Synthesis of Tetranuclear Iron–Sulphur Protein Analogues with Tetrathiol Ligands attached to Macrocycles which provide Intramolecular Hydrophobic Domains†

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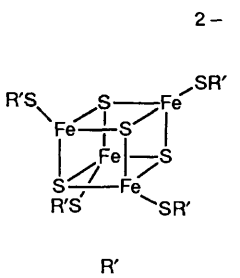
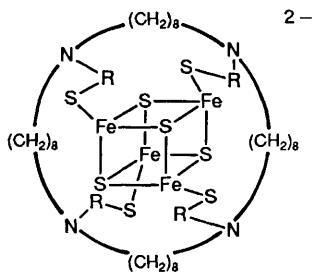
A new type of active-site analogue for 4Fe–4S iron-sulphur proteins is introduced, where the active site core is surrounded by an intramolecular hydrophobic domain formed by a 36-membered ring consisting of a methylene backbone. An efficient synthesis of the macrocyclic ligands 1,10,19,28-tetra(4-mercaptobenzoyl)-1,10,19,28-tetra-azacyclohexatriacontane, 1,10,19,28-[4-(mercaptomethyl)benzoyl]-1,10,19,28-tetra-azacyclohexatriacontane and 1,10,19,28-tetra-(3-mercapto-3-methylbutanoyl)-1,10,19,28-tetra-azacyclohexatriacontane is described. Their reaction with $[Fe_4S_4(SBu^t)_4]^{2-}$ afforded novel clusters in good yields (70—90%) as black powders with m.p. > 300 °C. They dissolve in dimethylformamide, dimethyl sulphoxide, and propylene carbonate. Complex formation with Fe_4S_4 clusters was mainly demonstrated by u.v.–visible and n.m.r. studies and the properties of the new clusters are discussed.

Well known are many biological materials in which particular metals are stoicheiometrically involved, *e.g.* metalloenzymes (hydrolases, oxido-reductases, isomerases, and synthetases), haemoglobin, blue copper, and chlorophyll.[1] Among them non-haem iron–sulphur proteins are widely distributed in living organisms from bacteria to mammals,[2] and play very important roles in various biological electron transfers. They are involved in many fundamental reactions such as photosynthesis, biosynthesis of steroidal hormones, metabolisms of fatty acids and sulphur, and nitrogen fixation.[2] Of those, high-potential proteins[3–5] show their redox potentials (1− to 2−) near +0.35 V *vs.* normal hydrogen electrode (n.h.e.) at pH 7 in water, although the structure of the 4Fe site analogue itself is very close to that of low-potential 4Fe ferredoxins, which exhibit redox potentials (2− to 3−) near −0.4 to −0.6 V.[2,6,7] It has been shown that the site cores in high-potential proteins are surrounded by proteins consisting largely of hydrophobic amino acids.[8,9] This may imply an important contribution of the hydrophobic environment to stabilizing the Fe_4S_4 cores, especially for high-potential proteins. Our preliminary reports demonstrated reliable synthetic routes to tetrathiol ligands[10] and the promising results of complexation with 4Fe–4S clusters[11] as well as characterization of the clusters.[12] Therefore, we examined the environmental effects on the FeS core in detail using macrocyclic tetrathiol ligands for modeling the proteins instead of the conventional small alkane- and arene-thiols [for example (**1**)—(**3**)]. Consequently we fully describe here the synthesis of tetrathiol ligands anchored to a 36-membered ring consisting of a methylene backbone macrocycle L^1—L^3 and their application to Fe_4S_4 clusters (**4**)—(**6**).

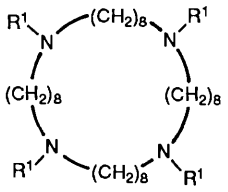


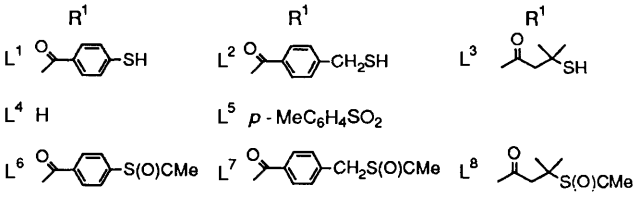
R′

(1) Ph
(2) CH_2Ph
(3) Bu^t



(4) R = (-S)-C(=O)-Ph
(5) R = (-S)-CH_2-C(=O)-Ph
(6) R = (-S)-C(=O)-CMe_3



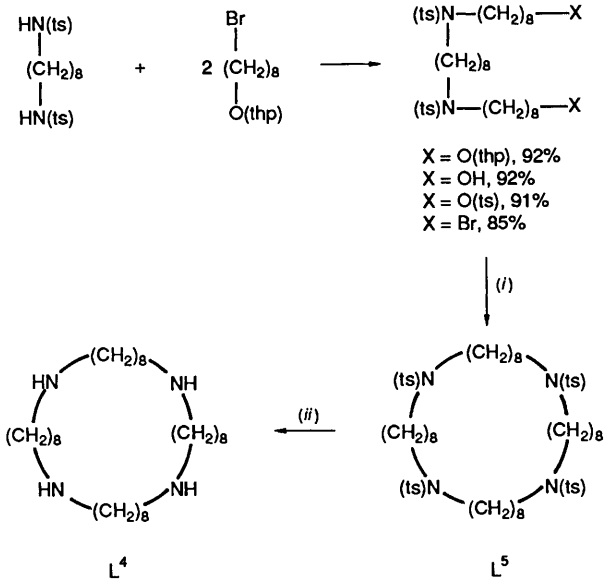


Results and Discussion

Synthesis of a 36-Membered Cyclic Tetra-amine with a Methylene Backbone (L^4).—The tetra-amine L^4 was synthesized as in Scheme 1. Treatment of *N,N′*-ditosyloctane-1,8-diamine with 1-bromo-8-(tetrahydropyran-2-yloxy)octane gave 1,26-bis(tetrahydropyran-2-yloxy)-9,18-ditosyl-9,18-diazahexacosane. Removal of the tetrahydropyranyl groups, tosylation and treatment with LiBr gave 1,26-dibromo-9,18-ditosyl-9,18-diazahexacosane. Double condensation[13] between the latter and *N,N′*-ditosyloctane-1,8-diamine proceeded smoothly in dimethyl formamide to afford L^5. The reaction can be carried out with a 10 mmol dm^{-3} concentration without use

† *Non S.I. unit employed*: mmHg ≈ 133 Pa.

of high dilution, and gave the corresponding macrocycle in excellent yields.[14] This tosylate was then converted into the free tetra-amine L^4 with HBr–phenol. Thus L^4 was obtained in 45.9% overall yield in six steps. The corresponding 2 + 2 cyclization[15,16] gave very poor yields; for example, only 9% of L^5 was obtained, while the corresponding 1 + 1 adduct was isolated in 72% yield.

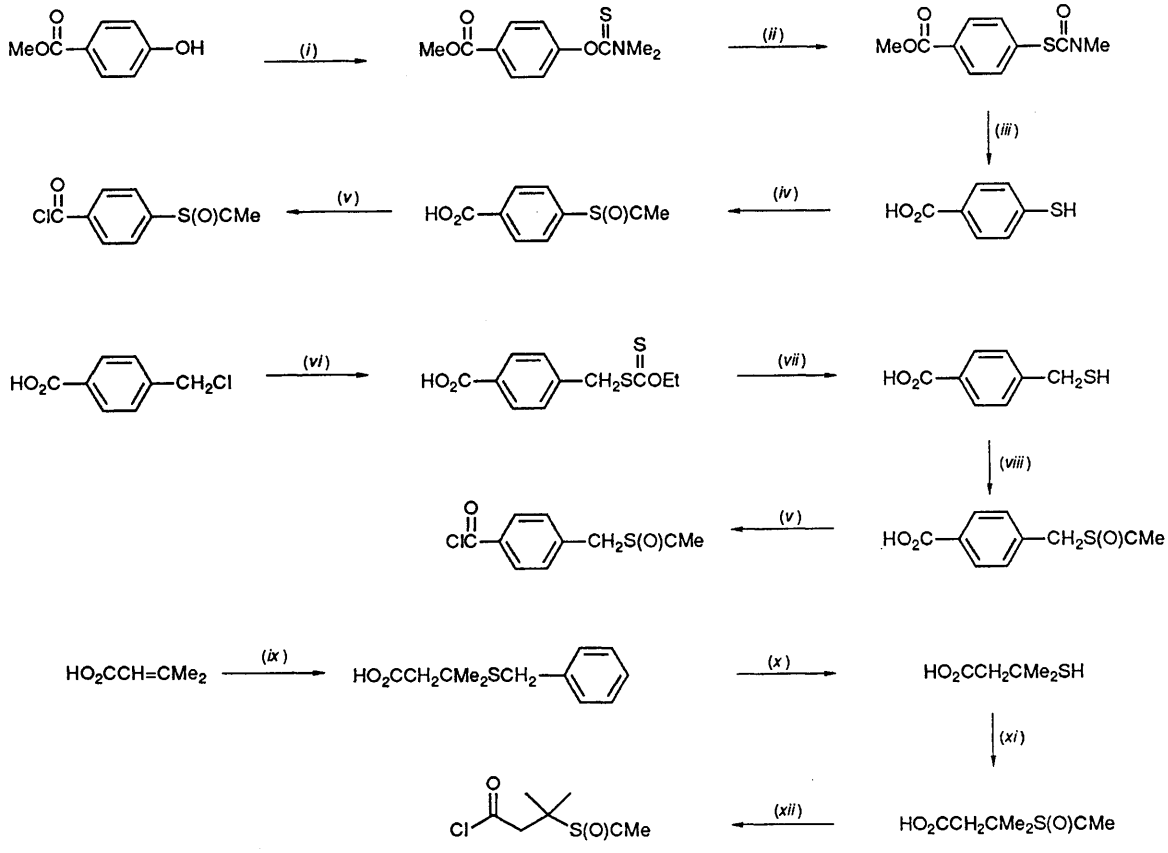


Scheme 1. ts = tosyl, thp = tetrahydropyran-2-yl. (*i*) 10 mmol dm^{-3} (ts)$HN(CH_2)_8NH$(ts), 77%; (*ii*) HBr–phenol, 91%.

Synthesis of the Macrocyclic Tetrathiol Ligands L^1—L^3.—The following synthetic routes for the acid chloride derivatives bearing thiol functions have been developed. As shown in Scheme 2 *p*-acetylthiobenzoyl chloride, *p*-acetylthiomethylbenzoyl chloride, and 3-acetylthio-3-methylbutanoyl chloride were synthesized from methyl *p*-hydroxybenzoate, 4-chloromethylbenzoic acid, and 3,3-dimethylacrylic acid as starting materials, respectively, in overall yields of 53 (five steps), 42 (four steps), and 37% (four steps). The tetrathiol derivatives L^6—L^8 were then synthesized by acylation of the macrocycle L^4 with the corresponding acid chlorides. The acylating reactions at four sites simultaneously with *p*-acetylthiobenzoyl chloride and *p*-acetylthiomethylbenzoyl chloride proceeded smoothly to afford L^6 and L^7 in the presence of NEt_3 as a base. When 3-acetylthio-3-methylbutanoyl chloride is used as an acylating agent no desired products result with NEt_3, but compound L^8 can be obtained in excellent yields with K_2CO_3 in dichloromethane. The results are summarized in Table 1.

Deprotection (deacetylation) of L^6—L^8 can be achieved under basic conditions. However the produced thiol groups are susceptible to oxidation to form the disulphide, and careful manipulations under an inert atmosphere are necessary. The removal of the acetyl groups is readily achieved under mild acidic conditions with HCl–methanol, and the products L^1—L^3 can be prepared without difficulty. These results are summarized in Table 2.

In the i.r. spectra the presence of SH and amide groups is shown around 2 500 and 1 630 cm^{-1} respectively (Table 3). Distinct SH stretching bands are observed for the 36-membered ring compounds L^1—L^3 with methylene backbones. In addition, both n.m.r. spectra and colorimetric measurements



Scheme 2. (*i*) $Me_2NC(S)Cl$, 80%; (*ii*) 220 °C, 97%; (*iii*) 10% NaOH–MeOH, 97%; (*iv*) $(MeCO)_2O$, 88%; (*v*) $(COCl)_2$, 80%; (*vi*) KS_2COEt, 91%; (*vii*) $H_2N(CH_2)_2NH_2$, quantitative; (*viii*) $(MeCO)_2O$, 76%; (*ix*) $PhCH_2SH$, 73%; (*x*) Na–NH_3, 92%; (*xi*) $(MeCO)_2O$, 69%; (*xii*) $(COCl)_2$, 89%

Table 1. Synthesis of L^6—L^8

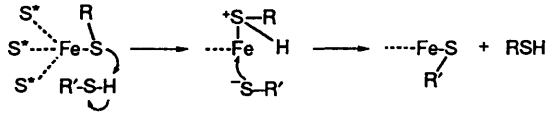
Compound	Substrates	Base	Yield (%)
L^6	L^4 + 4-MeC(O)SC_6H_4COCl (1.2 equiv.)	NEt_3	90
L^7	L^4 + 4-MeC(O)$SCH_2C_6H_4COCl$ (2.0 equiv.)	NEt_3	85
L^8	L^4 + CMe_2[MeC(O)S]CH_2COCl (1.5 equiv.)	K_2CO_3	68

Table 2. Synthesis of L^1—L^3 by deacetylation in 1 mol dm^{-3} HCl–methanol

Compound	T/°C	t/h	Yield (%)
L^1	60	3	Quantitative
L^2	70	3	Quantitative
L^3	60	2	89

Table 3. Determination of SH Groups in L^1—L^3 by i.r., n.m.r. spectroscopy and colorimetry

Compound	I.r. (cm^{-1})	N.m.r. (δ)	Colorimetry (no. of SH)
L^1	2 500 (m), 1 615	3.55 (s, 4 H)	3.98
L^2	2 500 (m), 1 620	1.77 (t, 4 H, J = 7.7 Hz)	3.90
L^3	2 550 (m), 1 630	2.68 (s, 4 H)	3.82



Scheme 3. S* = core atom

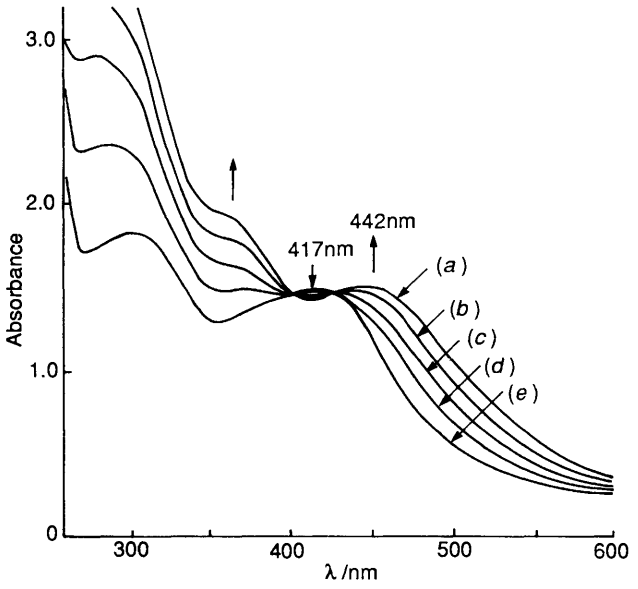


Figure. U.v.–visible titration spectra illustrating ligand exchange (**3**) + $\frac{n}{4}L^1$ ⟶ (**4**) in dmf, where n = ⩾4 (*a*), 3 (*b*), 2 (*c*), or 1 (*d*); (*e*) $[Fe_4S_4(SBu^t)_4]^{2-}$ (**3**) (n = 0)

with 5,5′-dithiobis(2-nitrobenzoic acid)[17] clearly showed the appropriate numbers of SH groups in these molecules. In the 270-MHz ^1H n.m.r. spectra in $CDCl_3$ singlet signals due to SH groups are observed for L^1 and L^3, at δ 3.55 and 2.68 respectively, and a triplet at δ 1.77 (J = 7.7 Hz) for L^2 with the appropriate integration. Interestingly the N_α protons in L^1 and L^2 were resolved due to hindered rotation, but not for L^3. At 80 °C a broad single peak was observed at δ 3.3 for L^1 in $(CD_3)_2SO$. Furthermore, the number of SH groups in the molecule was confirmed by colorimetry. The results are summarized in Table 3.

The ligand L^2 has been characterized by positive-ion fast-atom-bombardment mass spectrometry in *m*-nitrobenzyl alcohol + 0.2 mol dm^{-3} trifluoroaceitc acid. The molecular ion peak [M + H^+] at m/z 1 109.9 supports the expected formula.

4Fe–4S *Clusters with Macrocyclic Tetrathiol Ligands*, (**4**)—(**6**).—*Synthesis.* The novel 4Fe–4S site analogues (**4**)—(**6**) were prepared by a ligand-substitution reaction[18] using the macrocyclic tetrathiol compounds L^1—L^3, and $[Fe_4S_4(SBu^t)_4]^{2-}$ (**3**).[19] The reaction was performed in dimethylformamide (dmf), and all manipulations were carried out under pure nitrogen. Typical experimental procedures are as follows.

A slight excess (× 1.02 equivalents) L^1—L^3 in dmf is added into a solution of compound (**3**), and the mixture kept at 40 °C for 30 min under reduced pressure with stirring to remove the liberated Bu^tSH. The reaction is likely to proceed according to Scheme 3,[20] and a rapid colour change (brown to reddish brown) is observed after the addition of L^1, which suggests rapid ligand exchange with the cyclic phenyl ligands to form the new species. For the corresponding phenylmethane- and alkane-thiol derivatives no marked colour change is observed, but the solution turns slightly greenish brown. In these cases the difference in acidity of the Bu^tSH and the macrocyclic ligand thiols is not as great as that for the benzenethiols present in compound L^1. However, the substitution reactions proceeded smoothly by removing the volatile Bu^tSH liberated. A favourable macrocyclic effect towards formation of the complexes is also expected.

The product was then precipitated by addition of tetrahydrofuran, washed subsequently with acetonitrile, methanol, dichloromethane, and diethyl ether, and purified by two re-precipitations from dmf–tetrahydrofuran.

In the same manner, a series of new 4Fe–4S clusters with macrocyclic tetrathiol ligands, (**4**)—(**6**) was obtained in good yields (70—90%) as black powders with m.p. > 300 °C. These clusters are only soluble in solvents such as dmf, dimethyl sulphoxide (dmso), and propylene carbonate.

U.v.-visible absorption spectra. The Figure illustrates the results of u.v.–visible titration. Namely, an increasing amount of ligand L^1 in dmf was added to a solution of compound (**3**) in dmf. The u.v.–visible spectra obtained after addition of the ligand (0.25, 0.5, 0.75, 1, 1.25, and 1.5 equivalents) are shown. After reaching the 1:1 stoicheiometry, addition of a further amount of ligand does not produce any significant change. Furthermore the spectrum of the species thus formed corresponds to that of complex (**4**) dissolved in dmf. One can also observe that the absorption at 417 nm of (**3**) is shifted to 442 nm for (**4**). Two isosbestic points have been observed at 405 and 429 nm, which strongly supports the formation of a single complex.

The existence of the 4Fe–4S core in these products is also confirmed by the core-extrusion method;[18] for example, a series of spectral changes are observed from the initial spectrum of compound (**3**) ($\lambda_{max.}$ 417 nm) indicating the final formation of the known phenyl derivative $[Fe_4S_4(SPh)_4]^{2-}$ (**1**);[21] based on its known ε value, 95% of (**1**) was obtained on addition of excess of PhSH (× 150 mol) to a solution of (**4**)—(**6**).

Compared with the corresponding complexes without a

Table 4. Isotropic shifts of the protons of compounds (**4**)—(**6**)

Compound	Isotropic shift (p.p.m.)*
(**4**)	+1.50 (*ortho* to S), −0.57 (*meta* to S)
(**5**)	−9.46 ($PhCH_2S$), −0.06 (*ortho* to S)
	−0.13 (*meta* to S)
(**6**)	−1.14 (CH_3)

* Compared with the corresponding thiol ligand in $(CD_3)_2SO$ at 22 °C

macrocycle, a considerable blue shift of the maximum in the visible region is observed for compound (**4**) [$\lambda_{max.}$ (log ε): 442 (14.3) and 365 nm (sh) (21.1); *cf.* for (**1**), 457 nm (17.7)[21]], but virtually no shift for the others. This may reflect the nature of the electron-deficient sulphur of (**4**) due to the attached macrocycle. For the benzyl cluster, no remarkable changes were observed. The butyl analogues with or without the macrocycle, (**6**) and (**3**), gave essentially the same electronic spectra with similar ε values.

The above differences in absorption spectra are attributed to both the nature of the thiol ligands and the effect of the macrocycles. So, it is important to examine various combinations of thiols with different characters and a series of ring sizes, which may open the door to the criteria for environmental effects on the active sites of biometallo molecules.

Mass spectra. The mass spectrum of compound (**5**) could only be obtained using the positive-ion fast-atom bombardment technique with *m*-nitrobenzyl alcohol as the matrix; surprisingly, attempts to detect the negative ion spectrum were unsuccessful. The molecular peak of the anion complex could not be detected, most likely due to a classical reaction of the complex with the matrix. However, all the observed fragment peaks could be interpreted within experimental errors due to the broadness of some peaks. The highest parent peak observed at *m/z* 1 348 (±4) is attributed to $M^+ - 2Fe$ (expected value 1 345). The complete sequence is then as follows: $(M^+ - 2Fe) - S$ *m/z* 1 316 (calc 1 313), $(M^+ - 2Fe) - 2S$ 1 285, (1 281), $(M^+ - 2Fe) - 2S - Fe$ 1 225 (1 225), $(M^+ - 2Fe) - 3S - Fe$ 1 195 (1 193), $(M^+ - 2Fe) - 4S - Fe$ 1 161 (1 161), and $(M^+ - 2Fe) - 4S - 2Fe$ 1 105 (1 105), which corresponds to the deprotonated ligand L^2. If a polymeric structure cannot be completely ruled out, then based on satisfactory interpretation of all observed peaks we suggest a monomeric structure for complex (**5**) and by extension for the entire series. Attempts are being made to obtain crystals suitable for single-crystal *X*-ray analysis.

N.m.r. and Mössbauer spectra. When a solution of the tetrathiol ligand L^1 is added to compound (**3**) ligand substitution takes place in an aprotic solvent (such as dmf and dmso).[18,20] The original SH signal of (**3**) at δ 3.55 disappears, and new singlet signals at 1.4 (Bu^t) and 2.0 (SH) due to liberated Bu^tSH are observed in the ^1H n.m.r. spectrum. The spectrum of compound (**4**) was obtained after evaporation of Bu^tSH at 40 °C for 30 min under reduced pressure.

As mentioned before the N_α protons of ligand compound L^1 were resolved at δ 3.15 and 3.43 owing to hindered rotation, but the corresponding protons of (**4**) gave a single peak at δ 3.18. This may imply that the conformational change after complexation has the advantage of permitting an equal environment for the N_α protons. Similar behaviour is observed for (**6**). The rest of the methylene protons in the backbone occur around δ 1.3 together with methyl protons of the tetraethylammonium counter cation.

The characteristic features are broad signals and large downfield shifts of the α-protons to the ligand sulphur due to the paramagnetic nature of the FeS core.[22] Upfield shifts of *ortho* (δ 7.2—5.8) and downfield shifts of *meta* (δ 7.3—8) protons are also observed for the thiophenol derivative (**4**).[22] The isotropic shifts observed for the protons in (**4**)—(**6**) are summarized in Table 4.

A trace of dmf (*ca.* 5%) which is hardly removable from the solids is indicated[23] by peaks at δ 2.73, 2.89, and 7.93.

A similar explanation is applicable to the 270-MHz n.m.r. spectra of clusters (**5**) and (**6**), and the data are given in the Experimental section.

The Mössbauer spectrum (natural iron film as a standard) of compound (**5**) at room temperature was very similar to that of (**3**), and the isomer shifts (mm s^{-1}), quadrupole splittings (mm s^{-1}), and half-widths (mm s^{-1}) determined by a Lorentzian least-squares fitting method were, respectively, 0.36, 0.84, and 0.54 for (**5**) and 0.32, 0.77, and 0.43 for (**3**). These results may support retention of the cluster structure in the new complexes.

Detailed studies of Mössbauer spectra at low temperature under a magnetic field of a series of the macrocyclic complexes as well as magnetic susceptibility measurements will be reported elsewhere.

Experimental

General Methods.—Melting points are uncorrected. Manipulations and measurements involving FeS clusters and thiols were carried out under an atmosphere of N_2 or Ar. Flash chromatographic separations were carried out as described[24] on silica gel 60 (230—400 mesh). Tetrahydrofuran and diethyl ether were distilled from sodium diphenylketyl, dmf, dichloromethane, acetonitrile, benzene, hexane, and chloroform from CaH_2, ethanol and methanol from Mg. Ethyl acetate and acetone were purified by distillation. *N,N'*-Dimethylaminopyridine (dmap) was recrystallized from benzene–hexane. Other materials were purchased from appropriate sources and used as received. 1-Bromo-8-(tetrahydropyran-2-yloxy)octane,[25] *O-p*-methoxycarbonylphenyl dimethylthiocarbamate,[26] *S-p*-methoxycarbonylphenyl dimethylthiocarbamate,[26] 3-benzylthio-3-methylbutanoic acid,[27] 3-mercapto-3-methylbutanoic acid,[27] and the clusters (**1**)—(**3**)[28] were prepared according to literature procedures.

Absorption spectra were recorded on a Cary 219 spectrophotometer, i.r. spectra with a JASCO IRA-2, and n.m.r. spectra on a JEOL JMN GX-270 or FX-100 spectrometer. Chemical shifts are relative to $SiMe_4$ as internal reference. Mass spectra were measured on a JEOL JMS-D300 spectrometer.

Syntheses.—*N,N'-Ditosyloctane-1,8-diamine.* To a dichloromethane (300 cm^3) solution of octane-1,8-diamine (10.1 g, 70 mmol), NEt_3 (14.9 g, 147 mmol), and dmap (18.0 g, 147 mmol) was added toluene-*p*-sulphonyl chloride (28.0 g, 147 mmol) in dichloromethane (50 cm^3) at 0 °C, and the mixture was stirred for 5 h at room temperature. After washing successively with 3 mol dm^3 HCl, saturated $NaHCO_3$, and brine the organic phase was dried ($MgSO_4$) and evaporated to dryness *in vacuo*. The product was purified by recrystallization from methanol to afford colourless crystals in 80% yield (25.5 g), m.p. 147—148 °C; $\nu_{max.}$(Nujol) 3 300, 1 320, and 1 155 cm^{-1}; $\delta_H(CDCl_3)$ 1.0—1.6 (m, 12 H, CH_2), 2.40 (s, 6 H, $C_6H_4CH_3$), 2.7—3.0 (d of t, 4 H, *J* 6.4, $N_\alpha CH_2$), 4.86 (t, 2 H, *J* 6.5, D_2O exchangeable, NH), 7.31 (d, 4 H, *J* 8.3, aromatic), and 7.77 (d, 4 H, *J* 8.3 Hz, aromatic) (Found: C, 58.30; H, 7.20; N, 6.10. $C_{22}H_{32}N_2O_4S_2$ requires C, 58.35; H, 7.10; N, 6.20%).

1,26-Bis(tetrahydropyran-2-yloxy)-9,18-ditosyl-9,18-diazahexacosane. To a solution of the above compound (13.6 g, 30 mmol) in dry dmf (200 cm^3) was added NaH (1.74 g, 73 mmol) in dmf (40 cm^3), which was kept under reduced pressure (20—25 mmHg) for 30 min at 60 °C to evacuate the gas evolved. 1-Bromo-8-(tetrahydropyran-2-yloxy)octane (18.5 g, 63

mmol)[25] in dmf (60 cm^3) was then added, and the mixture allowed to react at 60 °C for 3 h. A colourless solid was filtered off over Celite, and the filtrate was evaporated. The residue was then dissolved in ethyl acetate, washed twice with brine, and dried ($MgSO_4$). Evaporation of the solvent followed by chromatography on silica gel with n-hexane–ethyl acetate (5:2) gave the required compound (24.3 g, 92%) as a colourless oil: $\nu_{max.}(CHCl_3)$ 1 730, 1 600, 1 320, and 1 140 cm^{-1}; $\delta_H(CDCl_3)$ 0.9—2.0 (m, 48 H, CH_2), 2.42 (s, 6 H, $C_6H_4CH_3$), 3.10 (t, 8 H, *J* 7.5, $N_\alpha CH_2$), 3.2—4.0 (m, 8 H, OCH_2), 4.5—4.7 (m, 2 H, OCHO), 7.33 (d, 4 H, *J* 8.3, aromatic), and 7.73 (d, 4 H, *J* 8.3 Hz, aromatic) (Found: C, 65.75; H, 9.20; N, 3.15. $C_{48}H_{80}N_2O_8S_2$ requires C, 65.70; H, 9.20; N, 3.20%).

1,26-*Dihydroxy*-9,18-*ditosyl*-9,18-*diazahexacosane*. A methanol solution (300 cm^3) of the above compound (5.0 g, 5.7 mmol) was treated with toluene-*p*-sulphonic acid monohydrate (2.4 g, 12.6 mmol). The resultant solution was stirred at room temperature for 30 min. After evaporation of the solvent followed by the addition of saturated $NaHCO_3$, the residue was extracted with ethyl acetate. The combined extracts were washed with saturated $NaHCO_3$ and brine, and dried ($MgSO_4$). The crude product was chromatographed on silica gel with n-hexane–ethyl acetate (1:3) to afford the required compound (3.7 g, 92%) as a colourless solid. Recrystallization from dichloromethane–diethyl ether gave colourless needle-shaped crystals, m.p. 57—58 °C; $\nu_{max.}(CHCl_3)$ 3 610, 3 520, 1 725, 1 600, 1 325, 1 145, and 1 085 cm^{-1}; $\delta_H(CDCl_3)$ 0.9—1.7 (m, 36 H, CH_2), 2.05 (s, 2 H, D_2O exchangeable, OH), 2.41 (s, 6 H, $C_6H_4CH_3$), 3.09 (t, 8 H, *J* 6.8, $N_\alpha CH_2$), 3.61 (t, 4 H, *J* 6.1, CH_2O), 7.30 (d, 4 H, *J* 8.0, aromatic), and 7.69 (d, 4 H, *J* 8.0 Hz, aromatic) (Found: C, 64.35; H, 9.20; N, 3.90. $C_{38}H_{64}N_2O_6S_2$ requires C, 64.35; H, 9.10; N, 3.95%).

9,18-*Ditosyl*-1,26-*ditosyloxy*-9,18-*diazahexacosane*. To a mixture of the above compound (1.0 g, 1.4 mmol) and dmap (1.72 g, 14 mmol) in dry dichloromethane (30 cm^3) was added dropwise toluene-*p*-sulphonyl chloride (0.8 g, 4.2 mmol) in dichloromethane (10 cm^3), and the solution was stirred for 30 min at room temperature. After washing with 3 mol dm^{-3} HCl, saturated $NaHCO_3$, and brine, the solution was dried ($MgSO_4$) and evaporated to dryness *in vacuo*. The residue was purified on a silica gel column eluted with benzene–ethyl acetate (20:1) to give a colourless oil (1.3 g, 91%); $\nu_{max.}(CHCl_3)$ 1 600, 1 350, 1 330, 1 150, and 1 090 cm^{-1}; $\delta_H(CDCl_3)$ 1.0—1.8 (m, 36 H, CH_2), 2.41 (s, 6 H, $C_6H_4CH_3$), 2.44 (s, 6 H, $C_6H_4CH_3$), 3.08 (t, 8 H, *J* 7.1, $N_\alpha CH_2$), 4.01 (t, 4 H, *J* 6.3, OCH_2), 7.31 (d, 4 H, *J* 7.5, aromatic), 7.38 (d, 4 H, *J* 7.8, aromatic), 7.71 (d, 4 H, *J* 7.8, aromatic), and 7.82 (d, 4 H, *J* 8.3 Hz, aromatic) (Found: C, 61.50; H, 7.60; N, 2.70. $C_{52}H_{76}N_2O_{10}S_4$ requires C, 61.40; H, 7.55; N, 2.75%).

1,26-*Dibromo*-9,18-*ditosyl*-9,18-*diazahexacosane*. Treatment of the above compound (1.2 g, 1.2 mmol) with LiBr (0.31 g, 3.6 mmol) in dry acetone (30 cm^3) under refluxing for 4 h gave the dibromide, and the acetone was evaporated after removal of the solid by filtration over Celite. Water was added to the residue and extracted with ethyl acetate. The combined extracts were washed with water and brine. Evaporation of the solvent followed by SiO_2 chromatography with n-hexane–ethyl acetate (3:1) afforded a colourless solid (0.84 g, 85%). Recrystallization from diethyl ether–light petroleum (b.p. 35—60 °C) gave colourless needles, m.p. 36.5—37.5 °C; $\nu_{max.}(CHCl_3)$ 1 600, 1 330, 1 150, and 1 085 cm^{-1}; $\delta_H(CDCl_3)$ 1.0—2.0 (m, 36 H, CH_2), 2.42 (s, 6 H, $C_6H_4CH_3$), 3.09 (t, 8 H, *J* 7.4, $N_\alpha CH_2$), 3.39 (t, 4 H, *J* 6.9, CH_2Br), 7.31 (d, 4 H, *J* 8.0, aromatic), and 7.71 (d, 4 H, *J* 8.0 Hz, aromatic) (Found: C, 54.70; H, 7.55; N, 3.30. $C_{38}H_{62}Br_2N_2O_4S_2$ requires C, 54.65; H, 7.50; N, 3.35%).

1,10,19,28-*Tetratosyl*-1,10,19,28-*tetra-azacyclohexatriacontane*, L^5. *N,N'*-Ditosyloctane-1,8-diamine (1.08 g, 2.39 mmol) was treated with NaH (138 mg, 5.75 mmol) in dry dmf (300 cm^3) at 60 °C under reduced pressure (20—25 mmHg). After 30 min Cs_2CO_3 (940 mg, 2.89 mmol) was added, and the solution stirred at 60 °C for 30 min under nitrogen. To the mixture was then added 1,26-dibromo-9,18-ditasyl-9,18-diazahexacosane (2 g, 2.40 mmol) in dmf (35 cm^3) and allowed to react at 60 °C for 3 h under nitrogen. After evaporation of the solvent, the residue was poured into 1 mol dm^{-3} HCl, and extracted with dichloromethane. The extracts were washed with brine, dried ($MgSO_4$), and purified on a silica gel column eluted with dichloromethane–ethyl acetate (20:1) to give a colourless solid (2.08 g, 77%). Recrystallization from chloroform–methanol afforded colourless leaflets, m.p. 140.5—142 °C; field desorption mass spectrum): *m/z* 1 125 [M^+ + H]; $\nu_{max.}(CHCl_3)$ 1 600, 1 325, 1 145, and 1 085 cm^{-1}; $\delta_H(CDCl_3)$ 1.24 (br s, 32 H, CH_2 (skeleton)], 1.3—1.7 (m, 16 H, $N_\beta CH_2$), 2.42 (s, 12 H, $C_6H_4CH_3$), 3.05 (t, 16 H, *J* 6.8, $N_\alpha CH_2$), 7.29 (d, 8 H, *J* 8.4, aromatic), and 7.69 (d, 8 H, *J* 8.4 Hz, aromatic) (Found: C, 64.20; H, 8.25; N, 4.80. $C_{60}H_{92}N_4O_8S_4$ requires C, 64.00; H, 8.25; N, 5.00%).

1,10,19,28-*Tetra-azacyclohexatriacontane*, L^4. The tosylamide L^5 (2.0 g, 1.8 mmol) and phenol (4.2 g in 48% HBr (84 cm^3) were refluxed for 8 h, and a dark red-violet oil separated. After cooling to room temperature, ethanol (30 cm^3) was added. Then a pale brown solid was collected by filtration and washed with ethanol and ether. A suspension of the above solid in 20% NaOH (60 cm^3) was refluxed for 1 h, and extracted with dichloromethane. The combined extracts were dried ($MgSO_4$), and evaporated to give the corresponding free amine as a colourless solid (0.82 g, 91%), m.p. 63—65 °C; $\nu_{max.}$(Nujol) 3 300 cm^{-1}; $\delta_H(CDCl_3)$ 1.32 (br, 36 H), 1.46 (br, 16 H), 2.59 (t, 16 H, *J* 7.1 Hz); electron impact high resolution mass spectrum *m/z*: 508.5415 (calc. for $C_{32}H_{68}N_4$: 508.5428). Data for the HCl salt are as follows: m.p. > 300 °C (Found: C, 58.50; H, 10.90; Cl, 21.55; N, 8.50. $C_{32}H_{72}Cl_4N_4$ requires C, 58.70; H, 11.10; Cl, 21.65; N, 8.55%).

4-*Mercaptobenzoic acid*. A solution of *S*-*p*-methoxycarbonylphenyl dimethylthiocarbomate (30 g, 0.12 mol)[26] in 10% NaOH–methanol and water (500 cm^3–4.5 cm^3) was refluxed under Ar for 3 h. After evaporation of methanol, the residue was acidified with 2 mol dm^{-3} HCl, extracted with ethyl acetate, washed with brine, and dried ($MgSO_4$). Recrystallization from benzene gave 18 g (97%) of pale yellow crystals, m.p. 214—215 °C; $\nu_{max.}$(Nujol) 1 660 cm^{-1}; $\delta_H(CDCl_3)$ 3.65 (s, 1 H), 7.32 (d, 2 H, *J* 8.8), and 7.96 (d, 2 H, *J* 8.7 Hz) (Found: C, 54.70; H, 3.90; S, 20.60. $C_7H_6O_2S$ requires C, 54.55; H, 3.90; S, 20.80%).

4-(*Acetylthio*)*benzoic acid*. The above compound (3.6 g, 23 mmol) was treated with acetic anhydride (3.6 cm^3, 38 mmol) in pyridine (3.6 cm^3) overnight under Ar. After evaporation of the solvent the residue was dissolved in ethyl acetate, washed with 2% HCl and brine, and dried (Na_2SO_4). Recrystallization from benzene gave colourless crystals (3.9 g, 88%), m.p. 183—185 °C; $\nu_{max.}$(Nujol) 1 670—1 690 cm^{-1}; $\delta_H(CDCl_3)$ 2.46 (s, 1 H), 7.54 (d, 2 H, *J* 8.5), and 8.14 (d, 2 H, *J* 8.6 Hz) (Found: C, 55.20; H, 4.05; S, 16.35. $C_9H_8O_3S$ requires C, 55.10; H, 4.10; S, 16.35%).

4-(*Acetylthio*)*benzoyl chloride*. A mixture of the above compound (5 g, 25.5 mmol) and oxalyl chloride (20 cm^3, 240 mmol) in dry benzene (100 cm^3) was refluxed for 1 h. Vacuum distillation afforded colourless crystals (4.4 g, 80%), b.p. (0.015 mmHg) 115—120 °C, m.p. 73—74.5 °C; $\nu_{max.}$(Nujol) 1 760 and 1 710 cm^{-1}; $\delta_H(CDCl_3)$ 2.49 (s, 3 H), 7.58 (d, 2 H, *J* 8.8), and 8.14 (d, 2 H, *J* 8.6 Hz) (Found: C, 50.45; H, 3.15; Cl, 16.35; S, 15.10. $C_9H_7ClO_2S$ requires C, 50.35; H, 3.30; Cl, 16.50; S, 14.95%).

4-(*Ethoxythiocarbonylthiomethyl*)*benzoic acid*. A mixture of 4-(chloromethyl)benzoic acid (5.0 g, 29 mmol) and potassium dithiocarbonate (7.0 g, 44 mmol) in acetone (120 cm^3) was refluxed for 3 h. The solvent was removed by evaporation, and the residue dissolved in ethyl acetate and washed with 10% HCl

and brine. Recrystallization from ethyl acetate–hexane gave colourless crystals (6.8 g, 91%), m.p. 125—126 °C; $\nu_{max.}$(Nujol) 1 680 cm^{-1}; $\delta_H(CDCl_3)$ 1.42 (t, 3 H, *J* 7.1), 4.42 (s, 2 H), 4.66 (q, 2 H, *J* 7.1), 7.44 (d, 2 H, *J* 8.5), and 8.07 (d, 2 H, *J* 8.5 Hz).

4-(*Mercaptomethyl*)*benzoic acid.* The above compound (8.0 g, 31 mmol) in ethylenediamine (10 cm^3) was stirred at room temperature for 5 h under Ar. The resultant solution was then poured into cold 10% HCl (150 cm^3). The reaction mixture was extracted with ethyl acetate (3 × 100 cm^3) and washed with brine (3 × 100 cm^3). Evaporation of the solvent yielded pale yellow crystals (5.2 g, quantitative), m.p. 155.5—157 °C; $\nu_{max.}$(Nujol) 1 680 cm^{-1}; $\delta_H(CDCl_3)$ 1.80 (t, 1 H, *J* = 7.8), 3.80 (d, 2 H, *J* = 7.8), 7.43 (d, 2 H, *J* = 8.5), and 8.07 (d, 2 H, *J* = 8.3 Hz).

4-(*Acetylthiomethyl*)*benzoic acid.* A dichloromethane solution (100 cm^3) containing the above acid (5.0 g, 30 mmol), NEt_3 (4.5 g, 44 mmol), and acetic anhydride (3.7 g, 36 mmol) was stirred at room temperature for 6 h under Ar. After vacuum evaporation of solvent, the residue in ethyl acetate (150 cm^3) was washed with 10% HCl and brine, and dried (Na_2SO_4). Recrystallization from ethyl acetate–light petroleum gave colourless crystals (4.83 g, 76%), m.p. 144—145 °C; $\nu_{max.}$(Nujol) 1 680 cm^{-1}; $\delta_H(CDCl_3)$ 2.30 (s, 3 H), 4.09 (s, 2 H), 7.32 (d, 2 H, *J* 8.6), and 7.97 (d, 2 H, *J* 8.5 Hz) (Found: C, 57.00; H, 4.80; S, 15.05. $C_{10}H_{10}O_3S$ requires C, 57.15; H, 4.80; S, 15.25%).

4-(*Acetylthiomethyl*)*benzoyl chloride.* A suspension of the above acid (1.60 g, 7.6 mmol) and oxalyl chloride (10 g, 79 mmol) in benzene (20 cm^3) was refluxed for 1 h. Vacuum distillation gave colourless crystals (1.40 g, 80%), b.p. (0.025 mmHg) 138—140 °C, m.p. 32—32.5 °C; $\nu_{max.}$(Nujol) 1 670 and 1 760 cm^{-1}; $\delta_H(CDCl_3)$ 2.36 (s, 3 H), 4.14 (s, 2 H), 7.43 (d, 2 H, *J* 8.5), and 8.05 (d, 2 H, *J* 8.5 Hz) (Found: C, 52.40; H, 3.90; Cl, 15.40; S, 13.80. $C_{10}H_9ClO_2S$ requires C, 52.50; H, 3.95; Cl, 15.50; S, 14.00%).

3-*Acetylthio*-3-*methylbutanoic acid.* 3-Mercapto-3-methylbutanoic acid (5.20 g, 38.6 mmol)[27] was treated with acetic anhydride (4.2 cm^3) in pyridine (4.2 cm^3) at room temperature. After 8 h, 0.3 mol dm^{-3} HCl was gradually added at 0 °C, and stirred at room temperature for 2 h. The solution was then extracted into ether, and the extracts were washed with brine and dried ($MgSO_4$). Vacuum distillation gave a colourless oil (4.71 g, 69%), b.p. (0.8 mmHg) 106—108 °C; $\nu_{max.}$(Nujol) 2 500—3 000, 1 680—1 700 cm^{-1}; $\delta_H(CDCl_3)$ 1.56 (s, 6 H), 2.26 (s, 3 H), and 2.99 (s, 2 H).

3-*Acetylthio*-3-*methylbutanoyl chloride.* Treatment of the above acid (1.50 g, 8.5 mmol) with oxalyl chloride (2.34 cm^3, 18 mmol) in benzene (7 cm^3) at room temperature for 1.5 h afforded the corresponding acid chloride. A colourless oil (1.47 g, 89%) was obtained after distillation *in vacuo*, b.p. (0.6 mmHg) 60—61 °C; $\nu_{max.}$(Nujol) 1 800 and 1 680 cm^{-1}; $\delta_H(CDCl_3)$ 1.53 (s, 6 H), 2.26 (s, 3 H), and 3.64 (s, 2 H).

1,10,19,28-*Tetra*[4-(*acetylthio*)*benzoyl*]-1,10,19,28-*tetra-azacyclohexatriacontane*, L^6. To a mixture of tetra-amine hydrochloride L^4 (500 mg, 0.763 mmol) and NEt_3 (930 mg, 9.19 mmol) in dichloromethane (12 cm^3) was added portionwise at 0 °C 4-acetylthiobenzoyl chloride (790 mg, 3.68 mmol) and the mixture stirred at room temperature for 2.5 h. The solution was washed with saturated $NaHCO_3$, 5% HCl, and brine, and dried ($MgSO_4$). Chromatographic purification over a silica gel column with methanol–hexane–chloroform (1:5:2) gave 843 mg (89%) of a pale yellow solid, m.p. 165—166 °C (ethyl acetate); $\nu_{max.}$(Nujol) 1 700 and 1 630 cm^{-1}; $\delta_H(CDCl_3)$ 1.12—1.61 (m, 48 H), 2.43 (s, 12 H), 3.18 (br, 8 H), 3.45 (br, 8 H), and 7.35—7.47 (m, 16 H) (Found: C, 66.80; H, 7.65; N, 4.50; S, 10.30. $C_{68}H_{92}N_4O_8S_4$ requires C, 66.85; H, 7.60; N, 4.60; S, 10.50%).

1,10,19,28-*Tetra*[4-(*acetylthiomethyl*)*benzoyl*]-1,10,19,28-*tetra-azacyclohexatriacontane*, L^7. Compound L^4 hydrochloride (100 mg, 0.153 mmol) and NEt_3 (186 mg, 1.84 mmol) were allowed to react in dichloromethane (5 cm^3) for 30 min at 0 °C, and then 4-acetylthiomethylbenzoyl chloride (280 mg, 1.22 mmol) was added in portions and stirred at room temperature. After 2 h the reaction mixture was washed with saturated $NaHCO_3$, 5% HCl, and brine. Purification by column chromatography over silica gel eluted with methanol–hexane–chloroform (1:6:2) afforded a pale yellow oil (166 mg, 85%); $\nu_{max.}$(neat) 1 680 and 1 620 cm^{-1}; field-desorption mass spectrum: 1 278 (M^+ + 1, 74.3), 1 277 (M^+, 100%), 1 204 (M^+ − 73, 55.6), 1 203 (M^+ − 74, 51.8), and 639 (M^+ − 638, 59.5%); $\delta_H(CDCl_3)$ 1.11—1.59 (m, 48 H), 2.35 (s, 12 H), 3.17 (br, 8 H), 3.44 (br, 8 H), 4.11 (s, 8 H), and 7.25—7.32 (m, 16 H) (Found: C, 67.15; H, 7.95; N, 4.00; S, 9.45. $C_{72}H_{100}N_4O_8S_4 \cdot H_2O$ requires C, 66.75; H, 7.95; N, 4.30; S, 9.90%).

1,10,19,28-*Tetra*(3-*acetylmercapto*-3-*methylbutanoyl*)-1,10,19,28-*tetra-azacyclohexatriacontane*, L^8. To a dichloromethane solution (50 cm^3) of L^4 (free amine; 400 mg, 0.79 mmol) and K_2CO_3 (650 mg, 4.7 mmol) was added dropwise 3-acetylthio-3-methylbutanoyl chloride (1.6 g, 8.2 mmol) in dichloromethane (50 cm^3) over a period of 30 min at 0 °C, and stirred overnight (16 h) at room temperature. The inorganic salts were filtered off, and the filtrate was washed with saturated $NaHCO_3$, 5% HCl, and brine, and dried ($MgSO_4$). Chromatographic purification over silica gel eluted with methanol–hexane–chloroform (1:10:2) gave a colourless oil (617 mg, 68%), $\nu_{max.}$(neat) 1 640 and 1 680 cm^{-1}; $\delta_H(CDCl_3)$ 1.31—1.40 (m, 32 H), 1.58 (s, 24 H), 1.40—1.65 (br, 16 H), 2.25 (s, 12 H), 2.92 (s, 8 H), and 3.30 (br, 16 H) (Found: C, 63.50; H, 9.70; N, 4.90; S, 11.35. $C_{60}H_{108}N_4O_8S_4$ requires C, 63.70; H, 9.55; N, 4.90; S, 11.25%).

1,10,19,28-*Tetra*(4-*mercaptobenzoyl*)-1,10,19,28-*tetra-azacyclohexatriacontane*, L^1. The acetyl compound L^6 (720 mg, 0.589 mmol) in deaerated 1 mol dm^{-3} HCl–methanol (150 cm^3) was heated at 60 °C under Ar for 3 h. After removal of the solvent *in vacuo* the residue was dissolved in chloroform (300 cm^3), washed with brine, and dried (Na_2SO_4). Evaporation of the solvent gave a pale yellow oil (620 mg, quantitative); $\nu_{max.}$(Nujol) 2 500 and 1 615 cm^{-1}; $\delta_H(CDCl_3)$ 1.22 (m, 32 H, CH_2), 1.55 (m, 16 H, $N_\beta CH_2$), 3.15 (br, 8 H, $N_\alpha CH_2$), 3.43 (br, 8 H, $N_\alpha CH_2$), 3.55 (s, 4 H, SH), and 7.20—7.33 (m, 16 H, Ph) (Found: C, 65.90; H, 7.95; N, 5.00; S, 12.05. $C_{60}H_{84}N_4O_4S_4 \cdot 2H_2O$ requires C, 66.15; H, 8.15; N, 5.15; S, 11.75%).

1,10,19,28-*Tetra*[4-(*mercaptomethyl*)*benzoyl*]-1,10,19,28-*tetra-azacyclohexatriacontane*, L^2. Compound L^7 (500 mg, 0.391 mmol) in deaerated 1 mol dm^{-3} HCl–methanol (100 cm^3) was heated at 70 °C for 3 h under Ar. The mixture was then evaporated to dryness *in vacuo*, dissolved in chloroform (200 cm^3), washed with brine, and dried (Na_2SO_4). Vacuum evaporation of the solvent yielded a pale yellow oil (437 mg, quantitative); $\nu_{max.}$(neat) 2 500 and 1 620 cm^{-1}; $\delta_H(CDCl_3)$ 1.23 (m, 32 H, CH_2), 1.62 (m, 16 H, $N_\beta CH_2$), 1.77 (t, 4 H, *J* 7.6, SH), 3.21 (br, 8 H, $N_\alpha CH_2$), 3.45 (br, 8 H, $N_\alpha CH_2$), 3.75 (d, 8 H, *J* 7.4 Hz, SCH_2), and 7.23—7.44 (m, 16 H, Ph); positive-ion fast-atom bombardment mass spectrum (matrix: *m*-$NO_2C_6H_4CH_2OH$ + 0.2 mol dm^{-3} CF_3CO_2H): *m/z* 1 109.88 [Calc. 1 109.61 (M^+ + H)] (Found: C, 68.70; H, 8.40; N, 5.00; S, 11.25. $C_{64}H_{92}N_4O_4S_4 \cdot 1.5H_2O$ requires C, 68.70; H, 8.40; N, 5.00; S, 11.45%).

1,10,19,28-*Tetra*(3-*mercapto*-3-*methylbutanoyl*)-1,10,19,28-*tetra-azacyclohexatriacontane*, L^3. Compound L^3 as a colourless oil (302 mg, 89%) was obtained in the manner described above using L^8 (387 mg, 0.339 mmol) by heating at 60 °C for 2 h. Dichloromethane was employed in lieu of chloroform in this case. $\nu_{max.}$(neat) 2 550 and 1 630 cm^{-1}; $\delta_H(CDCl_3)$ 1.31 (m, 32 H, CH_2), 1.56 (m, 16 H, $N_\beta CH_2$), 1.60 [s, 24 H, $C(CH_3)_2$], 2.60 (br, 8 H, $COCH_2$), 2.68 (s, 4 H, SH), and 3.28 (br, 16 H, $N_\alpha CH_2$) (Found: C, 63.40; H, 10.40; N, 5.55. $C_{52}H_{100}N_4O_4S_4 \cdot H_2O$ requires C, 63.00; H, 10.35; N, 5.65%).

Complex (**4**). To a dmf (30 cm^3) solution of compound (**3**)

(157 mg, 0.124 mmol), L^1 (150 mg, 0.142 mmol) in dmf (30 cm^3) was added dropwise, and the liberated Bu^tSH was distilled off *in vacuo* at 40 °C for 30 min. Then tetrahydrofuran (300 cm^3) was added, and the mixture kept at −20 °C overnight. The precipitate was collected by filtration, then washed with methanol, dichloromethane, and ether to afford 174 mg (74%) of a black powder, m.p. >300 °C (dmf–tetrahydrofuran); $\delta_H[(CD_3)_2SO]$ 1.07—1.49 [br, 24 H + 48 H, CH_3(cation) + CH_2(skeleton)], 3.16—3.37 [br, 16 H, N_α(skeleton) CH_2], 3.18—3.20 [br, 16 H, N_α(cation)CH_2], 5.8 [br, 8 H, aromatic (*ortho* to S)], and 8.0 [br, 8 H, aromatic (*meta* to S)]; $\lambda_{max.}$(dmf) 442 (ε 14 300 and 365 nm (sh, 21, 100 dm^3 mol^{-1} cm^{-1}) (Found: C, 51.20; H, 6.95; N, 4.65; S, 14.20. $C_{76}H_{120}Fe_4N_6O_4S_8 \cdot 6H_2O$ + 5% dmf requires C, 51.55; H, 7.50; N, 4.80; S, 14.45%); $E_{\frac{1}{2}}$ *vs.* s.c.e. in d.m.s.o. −0.36, (1− to 2−) −0.85 (2− to 3−), 1.64 V (3− to 4−).

The following clusters were synthesized similarly: (**5**) (560 mg, 89%) using (**3**) (370 mg, 0.382 mmol, 10 cm^3 dmf), and L^2 (437 mg, 0.391 mmol, 10 cm^3 dmf), precipitated with ethyl acetate–hexane (1:20, 300 cm^3), and washed with acetonitrile and dichloromethane, m.p. >300 °C (dmf–tetrahydrofuran); $\delta_H[(CD_3)_2SO]$ 1.10—1.49 [br, 24 H + 48 H, CH_3(cation) + CH_2(skeleton)], 3.1—3.4 [br, 16 H + 16 H, N_α(skeleton)-CH_2 + N_α(cation)CH_2], 7.3 (br, 8 H, aromatic), 7.5 (br, 8 H, aromatic), and 13.2 (br, 8 H, $PhCH_2S$); $\lambda_{max.}$(dmf) 420 (ε 15 300) and 315 nm (sh, 22 300 dm^3 mol^{-1} cm^{-1}); $E_{\frac{1}{2}}$ *vs.* s.c.e. in dmso −0.35 (1− to 2−), −1.12 (2− to 3−), and −1.86 V (3− to 4−); (**6**) (50 mg, 70%) using (**3**) (43.5 mg, 0.0449 mmol, 10 cm^3 acetonitrile) and L^3 (43.7 mg, 0.0449 mmol, 10 cm^3 dmf), precipitated with tetrahydrofuran (600 cm^3), and washed with acetonitrile and dichloromethane, m.p. >300 °C (dmf–tetrahydrofuran); $\delta_H[(CD_3)_2SO]$: 1.02—1.77 [br, 24 H + 48 H, CH_3(cation) + CH_2(skeleton)], 2.50 (s, 8 H, $COCH_2$), 2.63 [br, 24 H, CH_3(ligand)], and 3.15—3.4 [br, 16 H + 16 H, N_α(skeleton)CH_2 + N_α(cation)CH_2]; $\lambda_{max.}$(dmf) 416 (ε 16 200) and 302 nm (sh, 21 100 dm^3 mol^{-1} cm^{-1}); (Found: C, 54.75; H, 5.50; N, 4.85; S, 14.90. $C_{78}H_{92}Fe_4N_6O_4S_8 \cdot 3H_2O$ + 5% dmf requires C, 54.75; H, 5.80; N, 4.95; S, 14.95%); $E_{\frac{1}{2}}$ *vs.* s.c.e in dmso +0.25 (1− to 2−), −1.13 V (2− to 3−).

Colorimetric SH *Determination.*[17]—Ligand L^1 (3.0 cm^3; 1.477 mg, 1.40 μmol in 50.0 cm^3 methanol) was mixed with phosphate buffer (2.0 cm^3, 0.1 mol dm^{-3}, pH 8.0) and water (5.0 cm^3). To a solution of the above mixture (3.0 cm^3), 5,5′-dithiobis(2-nitrobenzoic acid) (20 μl, 10 mmol dm^{-3} in phosphate buffer, pH 7.0) was added, and the absorbance at 412 nm was determined after 40 min at room temperature. The same procedures were used for the other complexes with L^2 (0.720 mg, 0.650 μmol, 20.0 cm^3 methanol), and L^3 (1.076 mg, 1.105 μmol, 20.0 cm^3 methanol).

Conclusion

We have demonstrated the facile preparation of aromatic and alkyl tetrathiol ligands anchored to a 36-membered macrocycle consisting of a methylene backbone, which are suitable for capturing cubane-type cluster cores. Ligand-substitution reactions afford a new type of 4Fe–4S clusters surrounded by an intramolecular hydrophobic domain. Our current studies are devoted to the complexation of 3Fe clusters by macrocyclic trithiol ligands.

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