique. Les complexes du L_4 avec le nickel(II) et le cuivre(II) ont été caractérisés et la structure de l'ion Cu(II) telle que déterminée par diffraction des rayons X comporte un ion cuivre pentacoordiné malgré la présence de six atomes donneurs disponibles. Dans le cas du ligand N-(2-pyridylméthyl)-1,4,7-trithia-11-azacyclotétradécane (L_2) qui ne comporte qu'un seul azote donneur pendant, le complexe de nickel(II) se présente sous la forme d'un octaèdre déformé comportant une molécule d'acétonitrile sur le sixième site. On rapporte aussi les détails des données UV-vis, des spectres RPE et des études électrochimiques des complexes.

Mots clés : synthèse, bras pendant, macrocycles à donneurs mixtes S,N, cuivre, nickel.

[Traduit par la Rédaction]

Introduction

Historically, the most commonly studied macrocyclic ligands are tetraazatetradentate with cyclam as a typical example. X-ray diffraction studies show that most of these complexes have square-planar geometry in which the ligand cyclam encircles the metal ion in the equatorial plane (1–4). The coordination chemistry of the thia analogue (i.e.,

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It is a pleasure to recognize the many continuing contributions to chemistry in Canada by colleague and friend Arthur Carty.

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 $[14]aneS_4$) has been investigated (5) and solid-state studies show the free ligand isomorphs exhibit exo conformations of the S lone pairs. The chemistry of thioether ligands has also been reviewed (6).

In contrast to the N₄ and S₄ donor sets, there have been relatively fewer studies on macrocyclic ligands involving sulphur and nitrogen mixed donor sets (7, 8). Black and McLean (9) synthesized the macrocyclic sexadentate ligand 1,4,10,13-tetrathia-7,16-diazacyclooctadecane ([18]ane N_2S_4). The associated Co(II) and Ni(II) complexes were assumed to be octahedral with the N donors in the apical sites. Rorabacher and co-workers (10) have prepared a series of $N_x S_{4-x}$ donor sets (where x = 1-3) and also Cu complexes of cyclic polythiaethers. Kaden and co-workers (11, 12) have provided details of two sets of 12-, 14-, and 16-membered N₂S₂ macrocycles, dependent on the cis and trans arrangement of the donors within the ring, and have described the synthesis and solution chemistry of the Cu(II) and Ni(II) complexes. The use of mixed donor macrocycles as ligands for the selective interaction of Ag(I) has also been explored (13). In these laboratories, a focus has been on the synthesis of polymacrocylic ligands with these donors and the nature of the various oxidation states that may be stabilized owing to the mixed donor systems (14–16). Continuing interest in the coordination chemistry of these systems arises from the potential similarity of the coordination environment around metal centres in copper proteins. A recent review (17) has focussed on the role of macrocyclic ligands with pendant arms as Cu models related to electron transport and activation of small molecules in biological systems. In this paper, the synthesis of two macrocycles with attached pyridine moieties is described in an ongoing investigation of nitrogen and sulphur mixed donor macrocycles. The ability to complex a variety of metal ions in differing oxidation states is increased by the presence of both hard and soft donor centres within the macrocyclic framework.

Experimental

Ligand syntheses

The preparation of 1,4,7-trithia-11-azacyclotetradecane L_1 and the pendant-armed methylpyridine derivative L_2 have been reported previously (18).



N-Tosylbis(2-(tosyloxy)ethyl)amine (2)

Diethanolamine (1, 27.5 g, 0.262 mol) was dissolved in 500 mL of distilled CH_2Cl_2 in a three-necked flask. The solution was cooled to 0 °C in a stream of dry nitrogen and 122 mL of triethylamine (88.6 g, 0.88 mol) was added. With the temperature maintained at 0 °C, solid *p*-toluenesulfonyl chloride (157 g, 0.823 mol) was added in portions with vigorous stirring over the course of 5 h. The reaction mixture

was stirred at ambient temperature overnight. The Et₃NHCl formed was filtered off and the resulting pale yellow filtrate was washed three times with 1 mol/L HCl, followed by 5 × 200 mL portions of water and 5 × 200 mL portions of satd. NaHCO₃ solution. The organic layer was dried over anhydr. MgSO₄. Removal of the solvent by rotatory evaporation gave a white product (**2**). Yield: 120 g (ca. 80%), mp 98 °C. ¹H NMR (90 MHz, CDCl₃) δ : 7.2–7.9 (m, 12H, ArH), 4.14 (t, *J* = 6 Hz, 4H, CH₂OTs), 3.4 (t, *J* = 6 Hz, 4H, CH₂NTs), 2.47 (two singlets, 9H, ArCH₃). MS (CI): 568 [M + 1], 396 [M – OTs].

N-Tosylbis(2-bromoethyl)amine (3)

To a solution of the tritosylate **2** (43 g, 0.076 mol) in 250 mL of DMF was added NaBr (40 g, 0.39 mol). The resulting suspension was stirred in an oil bath at 120 °C for 4 h. After cooling to room temperature, the reaction mixture was concentrated to about 50 mL. The viscous milky product mixture was poured into a rapidly stirred ice–water mixture (1 L) where a white solid separated out. This material was filtered, washed with water, and air dried. Yield: 24 g (ca. 80%), mp 56–58 °C. ¹H NMR (90 MHz, CDCl₃) δ : 7.36–7.75 (m, 4H, ArH), 3.5 (s, 8H, CH₂NTs, CH₂Br), 2.45 (s, 3H, CH₃Ar). MS (EI): 383, 385, 387 [M⁺ in a ratio of 1:2:1].

N-Tosylbis(3-(tosyloxy)propyl)amine (4)

Bis(3-hydroxypropyl)amine (65 g, 0.488 mol) was dissolved in 800 mL of distilled CH₂Cl₂ in a 2 L, three-necked round bottom flask. The solution was cooled to -5 °C in a stream of dry nitrogen and triethylamine (218 mL, 1.56 mol) was added. With the temperature kept below 0 °C, solid ptoluenesulphonyl chloride (285 g, 1.49 mol) was added in portions to the above solution over the course of 2 h. The reaction mixture was stirred in an ice bath for 3 h and then at ambient temperature overnight. The white triethylamine hydrochloride formed was filtered off and washed with CH_2Cl_2 . The pale yellow filtrate was washed with water (5 × 250 mL), 1 mol/L HCl (5 × 250 mL), water (5 × 250 mL), and satd. NaHCO3 solution. The CH2Cl2 layer was dried over anhydr. MgSO₄. Removal of the solvent by rotatory evaporation resulted in a pale yellow viscous oil that was triturated to a white solid by the addition of diethyl ether. Yield: 232 g (80%), mp 68 to 69 °C. ¹H NMR (250 MHz, CDCl₃) δ : 7.74 (d, J = 8 Hz, 4H, ArH), 7.58 (d, J = 8 Hz, 4H, ArH), 7.25–7.39 (m, 6H, ArH), 4.00 (t, J = 7 Hz, 4H, CH₂OTs), 3.05 (t, J = 7 Hz, 4H, CH₂NTs), 2.42 (s, ArCH₃, 6H), 2.40 (s, ArCH₃, 3H), 1.84 (tt, J = 7 Hz, 4H, $CH_2CH_2CH_2$). ¹³C{¹H} NMR (CDCl₃) δ : 144.9, 143.6, 135.4, 132.7 (quat. ArC), 129.9, 129.8, 127.8, 127.1 (ArC), 67.62 (CH₂OTs), 45.76 (CH₂NTs), 28.62 (CH₂CH₂CH₂), 21.54, 21.41 (ArCH₃). MS (CI) 596 [M + 1], 424 [M + 1 -172]. An analytically pure sample was obtained by recrystallizing the white solid twice with hot ethanol. Anal. calcd. for C27H33NS3O8 (%): C 54.44, H 5.58, N 2.35, S 16.14; found: C 54.33, H 5.43, N 2.38, S 16.53.

N-Tosylbis(3-mercaptopropyl)amine (5)

To a solution of tritosylate (4) (20.2 g, 0.034 mol) dissolved in 200 mL of 95% ethanol in a 500 mL roundbottomed flask was added thiourea (5.6 g, 0.074 mol). The suspension was refluxed for 12 h. After cooling to room temperature, the reaction mixture was concentrated (rotovap) and pump-dried. A crystalline white solid of the isothiouronium salt was obtained. A solution of NaOH (13 g, 0.325 mol) in 215 mL of water (6% NaOH) was prepared and bubbled with nitrogen for 15 min. To the isothiouronium salt was added the deaerated 6% NaOH solution and the reaction mixture was well-stirred and refluxed in a nitrogen atmosphere for 2 h. After the mixture was cooled to room temperature, and subsequently in an ice bath, 6 mol/L HCl was added dropwise until the pH of the solution reached 1. The milky solution obtained was saturated with NaCl and extracted with 3×100 mL CH₂Cl₂. The organic layers were combined and dried with anhydr. MgSO₄, concentrated by rotovap, and pumped dry. The desired product was isolated as a colorless viscous oil. Yield: 90%. ¹H NMR (90 MHz, CDCl₃) δ: 7.35–7.75 (m, 4H, ArH), 3.20 (t, 4H, J = 6 Hz, CH₂NTs), 2.6 (q, 4H, J = 6 Hz, CH₂S), 2.40 (s, 3H, CH₂Ar), 1.90 (m, 4H, CH₂CH₂CH₂), 1.45 (t, 2H, J =6 Hz, SH). MS (CI): 318 [M + 1], 348 [M + 29], 360 [M + 41].

N,N'-Bistosyl-1,7-dithia-4,11-diazacyclotetradecane (6)

To a 5 L three-necked round flask equipped with a mechanical stirrer, condenser, and a dropping funnel was added oven-dried Cs₂CO₃ (14.8 g, 0.0454 mol) and 1 L of freshly opened DMF. The resulting suspension was stirred vigorously in a nitrogen atmosphere and warmed to 50 °C. A solution containing the dibromide (3) (4.82 g, 0.0125 mol) and dithiol (5) (4 g, 0.0125 mol) in 500 mL of DMF was prepared and bubbled in nitrogen for 20 min. This solution was then added to the Cs₂CO₃–DMF suspension via high dilution a rate of 4 to 5 mL/h. After the addition of all reactants, the mixture was stirred overnight. Upon cooling to room temperature, DMF was removed by rotatory evaporation. After extraction of the residual pale yellow solid with CHCl3 several times, the resultant yellow solution obtained was taken to dryness and evacuated, yielding a pale brown oil that was purified by column chromatography (silica gel, CH₂Cl₂-EtOAc, 95%:5%). Fractions with $R_f = 0.7$ were collected. The desired product was isolated as a white crystalline solid. Yield: 30%. ¹H NMR (90 MHz, CDCl₃) δ: 7.8 (m, ArH), 7.35 (m, ArH), 3.00-3.5 (m, CH₂NTs), 2.5-2.9 (m, CH₂S), 2.45 (s, CH₃Ar), 2.00 (m, CH₂CH₂CH₂). MS (CI): 543 [M + 1], 571 [M + 29].

1,7-Dithia-4,11-diazacyclotetradecane (L_3)

A sample of (6) (0.5 g, 0.92 mmol) was added slowly under a nitrogen atmosphere to a stirred suspension of LiAlH₄ (0.41 g, 10.8 mmol) in 40 mL of dry THF. The reaction mixture was stirred under reflux for 72 h. After cooling to room temperature, the excess LiAlH₄ was destroyed by dropwise addition of 30 mL of THF–H₂O (2:1 ν/ν). The mixture was filtered and the precipitate was carefully washed with CH₂Cl₂. Evaporation of the solvent afforded 150 mg of L₃ as a white crystalline waxy solid, which was used for subsequent reactions without further purification. ¹H NMR (90 MHz, CDCl₃) δ : 2.6–2.8 (m, 16H, CH₂S, CH₂N), 1.8 (m, 4H, CH₂CH₂CH₂), 1.45 (s, 2H, NH). MS (CI): 235 [M + 1], 263 [M + 29], 275 [M + 41].

N,N'-Bis(2'-pyridylmethyl)-1,7-dithia-4,11diazacyclotetradecane (L_4)

To a two-necked, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet was added a solution of L_3 (1.30 g, 6.1 mmol), triethylamine (4.5 mL, 32.3 mmol, 5 equiv.), and 2-(chloromethyl)pyridine hydrochloride (2 g, 12.2 mmol) in 50 mL of absolute ethanol. The solution was heated to a gentle reflux under a nitrogen atmosphere for 12 h. After cooling to room temperature, $CHCl_3$ (3 × 100 mL) was added to the orange-red reaction mixture. The organic phase was washed with water (5 \times 100 mL) and dried over anhydr. Na₂SO₄. CHCl₃ was removed by rotoevaporation and the brown oil obtained was purified by column (silica gel, EtOAc-CH₂Cl₂, 60%:40%). Fractions with a R_f value of 0.2 were collected. The title product was obtained as a pale yellow oil that yielded clear white crystals. Yield: 500 mg, 20%. ¹H NMR (250 MHz, CDCl₃) & 8.42, 7.61, 7.56, 7.38, 7.07 (m, 8H, pyridine Hs), 3.74 (s, 2H, CH₂-pyridine), 3.62 (s, 2H, CH₂-pyridine), 2.60–2.73 (m, 8H, CH_2S), 2.51 (t, J = 7 Hz, 8H, CH_2N), 1.75 (tt, J = 7 Hz, 4H, CH₂CH₂CH₂). ¹³C{¹H} NMR (CDCl₃) δ: 159.9, 159.6 (quat. ArC), 148.8, 136.3, 136.1, 122.7, 122.6, 121.8, 121.7 (ArC), 61.3, 61.0 (CH₂-pyridine), 52.6, 52.1 (CH₂N), 29.3, 29.2 (SCH₂), 27.1 (CH₂CH₂CH₂). MS (CI): 417 [M + 1], 445 [M + 29].

Syntheses of Co(II), Ni(II), and Cu(II) complexes

$[Co(L_2(CH_3CN)(NO_3)_2] \cdot CH_3CN (complex A)$

An acetonitrile solution of L_2 (0.06 g, 0.175 mmol) in a round-bottomed flask was purged with nitrogen for 20 min. A solution of $[Co(H_2O)_6](NO_3)_2$ (0.0496 g, 0.17 mmol) in acetonitrile was added dropwise to the ligand solution. The reaction mixture, now pink, was stirred at room temperature under a nitrogen atmosphere overnight to ensure complete complexation before concentration to ~1 mL on the rotovap. Slow evaporation of the solvent at room temperature yielded pink crystals of X-ray quality. Yield: 40 mg. Anal. calcd. for $C_{20}H_{32}N_6S_3O_6Co$ (%): C 39.51, H 5.31, N 13.83; found: C 38.91, H 5.20, N 13.46.

$[Co(L_2)(ClO_4)](ClO_4)$ (complex B)

A solution of 0.57 g (0.156 mmol) of $[Co(H_2O)_6](ClO_4)_2$ in dry nitromethane was added dropwise to a similar N₂purged solution of the ligand (0.0546 g, 0.159 mmol). The mixture turned deep red instantly and was refluxed gently under N₂ for about 1 h. After cooling, the solvent was removed and the resultant red oil was triturated with EtOH to a reddish-brown solid that was dried in vacuo. Yield: 0.089 g (92%). Anal. calcd. for C₁₆H₂₆N₂S₃O₈Cl₂Co (%): C 31.07, H 4.56, N 4.53; found: C 30.97, H 4.26, N 4.67.

Compounds A and B are stable in air and, when dissolved in acetonitrile or nitromethane, show different spectroscopic characteristics and electrochemical behavior.

$[Ni(L_2(CH_3CN)](ClO_4)_2 \cdot CH_3CN]$

An acetonitrile solution of L_2 (0.170 g, 0.496 mmol) was purged with nitrogen for 20 min and a solution of [Ni(H₂O)₆](ClO₄)₂ (0.145 g, 0.396 mmol) in acetonitrile was added dropwise to the ligand solution. The reaction mixture changed to purple and was stirred at room temperature under nitrogen overnight to ensure complete complexation after which it was concentrated to ~1 mL. Slow evaporation of the solvent at room temperature yielded purple crystals of X-ray quality. Yield: 200 mg (83%). Anal. calcd. for $C_{18}H_{32}N_4S_3Cl_2O_8Ni$ (%): C 35.20, H 4.73, N 8.21; found: C 35.05, H 4.60, N 7.79.

$[Cu(L_2)](ClO_4)_2$

A solution of L_2 (0.059 g, 0.172 mmol) in CH₂Cl₂ in a round-bottomed flask was purged with nitrogen for 20 min. An ethanolic solution of $[Cu(H_2O)_6](ClO_4)_2$ (0.060 g, 0.16 mmol) was added dropwise to the ligand solution. The reaction mixture changed to bluish green and was stirred at room temperature under nitrogen overnight to ensure complete complexation. The green precipitate formed was filtered, washed with diethyl ether, and air dried. Yield: 55 mg (57%). The green powder was recrystallized by dissolving it in EtOH–CH₃CN, yielding a microcrystalline green solid. Anal. calcd. for $C_{16}H_{26}N_2S_3O_8Cl_2Cu$ (%): C 31.76, H 4.33, N 4.63; found: C 31.86, H 4.18, N 4.69.

$[Cu(L_4](ClO_4)_2]$

A method similar to that described previously using solutions of L_4 (0.068 g, 0.164 mmol) in CH₂Cl₂ and [Cu(H₂O)₆](ClO₄)₂ (0.058 g, 0.156 mmol) in ethanol was used. Yield: 66 mg (66%). The powder was recrystallized by dissolving it in EtOH–CH₃CN, giving green crystals of X-ray quality. Anal. calcd. for C₂₂H₃₂N₄S₂O₈Cl₂Cu (%): C 38.91, H 4.75, N, 8.25; found: C 38.83, H 4.69, N 8.19.

$[Ni(L_4](ClO_4)_2]$

To a solution of the ligand (0.11 g, 0.0264 mmol) dissolved in a CH_2Cl_2 -MeCN (1:1) solution was added dropwise an acetonitrile solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.096 g, 0.262 mmol). The colour changed to blue and the mixture was stirred under N₂ at room temperature. After reduction to dryness, the resultant solid was dissolved in a MeOH-H₂O-acetone solution and a mixture of blue and purple solids was obtained. The latter was reduced to dryness, yielding a brown oil and a blue solid. Isolation of the blue material and dissolution in a minimum volume of ethanol yielded a blue solid that was washed with Et₂O and dried in vacuo. Anal. calcd. for $C_{22}H_{32}N_4S_2O_8Cl_2Ni$ (%): C 39.19, H 4.78, N 8.31; found: C 39.08, H 4.85, N 8.22.

(Caution: Perchlorate complexes may be hazardous and should be prepared in small quantities).

Electrochemistry

Cyclic voltammograms were recorded with a Princeton Applied Research model 273 potentiostat/galvanostat interfaced to an IBM PC computer. All measurements were carried out in acetonitrile, which was dried before use by distilling over calcium hydride overnight under a nitrogen atmosphere. A solution of 0.1 mol/L n-Bu₄NPF₆ in acetonitrile was used as the supporting electrolyte. Platinum beads were used as the working electrode and counter electrode. The reference electrode was Ag/AgNO₃ (0.01 mol/L in CH₃CN) linked to the cell via a salt bridge containing an acetonitrile solution of n-Bu₄NPF₆ (0.1 mol/L).

Crystallography

Crystals were mounted in glass Lindemann tubes. The unit cells and space groups were determined by using Weissenberg and precession photography after which the crystals were transferred to a Picker four-circle diffractometer automated with a PDP 11/10 computer or an Enraf Nonius CAD4 diffractometer to collect the data. Intensity measurements were obtained with Zr-filtered Mo radiation, $\lambda = 0.71069$ Å, or Cu radiation (1.542 Å). Background counting was introduced at the end of each scan. A set of three internal standard reflections preceded each batch of 50 measurements, with no noticeable change in intensity observed during the collection. The solution of the phase problem was achieved with MULTAN (19) and refined by direct methods with SHELX-76 (20). The atomic scattering factors used were those included in the SHELX-76 program together with the metal f curve from the International Tables (21). Completion and refinement of the structure was carried out by using difference electron density maps and leastsquares techniques. All atoms were refined anisotropically except for hydrogen atoms, which were observed and refined isotropically when possible; otherwise the H-atom positions were calculated. In general, the refinement converged with a maximum shift/esd of less than 0.2 on the final cycle.

Electron spin resonance

ESR spectra were obtained by use of a Varian E6 ESR spectrometer using DPPH as the external standard. Spectra were obtained at 77 K using a quartz insert dewar.

Nuclear magnetic resonance

¹H NMR spectra were recorded on a 90 MHz PerkinElmer R-32 instrument; high-field ¹H and ¹³C NMR spectra were obtained on either a Bruker WM 250 or AMX 360 instrument. Two-dimensional NMR spectra (e.g., ¹H COSY and ¹H–¹³C correlated spectra) were recorded on the Bruker AMX 360 instrument. All chemical shifts are reported relative to tetramethylsilane (TMS). Simulated ¹H and ¹³C NMR spectra were calculated using NMRPLOT (22).

Elemental analyses were performed by Canadian Microanalytical Services, Vancouver, British Columbia.

Results and discussion

Syntheses

The synthetic route leading to L_3 is summarized in Scheme 1. The tosylated amine 2 can be used directly for the cyclization or converted to the corresponding dibromide (Scheme 1) via nucleophilic substitution of tosyl oxy groups by NaBr in DMF. Both can serve as the leaving groups in the formation of C-S bonds in the cyclization. The dithiol (5) required for the cyclization was obtained in good yield (ca. 85%) by refluxing an ethanolic solution of 4 and thiourea for 12 h, followed by the base hydrolysis of the isothiuronium salt. The cyclization reaction leading to 6 was carried out under medium dilution conditions (final concentration of reagents ca. 0.01 mol/L) using Cs₂CO₃ as the base in dry DMF. Detosylation of 6 was complicated by the presence of thioether functional groups that are prone to cleavage when acidic procedures sufficient to remove tosyl groups were used. To avoid this problem, a reductive

Scheme 1.



detosylation involving LiAlH₄ was employed (23). Ligand L_3 was obtained in satisfactory yields (ca. 70%). The preparation of the bispyridine adduct (L_4) is shown in Scheme 2.

Two isomers of L_3 have been prepared previously (11, 12), and comparisons with the present metal-ion complexes are made. The nickel(II) and copper(II) complexes of L_2 were prepared by the reaction of equimolar quantities of the ligand with $[Ni(H_2O)_6](ClO_4)_2$ or $[Cu(H_2O)_6](ClO_4)_2$ in dry CH₃CN under a nitrogen atmosphere. X-ray quality crystals were obtained by slow diffusion of diethyl ether into the acetonitrile solution of the complexes. In the case of the cobalt(II) complex of L₂, two compounds were isolated vide infra.

Crystal structures

Experimental crystallographic data for three molecules are provided in Table 1.

$[Ni(L_2)CH_3CN)](ClO_4)_2$

The molecular structure is shown in Fig. 1, and significant interatomic distances and bond angles are given in Table 2. Complete details on distances and bond angles are provided in Supplementary tables S1-S5.³

As illustrated, the nickel centre is located in a pseudooctahedral environment, coordinated to the three thioether sulphur atoms and three nitrogen atoms (from the macrocycle, the pyridine ring, and acetonitrile) with differing Ni-N bond lengths observed. The Ni—N(1)pyr (2.04 Å) is slightly shorter than the ideal strain-free Ni—N bond length (2.10 Å) (24). However, it is close to the values found for related high spin mixed donor macrocyclic complexes reported (8, 11, 25). Three distinct Ni-S bond distances, ranging from 2.37 to 2.48 Å, are observed in the cation. The shortest, Ni(1)-S(1) trans to the pyridine N(1), the results from the trans inScheme 2.



fluence of a S atom being greater than the nitrogen donor. For S(3), trans to N(3), the bond length of Ni—S is 2.40 Å. This value is comparable to other mixed donor macrocyclic complexes such as Ni([9]aneNS₂)₂]²⁺ ([9]aneNS₂)₂ = 1-aza-4,7-dithiacyclononane) (2.41 Å) (26). The longest (Ni—S(2)) bond is consistent with earlier findings of the trans influence sequence thioether S > N(tert) > N(py). The folded structure has been observed in the Pd and Pt analogues (18).

$[Co(L_2)(NO_3)_2 \cdot CH_3CN] \cdot CH_3CN$

Attempts made at characterizing this complex crystallographically were not completely successful (R = 0.115, $R_w =$ 0.114). However, the broad outlines of the structure are identifiable and the proposed molecular structure is shown in Fig. S1,³ where it is seen that the cobalt ion is in an octahedral environment. It is coordinated to three nitrogen atoms from the macrocycle, the pyridyl ring, and the solvent acetonitrile. However, the remaining coordination sites are occupied by a monodentate and bidentate nitrate ion. These two modes of coordination have also been established by IR spectroscopy, with N-O stretches at 1360 and 1461 cm⁻¹ corresponding to a monodentate nitrate ion (27) and those at 1285 and 1021 cm⁻¹ consistent with a bidentate configuration. In contrast to the structure of the nickel(II) complex of L_2 discussed previously, none of the thioether sulphur atoms in the macrocycle L_2 is coordinated to the metal. The ligand adopts a conformation similar to that observed in the free ligand [14]aneS₄ (5), consistent with the lone pairs on the thioether atoms being directed out of the ring. This species is of interest in that it is an example of a rare precursor to complexation with the macrocyclic ligand.

Ligand L_4 and $[Cu(L_4)](ClO_4)_2$ Both the free ligand L_4 and its Cu(II) complex have been characterized crystallographically. The molecular structures are shown in Figs. 2 and 3, respectively, and crystallographic parameters for the copper(II) ion are listed in Table 2. Complete interatomic distances and bond angles of L_4 are provided in Tables S7–S9,³ and those of $[Cu(L_4)](ClO_4)_2$ are presented in Tables S10-S13.3

For the free ligand L_4 , the interatomic distances between the nitrogen and sulphur donor atoms inside the macrocyclic

³Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 4093. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 277077-277079 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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Complex	L_4	$[Cu(L_4)](ClO_4)_2$	$[N_1(L_2) \cdot CH_3 CN](ClO_4)_2 \cdot CH_3 CN$	
Empl. form.	$C_{22}H_{32}N_4S_2$	$C_{22}H_{32}Cl_2N_4O_8S_2Cu$	$C_{20}H_{32}Cl_2N_4O_8S_3Ni$	
Mol. wt.	416.64	679.1	682.3	
Crystal colour, habit	Clear white	Emerald green	Royal purple	
Crystal system	Monoclinic	Monoclinic	Monoclinic	
Space group	<i>P</i> 2 ₁ (No. 4)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	
Cell dimensions				
a (Å)	10.593(4)	15.632(1)	12.152(5)	
b (Å)	17.195(9)	9.753(3)	14.445(2)	
<i>c</i> (Å)	6.401(2)	18.713(2)	17.194(5)	
α (°)	90	90	90	
β (°)	97.72(4)	96.21(1)	109.84(3)	
γ (°)	90	90	90	
<i>V</i> (Å)	1155.29	2836.2	2839.1	
Ζ	2	4	4	
$D_{\text{calcd.}}$ (g cm ⁻³)	1.198	1.716	1.595	
<i>F</i> (000)	1104	1100.00	1896.00	
λ (Å)	0.710 69	1.542	0.710 69	
μ (cm ⁻¹)	2.44	44.5	11.07	
Crystal dimens. (mm)	1.051×0.098×0.427	0.105×0.136×0.546	0.64×0.20×0.25	
Transmission factors	0.893-0.927		0.598-0.664	
2θ Range (°)	2-50	2-120	4.0-45	
No. reflections measd.	2134	3774	3828	
No. reflections with $I > x\sigma(I)$	1464 ^{<i>a</i>}	2197 ^a	2992 ^b	
No. parameters	252	352	343	
R	0.085	0.0938	0.078	
R_w	0.084 7	0.0936	0.086	

Note: $T = 20^{\circ}$. $R = \Sigma ||F_{o}| - ||F_{c}||/\Sigma |F_{o}|$; $R_{w} = [(\Sigma w (|F_{o}| - |F_{c}|)^{2} / \Sigma w F_{o}^{2})]^{1/2}$. ^{*a*}x = 6.

Fig. 1. Crystal structure of [NiL₂(CH₃CN)]²⁺.



cavity are: $N(1)\cdots S(1) = 3.011$ Å, $S(1)\cdots N(2) = 4.511$ Å, $N(1)\cdots S(2) = 4.099$ Å, $N(2)\cdots S(2) = 4.737$ Å, $N(1)\cdots N(2) = 5.762$ Å, and $S(1)\cdots S(2) = 5.905$ Å. The average of the C—S bond distance is 1.833 Å, which is similar to that observed

in [14]aneS₄ (5). The geometry of the ligand in the solid state indicates that the S lone pairs are exocyclic and those on the nitrogen atoms are oriented in different directions such that binding to the metal centre requires conformational changes within the ligand.

In the complex ion $[Cu(L_4)]^{2+}$, the copper ion is in a distorted square-pyramidal environment (Fig. 3). It is coordinated by three nitrogen atoms and two thioether sulphur atoms. One tertiary nitrogen atom in the macrocycle is not coordinated. The Cu-N bond distances range from 2.00 to 2.14 Å. The apical Cu—S(1) bond distance is 2.51 Å, which is very close to the value in 17-thia-1,5,8,12-tetrazaabicyclo[10.5.2]nonadecane ([Cu(bicycloSN₄)]²⁺, 2.55 Å) (14b) where there is a similar N,S five-membered chelate ring. A comparison with the interatomic bond distances in L4 indicates that there are no major changes in bond lengths within the macrocycle upon coordination to copper. From the mean plane calculation (Table S12),³ the copper ion is 0.258 Å above the plane defined by the basal atoms N(1), N(3), and N(4). In addition, S(2) is 0.9059 Å below this plane. A consequence of the nonplanarity between the copper ion and the nitrogen and sulphur donor atoms is that the bond angle S(1)-Cu-S(2) is 130.5°. The bond angles in the equatorial plane are: N(4)pyr-Cu-S(2) = 90.2°, N(4)pyr-Cu-N(3) = 91.7°, S(2)-Cu-N(1)pyr = 86.8°, and N(1)-Cu-N(3)pyr = 81.7°, consistent with deviations from an ideal squarepyramidal structure that probably arises from the strain imposed by the ligand.

 $^{{}^{}b}x = 4.$

Table 2. Interatomic distances (Å) and bond angles (\circ) (standard deviations in parenthesis) for complex cations.

	$[Ni(L_2)CH_3CN)]^{2+}$	$[Cu(L_4)]^{2+}$			
Interatomic distances (Å)					
Ni(1)—S(1)	2.371(3)				
Ni(1)—S(2)	2.481(2)				
Ni(1)—S(3)	2.398(3)				
Ni(1)—N(1)	2.037(7)				
Ni(1)—N(2)	2.133(7)				
Ni(1)—N(3)	2.085(8)				
Cu(1)—S(1)		2.511(4)			
Cu(1)—S(2)		2.339(4)			
Cu(1)—N(1)		2.135(11)			
Cu(1)—N(3)		2.066(11)			
Cu(1) - N(4)		2.000(11)			
Bond angles (°)					
S(2)-Ni(1)-S(1)	84.8(1)				
N(1)-Ni(1)-S(1)	174.2(2)				
N(2)-Ni(1)-S(1)	91.9(2)				
N(3)-Ni(1)-S(1)	92.4(2)				
S(3)-Ni(1)-S(1)	96.2(1)				
N(1)-Ni(1)-S(2)	100.8(2)				
N(2)-Ni(1)-S(2)	176.0(2)				
N(3)-Ni(1)-S(2)	87.7(2)				
S(3)-Ni(1)-S(2)	82.6(1)				
N(1)-Ni(1)-S(3)	86.3(2)				
N(2)-Ni(1)-S(3)	95.5(3)				
N(3)-Ni(1)-S(3)	166.4(2)				
S(2)-Cu(1)-S(1)		130.5(2)			
N(1)-Cu(1)-S(1)		85.3(4)			
N(4)-Cu(1)-S(1)		107.8(3)			
N(4)-Cu(1)-N(3)		91.7(4)			
N(3)-Cu(1)-S(1)		84.3(3)			
N(1)-Cu(1)-S(2)		86.8(4)			
N(4)-Cu(1)-S(2)		90.2(3)			
N(3)-Cu(1)-S(2)		142.3(3)			
N(3)-Cu(1)-N(1)		81.7(5)			
N(4)-Cu(1)-N(1)		164.8(5)			

ESR spectra

The ESR spectral data for the Cu(II) and Co(II) complexes studied in this work are listed in Table 3. For the complexes $[Cu(\mathbf{L}_1)]^{2+}$ and $[Cu(\mathbf{L}_3)]^{2+}$ ($\mathbf{L}_3 = 1,7$ -diaza-4,10dithiacyclotetradecane), the ESR spectra are characteristic of a tetragonally distorted d⁹ ion in a tetragonal elongated environment, with $g_{\parallel} > g_{\perp}$. Hyperfine lines are also observed in the g_{\parallel} region, with the coupling constants ranging from 115 to 125 G. The g_{\parallel} value of $[Cu(\mathbf{L}_1)]^{2+}$ is greater than for $[Cu([14]aneS_4)]^{2+}$ ($g_{\parallel} = 2.10$; $A_{\parallel} = 165$ G) and also other Cu(II) N₂S₂ complexes prepared by Kaden and co-workers (12). Isotropic spectra were obtained even at 77 K for the copper(II) complexes with pyridine pendant arms, $[Cu(\mathbf{L}_2)]^{2+}$ and $[Cu(\mathbf{L}_4)]^{2+}$. The signals span a range of 500 G, and no hyperfine coupling was observed. A possible explanation for the spectra is that consistent with the structure of $[Cu(\mathbf{L}_4)]^{2+}$ shown in Fig. 3, the possibility exists of a dynamic exchange between the Cu-coordinated nitrogen

Fig. 2. Crystal structure of the ligand L_4 .



Fig. 3. Crystal structure of the $[CuL_4]^{2+}$ ion.



Table 3. ESR data for Cu(II) and Co(II) complexes (T = 77 K).

Complex	g_{\parallel} (A_{\parallel} in Gauss)	$g \bot$
$[Cu(L_1)]^{2+}$	2.467 (115)	2.121
$[Cu(L_2)]^{2+}$	2.070^{a}	
$[Cu(L_4)]^{2+}$	2.100^{a}	
$[Cu(L_3)]^{2+}$	2.167 (125)	1.983
$[Cu(L_5)]^{2+}$	2.146 (170)	2.121^{b}
$[Cu(L_6)]^{2+}$	2.162 (161)	2.121^{b}
$[Co(L_2)]^{2+}$	2.020 (75)	2.290

Note: $L_3 = 1,7,dithia-4,11-diazacyclotetradecane,$

 $L_5 = 1,4,dithia-8,11$ -diazacyclotetradecane, and $L_6 =$

4,12-diaza-1,8-dithiacyclotetradecane.

 ${}^{a}g_{iso}$ value shown.

^bReference 11.

atom from the pyridine and that of the tertiary amine. Although the crystal structure of $[Cu(L_2)]^{2+}$ is not available currently, a five-coordinate geometry is anticipated and a fluxional process may be present.

For the Co(II) complexes of L₂, only ion B, $[Co(L_2)(ClO_4)]^+$, is active. The spectrum at 77 K exhibits characteristics of a low spin d⁷ ion in a distorted octahedral environment, with $g_{\parallel} = 2.020$ and $g_{\perp} = 2.290$. This is consistent with a Co(II) ion coordinated to the N and S donor at-

Complex	Anion	λ_{max} (nm) (ϵ_{max} , (mol/L) ⁻¹ cm ⁻¹)
$[Ni(L_1)]^{2+}$	PF_6^-	282 (1700), 373 (38), 578 (23), 900 (31)
$[Ni(L_2)]^{2+}$	PF_6^-	282 (4870), 556 (28), 820 (24)
$[Ni(L_6)]^{2+}$	ClO_4^-	375 (32), 585 (17), >800 ^a
$[Ni(L_7)_2]^{2+b}$	ClO_4^-	297 (680), 524 (15), 840 (22) ^c
$[\mathrm{Cu}(\mathbf{L}_1)]^{2+a}$	PF_6^-	278 (2100), 368 (4500), 750 (430)
$[Cu(L_2)]^{2+}$	ClO_4^-	380 (5610), 704 (540), 871 (570)
$[Cu(L_4)]^{2+}$	ClO_4^-	356 (3020), 737 (390)
$[Co(L_2)(ClO_4)]^+$	ClO_4^-	261 (4410), 531 (32)
$[Co(L_2)(NO_3)_2(MeCN)]$	—	500 (396), 800 (153) ^b

Table 4. UV-vis spectra of metal complexes in acetonitrile.

^aReference 11.

^bSpectrum recorded in nitromethane.

 $^{c}L_{7} = 7$ -aza-1,4-dithiacyclononane (26).

oms from L_2 and perchlorate ion in a tetragonal elongated geometry. Since no hyperfine coupling from the nitrogen atoms was observed, the tertiary amine and pyridine moiety from the ligand are most likely coordinated in the equatorial plane of the distorted octahedron in a manner similar to the corresponding nickel(II) complex (Fig. 1). The eight hyperfine lines observed in the g_{\perp} region arise from the interaction of the unpaired electron with the Co nucleus (⁵⁹Co, I = 7/2). For the complex [Co(L_2)(NO₃)₂(CH₃CN)], no ESR signal was detected. Instead, a paramagnetic ¹H NMR spectrum spanning from -30 to +50 ppm was obtained, consistent with the persistence of the crystalline structure (Fig. S1)³ in solution, although the paramagnetic spectrum was not amenable to further analysis.

UV-vis spectra

The UV–vis spectral data for various Ni(II), Cu(II), and Co(II) complexes studied in this work are presented in Table 4. The Ni(II) complexes exhibit typical octahedral geometry, with solvent coordinated axially. Molar extinction coefficients, ranging in the visible from 20 to 40 (mol/L)⁻¹ cm⁻¹, are very similar to the Ni(II) complex of 1,8-dithia-5,11-diazacyclotetradecane, a ligand isomer reported in the literature (12), and are typical of octahedral geometry with solvent participation in the axial sites. This is confirmed by the similarity with the six-coordinate Ni(L₇)₂²⁺ ion (L₇ = 7-aza-1,4-dithiacyclononane) (26).

The Cu(II) complexes are green in acetonitrile and their UV–vis spectra show absorptions bands in the regions 324–380 nm and 704–760 nm that are assigned as ligand-to-metal charge transfer (LMCT) and d–d transitions, respectively. However, the presence of axial donors apparently induces a difference in spectra from the planar N_2S_2 systems (12).

The spectra of the two Co(II) complexes of L_2 show slightly different characteristics. Although both isomers have an absorption band around 500 nm, compound B has a slightly larger extinction coefficient. In addition, it has an additional absorption band at 800 nm. These observations can be rationalized by the different coordination environment at the cobalt centre in the two species. The ESR spectrum of B at 77 K is consistent with a Co(II) ion coordinated to all of the donor atoms in L_2 with weak interaction with an axial perchlorate ion. For A (Fig. S1),³ the nature of the primary coordination sphere is expected to produce a different ligand field at the metal centre.

Table 5. Electrochemical data.

Complex	E vs. Fc/Fc ⁺	ΔE (V)
Cu(II)/(I)		
$[Cu(L_2)]^{2+}$	$E_{1/2} = -0.024$	0.077
$[Cu(L_4)]^{2+}$	$E_{1/2} = -0.137$	0.086
$[Cu(L_5)]^{2+}$	$E_{1/2} = -0.045$	0.150
Ni(II)/(I)		
$[Ni(L_2)]^{2+}$	$E_{1/2} = -1.18$	а
$[Ni(L_4)]^{2+}$	$E_{1/2} = -1.23$	0.14
$[Ni(L_1)]^{2+}$	$E_{1/2} = -1.29$	а
Co(II)/(III)		
$[Co(L_2)]^{2+}(B)$	$E_{1/2} = 0.18$	0.23
$[Co(L_2)(NO_3)_2MeCN]$ (A)	$E_{1/2} = 1.71$	b
	$E_{\rm red} = -1.83$	а

Note: a = irreversible oxidation, b = irreversible reduction.

Electrochemistry

The redox chemistry of the Cu(II), Ni(II), and Co(II) complexes of L_2-L_4 was studied by cyclic voltammetry. The results are summarized in Table 5. For the Cu(II) complexes, the reduction to Cu(I) is, at best, quasi-reversible. It has been shown (28) that coordination geometry greatly influences redox potentials for these couples. Since Cu(II) complexes are generally tetragonal distorted and Cu(I) species prefer tetrahedral coordination, rearrangement of the structure of the complexes is required when Cu(II) is reduced to Cu(I). This process probably involves the "square scheme" discussed recently (10) that will contribute to the value of ΔE being greater than the theoretical value for a reversible one-electron reduction.

Both the cyclic voltammograms of $[Ni(L_2)]^{2+}$ and $[Ni(L_1)]^{2+}$ show irreversible reduction waves to Ni(I) at -1.18 and -1.29 V vs. Fc/Fc⁺, respectively. However, for the complex $[Ni(L_4)]^{2+}$, a quasi-reversible reduction from Ni(II) to Ni(I) is observed at -1.23 V with peak potentials separated by 0.14 V. In this case, since the ligand can impose octahedral geometry on the metal centre, there is less reorganizational energy required for the electron transfer.

For the complex $[Co(L_2)(ClO_4)]^+$ (compound B), a quasireversible oxidation to Co(III) was observed at $E_{1/2} = 0.18$ V vs. Fc/Fc⁺. The peak to peak separation is 0.23 V. This Co(II)/Co(III) couple occurs at a more positive value relative to other thioether complexes such as $[Co([9]aneS_3)]^{2+}$ (0.02 V vs. Fc/Fc⁺) (29) and $[Co([10]aneS_3)_2]^{2+}$ (0.01 V vs. Fc/Fc⁺) (30). A much more reversible situation is observed in preliminary observations of the reduction Co(II)/Co(I) of the hexacoordinate Co(L₄)²⁺ ion ($E_{1/2} = -1.33$ V, $\Delta E =$ 80 mV).

Conclusion

The preparation of mixed N,S-coordinating macrocycles has been achieved by reaction of thiols with either tosylated amines or the corresponding dibromides, where either can serve as the leaving groups in the formation of C-S bonds in the cyclization. Reductive detosylation, under mild conditions, results in satisfactory yields (ca. 70%). Complexes with pendant arms exhibit thermodynamic stabilities similar to their aza analogues. Interesting differences have been observed in the formation of cobalt(II) species dependent on the solvent used in the reaction. Although in the potentially hexacoordinating ligand with two pendant arms the S donors are exocyclic, in the copper(II) ion they are coordinated to the metal centre as are only three of the four other aza donors, confirming the preference for five-coordinate geometry at this metal centre. This observation contrasts with the corresponding Ni(II) complex where the octahedral ion permits possible access to Ni(I) and Ni(III) species.

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