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Synthesis, Structure, and Spectroscopy of Encapsulated Complexes of Cobalt(III) Derived from the Ligand 5-Methyl-5-(4-amino-2-thiabutyl)-3,7-diazanonane-1,9-diamine (N_5S)

James I. Bruce,[1a] Lawrence R. Gahan,*[1a] Trevor W. Hambley,[1b] and Robert Stranger[1a]

Chemistry Department, The University of Queensland, Brisbane, QLD, Australia 4072, and School of Chemistry, The University of Sydney, Sydney, NSW, Australia 2006

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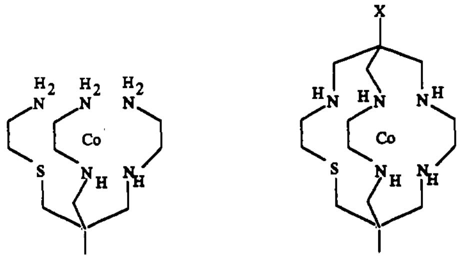
The synthesis of the N_5S ligand 5-methyl-5-(4-amino-2-thiabutyl)-3,7-diazanonane-1,9-diamine, and its complex with cobalt(III), is reported. Reaction of this complex with nitromethane and formaldehyde results in the nitro-capped encapsulated complex [(1-methyl-8-nitro-3-thia-6,10,13,16,19)-pentaazabicyclo[6.6.6]icosane)cobalt(III)] perchlorate, $[Co(NON_5Ssar)](ClO_4)_3$. The NH_3^+-capped complex $[Co(AMN_5SsarH)]Br_4{\cdot}2H_2O$ has been characterized by a single-crystal X-ray study: crystals are monoclinic, space group $P2_1/a$, with $Z = 4$, $a = 10.735(3)$ Å, $b = 18.699(7)$ Å, $c = 12.692(3)$ Å, $\beta = 91.25(2)°$, and $R = 0.031$ (1480 F). The low-temperature (11 K) absorption spectrum of $[Co(AMN_5SsarH)]^{4+}$ has been measured in Nafion film, and from the observed positions of both spin-allowed $^1T_{1g}$, $^1T_{2g}$ and spin-forbidden $^3T_{1g}$, $^3T_{2g}$ states, octahedral ligand-field parameters of $B = 565$ cm^{-1}, $C = 3300$ cm^{-1}, and $10Dq = 22\,900$ cm^{-1} were determined. Comparison with other sar type N_6, N_4S_2, N_3S_3, and S_6 encapsulated complexes indicates that B is reduced by approximately 30 cm^{-1} on replacement of a nitrogen with a thioether donor.

Introduction

The encapsulating ligands 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane (N_6sar)[2–4] and 3,6,10,13,16,19-hexathiabicyclo[6.6.6]icosane (Me_2S_6sar)[5] represent the two extremes of a possible set of seven ($N_{6-x}S_x$; x = 0–6) icosane encapsulating ligands. Extensive studies concerning the electrochemical,[6,7] redox,[8,9] spectroscopic, and magnetic properties[10,11] of the metal complexes of some of the ligands in this series have been reported. That a change in the number of thioether donors influences, in a progressive way, the properties of the metal complexes is exemplified by a comparison of the rate of electron transfer self-exchange for cobalt(III) and cobalt(II) complexes of Me_2S_6sar,[5] N_3S_3sar ($k_{11} \sim 10^4$ M^{-1} s^{-1}),[9] and N_6sar ($k_{11} < 10$ M^{-1} s^{-1}).[8] Of interest is the observation that the self-exchange rates for the S6 and N3S3 complexes are essentially identical and approximately 4 orders of magnitude greater than that observed for the N6 complexes, suggesting that the maximum effect of the change in the ratio of N/S donors may occur within the N6, N5S, N4S2, N3S3 part of the icosane series. The change in the rate of self-exchange electron transfer is not the only parameter which can be probed with these complexes; changes in redox potentials and ligand field parameters are also of interest.[10,11]

Chart I



$[Co(N_5S)]^{3+}$ $[Co(XN_5Ssar)]^{n+}$

We report in this paper the synthesis and characterization of the $N_{6-x}S_x$ (x = 1) segment of the icosane series, i.e. the N5S complex. Cobalt(III) complexes based on the ligand 5-methyl-5-(4-amino-2-thiabutyl)-3,7-diazanonane-1,9-diamine (N_5S) and, subsequently, the encapsulating ligand based on 3-thia-6,10,13,16,19-pentaazabicyclo[6.6.6]icosane (N_5Ssar) are reported. (The ligands described in this work are detailed in Chart I).

Experimental Section

^{1}H NMR spectra were recorded with a Varian M360 60-MHz spectrometer, sodium 3-(trimethylsilyl)propanesulfonate (NaTPS) in D_2O or tetramethylsilane (Me_4Si) in $CDCl_3$ being the internal reference. Fourier-transform $^{13}C[^1H]$NMR spectra were recorded with a Bruker AC200 FT spectrometer on internal lock (D_2O, $CDCl_3$), 1,4-dioxane and NaTPS (D_2O) or Me_4Si ($CDCl_3$) being the internal reference. Chemical shifts for the ^{13}C NMR spectra recorded in D_2O are reported in parts per million (δ) as positive downfield and negative upfield from the internal reference (dioxane); chemical shifts for the ^{13}C NMR spectra recorded in $CDCl_3$ are reported in parts per million (δ) as positive downfield from the internal reference Me_4Si. In the ^{13}C NMR assignments, the symbol C_q indicates a quaternary carbon atom. Visible spectra were recorded either with a Shimadzu UV-265 or a Cary 17 spectrophotometer (ϵ in M^{-1} cm^{-1}). For low-temperature spectra, samples were cooled down to ~10 K using a Leybold Heraeus ROK 10–300 closed-cycle helium cryostat. Nafion films (Aldrich Nafion 117 perfluorinated membrane, 0.0007-in. thick) of the metal complexes were prepared by placing the film in dimethylformamide solutions of the complex for 48 h. The films were removed from the solution, washed with solvent and distilled water, and dried on tissue paper. In order to observe the spin-forbidden bands it was necessary to stack several films on top of one another.

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(1) (a) The University of Queensland. (b) University of Sydney.

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Syntheses. The abbreviation Tosyl indicates the *p*-tolylsulfonyl moiety; *t*-Boc indicates the *tert*-butyloxycarbonyl protecting group. 1,3-(Dimethylmethylenedioxy)-2-methyl-2-hydroxymethylpropane and 1,3-(dimethylmethylenedioxy)-2-methyl-2-(methylene-*p*-tolylsulfonyl)propane were prepared as described previously.[12]

1,3-(Dimethylmethylenedioxy)-2-methyl-2-(4-amino-2-thiabutyl)propane (1). To a solution of sodium metal (4.5 g, 0.185 mol) in dry methanol (50 mL) was added 2-aminoethanethiol hydrochloride, and the solution was heated at reflux for 20 min. A methanol solution (100 mL) of 1,3-(dimethylmethylenedioxy)-2-methyl-2-(methylene-*p*-tolylsulfonyl)propane (24 g, 0.076 mol) was added dropwise to the refluxing solution, and the reflux was maintained for 4 h after the completion of the addition. After cooling, the white precipitate of sodium chloride and sodium tosylate was removed by filtration, and the solvent was removed from the filtrate under reduced pressure. The residue was dissolved in $CHCl_3$ (100 mL) and the organic layer washed with water (3 × 75 mL). The $CHCl_3$ solution was separated, dried over Na_2SO_4, and filtered and the solvent removed under reduced pressure leaving a pale brown oil (14.9 g). ^{13}C NMR ($CDCl_3$): δ 19.1 (2-CH_3), 20.4, 26.9 (1,3-CH_3), 34.0 (Cq), 38.0, 38.1 (CH_2–S), 41.1 (CH_2–N), 67.9 (CH_2–O), 97.8 (C_q). ^1H NMR ($CDCl_3$): δ 0.90 (2-CH_3, s), 1.42 (1,3-CH_3, s), 2.57–3.08 (–CH_2–, m), 3.53, 3.62 (–CH_2–).

1,3-(Dimethylmethylenedioxy)-2-methyl-2-(4-(*tert*-butyoxycarbonylamino)-2-thiabutyl)propane (2). **1** (14.9 g, 0.07 mol) was dissolved in the mixed solvent 1,4-dioxane (200 mL) and water (60 mL). The solution was cooled to 5 °C, and 3 M KOH (30 mL) was added. Di-*tert*-butyl carbonate (14.8 g, 0.071 mol) was added rapidly and the solution stirred at 5 °C for 30 min, during which time a white precipitate of K_2CO_3 formed. A second aliquot of KOH (30 mL) was added, and the solution was permitted to warm to room temperature. Stirring was continued while the solution was maintained at room temperature for 2 h. The white precipitate was removed by filtration and the filtrate extracted with ether (4 × 50 mL). The ether extracts were combined and the solvent removed under reduced pressure leaving a pale brown oil (14.3 g). ^1H NMR ($CDCl_3$): δ 0.85 (5-CH_3, s), 1.40 (2-CH_3), 1.43 (CH_3-*t*-Boc), 2.73 (–CH_2–, m), 3.60, 3.67 (-CH_2, s).

***N-tert*-Butoxycarbonyl-1,1-bis(hydroxymethyl)-1-methyl-3-thiahexanamine (3).** To a refluxing 50% ethanol/water (100 mL) solution of **2** (19.3 g, 0.061 mol) were added 10 drops of concentrated HCl, and the solution was heated at reflux for 5 min. The pH of the solution was adjusted to 7 with Na_2CO_3, and the solvents were removed under reduced pressure. The residue was dissolved in $CHCl_3$ (60 mL), and the mixture was washed with water (2 × 30 mL). The organic layer was separated and dried over Na_2SO_4, and after filtration the solvent was removed resulting in an oil (23.1 g). ^{13}C NMR ($CDCl_3$): δ 18.7 (–CH_3), 28.3 (CH_3-*t*-Boc), 33.74 (C_q), 39.2 (CH_2–S), 41.1, 41.3 (CH_2–NH_2), 68.8 (CH_2OH). ^1H NMR ($CDCl_3$): δ 0.83 (–CH_3, s), 1.43 (CH_3-*t*-Boc, s), 2.43–2.70 (–CH_2–, m), 3.55 (–CH_2–O).

***N-tert*-Butoxycarbonyl-1,1-bis(methylene-*p*-tolylsulfonyl)-1-methyl-3-thiahexanamine (4).** To a stirred solution of **3** (55.5 g, 0.196 mol) in dry pyridine (100 mL) cooled to –10 °C was added a solution of tosyl chloride (83.3 g) in dry pyridine (110 mL) dropwise over 3 h. The reaction mixture was permitted to warm to room temperature and then stirred for 24 h. The mixture was poured onto an ice–water slurry resulting in the precipitation of a brown oil, which was extracted with $CHCl_3$; the $CHCl_3$ extract was washed with water (3 × 75 mL) and, after separation, was dried over Na_2SO_4. Filtration and removal of the solvent under reduced pressure resulted in a brown oil, which was used without further purification (115 g). ^{13}C NMR ($CDCl_3$): δ 18.2 (CH_3), 21.6 (CH_3-tosylate), 28.3 (CH_3-*t*-Boc), 34.1 (C_q), 36.2 (CH_2–S), 69.7, 71.5 (CH_2–O–), 127.9, 129.5 (CH-tosylate), 132.1, 145.1 (Ar–C_q). ^1H NMR ($CDCl_3$): δ 0.90 (CH_3, s), 1.43 (CH_3-*t*-Boc), 2.43 (CH_3-tosylate, s), 3.1 (–CH_2–, m); 3.7 (O–CH_2, s); 3.77 (O–CH_2–, s); 7.5 (Ar–H, m).

5-Methyl-5-(4-*tert*-butoxycarbonylamino)-2-thiabutyl)-3,7-diazanonane-1,9-diamine (5). **4** (144 g, 0.244 mol) was heated to reflux with dry 1,2-diaminoethane (500 mL) for 24 h. At the completion of the reflux most of the 1,2-diaminoethane was removed by distillation, and the cooled residue was dissolved in methanol (250 mL) and a methanol solution (100 mL) of KOH (30.11 g) added. The dense white precipitate of potassium tosylate which formed was removed by filtration and the solvent removed from the filtrate. The heavy oil which remained was dissolved in $CHCl_3$ (200 mL), the organic layer was washed with water (3 × 50 mL) and dried over Na_2SO_4, and the solvent was removed under reduced pressure. A brown oil remained (45.4 g). ^{13}C NMR ($CDCl_3$): δ 22.3 (CH_3), 28.3 (CH_3-*t*-Boc), 33.2 (CH_2–N), 38.9 (C_q), 39.61, 39.9 (CH_2–S–), 41.25 (CH_2–NH_2), 52.8, 56.5 (CH_2–NH). ^1H NMR ($CDCl_3$): δ 0.97 (CH_3, s), 1.43 (CH_3-*t*-Boc), 1.53 (NH, s), 3.0 (CH_2, m).

5-Methyl-5-(4-amino-2-thiabutyl)-3,7-diazanonane-1,9-diamine (N_5S). **5** (45.4 g, 0.124 mol) was stirred for 4 h in dioxane (400 mL) which had previously been saturated with HCl (3.8 M). At the completion of the reaction period the solvent was removed under reduced pressure, and the residue was dissolved in water, the solution made basic by addition of KOH, and the mixture extracted with $CHCl_3$ (3 × 50 mL). The $CHCl_3$ extracts were combined and dried over Na_2SO_4. The $CHCl_3$ was removed under reduced pressure leaving the product as a yellow oil (26.7 g). ^{13}C NMR ($CDCl_3$): δ 22.2 (CH_3), 37.7, 39.9 (CH_2–S), 38.9 (C_q), 41.1, 41.3, (CH_2–NH_2), 56.6, 53.06 (CH_2–NH). ^1H NMR ($CDCl_3$): δ 0.97 (CH_3, s), 1.43 (NH, s), 2.5 (CH_2, m).

Caution! Perchlorate salts of metal complexes can be explosive and should be handled with care. They should not be heated as solids.

$[Co(N_5S)](ClO_4)_3\cdot 2H_2O$. A methanol solution (100 mL) of cobaltous nitrate (32.5 g) was added slowly to the crude ligand mixture (94 g) dissolved in methanol (200 mL). A stream of air was bubbled through the reaction during the course of the addition and subsequently for a further 4 h. The methanol was removed and the residue dissolved in water and filtered. After dilution to large volume (2 L), the red solution was loaded on to Dowex cation-exchange resin 50W-X2 (200–400 mesh), H^+ form, and the column was washed with water and 1 M HCl to remove minor products. Elution with 2 M HCl removed a purple product, which was discarded. The major orange band which was removed after washing with 3 M HCl was collected and freed of solvent to give an orange solid, which was dissolved in a large volume of water (2 L) and rechromatographed on Sephadex C-25 cation exchange resin (Na^+ form). After being washed with 0.2 M NaCl solution to remove minor green and purple bands, the major orange band which eluted with 0.3 M NaCl was collected on Dowex 50W-X2 cation exchange resin, washed with 0.5 M HCl, and eluted with 3 M HCl. The orange solid obtained upon evaporation of the solvent was collected (9.1 g). This product was determined from ^{13}C NMR to be a mixture of the desired compound $[Co(N_5S)]Cl_3$ and $[Co(N_4S_2)]Cl_3$, in the ratio 10:1. Chromatographic separation of the mixture was achieved on Sephadex C-25 cation exchange resin (Na^+ form) with 0.03 M sodium citrate solution. The first band eluted from the column, after collection on Dowex cation exchange resin, was washed with dilute HCl and eluted with 3 M HCl. Removal of the solvent resulted in the isolation of a product identified as $[Co(N_5S)]Cl_3$ from the ^{13}C NMR spectrum. The product was crystallized from aqueous solution with $NaClO_4$. Anal. Calcd for $[(C_{11}H_{29}N_5SCo)](ClO_4)_3\cdot 2H_2O$: C, 20.1; H, 5.07; N, 10.7. Found: C, 20.3; H, 4.86; N, 10.9. Visible spectrum [λ_{max}, nm (ϵ_{max}) in H_2O]: 478 (115), 349 (122). ^1H NMR (D_2O): δ 1.1 (CH_3, s), 3.1 (CH_2, m). ^{13}C NMR (in D_2O): δ –9.90, –10.7, –11.4, –12.1 (CH_2–NH–), –21.6, –23.5, –24.0 (CH_2–NH_2), –27.09, –27.19 (CH_2–S), –24.3 (C_q), –43.6 (CH_3). The crude mixture of metal complexes could also be employed in the next step.

$[Co(NON_5Ssar)](ClO_4)_3\cdot H_2O$. The nitro-capped encapsulated complex was prepared from the reaction of the mixture of $[Co(N_5S)]^{3+}$ and $[Co(N_4S_2)]^{3+}$ (5.0 g) in aqueous solution (300 mL) with nitromethane (8.0 g), 37% aqueous formaldehyde solution (61 g, 37% solution), and Na_2CO_3 (2.80 g) as described.[4,11] At the completion of the reaction the solution was diluted to large volume and loaded on to a Dowex 50W-X2 cation exchange column (H^+ form), the column washed with water (1 L), 1 M HCl (1 L), and the orange band eluted with 3 M HCl. Removal of the solvent under reduced pressure resulted in an orange red solid. The solid was dissolved in a large volume of water (1 L) and loaded on a column of Sephadex C25 cation exchange resin (Na+) form; the column was washed with water and then eluted with 0.05 M Na_2SO_4, resulting in the separation of a leading major red-orange and a minor red band. The major band was collected, freed of eluent using Dowex cation exchange resin, and eluted with 3 M HCl. Removal of the solvent resulted in an orange solid which was crystallized from aqueous sodium perchlorate solution, 1.8 g. Anal. Calcd for $[(C_{15}H_{32}N_6O_2S)Co](ClO_4)_3\cdot H_2O$: C, 24.5; H, 4.66; N, 11.4. Found: C, 24.7; H, 4.81; N, 11.5. Visible spectrum [λ_{max}, nm (ϵ_{max}) in H_2O]: 484 (317), 354 (318). ^1H NMR (D_2O): δ 1.1 (CH_3, 3H, s), 3.3 (CH_2, 18H, m). ^{13}C NMR (D_2O): δ +20.6 (C_q–NO_2), –10.4, –11.1, –11.4, –11.8, –12.5, –13.5, –14.2, –15.0, –15.1 (CH_2-NH), –23.6 (C_q), –28.8, –28.9 (CH_2–S), –43.8 (CH_3).

$[Co(AMN_5SsarH)]Br_4\cdot 2H_2O$. The nitro cap was reduced to a protonated amine cap as previously described.[4,11] The product, after chromatographic purification, was crystallized from aqueous sodium bromide solution. Anal. Calcd for $[(C_{15}H_{35}N_6S)Co]Br_4\cdot 2H_2O$: C, 24.1; H, 5.27; N, 11.3; S, 4.3. Found: C, 23.7; H, 5.14; N, 10.9; S, 4.0. Visible

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Table I. Crystal Data for $[Co(AMN_5SsarH)]Br_4{\cdot}2H_2O$

cryst system	monoclinic
space group	$P2_1/a$
a, Å	10.735(3)
b, Å	18.699(7)
c, Å	12.692(3)
β, deg	91.25(2)
V, Å^3	2547(1)
D_{calc}, g cm^{-3}	1.951
empirical formula	$C_{15}H_{39}Br_4CoN_6O_2S$
fw	746.54
Z	4
μ, cm^{-1}	69.89
F(000), electrons	1480
habit	prisms
dimens, mm	0.20 × 0.20 × 0.325
λ, Å	0.71065
T, °C	21
R[a]	0.031
R$_w$[b]	0.033

[a] $R = (\sum\|F_o| - |F_c\|)/\sum|F_o|$. [b] $R_w = (\sum w^{1/2}\|F_o| - |F_c\|)/\sum w^{1/2}|F_o|$.

Table II. Positional Parameters for $[Co(AMN_5SsarH)]Br_4{\cdot}2H_2O$[a]

	x	y	z	B_{eq}, Å^2
Co(1)	0.2313(1)	0.1332(1)	0.2818(1)	1.30
S(1)	0.3898(1)	0.0892(1)	0.1930(1)	2.09
N(1)	0.1027(4)	0.0830(2)	0.1943(3)	1.79
N(2)	0.2226(4)	0.2143(2)	0.1833(3)	1.87
N(3)	0.2539(4)	0.0508(2)	0.3794(3)	1.76
N(4)	0.0901(3)	0.1684(2)	0.3671(3)	1.68
N(5)	0.3483(4)	0.1918(2)	0.3684(3)	1.93
N(6)	0.2321(4)	0.1471(2)	0.6388(3)	2.33
C(1)	0.1955(6)	0.1216(4)	−0.0916(5)	3.98
C(2)	0.2165(5)	0.1234(3)	0.0321(4)	2.24
C(3)	0.3514(6)	0.0927(3)	0.0548(4)	2.65
C(4)	0.1186(5)	0.0747(3)	0.0792(4)	2.61
C(5)	0.2041(5)	0.2001(3)	0.0676(5)	2.94
C(6)	0.3700(5)	−0.0016(3)	0.2336(4)	2.55
C(7)	−0.0206(5)	0.1179(3)	0.2185(4)	2.48
C(8)	0.3347(5)	0.2593(3)	0.2055(5)	2.88
C(9)	0.3615(5)	0.0034(3)	0.3511(4)	2.31
C(10)	−0.0245(5)	0.1280(3)	0.3350(5)	2.43
C(11)	0.3480(6)	0.2654(3)	0.3219(5)	2.90
C(12)	0.2551(6)	0.0659(3)	0.4930(4)	2.83
C(13)	0.1055(5)	0.1713(3)	0.4819(4)	2.95
C(14)	0.3342(5)	0.1932(3)	0.4842(4)	2.82
C(15)	0.2324(5)	0.1440(3)	0.5212(4)	1.85
Br(1)	0.1398(1)	0.3642(1)	−0.0760(1)	2.99
Br(2)	−0.0009(1)	0.3207(1)	0.2582(1)	3.45
Br(3)	0.4637(1)	0.4331(1)	0.1878(1)	3.49
Br(4)	−0.2883(1)	0.0976(1)	0.0306(1)	4.34
O(1)	0.1522(5)	0.2792(3)	0.6979(4)	4.41
O(2)	0.1894(5)	0.5006(3)	0.7655(4)	4.59

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Table III. Bond Lengths (Å) for $[Co(AMN_5SsarH)]Br_4{\cdot}2H_2O$

S(1)–Co(1)	2.219(1)	N(1)–Co(1)	1.990(4)
N(2)–Co(1)	1.967(4)	N(3)–Co(1)	1.989(4)
N(4)–Co(1)	1.994(4)	N(5)–Co(1)	1.982(4)
C(3)–S(1)	1.794(6)	C(6)–S(1)	1.791(5)
C(4)–N(1)	1.483(7)	C(7)–N(1)	1.513(6)
C(5)–N(2)	1.501(7)	C(8)–N(2)	1.490(6)
C(9)–N(3)	1.504(6)	C(12)–N(3)	1.469(7)
C(10)–N(4)	1.493(6)	C(13)–N(4)	1.464(7)
C(11)–N(5)	1.497(6)	C(14)–N(5)	1.481(7)
C(15)–N(6)	1.494(6)	C(2)–C(1)	1.583(8)
C(3)–C(2)	1.579(8)	C(4)–C(2)	1.522(7)
C(5)–C(2)	1.509(7)	C(9)–C(6)	1.500(7)
C(10)–C(7)	1.492(8)	C(11)–C(8)	1.486(8)
C(15)–C(12)	1.526(7)	C(15)–C(13)	1.528(7)
C(15)–C(14)	1.511(7)		

spectrum [λ_{max}, nm (ϵ_{max}) in H_2O]: 484 (322), 353 (319). ^1H NMR (D_2O): δ 1.1 (CH_3, 3H, s), 3.02 (CH_2, 24H, m). ^{13}C NMR (D_2O): δ −11.0 (C_q), −11.4, −11.6, −12.0, −12.8, −13.2, −13.9, −15.1 (CH_2–NH), −23.8 (C_q); −28.6, −28.9 (CH_2–S), −43.9 (CH_3).

AMN$_5$Ssar. The metal ion, as cobalt(II), was removed from the encapsulating ligand using NaCN under an inert atmosphere of nitrogen.[11] In a typical experiment the $[Co(AMN_5SsarH)]Br_4{\cdot}2H_2O$ complex (5 g) was dissolved in water and reduced with Zn powder (0.3 g) under a stream of nitrogen. Solid NaCN (3 g) was added and the reaction permitted to proceed for 24 h. The mixture was made strongly basic (KOH) and extracted with $CHCl_3$. Removal of the solvent under reduced pressure resulted in a white solid (3 g). Anal. Calcd for $C_{15}H_{34}N_6S$: C, 54.5; H, 10.4; N, 25.4; S, 9.7. Found: C, 54.0; H, 11.0; N, 25.6; S, 9.4. Mass spectrum, m/e: calcd, 330.543; found, 330.257. ^1H NMR ($CDCl_3$): δ 0.81 (CH_3, 3H, s), 2.8 (CH_2, 34H, m). ^{13}C NMR ($CDCl_3$): δ 23.4 (CH_3), 34.0, 39.8 (CH_2-S), 40.3 (C_q), 48.9, 51.0, 51.75, 60.4, 61.6, 62.4 (CH_2–N), 53.5 (C_q).

X-ray Crystallography. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. The crystallographic data are summarized in Table I. Data were reduced and Lorentz, polarization and absorption corrections were applied using the Enraf-Nonius structure determination package (SDP).[13] The structure was solved by direct methods using SHELXS-86[14] and was refined by block matrix least squares analysis with SHELX-76.[15] Hydrogen atoms were included at calculated sites (C–H 0.97 Å) with individual isotropic thermal parameters. All other atoms were refined anisotropically. Scattering factors for Co (neutral Co) were taken from ref 16; for all others the values supplied in SHELX-76 were used. Non-hydrogen atom coordinates are listed in Table II, bond lengths and bond angles are listed in Tables III and IV, respectively. The atomic nomenclature is defined in Figure 1.[17]

Results and Discussion

Nomenclature. The hexadentate ligand 5-methyl-5-(4-amino-2-thiabutyl)-3,7-diazanonane-1,9-diamine is given the abbreviation N_5S, consistent with the previously adopted abbreviation for the analogous ligand 5-methyl-5-(4-amino-2-azabutyl)-3,7-dithianonane-1,9-diamine, N_4S_2.[11] Similarly, the abbreviation for the nitro-capped complex becomes NON$_5$Ssar, and that for the amine capped ligand is AMN$_5$Ssar;[11] protonation of the NH_2-cap is described by the suffix H, e.g., $[Co(AMN_5SsarH)]^{4+}$.[6] That the second trigonal cap contains a methyl group is dictated by the synthetic procedures and is not included in the nomenclature.

Ligand Synthesis. The potentially hexadentate ligand 5-methyl-5-(4-amino-2-thiabutyl)-3,7-diazanonane-1,9-diamine has been synthesized in a reaction scheme in which one 4-amino-2-thiabutyl and two 4-amino-2-azabutyl moieties are selectively placed on the trigonal cap 1,1,1-tris(hydroxymethyl)ethane, (Scheme I). The synthetic scheme utilizes two protecting groups to permit selective reaction at different stages of the procedure. The formation of the cyclic acetal permitted the "one-site" addition of 2-aminoethanethiol. The second protecting group (t-Boc) permitted selective protection of the primary amine against both tosylation, in subsequent stages of the scheme, and intramolecular ring closing reactions previously observed in the syntheses of these types of ligands.[18] The desire to avoid preparing the toluenesulfonate derivative of the pendant amine stems from the observation of extensive ligand degradation during removal (HBr/acetic acid; H_2SO_4) of this protecting group. The final product of the synthesis was shown to contain byproducts, one of which

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(17) Figures were drawn with ORTEP (Johnson, C. K. *ORTEP, A Thermal Ellipsoid Plotting Program*; Oak Ridge National Labs.: Oak Ridge, TN, 1965.

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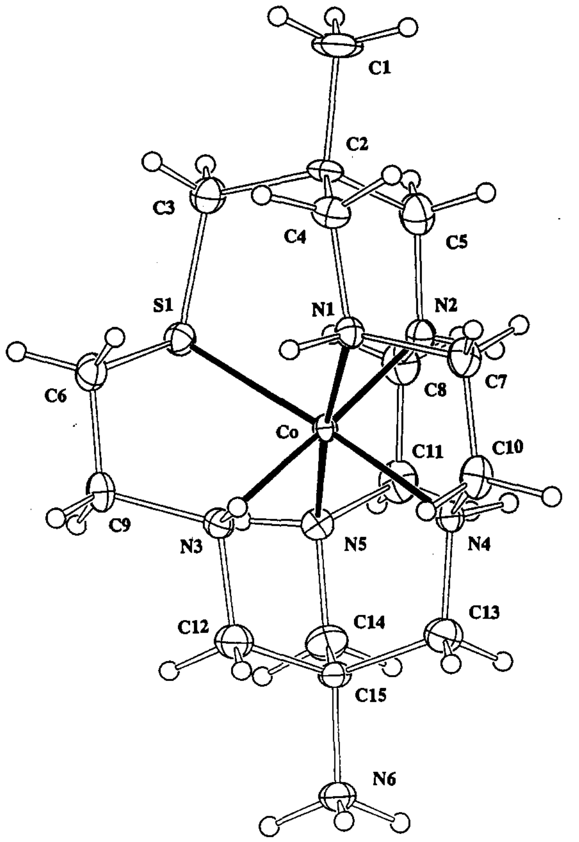


Figure 1. ORTEP plot of the complex cation of [Co(AMN$_5$SsarH)]Br$_4$·2H$_2$O, giving the crystallographic atom numbering. Probability ellipsoids of 30% are shown.

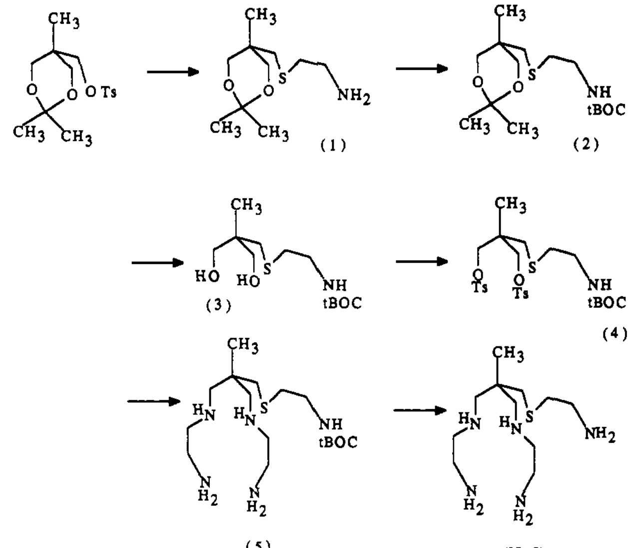
Table IV. Bond Angles (deg) for [Co(AMN$_5$SsarH)]Br$_4$·2H$_2$O

N(1)–Co(1)–S(1)	94.1(1)	N(2)–Co(1)–S(1)	89.4(1)
N(2)–Co(1)–N(1)	89.2(2)	N(3)–Co(1)–S(1)	86.8(1)
N(3)–Co(1)–N(1)	93.2(2)	N(3)–Co(1)–N(2)	175.7(2)
N(4)–Co(1)–S(1)	176.9(1)	N(4)–Co(1)–N(1)	86.1(2)
N(4)–Co(1)–N(2)	93.7(1)	N(4)–Co(1)–N(3)	90.1(2)
N(5)–Co(1)–S(1)	90.2(1)	N(5)–Co(1)–N(1)	174.2(2)
N(5)–Co(1)–N(2)	87.0(2)	N(5)–Co(1)–N(3)	90.9(2)
N(5)–Co(1)–N(4)	89.8(2)	C(3)–S(1)–Co(1)	108.8(2)
C(6)–S(1)–Co(1)	96.2(2)	C(6)–S(1)–C(3)	106.9(3)
C(4)–N(1)–Co(1)	120.4(3)	C(7)–N(1)–Co(1)	106.4(3)
C(7)–N(1)–C(4)	111.4(4)	C(5)–N(2)–Co(1)	119.3(3)
C(8)–N(2)–Co(1)	106.7(3)	C(8)–N(2)–C(5)	112.0(4)
C(9)–N(3)–Co(1)	113.1(3)	C(12)–N(3)–Co(1)	117.4(3)
C(12)–N(3)–C(9)	110.9(4)	C(10)–N(4)–Co(1)	108.4(3)
C(13)–N(4)–Co(1)	118.8(3)	C(13)–N(4)–C(10)	111.4(4)
C(11)–N(5)–Co(1)	107.0(3)	C(14)–N(5)–Co(1)	118.9(3)
C(14)–N(5)–C(11)	112.1(4)	C(3)–C(2)–C(1)	106.4(5)
C(4)–C(2)–C(1)	107.0(5)	C(4)–C(2)–C(3)	110.4(4)
C(5)–C(2)–C(1)	107.7(5)	C(5)–C(2)–C(3)	112.2(5)
C(5)–C(2)–C(4)	112.7(5)	C(2)–H(2A)–C(1)	173.0(8)
C(3)–H(2B)–C(2)	165.1(7)	C(2)–C(3)–S(1)	112.4(4)
C(2)–C(4)–N(1)	114.8(4)	C(2)–C(5)–N(2)	116.7(4)
C(9)–C(6)–S(1)	103.6(4)	C(10)–C(7)–N(1)	107.4(4)
C(11)–C(8)–N(2)	106.9(4)	C(6)–C(9)–N(3)	109.8(4)
C(7)–C(10)–N(4)	107.1(4)	C(8)–C(11)–N(5)	108.7(4)
C(15)–C(12)–N(3)	114.6(4)	C(15)–C(13)–N(4)	113.1(4)
C(15)–C(14)–N(5)	112.8(4)	C(12)–C(15)–N(6)	105.9(4)
C(13)–C(15)–N(6)	107.0(4)	C(13)–C(15)–C(12)	112.9(4)
C(14)–C(15)–N(6)	107.7(4)	C(14)–C(15)–C(12)	112.9(4)
C(14)–C(15)–C(13)	110.0(5)		

has been identified (<10%) as 5-methyl-5-(4-amino-2-azabutyl)-3,7-dithianonane-1,9-diamine, the N$_4$S$_2$ analogue.[11]

Oxidation of a mixture of a cobalt(II) salt and the crude ligand mixture, in methanol, with O$_2$ resulted in a mixture of [Co(N$_5$S)]$^{3+}$ and [Co(N$_4$S$_2$)]$^{3+}$. Separation using cation exchange chromatography afforded a pure sample of the desired complex. Alternatively, encapsulation procedures employing formaldehyde and nitromethane, in the presence of base,[4] followed by cation-exchange chromatography, resulted in the nitro-capped complex. Reduction of the nitro group, using previously described procedures,[4,11] resulted in the complex [Co(AMN$_5$SsarH)]Br$_4$·2H$_2$O.

Scheme I



Discussion of the Structure. The structure of [Co(AMN$_5$SsarH)]Br$_4$·2H$_2$O consists of the complex cation, four Br anions, and two water molecules. The conformation of the complex cation is described as *lel*$_3$ since the C–C vectors of the N–C–C–E (E = N or S) chelate rings are parallel to the pseudo-C_3 axis of the complex. Each of the cap atoms approximately eclipses the atoms to which they are bonded. The caps are staggered with respect to each other, and the conformation is similar to that previously observed for the N$_4$S$_2$,[11] N$_3$S$_3$,[19] and N$_6$[4] analogues of this complex.

The Co–S bond length in this structure (2.219(1) Å) is similar to that reported for analogous complexes (N$_4$S$_2$sar, average 2.214 Å;[11] N$_3$S$_3$sar, 2.226(1) Å[19]). In each case the bond length is at the short end of the range observed for Co–S bonds.[20,21] The Co–N bond lengths (average 1.984 Å) are shorter than those observed in [Co(NON$_4$S$_2$sar)]$^{3+}$ (average 2.008 Å)[11] and are similar to those reported for [Co(sep)]$^{3+}$ (1.990 Å).[2] The bond angles at the bridgehead methylene carbon atoms, e.g. C(4)–C(2)–C(3) and C(12)–C(15)–C(13), are expanded somewhat from the tetrahedral values, as are the bond angles at the methylene carbon atoms, e.g. C(2)–C(3)–S(1) and C(15)–C(12)–N(3), possibly as a consequence of the incorporation of a thioether in the macrobicyclic ring. An additional effect of the incorporation of the thioether donor is to increase the torsion angle at the central carbon–carbon bond (N(2)–C(8)–C(11)–N(5) and N(1)–C(7)–C(10)–N(4)) from 53.3(5) and 54.2(4)°, respectively, to 58.8(4)° for S(1)–C(6)–C(9)–N(3), similar to that observed in other mixed nitrogen/sulfur complexes.[19]

^{13}C NMR. The ^{13}C NMR spectra displayed reflect the general lack of symmetry in the complexes. For the [Co(N$_5$S)]$^{3+}$ complex the ^{13}C NMR spectrum displays 11 lines. Resonances at -9.90, -10.7, -11.4, and -12.1 ppm are assigned as methylene carbon atoms adjacent to coordinated secondary amines; resonances at -21.6, -23.5, and -24.0 ppm arise from methylene carbon atoms adjacent to coordinated primary amines. Resonances at -27.09 and -27.19 pm are assigned as arising from methylene carbon

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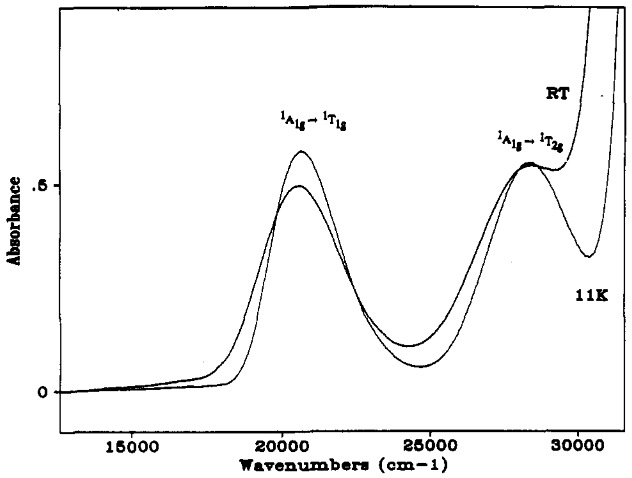

Figure 2. Absorption spectrum of the spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$, $^1T_{2g}$ transitions in $[Co(AMN_5SsarH)]^{4+}$ (Nafion film; room temperature and 11 K).

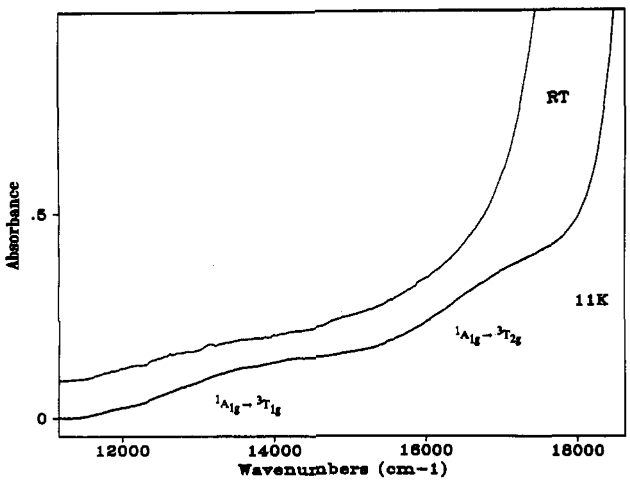

Figure 3. Absorption spectrum of the weak spin forbidden $^1A_{1g} \rightarrow {}^3T_{1g}$, $^3T_{2g}$ transitions in $[Co(AMN_5SsarH)]^{4+}$ (Nafion film; room temperature and 11 K).

atoms adjacent to the coordinated thioether.[19,22] The resonance at −24.3 ppm is assigned to the quaternary carbon atom in the trigonal cap. The encapsulation reaction to produce the nitro-capped complex results in the disappearance of the resonances around −23 ppm, except for that assigned to the quaternary carbon. The appearance of a more complex pattern of resonances in the region of the spectrum associated with carbon atoms adjacent to coordinated secondary amines, and the appearance of a resonance at +20.6 ppm, assigned to the quaternary carbon adjacent to the nitro group,[4,11,19] confirms the formation of the encapsulated complex. Reduction of the nitro group to a protonated amine results in loss of the +20.6 ppm resonance and the appearance of a new resonance at −11.0 ppm, as expected.[4,11,19] In most of the ^{13}C NMR spectra, small splittings (<0.5 Hz) were observed for resonances due to carbon atoms α and β to coordinated primary and secondary amines. This splitting has been ascribed to an isotopomeric effect resulting from a proton–deuterium exchange occurring at the amine centres.[23]

Visible Spectra. The visible spectra of these complexes are characteristic of low-spin octahedral cobalt(III) with two spin-allowed absorption bands corresponding to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ d–d transitions. As noted previously,[24] the nature of the apical donor has little influence on the position of the d–d bands.

The absorption spectrum of $[Co(AMN_5SsarH)]^{4+}$ in Nafion film at room temperature and 11 K is shown in Figure 2. At room temperature, the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition is almost obscured by the intense low-energy Co–S charge transfer transition, but at low temperatures this transition is clearly resolved. It is apparent from the two spectra that a vibronic mechanism is contributing to the transition intensity; however, due to the thermal contraction and expansion of the Nafion film with change in temperature, it is not possible to quantify this effect.

In order to locate the much weaker spin-forbidden transitions in $[Co(AMN_5SsarH)]^{4+}$, a more concentrated spectrum in Nafion film was measured at room temperature and 11 K. The spectra are shown in Figure 3 where, at low temperature, both the $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$ spin-forbidden transitions are observed. From a band analysis, the $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$ transitions are centred at approximately 13 750 and 17 500 cm^{-1}, respectively.

Assuming approximate octahedral O_h symmetry, the octahedral ligand field parameters $10Dq$, B, and C can be determined using the following perturbation expressions corrected for configuration interaction:[11]

$$E(^1A_{1g} \rightarrow {}^1T_{1g}) = 10Dq - C + (5BC + 7B^2 + C^2)/5Dq$$

$$E(^1A_{1g} \rightarrow {}^1T_{2g}) = 10Dq - C + 16B + (3BC - 27B^2 + C^2)/5Dq$$

$$E(^1A_{1g} \rightarrow {}^3T_{1g}) = 10Dq - 3C + (5BC - 11B^2 + C^2)/5Dq$$

$$E(^1A_{1g} \rightarrow {}^3T_{2g}) = 10Dq - 3C + 8B + (3BC - 21B^2 + C^2)/5Dq \quad (1)$$

From the observed band positions in the low-temperature spectrum, the above energy expressions give the best-fit values of $B = 557$, $C = 3240$, and $10Dq = 21\,950$ cm^{-1}. These may be compared with the values $B = 565$, $C = 3300$ and $10Dq = 22\,880$ cm^{-1} determined from a complete d^6 ligand field calculation.[25] Again, as was found for other $Co(N_6)^{3+}$ complexes,[24] the C/B ratio is approximately 6 compared with 4.8 for the free ion.[26,27]

The systematic replacement of amine donors with thioether donors in the cage system, keeping all else constant, affords the opportunity to examine the ligand dependence of 10Dq and the Racah B electron repulsion parameter. Table V lists the position of the $^1A_{1g} \rightarrow {}^1T_{1g}$, $^1T_{2g}$ spin-allowed transitions and $10Dq$ and B for the N_6, N_5S, N_4S_2, N_3S_3, and S_6 cage complexes. To be consistent, the room-temperature band positions are used in calculating the ligand field parameters. Since the $^1A_{1g} \rightarrow {}^3T_{1g}$, $^3T_{2g}$ spin-forbidden transitions have not been reported for the N_6, N_4S_2, N_3S_3, and S_6 cage complexes, the first two equations in expression 1 are used with the assumption of $C = 6B$ in order to determine $10Dq$ and B.

Examination of the results in Table V reveals that although there is a significant reduction of approximately 400 cm^{-1} in $10Dq$ from the N_6 to the N_5S complex, thereafter the value of $10Dq$ remains relatively constant with only a reduction of around 300 cm^{-1} from the N_5S to the S_6 complex. Clearly, the thioether ligand exerts a ligand field strength quite similar to that of a saturated amine donor ligand. The origin of the 400-cm^{-1} reduction in $10Dq$ in going from the N_6 to N_5S cage complex is

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Table V. Ligand Field Spectra of Co(III) Encapsulated Complexes[a]

ligand (donors)	*E* $(^1A_{1g}-^1T_{1g})^b$	*E* $(^1A_{1g}-^1T_{2g})^b$	$10Dq^b$	B^b	ref
diAMN$_6$sar(6N)	21050	29100	22300	594	28
AZAMEN$_6$sar (6N)	21300	29250	22600	583	28
AMMEN$_6$sarH (6N)	21200	29000	22510	571	28
AMN$_5$Ssar (5NS)	20660	28330	21930	562	*c*
NON$_5$Ssar (5NS)	20660	28250	21940	555	*c*
AZAN$_4$S$_2$sar (4N2S)	20450	27500	21770	509	11
AMN$_4$S$_2$sarH (4N2S)	20450	27700	21750	526	11
NON$_4$S$_2$sar (4N2S)	20450	27700	21750	526	11
CLN$_4$S$_2$sar (4N2S)	20450	27700	21750	526	11
HN$_4$S$_2$sar (4N2S)	20490	27550	21810	510	11
AZAN$_3$S$_3$sar (3N3S)	20450	26800	21790	451	28
AMN$_3$S$_3$sarH (3N3S)	20500	27150	21840	475	28
NON$_3$S$_3$sar (3N3S)	20450	27050	21790	471	28
Me$_2$S$_6$sar (6S)	20240	26315	21580	426	5

[a] Values of $10Dq$ and B were calculated from solution data (reported in the references) using expressions (1) with $C = 6B$ given in the text of this work. [b] All units are in cm^{-1}; band positions are measured at room temperature. [c] This work.

unclear, although it is noted that the average Co–N bond length in the N$_5$S complex is approximately 0.01 Å longer than that for the deprotonated NON$_6$sar cage complex.

The relative insensitivity of $10Dq$ to the number of thioether donors is not mirrored by the Racah B parameter. Figure 4 reports a plot of the Racah B parameter against the number of thioether donors for the complexes listed in Table V. Clearly, there is a systematic reduction in B from ~590 cm^{-1} for the N$_6$ donor set through to ~425 cm^{-1} for the S$_6$ donor set. However, although B is reduced by approximately 120 cm^{-1} from N$_6$ through to N$_3$S$_3$, corresponding to half of the amine donors replaced by thioether donors, a further reduction of only ~50 cm^{-1} occurs from N$_3$S$_3$ through to S$_6$ coordination. On the basis of the line of best fit drawn in Figure 4, the value of B is reduced by at least 30 cm^{-1} for each thioether donor present, and this trend is consistent with the reduction in B reported for a number of nickel(II) cyclononane complexes involving mixed nitrogen and sulfur coordination.[29]

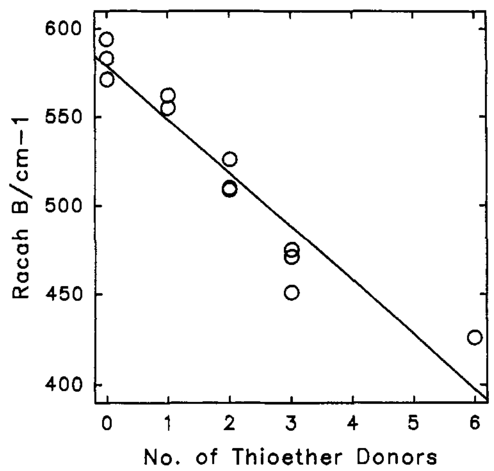

Figure 4. Plot of the Racah B parameter against the number of thioether donors (complexes listed in Table V).

It must be pointed out that as the number of thioether donors increases, the overlap of the $^1A_{1g} \rightarrow {}^1T_{2g}$ d–d transition with the lower energy wing of the Co(III)–S charge transfer transition generally increases, making any accurate estimate of the former d–d transition difficult. Since the value of B is basically determined by the energy separation of the $^1T_{1g}$ and $^1T_{2g}$ states (see expression 1), a reliable estimate of the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition energy is necessary. Obviously, the measurement of low-temperature spectra will help resolve this problem and provide a better estimate of the Racah B parameters, particularly for the N$_3$S$_3$ and S$_6$ complexes where the overlap problem is more severe.

Supplementary Material Available: Listings of full crystal data (Table S1), thermal parameters (Table S2), hydrogen positional and thermal parameters (Table S3), and torsion angles (Table S4) (6 pages). Ordering information is given on any current masthead page.

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