Table I. Quantum Yields of Co(II) in Various CH_3CN-H_2O Mixtures

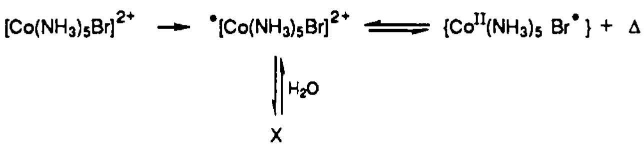
Φ(Co(II)[a-c]	$X(CH_3CN)$	η[d]	$1/\epsilon$[e]
0.28 (0.02)[5]	0.0000	0.890	0.0127
0.37 (0.02)[10]	0.0795	0.959	0.0147
0.34 (0.02)[5]	0.1872	0.819	0.0172
0.43 (0.03)[6]	0.3413	0.595	0.0207
0.48 (0.05)[5]	0.5801	0.430	0.0241
0.39 (0.03)[7]	0.8678	0.360	0.0267
0.47 (0.04)[5]	0.9442	0.341	0.0274
0.90 (0.06)[9]	1.0000	0.341	0.0278

[a] The number in parentheses refers to the standard deviation. [b] The superscript refers to the number of runs in each data set. [c] The literature value for Φ(Co(II)) in water is 0.32 (4). [d] The viscosity data were obtained from ref 11. [e] The dielectric constant data were obtained from ref 11.

implies that it is not important which salt is used in the final interpretation of the data. In addition, it may be noted that the conclusions drawn regarding the solvent dependence are based predominantly on the data obtained with the tetraphenylborate salt, as major changes in the quantum yield of Co(II) happen only above an acetonitrile mole fraction of 0.9442.

The results of the photolysis experiments are listed in Table I. Note that the data for mole fractions of acetonitrile up to and including 0.5801 were obtained by using the nitrate salt; the data for mole fractions of acetonitrile greater than and including 0.8678 were obtained by using the tetraphenylborate salt. These results exhibit several interesting features: (1) It was found that there was little change in the quantum yield of Co(II) over a factor of 2 solvent viscosity, η, in the region $0.08 \leq X(CH_3CN) \leq 0.58$. Thus, arguments based on classical solvent dynamics do not offer viable explanations of the manner in which the quantum yield of Co(II) varies with solvent composition. (2) Similarly, the quantum yield of Co(II) does not change significantly over a factor of 2 change in the inverse dielectric constant between $1/\epsilon = 0.014$ and $1/\epsilon = 0.028$. This suggests that the solvent polarity cannot be used to provide a reasonable explanation of the behavior of $[Co(NH_3)_5Br]^{2+}$ in the acetonitrile–water solvent system. A large change in the quantum yield is, however, observed for a change of solvent in which both η and $1/\epsilon$ remain essentially constant. Consequently, we must formulate a new hypothesis for the origin of the solvent effect on the photochemical behavior of this complex.

Suppose that the role of water is the specific promotion of a quenching process leading to an unreactive state called X, since its precise character is unknown. Then the reaction scheme can be written



$$[Co(NH_3)_5Br]^{2+} \longrightarrow {}^{\bullet}[Co(NH_3)_5Br]^{2+} \rightleftharpoons \{Co^{II}(NH_3)_5\ Br^{\bullet}\} + \Delta$$
$$\downarrow\uparrow H_2O$$
$$X$$

The wavelength dependence can lie in the probability of dissociation of the caged radicals, and the main solvent effect can lie in the competition between dissociation and trapping leading to X. In this model, if trapping is unimportant in acetonitrile, the quantum yield should *approach unity at high energy*, as is observed. It is, however, important to remember that the role of the solvent occurs very early in this process, specifically, faster than exchange between primary and secondary coordination spheres (~1 ns). That is, it occurs before the solvent can diffuse into the radical cage. Hence, it may be concluded that the solvent effects are not due simply to the intrusion of the solvent into the radical cage and the formation of a solvento adduct (i.e. the pentacoordinate Co species plus one solvent molecule).

If the quenching effect of water is molecular and dependent on a single water molecule, it will depend on the probability of a water molecule being in appropriate encounter with the complex at the time of excitation, since the existence of wavelength dependence implies initial steps that are fast in comparison to diffusional dissociation. This is an equilibrium process and proportional in simplest form to the activity of water, measured from the relative vapor pressure, P/P°.[10] In Figure 1, the dashed line shows the expectations for the simple model where the quantum yield decreases from the theoretical limit of 1 in acetonitrile to the experimentally well-defined limit of 0.32 in water,[4] proportionately to water activity. The line is not far from the experimental trend. The existing significant departure suggests that bulk solvent effects are not completely negligible. Nevertheless, the simple model appears capable of describing the principal effect.

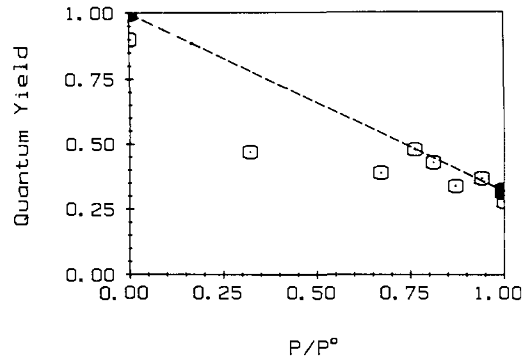


Figure 1. Quantum yield vs activity of water for $[Co(NH_3)_5Br]^{2+}$. The dashed line represents the theoretical curve. The activity of water is measured as P/P°, the vapor pressure over the mixture compared to the vapor pressure of pure water.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada and by the Ministre de enseignment superieur et de la science du Quebec.

Registry No. $[Co(NH_3)_5Br]^{2+}$, 14970-15-1; Co(II), 22541-53-3; H_2O, 7732-18-5; CH_3CN, 75-05-8.

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Synthesis, X-ray Crystal Structure, and Metal Ion Extraction from a Nitrogen–Sulfur "Pendant Arm" Encapsulated Complex of Cobalt(III)

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Received August 15, 1989

The synthesis of macrocyclic ligands that contain appended side chains incorporating potentially reactive donor functions has been of recent interest. The bifunctional nature of these ligands, with one site possessing a high affinity for the metal ion and a second site with a chemically reactive group suitable for further elaboration, has found many applications in the attachment of the ligands to polymers and biomolecules.[2-18] There are, however,

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0020-1669/90/1329-1451$02.50/0

few examples of similarly modified macrobicyclic ligands of the "sepulchrate"[19] type. The presence of an appendage on these ligands would introduce the possibility of the preparation of polymer-bound encapsulated complexes, the attachment of lipophilic chains, or the attachment to biological substrates, in each case through a reactive group at a site separated by a "spacer" from the neopentyl carbon in the trigonal cap of the cage.

This paper reports the synthesis of the ligand 5,5-bis(4-amino-2-thiabutyl)-3,7-dithianonane-1,9-diamine, the characterization of the octahedral complex monoprotonated [(5,5-bis-(4-amino-2-thiabutyl)-3,7-dithianonane-1,9-diamine)cobalt-(III)](4+), $[Co(L1)]^{4+}$, and the encapsulation reaction with nitromethane and formaldehyde, in the presence of base, to form macrobicyclic complexes. The nitro-capped encapsulated complex has been characterized by a single-crystal X-ray structure analysis. After reduction of the nitro group to an amine, removal of the metal ion from the complex results in 1-amino-8-(4-amino-2-thiabutyl)-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosane, a macrobicyclic ligand with sulfur and nitrogen donors, containing a five-atom arm with a pendant primary amine.

Experimental Section

^1H NMR spectra were recorded with a Varian EM360 60-MHz spectrometer on external lock, sodium 3-(trimethylsilyl)propanesulfonate (NaTPS) or tetramethylsilane (Me_4Si) being the internal reference. Fourier-transform $^{13}C[^1H]$ NMR spectra were recorded with a JEOL FX100 FT spectrometer on external lock (D_2O), 1,4-dioxane and NaTPS (D_2O) or Me_4Si ($CDCl_3$) being the internal reference. Chemical shifts are given as positive downfield relative to these standards. A complete assignment of the proton-decoupled ^{13}C spectra was possible by using the pulse sequence INEPT.[20] In the ^{13}C NMR assignments, the symbol (C_q) indicates a quaternary carbon atom. Visible spectra were recorded with a Hewlett Packard 8450 UV/vis spectrophotometer attached to a Hewlett Packard 7225B plotter and 8290/M flexible disk drive (ϵ in M^{-1} cm^{-1}).

Syntheses. Tetrabromopentaerythritol,[21] monoprotonated [(1-amino-8-methyl-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosane)cobalt-(III)](4+) chloride ($[Co(AMcapten)]Cl_4$),[22] and 1-amino-8-methyl-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosane (AMcapten)[23] (^{13}C NMR (in $CDCl_3$ (Me_4Si)): δ 62.3, 50.9 (CH_2); 54.1 (C_q); 44.6, 36.1 (CH_2); 39.9 (C_q); 25.7 (CH_3)) were prepared as described.

5,5-Bis(4-amino-2-thiabutyl)-3,7-dithianonane-1,9-diamine (L1). Sodium metal (9.5 g) was dissolved in absolute ethanol (100 mL) in a flask protected with a $CaCl_2$ drying tube. 2-Aminoethanethiol hydrochloride (23.42 g) was added and the resulting mixture heated to reflux for 0.5 h. The cooled reaction mixture was filtered to remove precipitated NaCl, which was washed with absolute ethanol (5 mL). An aliquot (20 mL) of the filtrate was added to a thick-walled glass tube containing tetrabromopentaerythritol (4 g) and the tube sealed with a Rotaflow Teflon tap. Five such tubes were prepared. The tubes were shaken and degassed by employing freeze–thaw cycles, after being cooled in liquid N_2. After being warmed to room temperature, the tubes were heated at 100 °C in an oil bath for 2 h after which time they were removed, cooled, and then carefully opened. The contents were separated by filtration and the filtrate was collected, freed of solvent on a rotary evaporator, and the residue was dissolved in water (100 mL). The solution was made alkaline by addition of solid KOH, then extracted with $CHCl_3$ (3 × 50 mL). After treatment with decolorizing charcoal, the solvent was removed on a rotary evaporator, resulting in a yellow oil, which solidified upon cooling. The ligand was sufficiently free of impurities, as judged from the ^{13}C NMR spectrum, for preparation of the metal complexes. ^{13}C NMR (in $CDCl_3$ (Me_4Si)): δ 32.6, 38.5, 40.0 (CH_2); 44.1 (C_q).

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

Monoprotonated [(5,5-Bis(4-amino-2-thiabutyl)-3,7-dithianonane-1,9-diamine)cobalt(III)](4+) {$[Co(L1)](ClO_4)_3\cdot HClO_4$}. A solution of $CoBr_2\cdot 6H_2O$ (15.78 g) in methanol (300 mL) was added dropwise to a solution of L1 (18 g) in methanol (300 mL) while a vigorous stream of air was drawn through the mixture. The aeration was continued for a further 5 h, after which time the solution was diluted to a large volume, filtered, and loaded on a column of Dowex 50W-X2 cation-exchange resin (H^+ form, 200–400 mesh). A fast moving pink band was eluted by washing with H_2O and 1 M HCl. The major red band eluted with 3 M HCl was collected and the solvent removed. The resulting red oil was redissolved in a large volume of water and chromatographed on Sephadex C25 cation-exchange resin (Na^+ form). Elution with 0.1 M NaCl solution resulted in the separation of two bands: the first a minor pink band; the second a major red band. The second band was freed of eluent after chromatography on Dowex 50W-X2 cation-exchange resin, washing with 1 M HCl, and elution with 3 M HCl. Removal of the solvent under reduced pressure resulted in a red solid, which was crystallized from aqueous ethanol with $NaClO_4$ (8.2 g, 20%). Anal. Calcd for $C_{13}H_{33}CoN_4S_4(ClO_4)_3\cdot HClO_4$: C, 18.8; H, 4.1; N, 6.7; S, 15.4. Found: C, 18.6; H, 4.0; N, 6.3; S, 15.7. ^{13}C NMR (in D_2O (Me_4Si)): δ 47.6, 45.7, 43.2, 42.8, 39.5, 38.9, 31.5. Visible spectral data [λ_{max}, nm (ϵ_{max}) in H_2O]: 483 (575), 364 (870).

Monoprotonated [(1-Nitro-8-(4-amino-2-thiabutyl)-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosane)cobalt(III)](4+) {$[Co(L2)](ClO_4)_3\cdot HClO_4\cdot 3H_2O$}. To an aqueous solution (300 mL) of $[Co(L1)]Cl_3\cdot HCl$ (3 g) were added anhydrous Na_2CO_3 (5.51 g), CH_3NO_2 (3.2 g) and formaldehyde solution (37%, 50 mL) in quick succession, and the resulting purple solution was stirred. After 2 h, the reaction mixture was acidified with acetic acid and the resulting red solution diluted to large volume, filtered, and loaded on a column of Dowex 50W-X2 cation-exchange resin (200-400 mesh, H^+ form). After the resin was washed with H_2O and 1 M HCl, a major red band was removed with 4 M HCl. The solvent was removed and the resulting red solid dissolved in a large volume of H_2O and applied to a Sephadex C25 cation-exchange resin (Na^+ form). Washing with 0.1 M NaCl removed a minor dark brown band, and the major red band was removed with 0.3 M NaCl. The band was collected on Dowex 50W-X2 resin and freed of eluent after washing with 1 M HCl. Elution with 3 M HCl removed the major red band. The red solid obtained upon evaporation of the solvent was crystallized from aqueous $NaClO_4$ solution upon standing at 0 °C (1.9 g, 39%). Anal. Calcd for $C_{17}H_{35}CoN_5O_2S_4(ClO_4)_3\cdot HClO_4\cdot 3H_2O$: C, 20.8; H, 4.3; N, 7.1; S, 13.1. Found: C, 20.5; H, 4.2; N, 6.8; S, 13.5. ^{13}C NMR (in D_2O (Me_4Si)): δ 88.2 (C_q); 56.1, 53.2, 41.5, 38.4, 31.7, 39.4, 42.8 (CH_2); 47.9 (C_q). Visible spectral data [λ_{max}, nm (ϵ_{max}) in H_2O]: 488 (830), 364 (sh).

Diprotonated [(1-Amino-8-(4-amino-2-thiabutyl)-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosane)cobalt(III)](5+) {$[Co(L3)](ClO_4)_2Cl_3\cdot 3H_2O$}. $[Co(L2)](ClO_4)_3\cdot HClO_4\cdot {}^1/_2H_2O$ (1 g) was dissolved in H_2O (50 mL) and the solution purged with N_2. Zinc powder (1 g) was added, and concentrated HCl (5 mL) was slowly added to the purple solution. Stirring was continued for 1 h. H_2O_2 (30%, 1.5 mL) was added and the solution warmed at 60 °C for $^1/_4$ h. The solution was filtered, diluted to a large volume, and chromatographed on Dowex 50W-X2 cation-exchange resin as described previously. The red band that eluted was collected, freed of solvent, and rechromatographed on Sephadex C25 cation-exchange resin. The major red band, which separated from two minor fast moving bands, was collected and freed of eluent by treatment on Dowex cation-exchange resin, and after removal of solvent, the red solid was crystallized from aqueous $NaClO_4$ (0.23 g, 25% yield). Anal. Calcd for $(C_{17}H_{39}N_5S_4)Co(ClO_4)_2Cl_3\cdot 3H_2O$: C, 23.7; H, 5.3; N, 8.1; S, 14.9; Cl (ionic), 12.4. Found: C, 23.5; H, 5.0; N, 7.9; S, 14.4; Cl (ionic), 12.1. ^{13}C NMR (in D_2O (Me_4Si)): δ 56.5 (C_q), 55.7, 53.2, 42.9, 41.7, 39.6, 38.1, 31.7 (CH_2), 48.2 (C_q). Visible Spectral data [λ_{max}, nm (ϵ_{max}) in H_2O]: 488 (901), 364 (sh).

1-Amino-8-(4-amino-2-thiabutyl)-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosane (L3). $[Co(L3)]Cl_5$ (2.5 g) was dissolved in H_2O (50

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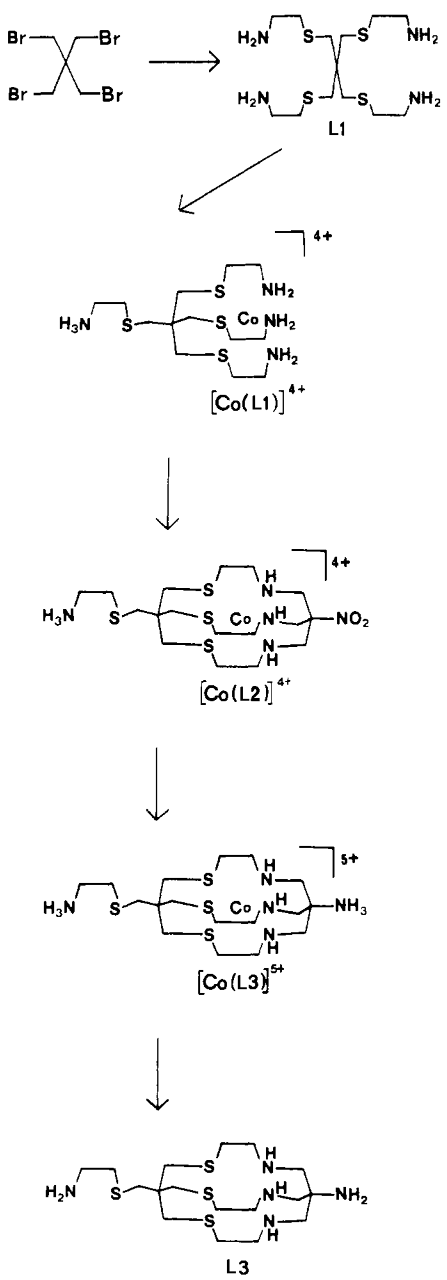
Table I. Crystal Data

cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.141 (6)
b, Å	19.219 (4)
c, Å	21.124 (5)
α, deg	99.34 (2)
β, deg	98.44 (3)
γ, deg	90.69 (3)
V, Å^3	3620 (1)
D_{calc}, g cm^{-3}	1.801
empirical formula	$C_{17}H_{42}Cl_4CoN_5O_{21}S_4$
fw	981.58
Z	4
$F(000)$, e	2024
cryst color	red
abs coeff, cm^{-1}	14.54
habit	needles
dimens, mm	0.45 × 0.30 × 0.25
transm factors	0.65, 0.72
temp, K	294
diffractometer	Enraf-Nonius CAD4-F, four circle
radiation	Mo Kα (λ = 0.71069 Å)
monochromator	graphite
scan mode	ω–θ
2θ range, deg	1.0–50.0
no. of reflcns measd	13985
range of hkl	0 to 10, −22 to 22, −25 to 25
merging R	0.01
no. of reflcns used ($I > 2.5\sigma(I)$)	10012
no. of variables	804
R	0.052
R_w	0.063
$w[=g/(\sigma^2F_o + kF_o^2)]$: g, k	3.02, 8.5 × 10^{-4}
shift/esd	<0.1
residual extrema, e Å^{-3}	0.90, −0.90

Scheme I



mL) and the reaction vessel maintained under an inert atmosphere of N_2. Zinc dust (2 g) was added, and after $^1/_4$ h, solid NaCN (2 g) was added to the purple solution. The solution was maintained under a stream of nitrogen as the color changed from purple to green over a period of 5 days, after which time the green solution was made strongly alkaline with solid KOH and extracted with $CHCl_3$ (3 × 50 mL). The $CHCl_3$ extract was dried over anhydrous Na_2SO_4, and the solution was filtered. Removal of the solvent yielded a pale yellow oil (1.2 g, 62%). (Found: M^+ = 439.21; $C_{17}H_{37}N_5S_4$ requires M = 439.83.) ^{13}C NMR (in $CDCl_3$ (Me_4Si)): δ 62.7, 50.6 (CH_2); 53.9 (C_q); 43.8 (C_q); 42.3, 41.0, 40.8, 37.9, 36.7 (CH_2).

Diprotonated [(1-Amino-8-(4-amino-2-thiabutyl)-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosane)cobalt(III)](5+) {[Co(L3)]Cl$_5$}. To a methanolic solution (15 mL) of L3 (0.2 g) was added a methanol solution of $CoBr_2\cdot 6H_2O$ (0.2 g, 10 mL), and a slow stream of air was drawn through the mixture. A red precipitate formed almost immediately upon addition. After 2 h, the solution was diluted with a large volume of water and chromatographed on Dowex cation-exchange resin. Elution with 4 M HCl resulted in a single red band. This band was collected and the solvent removed on a rotary evaporator, leaving a red solid (0.26 g, 80%). ^{13}C NMR (in D_2O (Me_4Si)): δ 56.5 (C_q), 55.7, 53.2, 42.9, 41.7, 39.6, 38.1, 31.7 (CH_2), 48.2 (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 decomposition corrections (5%) were applied by using a local data reduction program. The structure was solved by direct methods and was refined by blocked-matrix least-squares analysis with SHELX-76.[24] The solution and refinement of the structure was complicated by the presence of two molecules in the asymmetric unit, making it a very large structure (formula weight 1963), and by the disorder of perchlorate anions and complex cations. The complex cations were found to be disordered by rotation about the approximate C_3 axis as has been observed previously for similar structures.[22] This disorder amounts to less than 5% in each of the two complex cations and was only evident as alternative sites for the S donor atoms. These were refined with occupancies complementary to the major sites. The pendant arm of the second of the complex cations was also found to be disordered over two sites with occupancies of 84% and 16%. The disorder of the perchlorate anions was much more extensive, generally taking the form of rotation about the Cl atom but in one case involving movement of the entire anion. The disorder was modeled by assigning sets of oxygen atoms group occupancy parameters. Hydrogen atoms were included at calculated sites (C–H = 0.97 Å; N–H = 0.91 Å) with group isotropic thermal parameters, all other atoms except minor contributors to disordered groups were refined anisotropically. Scattering factors and anomalous dispersion corrections for Co were taken from ref 25 and for all others the values supplied in SHELX-76 were used. Absorption correction was by numerical integration.[26] The atomic nomenclature is defined in Figure 1.[27]

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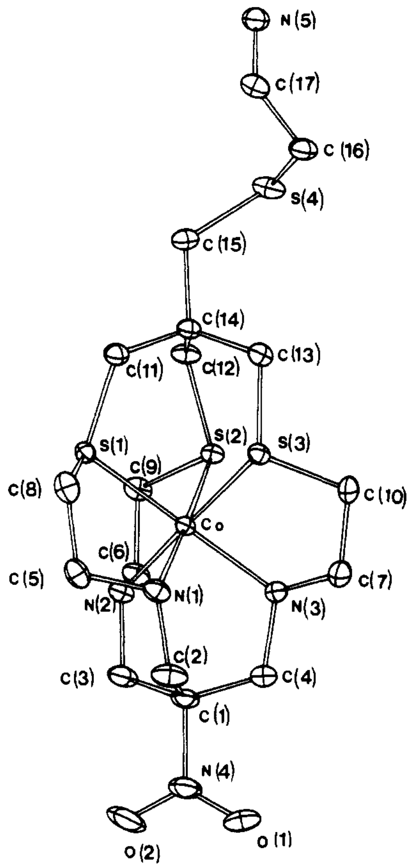

Figure 1. ORTEP diagram of the $[Co(L2)]^{4+}$ cation. Numbers for the second molecule are 20 plus the number of the first molecule (with the exception of O1 and O2, which become O3 and O4).

Results and Discussion

The reaction sequence is shown in Scheme I. The ligands in these complexes may be the free or monoprotonated amines, and the abbreviations L1, L2, and L3 are used for the ligands whatever the degree of protonation. The abbreviations L2 and L3 also indicate the presence of the 4-amino-2-thiabutyl and nitro (L2) and the 4-amino-2-thiabutyl and amine substituents (L3) at apical positions on the encapsulating ligands.

The ligand L1 is similar to the octaaza ligand 5,5-bis(4-amino-2-azabutyl)-3,7-diazanonane-1,9-diamine, where both possess the capacity to coordinate as either binucleating tetradentate, or mononucleating octahedral, ligands.[28-33] Careful control of reaction conditions permits octahedral hexadentate coordination of these ligands to cobalt(III).[31,32] The octahedral $[Co(L1)]Cl_4$ complex possesses three facially arranged primary amine donors and undergoes reaction with nitromethane and formaldehyde, in the presence of base,[22,34,35] resulting in the encapsulated complex monoprotonated [(1-(4-amino-2-thiabutyl)-8-nitro-3,6,10-trithia-13,16,19-triazabicyclo[6.6.6]icosane)-cobalt(III)](4+), $[Co(L2)]^{4+}$. The amine-capped cobalt(III) complex $[Co(L3)]^{5+}$ was isolated after reduction of the nitro group with zinc and acid.[22,35] Reaction of $[Co(L3)]^{4+}$, the cobalt(II) complex, with excess sodium cyanide results in extraction of the metal ion.

The structure of $[Co(L2)](ClO_4)_3{\cdot}HClO_4{\cdot}3H_2O$ consists of two complex cations, eight perchlorate anions, and six water molecules. Hydrogen bonds involving all moieties stabilize the structure. The complex cations have a Co(III) atom encapsulated by the macrobicyclic ligands which coordinate via three S(thioether) and three N(amine) donor atoms. A pendant arm attached to one cap carries an uncoordinated S(thioether) atom and an evidently protonated primary amine. The geometry of macrobicyclic ligands of this type has previously been described by the orientation of the C–C vectors of the S–C–C–N (or N–C–C–N) groupings with respect to the C_3 axis of the complex and by the dispositions of the two caps with respect to one another and with respect to the first coordination sphere. In the present structure the C–C vectors are all parallel to the C_3 axis and thus the conformation is described as C_3lel_3. The caps are staggered with respect to one another and eclipsed with respect to the adjacent three donor atoms, a conformation almost identical with that observed for $[Co(azacapten)]^{3+}$.[22]

The Co–S bond lengths (average 2.215 Å) are at the short end of the range of Co(III)–S(thioether) bonds [2.217 (2)–2.301 (1) Å][36] and are similar to those in $[Co(azacapten)](ZnCl_4)Cl$ [2.226 (1) Å].[22] The Co–N bond lengths (average 2.007 Å) are at the longer end of the range of Co(III)–N(amine) bond lengths [1.937 (2)–2.040 (6) Å],[37] also similar to the situation in $[Co(azacapten)](ZnCl_4)Cl$ [2.009 (3) Å].[22] The pendant arm is in the extended conformation, unlike for the $[Co(NOasar)]I_4{\cdot}3H_2O$ complex where the cis conformation is observed, apparently stabilized by hydrogen bonding to both iodide anions and water molecules.[31]

The ^{13}C NMR spectra of cobalt(III) complexes derived from L1 are similar to those reported previously for complexes of the analogous ligand 5-(4-amino-2-thiabutyl)-5-methyl-3,7-dithianonane-1,9-diamine (ten).[22] In both cases, reaction with nitromethane and formaldehyde results in the disappearance in the ^{13}C NMR spectrum of the starting material of a signal indicative of a methylene carbon α to the primary amine, replaced by a signal at 53.2 ppm indicative of a methylene adjacent to a secondary amine, both bound to cobalt(III).[22,32] Resonances assigned to the methylene carbon atoms in the pendant arm in $[Co(L1)]^{4+}$ are unaltered in the encapsulation reaction. The appearance of a resonance at 88.2 ppm in the spectrum of $[Co(L2)]^{4+}$ is characteristic of a quaternary carbon atom adjacent to the electron-withdrawing nitro group.[22,32]

Removal of the metal ion from $[Co(L3)]^{5+}$ results in a product that exhibits a nine-line ^{13}C NMR spectrum. The spectra of both AMcapten and L3 exhibit resonances indicative of methylene carbon atoms adjacent to secondary amine (62.3, 50.9; 62.7, 50.6 ppm), thioether (36.1, 44.6; 36.7, 42.3 ppm), and quaternary carbon atoms (54.1; 53.9 ppm) bearing the trigonal NH_2 cap, respectively. In the ^{13}C NMR spectrum of the L3 ligand the quaternary carbon cap bearing the pendant $NH_2CH_2SCH_2$ displays a resonance at 43.8 ppm; in addition, resonances at 41.0, 40.8, and 37.9 ppm are assigned to the methylene carbon atoms in the pendant arm. L3 reacts readily with a cobalt(II) salt in the presence of air to produce a cobalt(III) complex, which exhibited a ^{13}C NMR spectrum identical with that displayed by $[Co(L3)]^{5+}$, prior to metal removal.

Acknowledgment. L.R.G. acknowledges financial support from the Australian Research Grants Scheme.

Supplementary Material Available: Tables listing positional parameters, interatomic distances and angles, thermal parameters, calculated hydrogen atom positions and thermal parameters, and close intermolecular contacts (12 pages); a listing of calculated and observed structure factors (59 pages). Ordering information is given on any current masthead page.

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