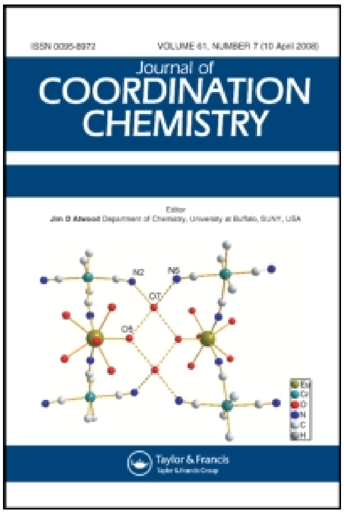

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Synthesis, spectroscopic and electrochemical investigations of a tetrathiamacrocycle and its copper(II) and nickel(II) complexes

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Synthesis, spectroscopic and electrochemical investigations of a tetrathiamacrocycle and its copper(II) and nickel(II) complexes

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A new tetrathiomacrocycle possessing four peripheral pendant cyano groups has been synthesized in high yield by the metal-templated cyclization of $Na_2S_2C_2(CN)_2$ and 1,3-dichloropropane in refluxing DMF followed by demetalation. The initially formed complexes $[Ni\{(CN)_4[14]eneS_4\}]Cl_2$ (**1**) and $[CuCl_2\{(CN)_4[14]eneS_4\}]$ (**2**) underwent demetalation upon reaction with CN^- or H_2S, respectively. Both **1** and **2** reacted with $[CpRu(PPh_3)_2Cl]$ to form cationic dinuclear complexes **3** and **4**, which were isolated as PF_6^- salts. All complexes, as well as the metal-free tetrathiamacrocycle, were characterized by IR, electronic and ^1H NMR spectroscopy. Redox characteristics of the complexes were investigated using cyclic voltammetry.

Keywords: Copper; Nickel; Maleonitrile dithiolate; Tetrathiamacrocycle; Ruthenium adduct; Cyclic voltammetry

1. Introduction

Sulfur donor ligands act as soft bases. Therefore, it is not surprising that thiacrown macrocycles of the type $[14]aneS_4$, L^1, as well as other higher members, preferentially interact with bivalent soft acid cations such as Fe^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} [1–6] and thus are used to facilitate transport of such metal ions [7–9] across organic phases. Tetrathiacrowns covalently linked to an anthracenyl fluorophore, L^2, act as fluorescent sensing agents for redox-active soft metal ions such as Cu^{2+} [10]. The cavity size in L^1 is more flexible because of the saturated alkyl chain and is therefore expected to interact non-discriminatively with any soft metal ion irrespective of its size. If a certain degree of rigidity is introduced in the macrocycle framework, for example through the introduction of double bonds, size-dependent selectivity could be introduced. Staeb *et al.* [11] have recently reported the synthesis of several cyclic

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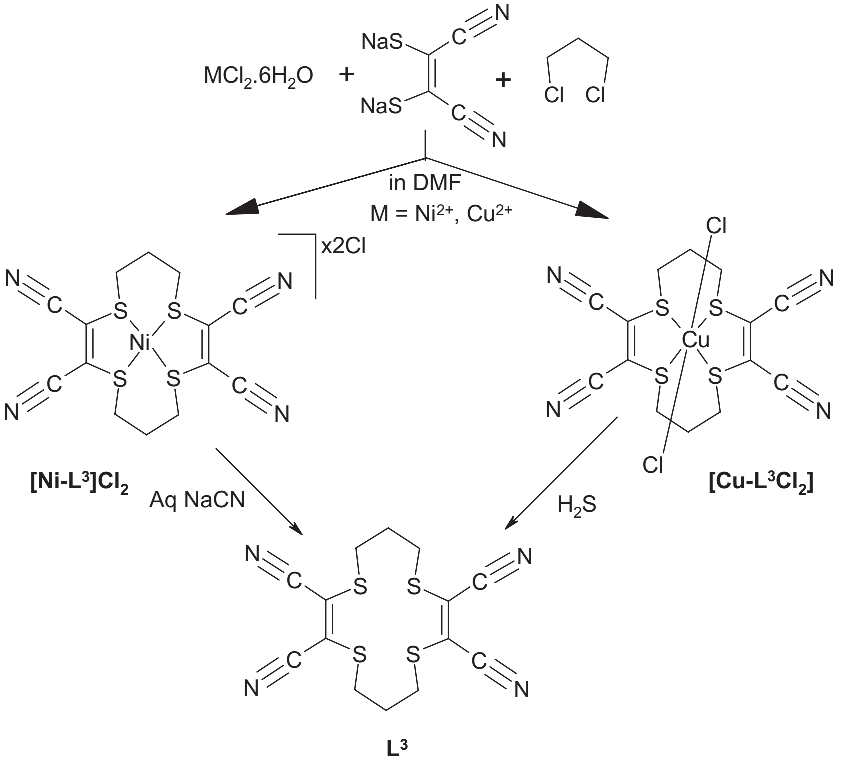


Scheme 1.

tetrathiadienes and tetrathiaenynes. However, for synthesizing alkenic thiacrowns, maleonitriledithiolate(2–), $S_2C_2(CN)_2^{2-}$, would be a convenient choice of reagent because of its ease of synthesis. Although $Na_2S_2C_2(CN)_2$ has been known for a some time [12, 13], its macrocylization to obtain thiacrowns has only been attempted very recently. Spannenberg *et al.* [14] have used high dilution techniques to react $Na_2S_2C_2(CN)_2$ and 1,3-dibromopropane in dioxane to obtain the macrocyclic thioether L^3 (scheme 1) in less than 10% yield. The compound undergoes intramolecular [2 + 2] photoaddition to give a tricyclo product.

We have been working on maleonitriledithiolate and its thioether complexes for over a decade [15–18]. In an extension of earlier work we report the templated synthesis of cyclic tetrathiaether complexes of Ni^{2+} and Cu^{2+} as well as the metal-free macrocycle L^3 in high yield (scheme 1). The spectroscopic and redox behavior of all the compounds is described.

2. Experimental

All common chemicals of AR grade and 1,3-dichloropropane (Fluka) and Et_4NClO_4 (TEAP) (Fluka) were used as received. $Na_2S_2C_2(CN)_2$ was prepared using a literature method [19]. Acetone used in the conductivity measurements was dried and stored over activated 3–4 Å molecular sieves. MeCN used in cyclic voltammetry (CV) studies was dried by passing it through activated, neutral Al_2O_3 that had been preheated at 450° C for 24 h. All synthetic manipulations were carried out under an N_2 atmosphere. Physical and spectroscopic measurements were carried out as described elsewhere [20]. Conductances were measured on a Tonshiwal TCM-15 conductivity meter. Cyclic voltammograms were recorded on a CHI-600A electrochemical analyzer using a three-electrode assembly (Pt wire auxiliary electrode, Ag/AgCl reference electrode and glassy carbon working microelectrode) in the presence of 0.1 M TEAP (in MeCN) as supporting electrolyte.

2.1. *[Ni{(CN)$_4$[14]eneS$_4$}]Cl$_2$, 1*

A suspension of $NiCl_2 \cdot 6H_2O$ (2.38 g, 10 mmol) and 1,3-dichloropropane (1.0 cm^3, 20 mmol) in DMF (50 cm^3) was heated at reflux for 30 min whereupon a yellowish green solution formed. To this was added a solution of $Na_2S_2C_2(CN)_2$ (3.72 g, 20 mmol), dissolved in 50 cm^3 of DMF, dropwise over a period of 2 h while refluxing and stirring continued. The mixture was heated further at reflux for 8 h, whereupon the color of the solution changed to brown and finally to orange–red. Solvent was distilled off at reduced pressure and the dry residue was extracted into methanol, yielding an orange-red solution. The solution was filtered and evaporated to dryness. The residue was extracted into acetone and purified by passing it through a neutral alumina column (eluant 1 : 1 v/v $CH_2Cl_2 : Me_2CO$). Yield: 2.5 g (43%); mp 188°C; Λ_M: 430 $^{-1}$ cm^{-1}. Electronic spectrum (DMF): λ_{max} 276 nm (ε_{max} 2.3×10^4 M^{-1} cm^{-1}), 314 (1.5×10^4), 385 (4.0×10^3), 480 (3.2×10^3). ES-MS: *m*/*z* 429, 215 (calcd. for $[M-2Cl]^+$ 422–432 and $[M-2Cl]^{2+}$ 211–216). IR (in KBr): 2933w, 2234vs, 1653vs, 1475s, 1429w, 1380s, 1252w, 1155w, 1111s, 1060vw, 876w, 689s, 512w cm^{-1}. Anal. Calcd. for $C_{14}H_{12}N_4S_4Cl_2Ni$(%): C, 34.0; H, 2.4; N, 11.3; S, 24.9; Cl, 14.4; Ni, 11.9. Found: C, 34.0; H, 1.8; N, 11.6; S, 25.3; Cl, 15.0; Ni, 12.4. ^{1}H NMR ($CDCl_3$): δ 2.7(br, CH_2), 3.7 (t, S-CH_2) ppm. CV (DMF): E_p−1.10 (irr.), 0.28 (rev.) and 1.17 (irr.) V *vs* Ag/AgCl.

2.2. *[CuCl$_2${(CN)$_4$[14]eneS$_4$}], 2*

This complex was prepared analogously to **1** by the reaction of $CuCl_2 \cdot 2H_2O$ (1.70 g, 10 mmol), 1,3-dichloropropane (1.0 cm^3, 20 mmol) and $Na_2S_2C_2(CN)_2$ (3.72 g, 20 mmol) in DMF. The initial bluish green color changed to brown and finally to deep greenish yellow. Solvent was distilled off at reduced pressure and the residue extracted into acetone. The complex was purified by passing the solution through a neutral alumina column (eluant 1 : 1 v/v $CH_2Cl_2 : Me_2CO$). Yield: 2.3 g (38%); mp 193°C; Λ_M: 17 Ω^{-1} cm^{-1}. Electronic spectrum (DMF): λ_{max} 271 nm (ε_{max} 6.3×10^3 M^{-1} cm^{-1}), 350 (6.8×10^3). ES-MS: *m*/*z* 219 (calcd. for $[M-2Cl]^{2+}$ 214–219). IR (KBr): 2917vw, 2209vs, 1731w, 1713w, 1625s, 1448vs, 1409vs, 1265vw, 1155s, 1052w, 678w, 613vw, 508s cm^{-1}. Anal. Calcd. for $C_{14}H_{12}N_4S_4Cl_2Cu$(%): C, 33.7; H, 2.4; N, 11.2; S, 25.6; Cl, 14.2; Cu, 12.7. Found: C, 34.0; H, 1.9; N, 11.3; S, 25.0; Cl, 14.7; Cu, 12.5. CV (DMF): E_p−1.30 (irr.), 0.79 (irr.) and 1.27 (irr.) V *vs* Ag/AgCl.

2.3. *$(CN)_4[4]eneS_4$, L^3*

The metal-free macrocycle was obtained by demetalating the nickel(II) complex using aqueous NaCN or the copper(II) complex using H_2S, as described below.

2.3.1. Method A.

Complex **1** (1.0 g, 2.0 mmol) and NaCN (1.0 g) were refluxed for 2 h in 50 cm^3 of water. The initial orange–red solution gradually turned turbid and subsequently a brown residue separated out. The solution was concentrated to *ca* 5 cm^3 by evaporation and cooled. The residue was extracted with $5 \times 10\,cm^3$ of dichloromethane and all the dichloromethane extracts were combined and evaporated to dryness. The residue was purified by passing a CH_2Cl_2 solution through a neutral alumina column eluting with CH_2Cl_2. Yield: 0.47 g (65%).

2.3.2. Method B.

Complex **2** (1.0 g, 2.0 mmol) was dissolved in 50 cm^3 of 1 : 1 (v/v) aqueous methanol and H_2S was passed through the solution for 20 min. The volume of solution was reduced to *ca* 5 cm^3 by evaporation and the resulting viscous fluid extracted with $5 \times 10\,cm^3$ portions of dichloromethane. The compound was purified as described above. Yield: 0.43 g (59%); mp 108–109°C. Electronic spectrum (DMF): λ_{max} 273 nm (ε_{max} 5.5×10^4 $M^{-1}cm^{-1}$), 320 (3.3×10^4). ES-MS: *m/z* 364 and 183 (calcd. for $[M]^+$ 364–372 and M^{2+} 182–186). IR (KBr): 2930w, 2224s, 1653vs, 1476s, 1380s, 1252w, 1111s, 686s cm^{-1}. Anal. Calcd. for $C_{14}H_{12}N_4S_4$(%): C, 46.1; H, 3.3; N, 15.4; S, 35.2. Found: C, 45.7; H, 3.8; N, 15.0; S, 34.8. ^1H NMR ($CDCl_3$): δ 2.0 (br, 4H, CH_2), 3.2 (m, 8H, S-CH_2) ppm.

2.4. *$[Ni\{(CN)_4[14]eneS_4\}\{RuCp(PPh_3)_2\}][PF_6]_3$, 3, and $[CuCl_2\{(CN)_4[14]eneS_4\}\{RuCp(PPh_3)_2\}][PF_6]$, 4*

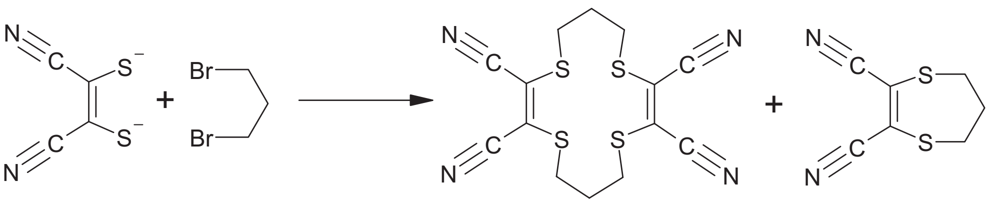
Complex **1** or **2** (0.5 g, 1.0 mmol) and $[CpRu(PPh_3)_2Cl]$ (0.7 g, 1.0 mmol) were added to 50 cm^3 of methanol and the suspension stirred for 10 h, whereupon a clear yellow–orange solution was obtained. To this was added solid NH_4PF_6 (0.8 g, 4.9 mmol) and the solvent removed at reduced pressure. The dry residue was extracted in dichloromethane and purified by passing it through a neutral alumina column, eluting with dichloromethane. Yield: *ca* 1.0 g (71%).

$[Ni\{(CN)_4[14]eneS_4\}Cl_2\{RuCp(PPh_3)_2\}][PF_6]$, **3**: Electronic spectrum (DMF): λ_{max} 237 nm (ε_{max} 1.6×10^4 M^{-1} cm^{-1}), 270 (1.4×10^4), 354 (1.5×10^4), 425 (sh), 570 nm (sh). ES-MS (PF_6^- salt): *m/z* 1318 (calcd. for $[M+2PF_6]^+$ 1313–1330). IR (KBr): 2186w, 1634s, 1474w, 1401vs, 1165w, 1090s, 747s, 697vs, 519s cm^{-1}. ^1H NMR (in $CDCl_3$): δ 2.7 (br, CH_2), 3.7 (t, S-CH_2), 4.1, 4.4, 4.6 (s, Cp-H), 7.0–8.0 (M, Ph-H) ppm. CV (DMF): E_p −1.09 (irr.), 0.60 (irr.) and 1.30 (irr.) V *vs* Ag/AgCl.

$[CuCl_2\{(CN)_4[14]eneS_4\}\{RuCp(PPh_3)_2\}][PF_6]$, **4**: Electronic spectrum (in DMF): λ_{max} 273 nm (ε_{max} 5.5×10^3 $M^{-1}cm^{-1}$), 360 (1.3×10^4). ES-MS: *m/z* 1192 (calcd. for $[M]^+$ 1182–1204). IR (in KBr): 2191w, 1632s, 1468s, 1394vs, 1241w, 1020w, 935w, 747s, 550s, 504s cm^{-1}. Anal. Calcd. for $C_{55}H_{47}N_4S_4P_3F_6Cl_2CuRu$(%): C, 53.9; H, 3.8; N, 4.6; S, 10.5; Cl, 8.7; Cu, 5.2. Found: C, 53.8; H, 4.2; N, 4.4; S, 10.1; Cl, 9.2; Cu, 5.2. CV (DMF): E_p −1.28 (irr.), 0.60 (irr.) and 1.10 (irr.) V *vs* Ag/AgCl.

3. Results and discussion

Direct reaction between $N_2S_2C_2(CN)_2$ and 1,3-dibromopropane yields predominantly the cyclic thioether 1,4-dithiohept-2-ene-2,3-dicarbonitrile L^4, and even by using high dilution techniques only a low yield of L^3 is obtained [14]. However, by using metal ions that have a propensity to form square planar complexes with $N_2S_2C_2(CN)_2$ as template, the reaction proceeds fairly well and yields greater amounts of the corresponding complexes. The method is convenient and efficient. It was found that nickel(II) formed a cationic complex that gave a conducting solution upon dissolution in polar solvents. The copper(II) complex and the metal-free macrocycle formed nonconducting solutions. The conductances of the cationic complexes are in agreement with literature data [21].


L^3, 10% **L^4, 90%**

All of the complexes exhibit a strong band between 2186 and 2234 cm^{-1} due to ν(CN) vibrations. This is observed as a very strong band in the mononuclear complexes but has moderate intensity in the dinuclear complexes. In the nickel(II) complex it is very strong and is observed at an unusually high frequency (2234 cm^{-1}). This is probably due to the metal-induced, forced, co-*facial* antiparallel arrangement between the $S_2C_2(CN)_2$ units and to the rigidity in the framework. Consequently, the antisymmetric stretch has a higher transition dipole. In the mononuclear copper(II) complex this band is observed at 2209 cm^{-1}. Upon binding of the additional $RuCp(PPh_3)_2$ fragment, the symmetry and rigidity of the macrocycle framework is perturbed, resulting in a shift of the ν(CN) band to lower frequencies. In the dinuclear complexes it is observed at 2186 and 2191 cm^{-1}, respectively, in nickel(II) and copper(II) complexes and lies in the range of simple related dinuclear thioether complexes [15–17]. This suggests decoupling of ν(CN) vibrations due to the asymmetry introduced by the binding of the second metal fragment. The metal-coordinated macrocycles showed a medium intensity band at *ca* 500 cm^{-1} due to M–S stretching.

^{1}H NMR spectra of the nickel(II) complex **1** and the free macrocycle showed two signals at $\delta \sim 2.7$ and ~ 3.7 ppm due to CH_2 and $S{-}CH_2{-}$ protons [22]. Upon binding the $RuCp(PPh_3)_2$ group to the CN nitrogen, a complex multiplet was observed at δ 7.0–8.0 ppm due to phenyl protons. Three additional signals were observed at δ 4.1, 4.4 and 4.6 ppm, attributed to cyclopentadienyl protons. The molecule has three conformers with both $S_2C_2(CN)_2$ units lying co-*facially* antiparallel, puckered or forming a boat (figure 1). Theoretical geometry optimization shows that these conformers have very small energy differences (8.36 kJ mol^{-1}) [23] and hence place the cyclopentadienyl group in three different magnetic environments.

Electronic spectra of **1** exhibit two strong absorptions at 276 and 314 nm and two weak bands at 385 and 480 nm. As the two strong UV region bands are also present

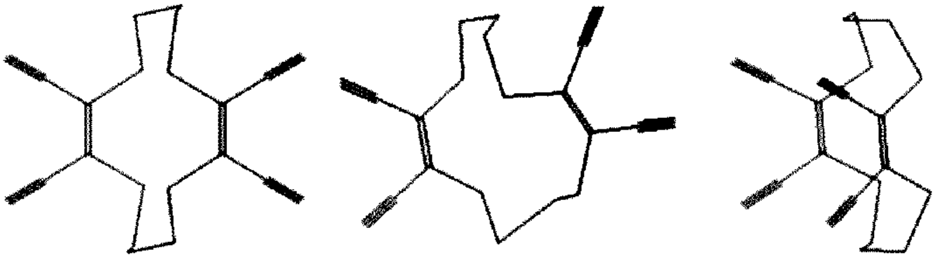


Figure 1. Three stable conformers of the metal-free $(CN)_4[14]eneS_4$ macrocycle.

in the free macrocycle, they are seen to arise from intraligand π–π^* transitions. The second π–π^* transition in **2** is shadowed by the strong Cl → Cu LMCT transition. Considering the intensity and position of the weak bands in **1**, they could be attributed to d–d transitions $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$. The $^3A_{2g} \rightarrow {}^3T_{2g}$ transition is observed as a very weak absorption at 865 nm. In the copper(II) complex the d–d transitions appear as shoulders on the long tail of the strong LMCT absorption. Upon binding of the $RuCp(PPh_3)_2$ fragment in complexes **3** and **4**, a new strong absorption band is introduced at 354 nm, overshadowing the longer wavelength intraligand π–π^* transitions.

Cyclic voltammograms of the complexes $[Ni\{(CN)_4[14]eneS_4\}]Cl_2$, $[CuCl_2\{(CN)_4[14]eneS_4\}]$, $Na_2[Ni\{S_2C_2(CN)_2\}_2]$ and $Na_2[Cu\{S_2C_2(CN)_2\}_2]$ were recorded for comparison. Unlike maleonitriledithiolate complexes, the tetrathiamacrocycle complexes exhibited a low-lying reversible and a *quasi*-reversible oxidation wave in the nickel(II) and copper(II) complexes. It seems that following the Cu(II)/Cu(III) process, the pseudo-octahedral complex undergoes dissociative removal of the coordinated chlorides. Therefore, it is oxidized at E_{pa} 0.79 V *vs* Ag/AgCl, while in the return sweep the dissociated species is reduced back to E_{pc} 0.36 V. The nickel(II) complex, being square planar, has no such ligand dissociation and hence exhibits a reversible wave. The second oxidation wave in both of the complexes is of an irreversible nature and is observed at E_{pa} 1.17, 1.27 V in nickel(II) and copper(II) complexes, respectively. Both complexes exhibit an irreversible reduction wave; at $E_{pc}-1.10$ and -1.30 V, respectively. Again the reduction wave in maleonitriledithiolate complexes is observed at -0.90 V. CV scans of the $RuCp(PPh_3)_2$-linked dinuclear complexes are composites of the CVs of the two fragments and thereby exhibit irreversible oxidation waves at E_{pa} 0.60, 1.30 and 0.60, 1.10 V for the nickel(II) and copper(II) complexes, respectively.

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