Carbon-functionalized 1,4,7-Trithiacyclononanes: Synthesis, Molecular Mechanics and Co-ordination Chemistry†

Raymond J. Smith,[a] **Spencer N. Salek,**[a] **Michael J. Went,**[a] **Philip J. Blower**[*,a]
and Neil J. Barnard[b]
[a] *Biological Laboratory and Chemical Laboratory, The University, Canterbury CT2 7NJ, UK*
[b] *Department of Chemistry, University of Essex, Colchester CO4 3SQ, UK*

A series of functionalized analogues of 1,4,7-trithiacyclononane has been synthesized and the effects of functionalization on their co-ordination chemistry investigated. The substituents were introduced *via* substituted 1,2-dibromopropanes, by cyclization with 3-thiapentane-1,5-dithiolate in the form of its molybdenum complex $[Mo(CO)_3(SCH_2CH_2SCH_2CH_2S)]^{2-}$. The functionalized macrocycles were then displaced from the metal by additional 3-thiapentane-1,5-dithiolate. A series of complexes $[ML_2]^{n+}$ (M = Ag, Hg, Cu, Ni, Co or Fe; L = 2-methyl-1,4,7-trithiacyclononane, the simplest of the new ligands) was prepared. Spectroscopic and electrochemical studies revealed that any effects of substitution on the ring conformational preferences were not manifested in the stability or electrochemistry of the complexes. Molecular-mechanics calculations suggest that no alterations in conformational preferences are caused by a single substitution. Attempts to synthesize analogues with two vicinal methyl groups yielded only polymeric products.

During the last decade, the macrocyclic thioether ligand 1,4,7-trithiacyclononane, [9]aneS_3, has become the focus of a great deal of interest compared with other linear and macrocyclic polythioethers, largely as a result of its conformational peculiarities.[1] Conformational analysis of polythioethers and polythioether macrocycles has revealed a preference for conformations which maximize the number of *gauche* placements at C–S bonds,[2] even in the absence of macrocyclic constraints,[3] and minimize the number of *gauche* placements at C–C bonds. The compound [9]aneS_3 is too small a macrocycle to possess sufficient flexibility to conform to these preferences. This has implications for both its synthesis and co-ordination chemistry in relation to other polythiamacrocycles. Thus, in the synthesis the ring-closure step must involve a relatively high-energy transition state, since even in the most favourable conformation it must contain a high proportion of *gauche* C–C and *anti* C–S bonds. This poses difficulties in synthesis of the 1,4,7-trithiacyclononane ring which are more severe than for other polythiamacrocycles {*e.g.* 1,4,7,10,13,16-hexathiacyclooctadecane ([18]aneS_6), 1,5,9-trithiacyclododecane, ([12]aneS_3) and 1,4,7-trithiacyclodecanes[1]} culminating in low yields.

However, it is these very conformational constraints which give [9]aneS_3 its exceptional chelating properties, and thus from which interest in it arises. It is widely accepted that the unusual properties of [9]aneS_3 complexes which distinguish them from other macrocyclic thioether complexes are due largely to the endodentate conformation peculiar to the nine-membered ring.[1] In other types of thiamacrocycles the *gauche*/*anti* preferences result in a tendency for the sulfur atoms to be exodentate in the ground-state conformation,[2] so that chelation is thermodynamically hampered by the enthalpy of the necessary ligand reorganization. For [9]aneS_3 complex formation this enthalpic contribution is absent or minimal since the endodentate conformation is the lowest[4,5] (or almost the lowest[5,6]) energy conformation in the solid, solution or gaseous state. As a result, [9]aneS_3 forms late-transition-metal complexes with high stability and unusual structural and electronic properties. These are now well documented in the review literature.[1]

It may be desirable to exploit these properties in the design of molecular devices such as bifunctional chelators and sensors. Whether this possibility is realistic or not depends on the ease of synthesis of multifunctional compounds incorporating the [9]aneS_3 unit, and on whether the necessary modification of these structures is detrimental to its co-ordinating ability, issues which have been addressed for the homologous ten-membered macrocycle.[7,8] Both of these factors could be influenced by substitutional modification of the carbon backbone. Any changes in the thermodynamic accessibility of endodentate conformations may be expected to be manifested in the synthetic yield of the compounds and in the stability, co-ordination number, and oxidation-state preferences of the transition-metal complexes, much as the change in ring size from 9 to 10 and 12 atoms does.[1] We have investigated this through synthesis of a series of substituted [9]aneS_3 compounds, synthesis and spectroscopic/electrochemical studies of their complexes, and molecular-mechanics studies of the free compounds. Some of this work has been reported previously in preliminary form.[9]

Results

Ligand Syntheses.—The synthetic routes to the functionalized [9]aneS_3 compounds L^1–L^7 are shown, and yields reported, in Scheme 1. The compounds were obtained by cyclization of the appropriate 1,2-dibromide with 3-thiapentane-1,5-dithiol. This was achieved by using either a molybdenum tricarbonyl template in acetonitrile[10] (method A, Scheme 3), or by a high-dilution technique (method B, Scheme 4).[11] The first of these methods was found to give higher yields. For example, the methylated analogue L^1 was prepared in 25% yield using method A, whereas using method B a polymeric material was the only product. All of the products obtained from cyclization reactions required silica gel chromatography as part of the work-up to remove 3-thiapentane-1,5-dithiol and other impurities. None of the cyclization reactions gave yields as high as analogous preparations of [9]aneS_3 itself. Attempts to prepare

---

† *Non-SI unit employed:* cal = 4.184 J.

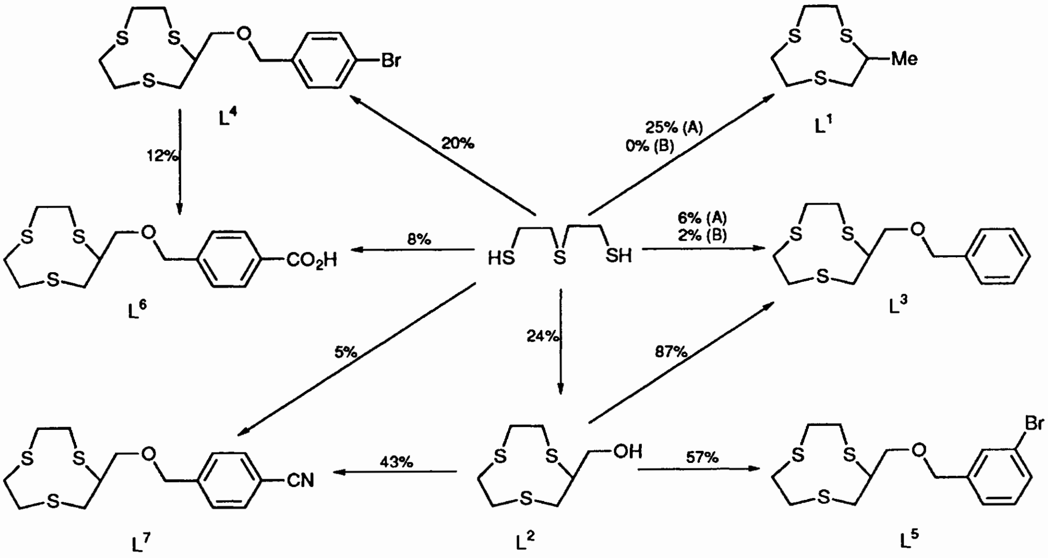
vicinally disubstituted [9]aneS$_3$ derivatives (*e.g.* 2,3-dimethyl-1,4,7-trithiacyclononane) by either route were unsuccessful.

The routes to the substituted 1,2-dibromopropanes and alkenes required in the synthesis are summarized, with yields, in Scheme 2. The 1,2-dibromides were made in racemic form by the addition of dibromine to the corresponding allyl benzyl ethers. The latter were synthesized from allyl alcohol and the required benzyl halide.[12] The preferred route to the *p*-carboxybenzyl derivative was *via* hydrolysis of the *p*-cyanobenzyl derivative. Of the allyl ethers, only the unsubstituted allyl benzyl ether has been previously reported.[13]

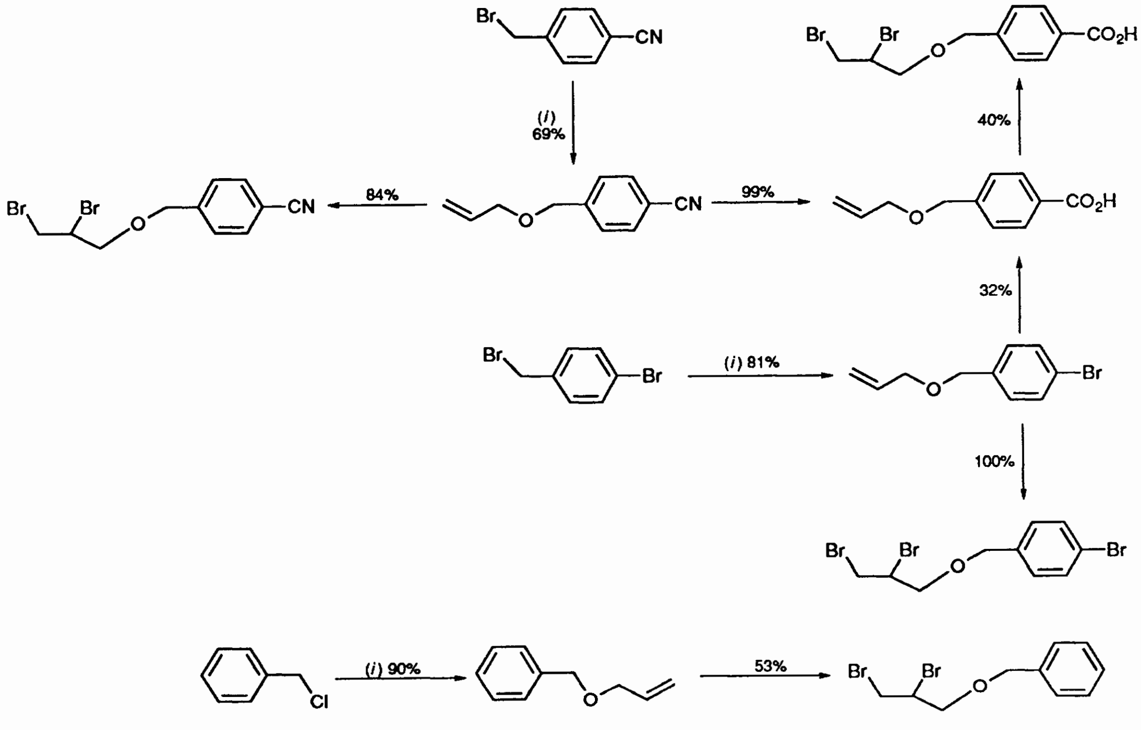
The hydroxyl group of L^2 was used to introduce a wider range of functionality by reaction of its sodium salt with substituted benzyl halides (Scheme 1). Reaction of the sodium salt of L^2 with benzyl chloride produced L^3 in good yield (87%). When ring-substituted (*p*-bromo, *p*-cyano) benzyl halides were employed, however, the yield was substantially reduced. As an alternative (lower-yield) route to the *p*-carboxy-substituted compound L^6 (previously synthesized by direct cyclization, method A, see above), the Grignard reagent of L^4 was treated with carbon dioxide.

Synthesis of Complexes.—The methyl and hydroxymethyl derivatives of [9]aneS$_3$ were used to prepare complexes of the type [ML$_2$]$^{n+}$ (M = Ag, Hg, Ni, Co, Fe or Cu) and of formula [MLCl$_3$] (M = Ru or Au), using methods adapted from those used for the parent [9]aneS$_3$ complexes. In general, a solution of the metal tetrafluoroborate, perchlorate, or trifluoromethanesulfonate was added to a solution containing a two-fold excess of the macrocycle in nitromethane, ethanol, methanol or acetonitrile. All complexes gave satisfactory elemental analysis.

Electronic Spectra.—The electronic spectra of the complexes, determined in acetonitrile except where comparison with the



Scheme 1 Synthesis of *C*-functionalized 1,4,7-trithiacyclononanes L^1–L^7. For reagents and conditions see text

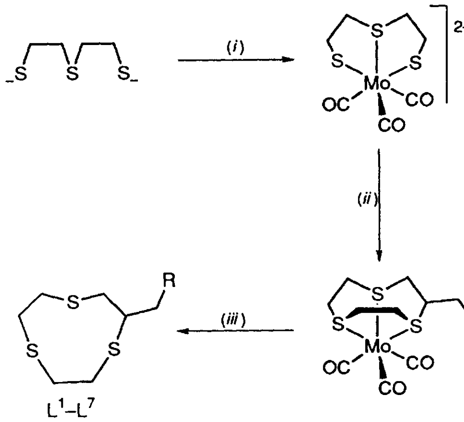


Scheme 2 Synthesis of allyl and 1,2-dibromoalkyl compounds. For reagents and conditions see text. (*i*) Allyl alcohol

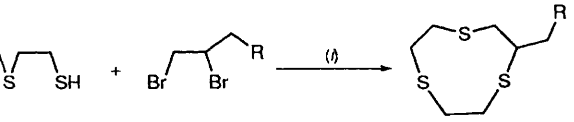
Table 1 Electronic spectral and cyclic voltammetric data for the complexes

Complex	$\lambda_{max}{}^{a}$/nm	ε/dm^3 mol^{-1} cm^{-1}	Colour	$E_{\frac{1}{2}}^{ox\,b,c}$/V	$E_{\frac{1}{2}}^{red\,b,c}$/V
$[AgL^1{}_2]^+$	—	—	White	+0.71^d	—
$[Ag([9]aneS_3)_2]^+$	—	—	White	+0.75^e	—
$[HgL^1{}_2]^{2+}$	231.3	21 835	White	—	—
$[Hg([9]aneS_3)_2]^{2+}$	236.5	16 827	White	—	—
$[CuL^1{}_2]^{2+}$	448.8	7 241	Brown	—	+0.23^f
$[CuL^2{}_2]^{2+}$	446.4	6 842	Brown	n.d.	n.d.
$[Cu([9]aneS_3)_2]^{2+}$	446.4	5 017	Brown	—	+0.21^f
$[NiL^1{}_2]^{2+}$	320.0	15 565	Pink	+1.02^f	−1.14^d
$[Ni([9]aneS_3)_2]^{2+}$	318.5	9 767	Pink	+0.97^f	−1.07^d
$[CoL^1{}_2]^{2+}$	480.0	136	Red	+0.03^f	−0.85^f
$[Co([9]aneS_3)_2]^{2+}$	478.0	93	Red	+0.05^f	−0.90^f
$[FeL^1{}_2]^{2+}$	265.3	22 051	Violet	+1.04^f	—
$[Fe([9]aneS_3)_2]^{2+}$	265.2	14 256	Violet	+0.97^f	—
$[AuCl_2L^1]^+$	n.d.	n.d.	Brown	n.d.	n.d.
$[AuCl_2([9]aneS_3)]^+$	n.d.	n.d.	Brown	n.d.	n.d.
$[RuCl_3L^1]$	n.d.	n.d.	Red-brown	n.d.	n.d.
$[RuCl_3([9]aneS_3)]$	n.d.	n.d.	Red-brown	n.d.	n.d.

n.d. = Not determined. ^{a} In acetonitrile. ^{b} *vs.* ferrocene–ferrocenium. ^{c} In nitromethane. ^{d} Quasi-reversible. ^{e} Irreversible. ^{f} Reversible.



Scheme 3 Molybdenum template method (A) of ring closure for substituted trithiacyclononanes. (*i*) $[Mo(CO)_3(MeCN)_3]$; (*ii*) $RCH_2CHBrCH_2Br$; (*iii*) 3-thiapentane-1,5-dithiolate



Scheme 4 High-dilution method (B) of ring closure for substituted trithiacyclononanes. (*i*) Cs_2CO_3, dimethylformamide (dmf)

literature required use of nitromethane, are reported in Table 1. Introduction of a methyl or hydroxymethyl group into the carbon backbone did not shift the absorption maxima significantly. Only the absorption coefficients are affected, and in all cases these are significantly increased, consistent with the expected relaxation of selection rules upon lowering the symmetry.

Cyclic Voltammetry.—The electrochemical behaviour of the iron, cobalt, nickel, copper and silver complexes was studied by cyclic voltammetry using nitromethane solutions. The reduction and oxidation potentials appear in Table 1. In all cases the corresponding properties of the parent $[9]aneS_3$ complexes were determined under the same conditions and are also listed for comparison. The half-wave potentials of the complexes of L^1 and of the parent $[9]aneS_3$ did not differ by more than 70 mV. The reversibility of the electrode processes, characterized by the separation of forward and reverse peak potentials and the ratio of the forward and reverse peak currents, were also qualitatively similar for the respective pairs.

Molecular Mechanics.—The four lowest-energy conformations (designated C_1, C_2, C_3 and D_3 according to the symmetry point group of the conformation) of $[9]aneS_3$ reported by Bloom *et al.*[5] (derived using the MM2 force field) were used to generate starting geometries for $[9]aneS_3$. These were then minimized using the MM+ force field in the HYPERCHEM (Release 3) package.[14] The energies of the minimized geometries (Fig. 1; C_1, 18.53; C_2, 20.51; C_3, 18.56; D_3, 20.89 kcal mol^{-1}) were all *ca.* 0.07 kcal mol^{-1} lower than those derived with MM2.[5] The effect of methyl substitution (as in L^1) was then modelled by substituting a single methyl group at all of the possible single sites in all the four minimized conformations derived for $[9]aneS_3$ and then minimizing. The C_1-derived models generated 12 distinct minima, the lowest being at 19.09 kcal mol^{-1}. As expected, the C_3-derived models generated four distinct minima with methyl groups at positions a, b, c and d (Fig. 1; the methyl group shown in the C_3-derived structure is in a position equivalent to a), the lowest being at 19.11 kcal mol^{-1}. Only one of these (with the methyl at position b) has significantly higher energy (25.40 kcal mol^{-1}) than those of the others, presumably as a consequence of transannular steric repulsion. With the methyl group at position c or d the energies (19.85 and 19.33 kcal mol^{-1}) were similar to that for position a. The minima obtained from the C_2- and D_3-derived models, with the methyl groups in the most favourable positions, were both considerably higher at 21.29 and 21.83 kcal mol^{-1}. These energies follow the same order as those of the corresponding conformations of $[9]aneS_3$ and are only 0.5–1 kcal mol^{-1} higher. The minimized macrocycle conformations were barely perturbed by methyl substitution. Fig. 2 shows the minimum for the C_3-derived conformation of L^1 with the methyl group in the most favoured position, superimposed on the minimized C_3 conformation of the parent $[9]aneS_3$; the two are barely distinguishable.

Discussion

Two approaches have been documented previously to overcome the difficulties of $[9]aneS_3$ synthesis, both designed to encourage cyclization rather than polymerization: a template reaction in which 3-thiapentane-1,5-dithiolate is constrained in a suitable conformation by facial co-ordination to a $Mo(CO)_3$ fragment[10] (method A), and a high-dilution approach employing caesium as the counter ion for the 3-thiapentane-1,5-dithiolate[11] (method B). Both employ 1,2-dihalogenoethanes as the electrophile. When applied to the synthesis of the

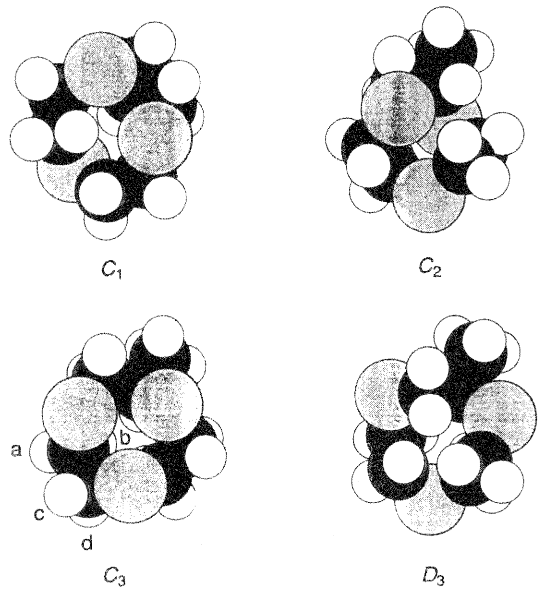


Fig. 1 Conformations of L[1] studied by molecular mechanics (identified by the symmetry designation of the analogous [9]aneS_3 conformations found to be the lowest-energy conformations of [9]aneS_3.[5] Hydrogen labels in the C_3 conformation refer to possible positions of methyl substitution: the methyl group shown is in a position equivalent to hydrogen atom a

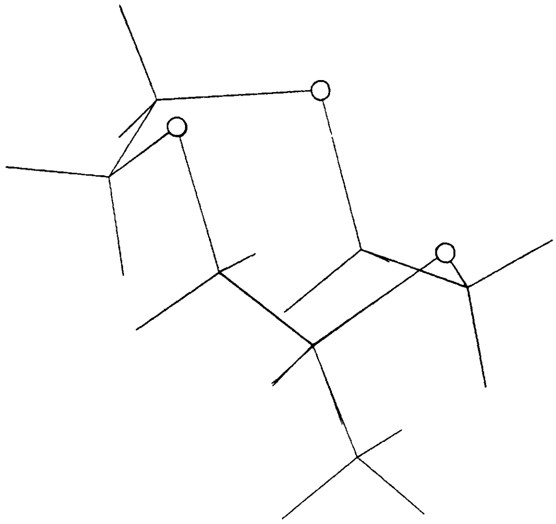


Fig. 2 Overlay diagram of the endodentate minimum found for L[1] superimposed on the analogous minimum for [9]aneS_3

substituted [9]aneS_3 derivatives investigated here, the molybdenum template approach to ring closure (method A) proved superior, but in all cases yields failed to match that obtained for [9]aneS_3 itself. These results suggest that substitution raises the transition-state energy for the ring-closure step (in the non-templated reaction) even further, perhaps by reducing the number of suitable conformations accessible (and hence imposing an unfavourable entropy of activation). The reduced yields in the templated reaction may be a result of steric hindrance by the substituent, since the final nucleophilic attack culminating in ring closure is at a secondary rather than a primary carbon. In both cases, intramolecular reaction would be disfavoured compared to intermolecular reaction as a result. The lack of success in the synthesis of vicinally disubstituted analogues is disappointing and is probably due to steric hindrance in the transition state of the templated ring-closure step.

Notwithstanding the reduced yields compared to those of the parent macrocycle, the template approach is remarkably successful in some cases. It is particularly surprising, and fortunate, in cases where the extremely reactive and electron-rich molybdenum dithiolate complex is treated with reactive and protic reagents. On the other hand, some cyclizations gave rather less satisfactory yields, suggesting that it may be preferable to seek a single, versatile functionalized [9]aneS_3 which can be synthesized in satisfactory yield, and can act as a central intermediate for further functionalization. The hydroxymethyl derivative L[2], for example, fulfils this role. It can be synthesized by method A in 24% yield and readily purified. The functionalized compounds made in this way are sufficiently robust for further functional group modification as in synthesis of L[3], L[5] and L[7].

The stoichiometry, electronic spectra (and hence probably co-ordination geometry in solution), and electrochemistry of the complexes are not significantly affected by the presence of a ring substituent. In particular, d^{10} (mercury and silver) complexes, which normally are not expected to achieve a co-ordination number higher than four, retain the spectroscopic (Hg) and electrochemical (Ag[15]) behaviour of the parent complexes, which each display six-co-ordination.[15,16] The ease and reversibility of oxidation of $[Ag([9]aneS_3)_2]^+$ are assumed to be the consequence of the high co-ordination number forced upon the metal by the conformational demands of the ligand.[15] Hence, the lack of sensitivity of the electrochemistry to substitution indicates that the conformational preferences in the [9]aneS_3 ring are similar whether the ring is substituted or not, at least as manifested in the co-ordination chemistry.

The molecular-mechanics results suggest that a single methyl substitution does not significantly affect the relative stabilities of the endo- and exo-dentate conformations when the methyl group is in its preferred position. Also, the ring torsional angles in the minimized structures are barely altered by substitution (Fig. 2). Hence, although the calculations have been limited to a few low-energy conformations previously identified for [9]aneS_3, conformational enthalpy considerations provide no cause for predicting changes in the co-ordination chemical properties thought to be dependent on preorganization of the ligand. On this basis the complexes would be expected to behave in a similar way to those of the parent [9]aneS_3. Conformational entropy effects may also play a significant role in determining the overall preferred structure; this has not been addressed in this study. Similar calculations on vicinally disubstituted analogues did not show significantly altered conformational preferences nor a significant increase in overall energy of the preferred conformations, supporting the suggestion that, in the templated ring closure, low yields are the results of steric hindrance at the metal centre (a kinetic effect) rather than additional thermodynamic ring strain in the product.

Conclusion

Molecular-mechanics studies over a limited range of favoured conformations of [9]aneS_3 suggest that substitution of a hydrogen for a methyl group does not significantly affect the conformational preferences of the ligand. This leads to the prediction that unusual features of the co-ordination chemistry of [9]aneS_3 believed to be a consequence of 'preorganization' would be preserved in its substituted analogues. This is borne out by the similarity of the properties of the complexes of [9]aneS_3 and L[1]. Synthetic yields of the substituted derivatives are practicable but always less than for [9]aneS_3 itself.

Experimental

All chemicals were of reagent grade obtained from Aldrich Chemical Company except the following: all solvents other than dimethylformamide and nitromethane (Fisons); nickel(II) tetrafluoroborate, copper(II) tetrafluoroborate (Fluorochem);

60–120 mesh silica used for column chromatography (BDH). Plastic-backed thin-layer chromatography sheets were supplied by Kodak. Acetonitrile and dmf were distilled from calcium hydride under a dinitrogen atmosphere, Me_2SO was dried with 4 Å molecular sieves, and tetrahydrofuran (thf) and diethyl ether were distilled from benzophenone and sodium. Column chromatography was carried out using a glass column (diameter 2.5 cm). Thin-layer chromatograms were developed on plastic-backed silica sheets and visualized with iodine vapour and/or with ultraviolet fluorescence. Elemental micro-analyses were performed either by Butterworths Laboratories (London) or by the Analytical Unit of the Chemical Laboratory at the University of Kent. The following instrumentation was used for spectroscopy: 60 MHz ^1H NMR, JEOL JNM-PMX 60 SI; 100 MHz ^1H NMR, JEOL JNM PS 100; 270 MHz ^1H and 67.8 MHz ^{13}C NMR, JEOL JNM GX 270 (all ^{13}C spectra were proton spin-decoupled, samples were dissolved either in a deuteriated solvent or carbon tetrachloride, and tetramethylsilane was used as an internal standard); IR, Perkin-Elmer 683 (samples either as Nujol mulls or liquid films between sodium chloride or potassium bromide plates, using a polystyrene film as standard); mass spectrometry, VG MS9, electron-impact (EI) ionization at an energy of 70 eV (1.12×10^{-17} J); UV/VIS, Philips PU8720, quartz cuvettes, acetonitrile or nitromethane solution. Cyclic voltammetry measurements were made under a dinitrogen atmosphere in a hemispherical glass cell containing the sample (2 mg) in 2 cm^3 of solvent (acetonitrile or nitromethane) containing 0.2 mol dm^{-3} tetrabutylammonium tetrafluoroborate as supporting electrolyte. Ferrocene was used as an internal standard and potentials are given relative to the ferrocene–ferrocenium redox potential. All measurements were at 20–22 °C unless stated otherwise. Platinum or glassy carbon working electrodes were used.

Molecular-mechanics calculations were carried out using HYPERCHEM (Release 3).[14] The structural parameters of the four lowest-energy conformers of [9]aneS_3 reported by Bloom *et al.*[5] were used to generate starting geometries for it. These were then minimized with conjugate gradients (Polak–Ribiere algorithm) using the MM+ force field until the gradients were less than 0.01 kcal mol^{-1} Å^{-1}. The methyl-substituted analogue L^1 was then modelled by substituting a single methyl group into the molecule at all the possible positions of all the four conformations and then minimizing each.

(R,S)-2-*Methyl*-1,4,7-*trithiacyclononane*(L^1).—(*R*,*S*)-1,2-Dibromopropane (4.04 g, 2.07 cm^3, 0.02 mol, in 20 cm^3 acetonitrile) was added dropwise to a suspension of $[Mo(CO)_3(SCH_2CH_2SCH_2CH_2S)]^{2-}$ **1** (0.02 mol) in acetonitrile (60 cm^3) over 5 min. The resulting brown suspension was stirred for 2 d at room temperature under dinitrogen, then the solvent was removed under vacuum. To the residue was added 0.02 mol bis(tetramethylammonium) 3-thiapentane-1,5-dithiolate dissolved in Me_2SO (60 cm^3). The product was stirred under dinitrogen for 2 d, then extracted with diethyl ether (4×40 cm^3). The combined extracts were washed with water (8×50 cm^3), dried over magnesium sulfate and evaporated down to an oil. Thin-layer chromatography of the material (toluene–hexane, 1 : 1; silica) showed two spots, $R_f = 0.45$ (3-thiapentane-1,5-dithiol) and 0.35 (L^1). The crude product was purified on a 20 g silica column with hexane–toluene (1 : 1) as eluent, yielding after solvent removal 0.97 g (25%) of compound L^1, which eluted after 3-thiapentane-1,5-dithiol (Found: C, 43.25; H, 7.35. $C_7H_{14}S_3$ requires C, 43.30; H, 7.25%). δ_H(CCl_4, 60 MHz) 3.5–2.9 (11 H, m, ring CH_2) and 1.35 (3 H, d, *J* 6.6 Hz, CH_3). δ_C($CDCl_3$, 67.8 MHz) 43.71 (s, CH_3C), 41.40, 35.57, 35.35, 34.09, 33.28 (all s, ring methylene C), and 22.75 (s, CH_3). ν_{max}(film) 2950s, 2895s, 2795w, 1445m, 1405s, 1340m, 1265m and 1240m cm^{-1}. *m*/*z* (EI) 194 (M^+), 135 ($M^+ - C_2H_3S$), 120, 105, 91 (base peak), 71 and 57.

(R,S)-2-*Hydroxymethyl*-1,4,7-*trithiacyclononane* (L^2).—(*R*,*S*)-2,3-Dibromopropan-1-ol (4.36 g, 2.06 cm^3, 0.02 mol) was added to a stirred suspension of complex **1** (0.02 mol) in acetonitrile (10 cm^3) over 5 min. After stirring for 2 d at room temperature the solvent was removed under vacuum and the product was treated with the dithiolate salt as above. The dark mixture was stirred for 1 d and the product extracted into diethyl ether (50 cm^3). The dimethyl sulfoxide phase was diluted with water (100 cm^3) and again extracted into diethyl ether (6×30 cm^3). The combined diethyl ether extracts were washed with water (2×100 cm^3), 1 mol dm^{-3} NaOH(aq) (2×100 cm^3), and water again (6×100 cm^3). The organic phase was dried over magnesium sulfate and evaporated down to an oil. Thin-layer chromatography of the crude product (chloroform, silica gel) gave three main spots with R_f 0.67 (3-thiapentane-1,5-dithiol), 0.30 (required product) and 0.09 (unknown). The mixture was chromatographed on a 35 g silica column with 5% methanol in chloroform to give 1.02 g (24%) of compound L^2, m.p. 30 °C, upon removal of solvent. The product crystallized upon standing in a refrigerator (Found: C, 40.00; H, 6.85. $C_7H_{14}OS_3$ requires C, 39.95; H, 6.70%). δ_H($CDCl_3$, 60 MHz) 3.8–2.7 (13 H, m, ring and exocylic methylene H), and 2.2 (1 H, br s, exchanged with D_2O, COH). ν_{max}(film) 3430s (br) (O–H), 2920s, 1420s, 1270m, 1060m and 1030m cm^{-1}. *m*/*z* (EI) 210 (M^+), 192 ($M^+ - H_2O$), 149 ($M^+ - C_2H_5S$), 119, 105, 91, 83, 73 and 61 (base peak).

Compounds L^3–L^7 were prepared similarly *via* the routes shown in Scheme 1. Experimental details are given elsewhere.[17]

Allyl Benzyl Ethers.—Allyl benzyl, allyl 4-bromobenzyl, allyl 4-carboxybenzyl, and allyl 4-cyanobenzyl ethers were prepared by methods similar to that given in the literature for allyl benzyl ether;[3] experimental details are given elsewhere.[17]

3-*Substituted* 1,2-*Dibromopropanes.*—1,2-Dibromo-3-(phenylmethoxy)-, (*R*,*S*)-1,2-dibromo-3-(4-bromophenylmethoxy)-, (*R*,*S*)-1,2-dibromo-3-(4-carboxyphenylmethoxy)- and (*R*,*S*)-1,2-dibromo-3-(4-cyanophenylmethoxy)-propane were prepared by bromination of the corresponding allyl benzyl ethers.[17]

Bis(*tetramethylammonium*) 3-*Thiapentane*-1,5-*dithiolate.*—A solution of 3-thiapentane-1,5-dithiol (3.09 g, 2.6 cm^3, 0.02 mol) in 25% methanolic tetramethylammonium hydroxide (16.85 cm^3, 0.04 mol) was prepared under dinitrogen at room temperature, and evaporated to dryness. The white residue was used for subsequent reactions without further purification.

Bis(*tetramethylammonium*) *Tricarbonyl*(3-*thiapentane*-1,5-*dithiolato*)*molybdate* **1**.[12]—Molybdenum hexacarbonyl (5.28 g, 0.02 mol) was stirred in refluxing acetonitrile (60 cm^3) under dinitrogen for 3 h to form a yellow solution of $[Mo(CO)_3(MeCN)_3]$. When cool this was added anaerobically to the above solid dithiolate (0.02 mol). The resulting bright yellow suspension of $[NMe_4]_2[Mo(CO)_3(SCH_2CH_2SCH_2CH_2S)]$ **1** was used *in situ* for reactions with 3-substituted 1,2-dibromopropanes as described above.

Complexes of [9]aneS_3.—All of these were prepared by literature methods.[15,16,18–20]

Bis[(R,S)-2-*methyl*-1,4,7-*trithiacyclononane*]*silver*(I) *Tetrafluoroborate.*—Compound L^1 (0.10 g, 0.52 mmol) was stirred in nitromethane (5 cm^3) while silver(I) trifluoromethanesulfonate (0.064 g, 0.25 mmol) was added. After stirring for 1 h tetrabutylammonium tetrafluoroborate (0.082 g, 0.27 mmol) was added, the solvent removed under vacuum, and the residue recrystallized from methanol to give 0.085 g (58%) of $[AgL^1{}_2]BF_4$ (Found: C, 28.6; H, 4.9. $C_{14}H_{28}AgBF_4S_6$ requires C, 28.8; H, 4.8%). ν_{max}(mull) 1410w, 1290w, 1280w, 1100w, 1055s, 1035m, 900w and 820w cm^{-1}.

Bis[(R,S)-2-*methyl*-1,4,7-*trithiacyclononane*]*mercury*(II) *Bis*(*perchlorate*).—Compound L^1 (0.12 g, 0.62 mmol) was stirred in nitromethane (5 cm^3) while mercury(II) perchlorate (0.12 g, 1.4 mmol) in nitromethane (5 cm^3) was added. After 1 h the product was crystallized by addition of diethyl ether (8 cm^3), and filtered off, yield 0.05 g (47%) of $[HgL^1{}_2][ClO_4]_2 \cdot 1.5MeNO_2$ (Found: C, 21.0; H, 3.8; N, 2.4. $C_{15.5}H_{32.5}Cl_2HgN_{1.5}O_{11}S_6$ requires C, 21.2; H, 3.7; N, 2.4%). ν_{max}(mull) 1410w, 1295w, 1255w, 1220w, 1180w, 1085s, 930w, 905w, 825w and 630m cm^{-1}.

Bis[(R,S)-2-*methyl*-1,4,7-*trithiacyclononane*]*nickel*(II) *Bis*(*tetrafluoroborate*).—Nickel(II) tetrafluoroborate (0.048 g, 0.14 mmol) in ethanol (4 cm^3) was added to a stirred solution of compound L^1 (0.565 g, 0.29 mmol) in ethanol (4 cm^3). The solution turned pale blue, then violet, and was boiled for 10 min whereupon it turned pink. On cooling the pink solid was filtered off, washed with ethanol and diethyl ether, and dried under vacuum to yield $[NiL^1{}_2][BF_4]_2$, 0.047 g (55%) (Found: C, 26.8; H, 4.20. $C_{14}H_{28}B_2F_8NiS_6$ requires C, 27.1; H, 4.5%). ν_{max}(mull) 1415m, 1285w, 1050s, 940w, 925w, 910w, 830w, 725w, 630w and 520w cm^{-1}.

Bis[(R,S)-2-*methyl*-1,4,7-*trithiacyclononane*]*copper*(II) *Bis*(*tetrafluoroborate*).—Compound L^1 (0.126 g, 0.65 mmol) in ethanol (10 cm^3) was stirred while copper(II) tetrafluoroborate (0.10 g, 0.29 mmol) was added. A brown precipitate formed which was collected and recrystallized from acetonitrile–diethyl ether to yield 0.069 g (38%) of $[CuL^1{}_2][BF_4]_2$ (Found: C, 26.7; H, 4.4. $C_{14}H_{28}B_2CuF_8S_6$ requires C, 26.9; H, 4.5%). ν_{max}(mull) 1415w, 1310w, 1285w, 1050s, 935w, 920w, 905w and 830w cm^{-1}.

Bis[(R,S)-2-*hydroxymethyl*-1,4,7-*trithiacyclononane*]*copper*(II) *Bis*(*tetrafluoroborate*).—Compound L^2 (0.08 g, 0.38 mmol) was stirred in ethanol (5 cm^3) while copper(II) tetrafluoroborate (0.043 g, 0.38 mmol) was added. A dark brown precipitate formed within a few seconds, and was collected, washed with ethanol and dried to give 0.067 g (57%) of $[CuL^2{}_2][BF_4]_2$ (Found: C, 25.2; H, 4.4. $C_{14}H_{28}B_2CuF_8O_2S_6$ requires C, 25.6; H, 4.3%). ν_{max}(mull) 3520m, 1410w, 1315w, 1300w, 1140w, 1060s, 930w, 910w, 870w and 835w cm^{-1}.

Bis[(R,S)-2-*methyl*-1,4,7-*trithiacyclononane*]*cobalt*(II) *Bis*(*perchlorate*).—Silver(I) perchlorate (0.059 g, 0.29 mmol) was stirred in acetonitrile (2 cm^3) while cobalt(II) chloride (18.5 mg, 0.142 mmol) in acetonitrile was slowly added. After stirring for 10 min the solid AgCl was filtered off. The pale pink cobalt(II) perchlorate solution was added to compound L^1 (55 mg, 0.0285 mmol) in diethyl ether (2 cm^3) and acetonitrile (2 cm^3). The resulting pink solution was evaporated to dryness and the residue recrystallized from nitromethane–diethyl ether to yield 45 mg (50%) of $[CoL^1{}_2][ClO_4]_2 \cdot 0.5MeNO_2$ (Found: C, 25.7; H, 4.4; N, 1.0. $C_{14.5}H_{29.5}CoCl_2N_{0.5}O_9$ requires C, 6.0; H, 4.2; N, 1.1%). ν_{max}(mull) 1540s, 1410m, 1260m, 1080s, 1025m, 945w, 925w, 905w, 860w, 825m, 720w, 655m, 635m and 620s cm^{-1}.

Dichloro[(R,S)-2-*methyl*-1,4,7-*trithiacyclononane*]*gold*(III) *Chloride*.—Compound L^1 (0.10 g, 0.52 mmol) was stirred in nitromethane (4 cm^3) while hydrogen tetrachloroaurate(III) trihydrate (0.098 g, 0.25 mmol) was added. A dark oily precipitate formed which redissolved upon addition of trifluoroacetic acid (1 cm^3). Addition of diethyl ether followed by stirring overnight afforded $[AuCl_2L^1]Cl$ as a yellow-brown solid which was collected and dried under vacuum, yield 0.052 g (42%) (Found: C, 16.5; H, 2.7. $C_7H_{14}AuCl_3S_3$ requires C, 16.9; H, 2.8%). ν_{max}(mull) 1400w, 1310w, 1145w, 1035w, 1010w, 925w, 900w, 815w, 800w, 725w and 665w cm^{-1}.

Trichloro[(R,S)-2-*methyl*-1,4,7-*trithiacyclononane*]*ruthenium*(III).—Compound L^1 (0.050 g, 0.257 mmol), ruthenium trichloride (0.065 g, 0.25 mmol) and trifluoroacetic acid (0.065 g, 0.25 mmol) in methanol were heated under reflux for 30 min. The brown suspension was cooled and the red-brown product filtered off and washed with propanone to yield $[RuCl_3L^1]$ (0.096 g, 83%) (Found: C, 20.8; H, 3.9. $C_7H_{14}Cl_3RuS_3$ requires C, 20.9; H, 3.5%). ν_{max}(mull) 1770w, 1740m, 1080w, 1045w and 995w cm^{-1}.

Acknowledgements

R. J. S. is grateful to the Cancer Research Campaign for a studentship, S. N. S. to the SERC for a studentship (no. 93316834). We thank Professor J. R. Dilworth for helpful discussion.

References

1 S. R. Cooper and S. C. Rawle, *Struct. Bonding* (*Berlin*), 1990, **72**, 1; M. Schröder, *Pure Appl. Chem.*, 1988, **60**, 517; S. R. Cooper, *Acc. Chem. Res.*, 1988, **21**, 141.
2 R. E. Wolf, jun., J. R. Hartman, J. M. E. Storey, B. M. Foxman and S. R. Cooper, *J. Am. Chem. Soc.*, 1987, **109**, 4328.
3 J. M. Desper, D. R. Powell and S. Gellman, *J. Am. Chem. Soc.*, 1990, **112**, 4321.
4 R. S. Glass, G. S. Wilson and W. N. Setzer, *J. Am. Chem. Soc.*, 1980, **102**, 5068; J. C. Lockhart and N. P. Tomkinson, *J. Chem. Soc., Perkin Trans. 2*, 1992, 533.
5 R. Bloom, D. W. H. Rankin, H. E. Robertson, M. Schröder and A. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1991, 773.
6 J. Beech, P. J. Cragg and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1994, 719.
7 W. N. Setzer, E. L. Cacioppo, Q. Guo, G. J. Grant, D. D. Kim, J. L. Hubbard and D. G. VanDerveer, *Inorg. Chem.*, 1990, **29**, 2672.
8 J. Buter, R. M. Kellog and F. van Bolhuis, *J. Chem. Soc., Chem. Commun.*, 1990, 282.
9 R. J. Smith, G. D. Admans, A. P. Richardson, H.-J. Küppers and P. J. Blower, *J. Chem. Soc., Chem. Commun.*, 1991, 475.
10 D. Sellmann and L. Zapf, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 807.
11 P. J. Blower and S. R. Cooper, *Inorg. Chem.*, 1987, **26**, 2009.
12 R. H. Baker, K. H. Cornell and M. J. Cron, *J. Am. Chem. Soc.*, 1948, **70**, 1490; F. P. Doyle and J. H. C. Nayler, *Chem. Ind.* (*London*), 1955, 714.
13 J. von Braun, *Chem. Ber.*, 1910, **43**, 1350.
14 J. L. Pazun, *J. Chem. Inf. Comput. Sci.*, 1993, **33**, 931.
15 J. Clarkson, R. Yagbasan, P. J. Blower, S. C. Rawle and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1987, 950.
16 A. J. Blake, A. J. Holder, T. I. Hyde, G. Reid and M. Schröder, *Polyhedron*, 1989, **8**, 2041.
17 R. J. Smith, Ph.D. Thesis, University of Kent, 1993.
18 W. N. Setzer, C. A. Ogle, G. S. Wilson and R. S. Glass, *Inorg. Chem.*, 1983, **22**, 223.
19 K. Wieghardt, H.-J. Küppers and J. Weiss, *Inorg. Chem.*, 1984, **24**, 3067.
20 A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1989, 876.

Received 11*th May* 1994; *Paper* 4/02803A