Synthesis and Cryptate Complexes of Azathia Macropolycyclic Ligands based on 12-Membered N_2S_2 and 15-Membered N_2S_3 Macrocyclic Subunits†

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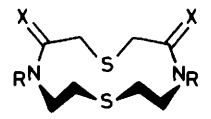
The cyclindrical macrotricyclic ligands 4,16-dioxa-10,22,27,32-tetrathia-1,7,13,19-tetra-aza-tricyclo[17.5.5.5^{7,13}]tetratriacontane (L^2) and 4,19-dioxa-10,13,25,28,33,38-hexathia 1,7,16,22-tetra-aza-tricyclo[20.8.5.5^{7,16}]tetracontane (L^7) have been synthesised by high-dilution condensation of macrocyclic ligands containing 12-membered N_2S_2 and 15-membered N_2S_3 subunits, following different reaction sequences. The macrocycles 4,10-dimethyl-1,7-dithia-4,10-diazacyclododecane and 7,13-dimethyl-1,4,10-trithia-7,13-diazacyclopentadecane and the macrotricycles L^2 and L^7 form respectively mono- and di-nuclear complexes with Cu^{II}, Ni^{II}, and Ag^{I}. The reduced Cu^{I} and Ni^{I} complexes are strongly stabilized whilst the dinuclear complexes function as dielectronic receptors, exchanging two electrons in a single wave.

Macropolycyclic ligands may form polynuclear cryptate complexes by inclusion of one or more metal ions within their intramolecular cavities.[1-3] In these systems the arrangement and distance between the metal ions may be regulated *via* the ligand structure. Macropolycycles involving only oxygen and nitrogen binding sites were primarily designed for the complexation of alkali and alkaline-earth cations.[4-7] In order to combine the rich chemistry of the transition-metal cations with the diverse array of macropolycyclic structures, nitrogen and sulphur binding sites have been introduced and a series of polyazapolythiamacrocycles was developed.[1,8-12] Within this series, the cyclindrical macrotricycles were particularly attractive as the lateral macrocycles could bind the cations while the central cavity was available for inclusion of a substrate of compatible size and suitable binding properties (see Figure 1 in ref. 1).

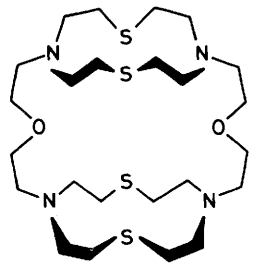
There has been relatively little published work concerned with the co-ordination chemistry of N_2S_2 macrocyclic ligands. Nickel complexes of a Schiff base[13] and its reduced form[14] as well as complexes with 14-, 15-, and 16-membered macrocycles have been reported.[15-17] More recently copper(II) complexes of a series of 12- to 16-membered N_2S_2 macrocycles have been described.[18] Some of the chemistry discussed herein has been reported in preliminary communications describing copper(II) complexes of the N_2S_2 monocycle L^{1c} and the dinucleating macrotricycle L^2.[8-11]

Results and Discussion

Synthesis of Ligands L^{1c}, L^2, L^3, *and* L^7.—The 12-membered N_2S_2 monocycle L^{1b} was obtained by high-dilution condensation[19] of $S(CH_2COCl)_2$ (L^{4a}) with 1,5-diamino-3-thiapentane (L^{4b}) in toluene (giving the diamide L^{1a}) followed by reduction with BH_3·SMe_2 in tetrahydrofuran (thf). The monocycle was converted into the dimethylated derivative L^{1c} using the Eschweiler–Clarke procedure. The overall yield of L^{1c} from acyclic precursors was 76%. High-dilution condensation of L^{1b} with $O(CH_2COCl)_2$ in toluene at −5 °C led to a mixture of the dimeric and trimeric macrocycles L^{5a} and L^{5b} which was reduced *in situ* with BH_3·thf to a mixture of the corresponding amines. Separation by chromatography on alumina gave the



L^{1a} ; X = O , R = H
L^{1b} ; X = H_2, R = H
L^{1c} ; X = H_2, R = Me



L^2

macrotricycle L^2 in 32% yield and the macrotetracycle L^3 in *ca.* 8% yield.* Figure 1 illustrates the ^1H n.m.r. spectra of L^{1c}, L^2, and L^3 consistent with the given structures.

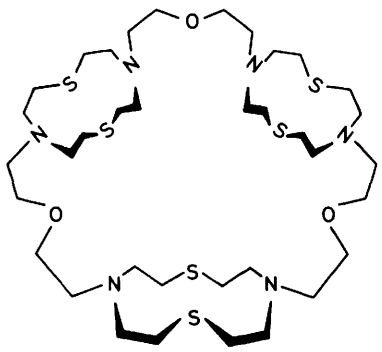
The macrotricyclic, ligand L^7 with a 15-membered N_2S_3 subunit was synthesised *via* a stepwise method introducing the macrocyclic units at different stages (see also Figure 7 in ref. 1).[1,8] The synthesis involves: reaction of L^{6b} with 3-oxaglutaric anhydride to form L^{6d} bearing two appendages; conversion of the terminal carboxylic acid functions into the activated esters (L^{6e}) with bis(*p*-nitrophenyl) sulphite; condensation of L^{6e} with L^{6b} under high dilution in refluxing pyridine to give the macrocyclic tetra-amide analogous to L^{5a}; reduction of the crude product with BH_3·SMe_2 to yield the macrotricycle L^7.

The structures assigned to the cylindrical macrotricycles L^2 and L^7 and to the macrotetracycle L^3 rest on their spectral (n.m.r., mass) and microanalytical properties as well as on the synthetic sequence (see *). Furthermore, the structure of L^2 has been confirmed by a crystal-structure determination of its dinuclear Cu^{II} complex.[11,20]

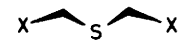
Mononuclear Complexes of L^{1c}.—While transition-metal complexes of macrocyclic ligands with N_4 or S_4 donors have been extensively documented,[21] the co-ordination chemistry of N_2S_2 macrocycles has received relatively little attention.[13-18] The ligand L^{1c} forms stable 1:1 complexes with the perchlorates of

† *Non-S.I. units employed:* mmHg ≈ 13.6 × 9.8 Pa, atm = 101 325 N m^{-2}, G = 10^{-4} T.

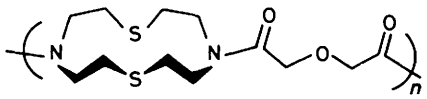
* This direct (2 + 2) condensation represents the most convenient preparation of L^2 and L^3, although initially L^2 had been prepared *via* a stepwise procedure.[8] The polyoxa-analogue L^8 has been obtained earlier by a similar reaction.[7] The stepwise procedure allowed a closer control of the synthetic sequence and gave the same material.[8]



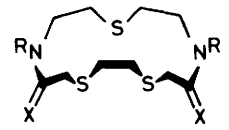
L^3

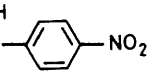


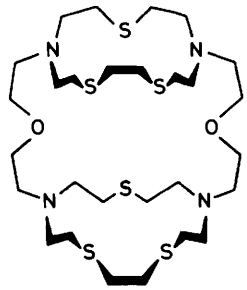
L^{4a}; X = COCl
L^{4b}; X = CH_2NH_2



L^{5a}; n = 2
L^{5b}; n = 3



L^{6a}; X = O, R = H
L^{6b}; X = H_2, R = H
L^{6c}; X = H_2, R = Me
L^{6d}; X = H_2, R = $COCH_2OCH_2CO_2H$
L^{6e}; X = H_2, R = $COCH_2OCH_2COO$–  –NO_2



L^7

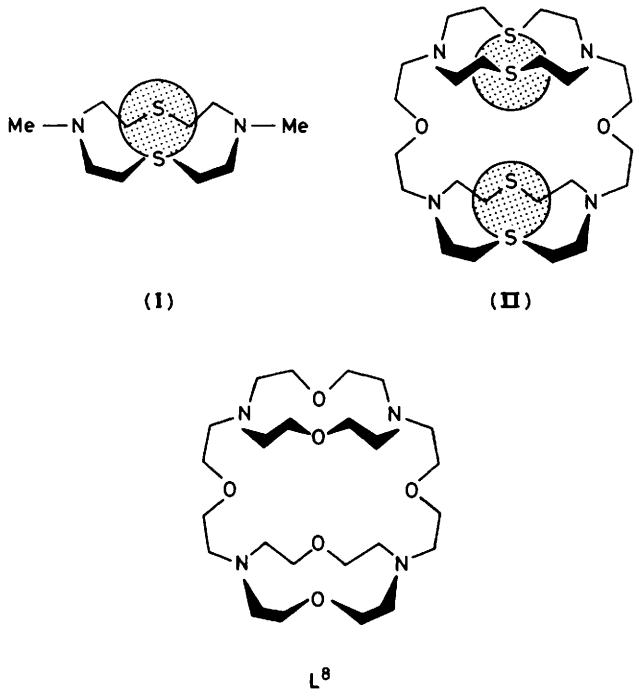
divalent nickel, copper, and zinc which may be schematically represented by structure (I) (dotted circle represents metal). The zinc complex was isolated as the dihydrate while the copper and nickel complexes crystallised from methanol as deep blue and green crystalline solids. The copper complex may be reduced to the Cu^I state electrochemically in aqueous solution [$E_{\frac{1}{2}}$ = +0.495 V, relative to standard hydrogen electrode (s.h.e.)], and the resultant colourless complex oxidises rapidly when exposed to air. Such a reduction potential is similar to those observed for related copper(II) complexes of polythiamacrocycles[22] and close to those found for several copper proteins.[23] The powder e.s.r. spectrum is of the axial type with $g_{\|}$ = 2.112 and $g_{\perp}$ = 2.047 (Figure 2), while in the frozen solution e.s.r. spectrum a normal $A_{\|}$ hyperfine splitting may be observed (0.015 cm^{-1}).

In propylene carbonate solution, the nickel(II) complex shows a quasi-reversible monoelectronic reduction step at −0.52 V (relative to s.h.e.). This relatively low value indicates that the N_2S_2 ligand is better able to stabilise the lower oxidation state of nickel than the more often studied cyclic tetra-amine ligands.[24] Using the related *N*-methylated 15-membered N_2S_3 monocycle[25] L^{6c} a dark blue nickel complex may also be isolated which exhibits a one-electron reduction wave at −0.30 V (relative to s.h.e.), indicative of further stabilization of the nickel(I) complex. The nickel(II) complex of L^{1c} has also been characterised by fast-atom bombardment (f.a.b.) mass spectrometry.[26] Positive-ion spectra recorded in a glycerol matrix showed peaks at *m/z* 292 due to the cation $[Ni(L^{1c})]^{+\cdot}$ and at 391 due to this cation plus one perchlorate. Theoretical and experimental isomer distributions showed good agreement. It was also possible to examine the negative-ion f.a.b. spectrum using thioglycerol as a matrix material. In this case a peak due to the cation with two perchlorate counterions at *m/z* 492 was observed which again showed good agreement with the theoretical isomer distribution (Figure 3). The ^1H n.m.r. spectrum of the nickel complex in CD_3CN shows broadened absorptions for the ligand protons and the electronic absorption spectrum in propylene carbonate contains two weak bands at 392 and 622 nm. It is evident that the nickel complex is paramagnetic with a high-spin d^8 configuration similar to several related polyazamacrocyclic complexes.[27]

Reaction of L^{1c} with the dimeric complex $[\{Rh(bhd)Cl\}_2]$ (bhd = bicyclo[2.2.1]hepta-2,5-diene) in dichloromethane followed by treatment with $NaBF_4$ gave a bright yellow cationic rhodium–diene complex (see Experimental section) which was characterised by elemental analysis and ^1H n.m.r. This diene complex, in which the two sulphurs presumably function as a *cis* chelate,[28] is remarkably stable to oxidative addition of hydrogen. The bhd could not be removed by hydrogenation[29] in methanol at 25 atm and 50 °C.

Finally L^{1c} forms a colourless crystalline complex on reaction with silver nitrate. The ^{13}C n.m.r. spectrum revealed only three resonances so that the silver ion is symmetrically disposed above the macrocyclic ring in solution. In the ^1H n.m.r. spectrum the geminal CH_2N protons are rendered diastereotopic by silver ion complexation forming a complex ABC_2 multiplet with $\Delta\delta_{AB}$ = 0.7 p.p.m.

Dinuclear Complexes of the Macrotricyclic Ligand L^2.—The cylindrical macrotricycle L^2 forms dinuclear complexes of Cu^{II}, Ni^{II}, and Ag^I, to which the dinuclear cryptate structure schematically represented by (II) may be assigned. L^2 forms the violet dinuclear copper(II) cryptate complex $[Cu_2(L^2)]^{4+}$, in which the two copper atoms are bound inside the macrotricyclic cavity with a Cu–Cu distance of 5.62 Å.[11,20] Each copper cation is in a distorted tetragonal pyramid environment with the cation



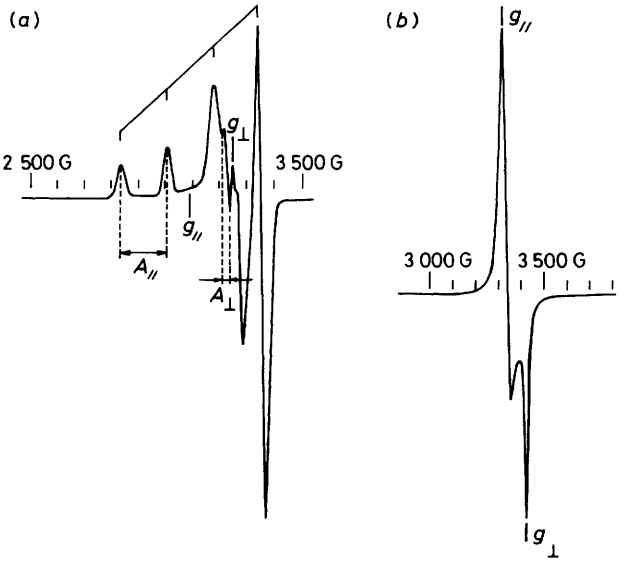


Figure 2. E.s.r. spectra of $[Cu(L^{1c})][ClO_4]_2$: (*a*) frozen solution [propylene carbonate–chloroform (1:1)] at −150 °C ($g_{\parallel}$ = 2.136, $g_{\perp}$ = 2.058, $A_{\parallel}$ = 0.015 cm^{-1}, $A_{\perp}$ = 0.0025 cm^{-1}); (*b*) powder spectrum at 25 °C ($g_{\perp}$ = 2.047, $g_{\parallel}$ = 2.112)

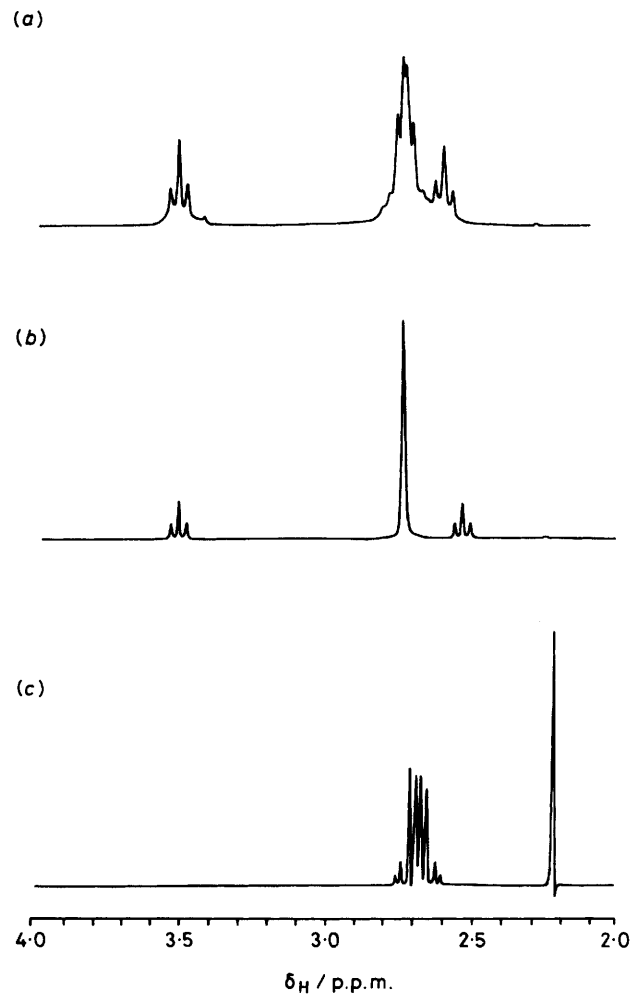


Figure 1. 200-MHz ^1H N.m.r. spectra of (*a*) L^3, (*b*) L^2, and (*c*) L^{1c} in $CDCl_3$

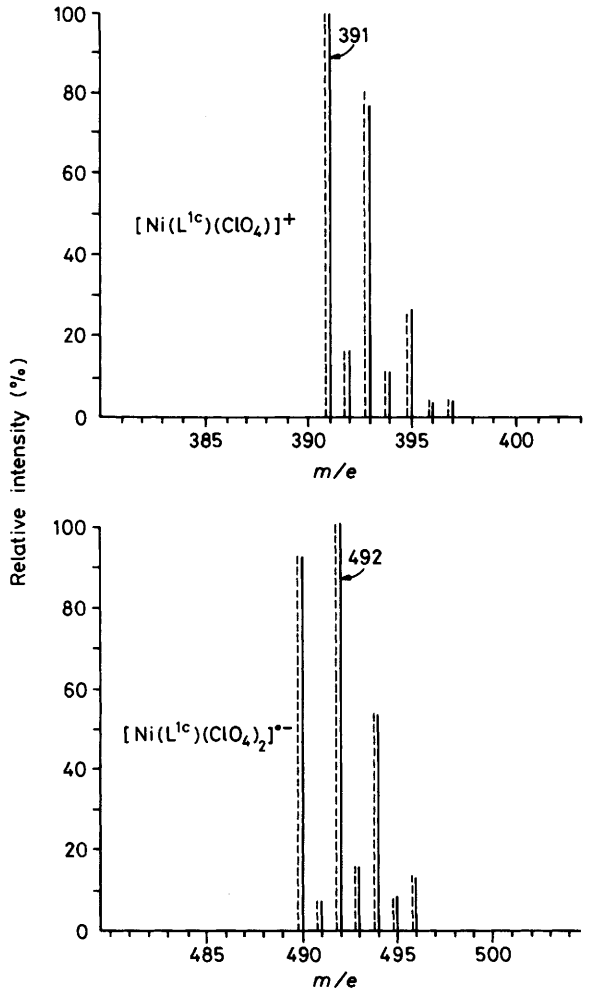


Figure 3. Fast-atom bombardment mass spectrum of $[Ni(L^{1c})][ClO_4]_2$: (*a*) positive-ion mode recorded in glycerol; (*b*) negative-ion mode recorded in thioglycerol: (——) experimental, (– – –) calculated

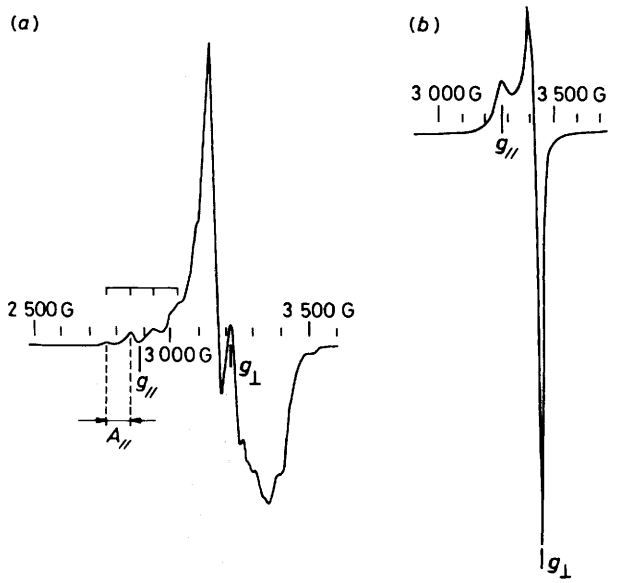


Figure 4. E.s.r. spectra of $[Cu_2(L^2)][ClO_4]_4$: (*a*) frozen solution [chloroform–propylene carbonate (1:1)] at −150 °C ($A_{||}$ = 0.008 cm^{-1}); (*b*) powder spectrum at 25 °C

lying 0.34 Å out of the N_2S_2 plane towards the axial oxygen atom. Cyclic voltammetric studies have revealed that the two redox centres behave independently, undergoing simultaneous reversible monoelectronic reduction at $E_{\frac{1}{2}}$ = +0.445 V (relative to s.h.e.),[9] a potential similar to that of type 3 copper sites in proteins.[23] The frozen solution e.s.r. spectrum, recorded at −150 °C, shows the small molecular $A_{||}$ value (0.008 cm^{-1}) expected for a triplet state resulting from the two identical copper(II) centres in the dimer.[10] The powder and frozen solution e.s.r. spectra are shown in Figure 4. Variable-temperature magnetic susceptibility measurements demonstrated that the two copper atoms are in fact coupled antiferromagnetically with an exchange term J = −54.5 cm^{-1}.[10] Addition of copper(II) perchlorate to L^2 (2:1) in propylene carbonate–chloroform (1:1) gave a violet solution with $\lambda_{max.}$ at 565 nm. The band at 565 nm is associated with the ligand-field transition ($d \longrightarrow d^*$)[30] while the other major band at 375 nm is a ligand-to-metal charge-transfer band [$\sigma_S \longrightarrow Cu^{2+}$].[31] pH-Metric titrations gave an overall stability constant of log β_2 = 18.5 in aqueous solution for the formation of the dinuclear copper cryptate.[32]

The ligand L^2 also forms a purple dinuclear nickel(II) complex in which the two nickel centres appear to behave independently during cyclic voltammetry, with $E_{\frac{1}{2}}$ = −0.54 V (s.h.e.) for the double monoelectronic reduction Ni^{2+}–Ni^{+}. Like the copper complexes of L^2, the nickel centres behave independently consistent with their large separation (≥5.5 Å). The dinuclear Cu^{II} and Ni^{II} complexes of L^2 may be regarded as *dielectronic receptors* which are able to exchange two electrons simultaneously. The analogous dinickel(II) complex of L^7 with two N_2S_3 cycles behaves as a (2 + 2) *tetraelectronic receptor* which exhibits two dielectronic reduction waves in propylene carbonate at −0.28 and −1.29 V (s.h.e.) giving respectively the dinickel(I) and dinickel(0) complexes.

Finally L^2 forms a disilver(I) cryptate in dichloromethane–acetonitrile (1:2). ^{13}C N.m.r. reveals only four resonances for this complex in D_2O, in agreement with a symmetrical structure in which both silver ions are bound within the macrotricyclic cavity. By analogy with the reported crystal structure for the disilver complex of the analogous ligand L^8,[33] presumably each silver atom sits on top of one of the lateral N_2S_2 rings. This disilver cryptate has been further characterised by fast-atom bombardment mass spectrometry.[25] In the positive-ion mode, using a glycerol matrix, peaks were observed at 830 for $[Ag_2(L^2)(NO_3)]^+$, at 768 for $[Ag_2(L^2)]^{++}$, and at 661 for $[Ag(L^2)]^+$. The observed and calculated isomer distributions showed good agreement.

In conclusion the 12-membered N_2S_2 and the 15-membered N_2S_3 macrocyclic subunits have proved to be versatile ligands for transition-metal ions, binding particularly well to relatively 'soft' cations. Complexation studies of the type described herein are the first steps towards investigating new chemical processes involving two or more metal cations arranged inside a macropolycyclic ligand.

Experimental

Reactions were carried out under an inert atmosphere, using nitrogen or argon purified by sequential passage through concentrated H_2SO_4, KOH pellets, and glass wool. Commercial solvents were distilled prior to use from an appropriate drying agent according to standard procedures.[34] Proton n.m.r. spectra were recorded using either a Bruker WP200 (200.13 MHz) or a Bruker WH360 spectrometer (360.13 MHz); carbon-13 spectra were recorded on either a Bruker WP200 (50.33 MHz) or a Varian XL100 spectrometer (25.8 MHz). Chemical shifts are given in p.p.m. relative to $SiMe_4$. Electronic spectra were obtained in the stated solvent on a Varian-Cary 118C spectrophotometer [$\lambda_{max.}$ in nm and ε(dm^3 mol^{-1} cm^{-1}) in parentheses]. Infrared spectra were recorded as Nujol mulls or in the stated solvent using a Perkin-Elmer 297 spectrophotometer. Mass spectra were recorded on LKB9000S and Thomson THW208 spectrometers. Fast-atom bombardment spectra were obtained on a Kratos MS8ORF instrument. Conductivities were measured on a Portland Electronics P335 conductivity meter. Cyclic voltammetry was performed using a Bioanalytical Systems CV-5 voltammograph using a glassy carbon or platinum working electrode.

$S(CH_2COCl)_2$ was prepared from $S(CH_2CO_2H)_2$ using thionyl chloride.[35]

1,5-Diamino-3-thiapentane may be prepared by reported methods[36,37] but is synthesised more efficiently by the following procedure. To 2-aminoethanethiol (76 g, 1.0 mol) in absolute ethanol (400 cm^3) was added aziridine (40 g, 1.0 mol) and the mixture stirred at room temperature (4 h). After standing overnight ethanol was removed under reduced pressure and the residue distilled *in vacuo* to give a colourless liquid (100 g, 83%), b.p. 70 °C (0.1 mmHg) (lit. 112—116 °C, 12 mmHg),[36] which was stored under nitrogen at −30 °C.

5,9-*Dioxo*-1,7-*dithia*-4,10-*diazacyclododecane*, L^{1a}.—To dry toluene (2 dm^3) in a high-dilution apparatus[19] cooled to −5 °C in an ice–salt bath, was added synchronously over a period of 12 h a solution of 1,5-diamino-3-thiapentane (20.0 g, 0.167 mol) in toluene (500 cm^3) and a solution of $S(CH_2COCl)_2$ (16.0 g, 0.083 mol) in toluene (500 cm^3) with vigorous stirring. The resulting suspension was filtered, the residues washed thoroughly with hot chloroform (8 × 200 cm^3), and the combined filtrates evaporated under reduced pressure to give L^{1a} as a white solid. This was washed with chloroform (5 × 5 cm^3) and toluene (2 × 10 cm^3) and dried *in vacuo* (0.2 mmHg), 14.7 g (76%), m.p. 196—197 °C (Found: C, 41.1; H, 6.05; N, 12.0. $C_8H_{14}N_2O_2S_2$ requires C, 41.0; H, 6.00; N, 12.0%); *m/e* 234 (M^+), 217, 201, 191, 144, and 132.

1,7-*Dithia*-4,10-*diazacyclododecane*, L^{1b}.—To a suspension of the dilactam L^{1a} (5.0 g, 21.4 mmol) in dry tetrahydrofuran (200 cm^3) a solution of BH_3·SMe_2 in tetrahydrofuran (10 cm^3, 40

mmol) was added by syringe under argon. After refluxing for 3 h, methanol (50 cm^3) was added slowly to the cooled suspension and solvent removed under reduced pressure. The white residue was dissolved in methanol and refluxed with hydrochloric acid (55 cm^3, 2 mol dm^{-3}) for 4 h. After removal of solvents under reduced pressure, the residue was shaken with chloroform (100 cm^3) and KOH solution (100 cm^3, 2 mol dm^{-3}) and the aqueous layer washed with chloroform (4 × 50 cm^3). The combined organic extracts were dried over anhydrous sodium sulphate, filtered, and evaporated under reduced pressure to give a residue which was chromatographed on basic alumina (Merck, activity II—III), eluting with toluene. Evaporation of the toluene eluates gave a residue which was recrystallised from hexane–chloroform to give L^{1b} as white needles, 4.0 g (94%), m.p. 78—79 °C (Found: C, 46.4; H, 8.80; N, 13.6. $C_8H_{18}N_2S_2$ requires C, 46.6; H, 8.75; N, 13.6%); *m/e* 206 (M^+), 207 (M^+ + 1), 173, 145, 138, and 116; δ_H ($CDCl_3$) 2.10 (2 H, br s, NH), 2.42 (16 H, br s, CH_2N + CH_2S); δ_C ($CDCl_3$) 32.6 (CH_2S), 40.2 (CH_2N).

4,16-*Dioxa*-10,22,27,32-*tetrathia*-1,7,13,19-*tetra-azatricyclo*-[17.5.5.5^{7,13}]*tetratriacontane*, L^2.—To dry toluene (1.5 dm^3) in a high-dilution apparatus[19] cooled to −5 °C was added, simultaneously over a period of 9 h, a solution of 1,7-dithia-4,10-diazacyclododecane (L^{1b}) (1.24 g, 6 mmol) and triethylamine (1.21 g, 12 mmol) in dry toluene (200 cm^3) and a solution of $O(CH_2COCl)_2$ (1.03 g, 6 mmol) in toluene (200 cm^3). After stirring for a further 2 h, the suspension was filtered and the residue washed with toluene (3 × 50 cm^3). Evaporation of the combined filtrates gave a white solid of low solubility, the tetramide L^{5a}, which was used without further purification for the reduction step. It was suspended in dry tetrahydrofuran (25 cm^3) and a solution of BH_3·thf in tetrahydrofuran (40 cm^3, 48 mmol) was added under argon. The mixture was refluxed (18 h) and excess borane destroyed by careful addition of water and methanol (1:1, 20 cm^3). After evaporation to dryness the residue was hydrolysed with hydrochloric acid (70 cm^3, 6 mol dm^{-3}) refluxing for 4 h, then solvent was removed under reduced pressure. After basification with excess aqueous KOH, the mixture was extracted with chloroform (8 × 40 cm^3), and the extracts dried over anhydrous sodium sulphate. Filtration and removal of solvent under reduced pressure gave a white solid residue (1.3 g) which was chromatographed on basic alumina (Merck, activity II—III), eluting with dichloromethane, and from which two homogeneous products were separated: L^2, 520 mg (32%); L^3 140 mg (8.5%).

L^2: R_f 0.62 [Al_2O_3; CH_2Cl_2–MeOH (98 : 2)], m.p. 161—162 °C (Found: C, 51.9; H, 8.90; N, 10.0; S, 23.0. $C_{24}H_{48}N_4O_2S_4$ requires C, 52.2; H, 8.70; N, 10.1; S, 23.2%); *m/e* 552 (M^+), 519, 424, 406, 390, and 372; δ_H ($CDCl_3$) 2.57 (8 H, t, CH_2N), 2.77 (32 H, br s, CH_2S + CH_2N), 3.53 (8 H, t, CH_2O); δ_C ($CDCl_3$) 27.4 (CH_2S), 54.9 (CH_2N), 55.4 (CH_2N), 69.5 (CH_2O).

L^3: R_f 0.42 [Al_2O_3; MeOH–CH_2Cl_2 (2:98)], oil; *m/e* 828 (M^+), 795, 709, 553, 277, and 275; δ_H ($CDCl_3$) 3.51 (12 H, t, CH_2O, *J* 5.7 Hz), 2.79—2.67 (48 H, m, CH_2N + CH_2S), 2.60 (12 H, t, CH_2N); δ_C ($CDCl_3$) 28.8, 54.7, 55.3, 69.8.

4,10-*Dimethyl*-1,7-*Dithia*-4,10-*diazacyclododecane*, L^{1c}.—(1,7-Dithia-4,10-diazacyclododecane L^{1b} (412 mg, 2.0 mmol) was heated on a steam-bath with formaldehyde (0.3 cm^3, 30% solution) and formic acid (0.32 cm^3, 8 mmol) for 4 h. Hydrochloric acid (1.0 mol dm^{-3}, 5 cm^3) was added to the cooled solution and the solution was evaporated to dryness under reduced pressure; the colourless solid residue was dissolved in water (3 cm^3) and the pH adjusted to 10 with KOH solution. After extraction into dichloromethane and drying ($MgSO_4$), solvent was removed to give a colourless residue which was recrystallised from chloroform–hexane to give colourless cubes of L^{1c} (450 mg, 96%), m.p. 67—68 °C (Found: C, 51.2; H, 9.40; N, 11.9. $C_{10}H_{22}N_2S_2$ requires C, 51.3; H, 9.40; N, 12.0%); δ_H ($CDCl_3$) 2.7 (16 H, m, CH_2N + CH_2S), 2.23 (6 H, s, CH_3N); δ_C ($CDCl_3$) 56.7 (CH_2N), 43.2 (CH_3N), 28.1 (CH_2S); *m/e* 234 (M^+), 235 (M^+ + 1), 201, 151, 104, 102, and 70.

1,4,10-*Trithia*-7,13-*diazacyclopentadecane*, L^{6b}.—To dry toluene (1 dm^3) in a high-dilution apparatus[19] cooled to 0 °C was added, synchronously over a period of 12 h, a solution of 1,5-diamino-3-thiapentane (15.0 g, 0.125 mol) in toluene (500 cm^3) and a solution of 3,6-dithiaoctanedioyl dichloride (15.4 g, 0.062 mol) in toluene (500 cm^3) with vigorous stirring. The resulting suspension was filtered, the residues washed thoroughly with chloroform, and the combined filtrates evaporated under reduced pressure to give a colourless solid (12.0 g, 66%) which was used directly without further purification. To the dilactam L^{6a} in thf (250 cm^3) a solution of BH_3·SMe_2 (15 cm^3, 150 mmol) in thf (50 cm^3) was added by syringe under argon and the mixture refluxed (3 h). To the cooled suspension was added methanol (100 cm^3) and solvent removed under reduced pressure. The residue was suspended in methanol (50 cm^3) and refluxed with hydrochloric acid (10 cm^3, 6 mol dm^{-3}) for 3 h. After removal of solvents the residue was taken up in water (100 cm^3) and basified with solid KOH, and the aqueous layer extracted with chloroform (3 × 100 cm^3). The combined organic extracts were dried over anhydrous sodium sulphate, filtered, and evaporated under reduced pressure to give a residue which was chromatographed on basic alumina (Merck, activity II—III), eluting with chloroform–toluene (1 : 1). Evaporation of the eluates gave a colourless solid (10.0 g, 93%), m.p. 70—72 °C (Found: C, 44.9; H, 8.15; N, 10.4. $C_{10}H_{22}N_2S_3$ requires C, 45.1; H, 8.25; N, 10.5%); *m/e* 266 (M^+), 267 (M^+ + 1), 233, 205, 174, 152; δ_H ($CDCl_3$) 2.27 (2 H, br s, NH), 2.93 (20 H, br s, CH_2N + CH_2S).

4,19-*Dioxa*-10,13,25,28,33,38-*hexathia*-1,7,16,22-*tetra-azatricyclo*[20.8.5.5^{7,16}]*tetracontane*, L^7.—The sequence of reactions was conducted directly through to the final compound L^7 using the crude intermediates, which were sufficiently pure. To a solution of L^{6b} (4.0 g, 15.3 mmol) in chloroform (150 cm^3) was added in portions 3-oxaglutaric anhydride (3.8 g, 33 mmol) and the mixture refluxed (1 h). After removal of solvent under reduced pressure, the residue was extracted with hot methanol (2 × 200 cm^3) to yield a colourless oil (7.6 g), L^{6d}, after evaporation of the methanol. The diacid L^{6d} was dissolved in dry pyridine (250 cm^3) and bis(*p*-nitrophenyl) sulphite[38] (10.5 g, 32.4 mmol) added, keeping the solution at 3 °C (20 h). After removal of pyridine the residue was taken up in chloroform (100 cm^3), washed with KOH solution (2 × 50 cm^3, 2 mol dm^{-3}) and hydrochloric acid (2 × 50 cm^3, 2 mol dm^{-3}), and solvent removed under reduced pressure to give a yellow foam (5.9 g, 55%), L^{6e}, which was used directly without further purification. To refluxing pyridine (500 cm^3) was added synchronously over 2 h a solution of L^{6e} (1.5 g, 2.1 mmol) in pyridine (50 cm^3) and a solution of L^{6b} (559 mg, 2.1 mmol) in pyridine (50 cm^3). After removal of solvent under reduced pressure the residue was taken up in hot chloroform (3 × 100 cm^3) and after evaporation of solvent was chromatographed on alumina. Eluting with dichloromethane–methanol (10:1) yielded a colourless solid (700 mg, 50%) of low solubility, the 2,6,17,21-tetra-amide corresponding to L^7, which was suspended in dry thf (100 cm^3). A solution of BH_3·SMe_2 (1.0 cm^3, 10 mmol) in thf (10 cm^3) was added and the mixture refluxed under nitrogen (1 h). After careful addition of methanol (5 cm^3) to the cooled solution, solvents were removed under reduced pressure and the residue hydrolysed by refluxing with hydrochloric acid (25 cm^3, 6 mol dm^{-3}) for 4 h. Following evaporation to dryness and basification with excess KOH solution (20 cm^3, 2 mol dm^{-3}), the

solution was extracted with chloroform (5 × 50 cm^3) and the extracts dried over anhydrous sodium sulphate. Filtration and evaporation of solvent gave a colourless residue (600 mg) which was chromatographed on basic alumina (Merck, activity II–III). Eluting with toluene–chloroform (1:1) gave a colourless solid which was recrystallised from dichloromethane–heptane (1:1) to give colourless crystals of L^7 (350 mg, 50%), m.p. 144–146 °C (Found: C, 49.9; H, 8.15; N, 8.25. $C_{28}H_{56}N_4O_2S_6$ requires C, 50.0; H, 8.35; N, 8.35%); δ_H ($CDCl_3$) 3.50 (8 H, t, CH_2O, J = 5 Hz), 2.89–2.58 (48 H, m, CH_2N + CH_2S); δ_C ($CDCl_3$) 30.5, 31.4, 32.8 (CH_2S); 55.0, 55.6, 56.1 (CH_2N); 70.3 (CH_2O); *m/e* 672 (M^+).

Complexes of 4,10-*Dimethyl*-1,7-*dithia*-4,10-*diazacyclododecane*, L^{1c}.—*Silver*(I) *complex*, $[Ag(L^{1c})][NO_3]$. To a solution of silver nitrate (17.0 mg, 0.1 mmol) in dry acetonitrile (1 cm^3) was added a solution of L^{1c} (23.4 mg, 0.1 mmol) in dichloromethane–acetonitrile (1:1, 2 cm^3). The colourless mixture was rapidly filtered and held at −25 °C in the dark. After 36 h, colourless crystals were collected by filtration, washed with dichloromethane (2 × 2 cm^3), and dried *in vacuo* (0.05 mmHg) (34 mg, 83%) (Found: C, 29.7; H, 5.45; N, 10.4. $C_{10}H_{22}AgN_3O_3S_2$ requires C, 29.9; H, 5.45; N, 10.4%); δ_C (25.1 MHz, CD_3OD), 55.3 (CH_2N), 44.8 (CH_3N), 31.5 (CH_2S); δ_H (200 MHz, CD_3OD), 2.95 (12 H, m, CH_2S + CHN), 2.35 (6 H, s, CH_3N), 2.25 (4 H, m, CHN); $\lambda_{max.}$ (H_2O) 260 (800).

Nickel(II) *complex*, $[Ni(L^{1c})][ClO_4]_2$. A solution of the ligand L^{1c} (23.4 mg, 0.1 mmol) in dry chloroform (0.5 cm^3) was added with stirring at room temperature to a solution of nickel perchlorate hexahydrate (50 mg, 0.14 mmol) in dry acetonitrile (2 cm^3). After 0.5 h, methanol (0.5 cm^3) was added and the green solution filtered and left to evaporate slowly. A green microcrystalline solid was collected by filtration, washed with chloroform (2 × 1 cm^3) and cold methanol (2 × 0.3 cm^3), and dried *in vacuo* (0.1 mmHg) (44 mg, 90%) (Found: C, 24.3; H, 4.70; N, 5.60. $C_{10}H_{22}Cl_2N_2NiO_8S_2$ requires C, 24.4; H, 4.45; N, 5.70%); $\lambda_{max.}$ (propylene carbonate), 392 (54); 622 (25); *m/e* (f.a.b. positive ion, glycerol) 391 $[Ni(L^{1c})(ClO_4)]^+$, 292 $[Ni(L^{1c})]^{\cdot+}$; $E_{\frac{1}{2}}^{c}$ [propylene carbonate, I = 0.1 mol dm^{-3} (NEt_4ClO_4)] −0.52 V (*vs.* s.h.e.); Λ (× 10^4) = 233 S m^2 mol^{-1} (0.001 mol dm^{-3}, H_2O).

Zinc(II) *complex*, $[Zn(L^{1c})][ClO_4]_2$. A solution of zinc perchlorate hexahydrate (30 mg, 0.081 mmol) in dry acetone (2 cm^3) was added to an acetone (1 cm^3) solution of the ligand L^{1c} (15 mg, 0.064 mmol) and the mixture stirred (0.5 h) at room temperature. After removal of solvent under reduced pressure, the residue was recrystallised from hot water (4 cm^3), giving a white crystalline product, which was collected by filtration and dried *in vacuo* (0.08 mmHg), 31 mg (91%) (Found: C, 22.5; H, 4.95; N, 5.50. $C_{10}H_{22}Cl_2N_2O_8S_2Zn{\cdot}2H_2O$ requires C, 22.6; H, 4.95; N, 5.30%); δ_H (200 MHz, D_2O) 2.94 (8 H, m, CH_2N), 2.79 (8 H, m, CH_2S); 2.34, 2.22 (6 H, s + s, NCH_3).

(*Bicyclo*[2.2.1]*hepta*-2,5-*diene*)(4,10-*dimethyl*-1,7-*dithia*-4,10-*diazacyclododecane*)*rhodium*(I) *tetrafluoroborate*. The ligand L^{1c}, as a solid (23.4 mg, 0.1 mmol), was added to a solution of $[\{Rh(bhd)Cl\}_2]$ (23.05 mg, 0.05 mmol) in dry dichloromethane (3 cm^3) and the mixture stirred (0.1 h) at room temperature. Excess $NaBF_4$ (200 mg) was then added; after filtration the solution was reduced in an argon stream and the resulting solution (1 cm^3) slowly added dropwise to dry ether (8 cm^3). The resulting bright yellow precipitate was filtered off, washed with ether (2 × 2 cm^3), and dried *in vacuo* (0.1 mmHg), 50 mg (97%) (Found: C, 39.5; H, 6.02; N, 5.75. $C_{17}H_{30}BF_4N_2RhS_2$ requires C, 39.5; H, 5.85; N, 5.45%); δ_H (250 MHz, CD_2Cl_2), 3.60 (2 H, br s, CH allylic), 3.25 (4 H, m, bound olefinic), 3.0–2.3 (16 H, m, CH_2N + CH_2S), 2.07 (6 H, s, CH_3N), 1.16 (2 H, s, CH_2).

Copper(II) *complex*, $[Cu(L^{1c})][ClO_4]_2$. To a solution of the ligand L^{1c} (46.4 mg, 0.2 mmol) in dry chloroform (1 cm^3) was added a solution of copper(II) perchlorate (100 mg) in methanol (2 cm^3) and the dark blue solution allowed to stand for 24 h. A dark blue precipitate formed, which was filtered off, washed with methanol (2 × 1 cm^3) and chloroform (2 × 1 cm^3), and dried *in vacuo* (0.06 mmHg), 82 mg (87%) (Found: C, 24.1; H, 4.50; N, 5.75. $C_{10}H_{22}Cl_2CuN_2O_8S_2$ requires C, 24.4; H, 4.45; N, 5.70%); $\lambda_{max.}$ (H_2O) 370 (5 000), 605 (1 200); $E_{\frac{1}{2}}$ {propylene carbonate, I = 0.1 mol dm^{-3} $[N(C_4H_{13})_4ClO_4]$} + 0.495 V (*vs.* s.h.e.).

Complexes of 4,16-*Dioxa*-10,22,27,32-*tetrathia*-1,7,13,19-*tetra-azatricyclo*[17.5.5.$5^{7,13}$]*tetratriacontane*, L^2.—*Disilver*(I) *complex*, $[Ag_2(L^2)][NO_3]_2$. To a solution of silver nitrate (8.5 mg, 0.05 mmol) in dry acetonitrile (1 cm^3) was added a solution of L^2 (13.8 mg, 0.025 mmol) in dry dichloromethane (0.5 cm^3) and the mixture stirred (0.1 h) at 273 K. After filtration, the solution was allowed to stand at −25 °C for 48 h in the dark; colourless crystals formed which were filtered off, washed with dichloromethane (2 × 1 cm^3), and dried *in vacuo* (0.1 mmHg). The complex may be recrystallised from warm water, 18 mg (81%) (Found: C, 32.1; H, 5.35; N, 9.45. $C_{24}H_{48}Ag_2N_6O_8S_6$ requires C, 32.3; H, 5.40; N, 9.40%); $\lambda_{max.}$ (H_2O) 296 (620); δ_C (50.3 MHz, D_2O), 68.1 (CH_2O), 53.3 (CH_2N), 51.5 (CH_2N ring), 30.3 (CH_2S); δ_H (200 MHz, CD_3OD), 3.75 (8 H, t, J = 4.8 Hz, CH_2O), 2.70 (16 H, m, CH_2S), 3.0–2.9 (24 H, m, CH_2N).

Dinickel(II) *complex*, $[Ni_2(L^2)][ClO_4]_4$. To a solution of nickel perchlorate (30 mg, 0.084 mmol) in dry acetone (1 cm^3) was added a solution of L^2 (10 mg, 0.018 mmol) in dry dichloromethane (0.5 cm^3). After addition of water (0.5 cm^3), the mixture was warmed to 40 °C, acetonitrile (0.5 cm^3) added, and the filtered solution allowed to stand; a green microcrystalline product was formed, collected by filtration, washed with water (2 × 1 cm^3), and dried *in vacuo* (0.1 mmHg) (16 mg, 81%) (Found: C, 26.3; H, 4.50; N, 5.20. $C_{24}H_{48}Cl_4N_4Ni_2O_{18}S_4{\cdot}H_2O$ requires C, 26.6; H, 4.60; N, 5.15%); $\lambda_{max.}$ 566 (30), 380 (120); $E_{\frac{1}{2}}^{c}$ [propylene carbonate, I = 0.1 mol dm^{-3} (NEt_4ClO_4)] −0.54 V (*vs.* s.h.e.).

Dicopper(II) *complex*, $[Cu_2(L^2)][ClO_4]_4$. To a solution of L^2 (30.4 mg, 0.05 mmol) in chloroform–methanol (1:1, 2 cm^3) was added copper(II) perchlorate (40 mg) in methanol (1 cm^3). After standing overnight, an intense violet microcrystalline solid was collected by filtration, washed with chloroform (3 × 1 cm^3) and methanol (2 × 1 cm^3), and dried *in vacuo* (0.1 mmHg), 40 mg (92%) (Found: C, 25.7; H, 4.90; N, 5.00. $C_{24}H_{56}Cl_4Cu_2N_4O_{18}S_4$ requires C, 25.4; H, 4.95; N, 4.95%); $\lambda_{max.}$ [propylene carbonate–chloroform (1:1)], 375 (3 500), 565 (1 200); $E_{\frac{1}{2}}^{c}$ [H_2O, I = 0.1 mol dm^{-3} (KCl)] + 0.445 V (*vs.* s.h.e.).

Nickel(II) *Complex of* 7,13-*Dimethyl*-1,4,10-*trithia*-7,13-*diazacyclopentadecane*, $[Ni(L^{6c})][ClO_4]_2$.—To a solution of nickel perchlorate hexahydrate (100 mg, 0.28 mmol) in dry acetonitrile (3 cm^3) was added dropwise a chloroform (2 cm^3) solution of L^{6c} (14.7 mg, 0.05 mmol). Water (0.5 cm^3) was added and the mixture warmed to 40 °C, filtered, and left to stand for 72 h; a dark blue crystalline solid formed which was filtered off, washed with water (2 × 2 cm^3) and chloroform (2 × 3 cm^3), and dried *in vacuo* (0.05 mmHg) (25 mg, 92%) (Found: C, 26.0; H, 4.80; N, 5.00. $C_{12}H_{26}Cl_2N_2NiO_8S_3$ requires C, 26.1; H, 4.70; N, 5.05%); $\lambda_{max.}$ (propylene carbonate) 596 (26); $E_{\frac{1}{2}}^{c}$ [propylene carbonate, I = 0.1 mol dm^{-3} (NEt_4ClO_4)] −0.30, −1.32 V (*vs.* s.h.e.).

Dinickel(II) *Complex of* 4,19-*Dioxa*-10,13,25,28,33,38-*hexathia*-1,7,16,22-*tetra-azacyclo*[20.8.5.$5^{7,16}$]*tetracontane*, $[Ni_2(L^7)][ClO_4]_4$.—To a solution of nickel perchlorate (50 mg, 0.14 mmol) in dry acetonitrile (2 cm^3) was added a solution of L^7 (15 mg, 0.022 mmol) in dichloromethane (1 cm^3). After filtration the solution was allowed to stand for several days to

give a blue crystalline solid, which was filtered off, washed with water (2 × 1 cm^3) and dichloromethane (2 × 1 cm^3), and dried *in vacuo* (0.1 mmHg) (22 mg, 85%) (Found: C, 27.8; H, 5.10; N, 5.00. $C_{28}H_{56}Cl_4N_4Ni_2O_{18}S_6$ requires C, 28.3; H, 4.75; N, 4.75%); $\lambda_{max.}$ (dimethyl formamide) 754, 663, 392; $E_{\frac{1}{2}}^{c}$ [propylene carbonate, I = 0.1 mol dm^{-3} (NEt_4ClO_4)] −0.28, −1.29 V (*vs.* s.h.e.).

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