Synthesis and Spectroscopic Properties of the Encapsulated Cobalt(III) Complexes Derived from the Unsymmetrically Substituted Ligand 5-Methyl-5-(4-amino-2-azabutyl)-3,7-dithianonane-1,9-diamine (N_4S_2)

Therese M. Donlevy,[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, University of Sydney, Sydney, NSW, Australia 2006

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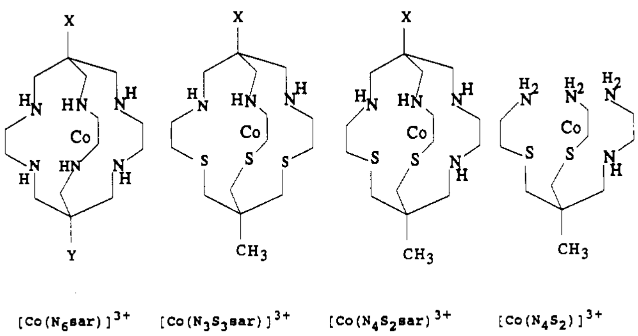
The cobalt(III) complex of the unsymmetrically substituted ligand 5-methyl-5-(4-amino-2-azabutyl)-3,7-dithianonane-1,9-diamine (N_4S_2) has been prepared. The complex reacts with formaldehyde and ammonia, and formaldehyde and nitromethane, to form the encapsulated complexes [(8-methyl-6,10-dithia-1,3,13,16,19-pentaazabicyclo[6.6.6]icosane)cobalt(III)] perchlorate ([Co(AZAN$_4$S$_2$sar)](ClO_4)$_3$) and [(1-methyl-8-nitro-3,13-dithia-6,10,16,19-tetraazabicyclo[6.6.6]icosane)cobalt(III)] perchlorate ([Co(NON$_4$S$_2$sar)](ClO_4)$_3$), respectively. The nitro-substituted encapsulated metal complex is readily reduced to the NH_3^+-substituted compound; this substituent is replaced to form, successively, chloro- and proteo-capped complexes. The uncapped and the nitro-capped complexes have been characterized by single-crystal X-ray study: crystals of the former complex are orthorhombic, space group, $P2_12_12_1$, a = 8.963 (2) Å, b = 13.293 (2) Å, c = 18.229 (6) Å, Z = 4, R = 0.030 (1756 F); crystals of the latter are monoclinic, space group, $P2_1/n$, a = 15.669 (6) Å, b = 9.620 (2) Å, c = 17.772 (2) Å, β = 105.26 (2)°, Z = 4, R = 0.040 (3317 F). The octahedral ligand-field parameters $10Dq$ and B are progressively reduced as the number of thioether donors increases, a result of the increased covalency associated with the thioether coordination. Comparison of the solution circular dichroism for Co($N_{6-n}S_n$) complexes reveals that the net positive rotational strength for the Λ absolute configuration increases with the number of thioether groups coordinated to the metal.

Introduction

The syntheses and characterization of the hexaazamacrobicyclic encapsulated complexes of cobalt(III) have been described previously.[2-5] The synthesis of ligands with mixed thioether–nitrogen donors resulted in macrobicyclic encapsulated complexes in which the chemical and spectroscopic properties displayed reflect the presence of the sulfur donors.[6] In an attempt to explore further aspects of the chemistry of encapsulated complexes, we have been concerned with the synthesis of a new type of encapsulating ligand in which the ratio of sulfur/nitrogen donors falls between 6 N and 3 N 3 S.[7] This paper reports the synthesis and characterization, by single-crystal X-ray analysis, of the cobalt(III) complex prepared from the ligand 5-methyl-5-(4-amino-2-azabutyl)-3,7-dithianonane-1,9-diamine, a ligand containing the N_4S_2 donor set. Encapsulated complexes of cobalt(III) with this ligand as precursor have been prepared and investigated. (For a description of the complexes detailed in this work, see Chart I).

Chart I



Experimental Section

^{1}H NMR spectra were recorded with a Varian EM360 60-MHz spectrometer, sodium 3-(trimethylsilyl)propanesulfonate (NaTPS) (D_2O) or tetramethylsilane (Me_4Si) ($CDCl_3$) being the internal reference. Fourier-transform $^{13}C[^1H]$ NMR spectra were recorded with a JEOL GX400 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 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; 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. A complete assignment of the proton-decoupled ^{13}C spectra was possible by using the pulse sequence INEPT.[8] 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. 1,1,1-tris(((tolylsulfonyl)oxy)methyl)ethane was prepared as described previously.[9]

5-Methyl-5-(((tolylsulfonyl)oxy)methyl)-3,7-dithianonane-1,9-diamine. Sodium metal (18.2 g) was dissolved in absolute ethanol (750 mL) in a flask protected with a $CaCl_2$ drying tube. 2-Aminoethanethiol hydrochloride (45.4 g) was added, and the resulting mixture was heated to reflux for 0.5 h. To the cooled reaction mixture was added 1,1,1-tris(((tolylsulfonyl)oxy)methyl)ethane (108 g) and the mixture heated under reflux for 2 h. The reaction mixture was cooled and filtered to remove the mixed precipitate of NaCl, sodium *p*-toluenesulfonate, and 1,1,1-tris(((tolylsulfonyl)oxy)methyl)ethane. The filtrate was freed of solvent on a rotary evaporator, the resulting oil was dissolved in water

(1) (a) The University of Queensland. (b) University of Sydney.
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(100 mL), and the solution was made alkaline by addition of solid KOH and then extracted with $CHCl_3$ (3 × 100 mL). Removal of the $CHCl_3$ under reduced pressure resulted in a heavy yellow oil (60.6 g), which from ^1H NMR was a mixture of the desired product and the expected statistical products. The oil was used without further purification.

5-Methyl-5-(4-amino-2-azabutyl)-3,7-dithianonane-1,9-diamine (N_4S_2). The product from the above reaction was reacted with 1,2-diaminoethane, and the mixture of products isolated essentially as described for the preparation of the analogous ligand 1,1,1-tris(4-amino-2-azabutyl)ethane (sen).[10] The ^1H NMR spectrum ($CDCl_3$) of the product, a yellow oil, indicated it to be a mixture of N_4S_2, 1,1,1-tris(4-amino-2-thiabutyl)-ethane,[6] and one further product, in the approximate ratio 2:1.5:1, respectively. The oil was used without further purification.

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

[(5-Methyl-5-(4-amino-2-azabutyl)-3,7-dithianonane-1,9-diamine)cobalt(III)] Chloride Diperchlorate, $[Co(N_4S_2)]Cl(ClO_4)_2$. A methanol solution (150 mL) of cobaltous acetate (34.8 g) was added slowly to the crude ligand mixture (40 g) dissolved in methanol (600 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 onto Dowex cation-exchange resin 50W-X2 (200–400 mesh), H^+ form, and the column 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 red band which was removed after washing with 3 M HCl was collected and freed of solvent to give a red solid which was dissolved in a large volume of water (2 L) and rechromatographed on Sephadex C-25 cation-exchange resin (Na^+ form). After washing with 0.2 M NaCl solution to remove a minor purple band, the major red 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 red solid obtained upon evaporation of the solvent was crystallized from water with $NaClO_4$. This product (13.35 g) was determined from ^{13}C NMR to be a mixture of $[Co(N_4S_2)]^{3+}$ and $[Co(N_3S_3)]^{3+}$.[6] Chromatographic separation of the mixture on a small scale was achieved on Sephadex C-25 cation-exchange resin (Na^+ form) with 0.067 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 and crystallization from water with $NaClO_4$ resulted in the isolation of a product subsequently identified as $[Co(N_4S_2)]Cl(ClO_4)_2$. Anal. Calcd for $[(C_{11}H_{28}N_4S_2)Co]Cl(ClO_4)_2$: C, 23.0; H, 4.92; N, 9.8; S, 11.2; Cl-(ionic), 6.2. Found: C, 22.5; H, 4.82; N, 9.2; S, 11.0; Cl(ionic), 6.9. Visible spectrum [λ_{max}, nm (ϵ_{max}) in H_2O]: 482 (352), 358 (414). ^1H NMR: δ 1.26 s (CH_3), 2.61–3.45 m (CH_2). ^{13}C NMR (in D_2O): δ −10.5, −11.6, −21.6, −22.3, −24.0, −25.2, −26.5, −26.8 (CH_2); −24.3 (C_q); −40.8 (CH_3). It was, however, found to be convenient to use the crude mixture of complexes in the reaction to prepare encapsulated complexes.

[(1-Methyl-8-nitro-3,13-dithia-6,10,16,19-tetraazabicyclo[6.6.6]icosane)-cobalt(III)] Perchlorate Monohydrate, $[Co(NON_4S_2sar)](ClO_4)_3\cdot H_2O$. The mixture of $[Co(N_4S_2)]^{3+}$ and $[Co(N_3S_3)]^{3+}$ (12 g) was dissolved in water (500 mL), and to the stirred solution was added in quick succession Na_2CO_3 (6.65 g), CH_3NO_2 (19.1 g), and HCHO (147 g, 37% solution). The purple mixture was stirred for 4 h, after which time the reaction was quenched with acetic acid. The mixture was filtered, diluted to large volume, loaded on a column of Dowex 50W-X2 cation-exchange resin (200–400 mesh, H^+ form), and washed with water and 1 M HCl to remove minor pink and green bands. The major red band was eluted with 3 M HCl. After removal of the solvent under reduced pressure the red solid obtained was dissolved in a large volume of water and loaded on a column of C-25 Sephadex cation-exchange resin (Na^+ form), which was subsequently washed with water. Elution of the column with 0.1 M Na_2SO_4 resulted in the immediate separation of two bands which were collected separately on Dowex 50W-X2 cation-exchange resin, washed with 0.5 M HCl, and eluted with 3 M HCl. The product obtained from the band eluted first from the Sephadex was crystallized from water with $NaClO_4$ and subsequently identified as $[Co(NON_4S_2sar)](ClO_4)_3\cdot H_2O$ (6.2 g). Anal. Calcd for $[(C_{15}H_{31}N_5O_2S_2)Co](ClO_4)_3.H_2O$: C, 24.0; H, 4.42; N, 9.3; S, 8.5. Found: C, 24.3; H, 4.60; N, 9.4; S, 8.9. Visible spectrum [λ_{max}, nm (ϵ_{max}) in H_2O]: 489 (504), 361 (504). ^1H NMR (in D_2O (DSS)): δ 1.27 s (CH_3), 2.47–4.06 m (CH_2). ^{13}C NMR (in D_2O): δ +20.5 (C_q); −10.1, −10.8, −11.0, −11.3, −13.3, −13.5, −14.1, −15.2, −27.1, −27.3, −27.9, −28.2 (CH_2); −23.8 (C_q); −41.2 (CH_3). The product from the second band eluted from the Sephadex was identified from the ^{13}C NMR spectrum as $[Co(NON_3S_3sar)]^{3+}$.[6]

$[Co(AMN_4S_2sarH)]^{4+}$. The nitro-capped complex $[Co(NON_4S_2sar)](ClO_4)_3\cdot H_2O$ (5 g) was reduced to the amine cap derivative $[Co(AMN_4S_2sarH)]^{4+}$ in aqueous solution under a stream of N_2 using granulated zinc and concentrated HCl essentially as described previously for similar complexes.[6] ^1H NMR (in D_2O (DSS)): δ 1.28 s (CH_3), 2.50–3.89 m (CH_2). ^{13}C NMR (in D_2O): δ −10.3 (C_q); −10.9, −11.0, −12.8, −13.1, −14.2, −15.1, −27.1, −27.3, −28.2, −28.5 (CH_2); −23.7 (C_q); −41.2 (CH_3).

$[Co(CLN_4S_2sar)](ClO_4)_3\cdot H_2O$. The NH_3^+– group was replaced by a halogen, after nitrosation, essentially as described previously.[11] The complex was isolated after chromatography on Dowex 50W-X2 cation-exchange resin and crystallized from an aqueous solution of $NaClO_4$. Anal. Calcd for $[(C_{15}H_{31}ClN_4S_2)Co](ClO_4)_3\cdot H_2O$: C, 24.3; H, 4.5; N, 7.5; S, 8.6. Found: C, 23.9; H, 4.6; N, 6.9; S, 8.6. Visible spectrum [λ_{max}, nm (ϵ_{max}) in H_2O]: 489 (570), 361 (588). ^1H NMR (in D_2O (DSS)): δ 1.25 s (CH_3), 2.44–3.77 m (CH_2). ^{13}C NMR (in D_2O): δ −5.7 (C_q); −9.8, −9.9, −10.1, −10.5, −10.6, −10.8, −11.4, −13.4, −27.2, −27.8, −28.0 (CH_2); −23.9 (C_q), −41.3 (CH_3).

$[Co(HN_4S_2sar)]^{3+}$. $[Co(CLN_4S_2sar)]^{3+}$ (1 g) was dissolved in water (100 mL) and the solution purged under a stream of nitrogen. Addition of nickel–aluminum alloy (0.6 g) and NaOH (0.6 g) caused an immediate purple color to develop in the solution. The mixture was stirred for 12 h, after which time concentrated HCl (15 mL) was added, and the solution filtered. The filtrate was diluted to large volume, absorbed on a column of Dowex 50W-X2 cation-exchange resin and washed with water and 1 M HCl to remove minor green bands. The single major red band which eluted with 3 M HCl was collected and the solvent removed. The red solid obtained was dissolved in a large volume of water and loaded onto a long Sephadex cation-exchange column (C-25, Na^+ form). Elution with a solution of 14.7 g/L Na_3 citrate resulted in the separation of four bands. The first, second, and fourth bands were orange, pink, and yellow in color, respectively, and represented minor products and were thus discarded. The third band was red in color and represented the major product and was collected. The band was collected on a short column of Dowex cation-exchange resin, washed with dilute HCl, and eluted with 3 M HCl. Removal of the solvent resulted in the isolation of a red solid which was crystallized from aqueous $NaClO_4$ solution. Anal. Calcd for $[(C_{15}H_{32}N_4S_2)]Co(ClO_4)_3$: C, 26.1; H, 4.7; N, 8.1; S, 9.3. Found: C, 26.1; H, 4.4; N, 7.8; S, 9.0. Visible spectrum [λ_{max}, nm (ϵ_{max}) in H_2O]: 488 (541), 363 (527). ^1H NMR (in D_2O (DSS)): δ 1.26 s (CH_3), 2.47–3.73 m (CH_2). ^{13}C NMR (in D_2O): δ −10.2, −10.9, −11.1, −11.4, −14.1, −15.2, −15.5, −17.6, −27.5, −27.8, −28.0, −28.2 (CH_2); −29.9 (C_q); −24.4 (C_q); −41.1 (CH_3).

$[Co(AZAN_4S_2sar)](ClO_4)_3$. The complex was prepared as described previously for similar complexes.[3] Anal. Calcd for $[(C_{14}H_{31}N_5S_2)Co](ClO_4)_3\cdot NaClO_4\cdot H_2O$: C, 20.2; H, 4.00; N, 8.4; S, 7.7. Found: C, 20.6; H, 4.21; N, 8.6; S, 8.1. Visible spectrum [λ_{max}, nm (ϵ_{max}) in H_2O]: 489 (483), 364 (545). ^1H NMR: δ 1.25 s (CH_3), 2.42–4.53 m (CH_2). ^{13}C NMR (in D_2O): δ +1.6, +1.0, +0.2, −9.6, −10.1, −12.8, −13.0, −15.0, −23.3 (C_9), −26.3, −27.7, −28.2, −28.5 (CH_2); −41.3 (CH_3).

AMN_4S_2sar. $[Co(AMN_4S_2sarH)]^{4+}$ (1 g) was dissolved in H_2O (50 mL) and the reaction vessel maintained under an inert atmosphere of N_2. Zinc dust (2 g) and, after $^1/_2$ h, solid NaCN were added to the purple solution, which was maintained under a stream of nitrogen as the color changed from purple to green over a period of $^1/_4$ h. The solution was maintained under a nitrogen stream for 2 h to ensure complete reaction. The resulting green solution was made strongly alkaline with solid KOH and extracted with $CHCl_3$ (3 × 50 mL). After the $CHCl_3$ extract was dried with anhydrous Na_2SO_4, the solution was filtered. Removal of the solvent yielded a colorless solid (0.62 g, 98%). (MS (EI): found for M^+, m/e 347; calcd for $C_{15}H_{33}N_5S_2$ (M), m/e 347.58.) ^{13}C NMR (in $CDCl_3$ (Me_4Si)): δ +61.9; +61.1; +59.5 (CH_2); +53.2 (C_q); +50.9, +50.0, +49.1, +43.6 (CH_2); +40.3 (C_q); +35.2 (CH_2); +25.7 (CH_3).

Resolution of $[Co(N_4S_2)]^{3+}$. The complex (0.10 g) was resolved into its enantiomeric forms through chromatography on Sephadex cation-exchange resin (Na^+ form) employing an aqueous solution of sodium $(+)_{589}$-tartrate as an ion-pairing reagent. The enantiomers were crystallized to constant rotation from aqueous solutions containing sodium perchlorate. The first fraction eluted from the column gave $\Delta\epsilon_{475}$ = +6.36 M^{-1} cm^{-1} and $\Delta\epsilon_{358}$ = −1.95 M^{-1} cm^{-1}. Anal. Calcd for $[(C_{11}H_{28}N_4S_2)Co]Cl(ClO_4)_2$: C, 23.0; H, 4.92; N, 9.8; S, 11.2. Found:

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Table I. Crystal Data

	$[Co(N_4S_2)]Cl(ClO_4)_2$	$[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$
space group	$P2_12_12_1$	$P2_1/n$
a, Å	8.963 (2)	15.669 (6)
b, Å	13.293 (2)	9.620 (2)
c, Å	18.299 (4)	17.772 (2)
β, deg		105.26 (2)
V, Å^3	2180.3	2584.5
fw	573.79	697.15
D_{calcd}, g cm^{-3}	1.748	1.791
empirical formula	$C_{11}H_{28}Cl_3CoN_4O_8S_2$	$C_{15}H_{33}Cl_5CoN_5O_3S_2Zn$
Z	4	4
absorp coeff, cm^{-1}	13.26	22.35
transm coeff	0.935–0.829	0.793–0.620
temp, °C	21	21
λ, Å	0.710 69	
$R(F_o)$	0.030	0.040
R_w	0.031	0.045

C, 23.1; H, 5.0; N, 9.9; S, 11.1. The second fraction gave $\Delta\epsilon_{475} = -6.27$ M^{-1} cm^{-1} and $\Delta\epsilon_{358} = +2.01$ M^{-1} cm^{-1}. Anal. Calcd for $[(C_{11}H_{28}N_4S_2)Co]Cl(ClO_4)_2$: C, 23.0; H, 4.92; N, 9.8; S, 11.2. Found: C, 23.2; H, 5.0; N, 10.0; S, 11.1.

X-ray Crystallography. Cell constants were determined by least-squares fits 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).[12] The structures were solved by direct methods using SHELXS-86[13] and were refined by full-matrix ($[Co(N_4S_2)]Cl(ClO_4)_2$) or blocked-matrix ($[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$) least-squares analysis with SHELX-76.[14] In $[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$, the water molecule and the chloride anion were found to be cooperatively disordered; minor sites for these atoms refined with occupancies of 0.13 (2). Hydrogen atoms in $[Co(N_4S_2)]Cl(ClO_4)_2$ were included at calculated sites (C–H = 0.97 Å) with individual isotropic thermal parameters, and those in $[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$ were refined, also with individual isotropic thermal parameters. All other atoms except minor contributors to disordered groups were refined anisotropically. The alternative absolute configuration of $[Co(N_4S_2)]Cl(ClO_4)_2$ refined with an R_w of 0.039. Scattering factors and anomalous dispersion corrections for Co and Zn were taken from ref 15, and for all others the values supplied in SHELX-76 were used. Non-hydrogen atom coordinates are listed in Tables II and III. The atomic nomenclatures are defined in Figures 1 and 2.[16]

Results and Discussion

Nomenclature. It is appropriate at this point to comment on the nomenclature employed for these ligands and their metal complexes. The designation N_4S_2 corresponds to the ligand structure 5-methyl-5-(4-amino-2-azabutyl)-3,7-dithianonane-1,9-diamine. An elegant and systematic nomenclature has been developed and generally accepted for the hexaaza encapsulated complexes.[17] However, the nomenclature requires modification in order to cater to the new encapsulating ligands with various chromophores. In keeping with the nomenclature reported for the encapsulating ligand 1,8-dimethyl-3,6,10,13,16,19-hexathiabicyclo[6.6.6]icosane (Me_2S_6sar),[18] we describe the ligand 1-methyl-8-nitro-3,13-dithia-6,10,16,19-tetraazabicyclo[6.6.6]-

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Table II. Positional Parameters (×10^4) for $[Co(N_4S_2)]Cl(ClO_4)_2$

	x	*y*	*z*
Co(1)	−70 (1)	431 (1)	8651 (1)
S(1)	1903 (2)	−204 (1)	9201 (1)
S(2)	−891 (2)	1040 (1)	9705 (1)
N(1)	−1373 (5)	−753 (3)	8818 (2)
N(2)	−1783 (6)	962 (4)	8088 (3)
N(3)	1057 (6)	1696 (4)	8525 (3)
N(4)	789 (5)	−105 (4)	7725 (3)
C(1)	−498 (10)	−1665 (5)	10776 (4)
C(2)	−278 (8)	−973 (4)	10103 (3)
C(3)	1237 (7)	−1213 (5)	9775 (4)
C(4)	−359 (8)	124 (4)	10404 (3)
C(5)	−1530 (7)	−1194 (5)	9568 (3)
C(6)	2792 (7)	−822 (6)	8439 (4)
C(7)	439 (9)	2057 (5)	9799 (3)
C(8)	−2883 (7)	−563 (5)	8495 (4)
C(9)	2432 (7)	−249 (5)	7755 (4)
C(10)	578 (8)	2495 (4)	9031 (3)
C(11)	−2697 (7)	104 (5)	7845 (3)
Cl(1)	113 (2)	210 (1)	5642 (1)
O(1)	177 (7)	1167 (3)	5299 (3)
O(2)	−207 (9)	−510 (4)	5090 (3)
O(3)	−1025 (6)	178 (5)	6184 (3)
O(4)	1489 (6)	0 (6)	5985 (3)
Cl(2)	4947 (2)	2584 (1)	8160 (1)
O(5)	1358 (5)	2135 (5)	1519 (3)
O(6)	−481 (6)	3337 (4)	1502 (3)
O(7)	−1124 (7)	1688 (5)	1678 (4)
O(8)	102 (12)	2566 (5)	2581 (3)
Cl(3)	9 (3)	2465 (1)	7025 (1)

Table III. Positional Parameters (×10^4) for $[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$[a]

	x	*y*	*z*
Co(1)	2374 (1)	2441 (1)	9965 (1)
S(1)	3753 (1)	2931 (1)	10619 (1)
S(2)	2306 (1)	571 (1)	10669 (1)
N(1)	1825 (2)	3595 (3)	10681 (2)
N(2)	2462 (3)	4063 (4)	9286 (3)
N(3)	2859 (2)	1187 (4)	9282 (2)
N(4)	1128 (3)	2134 (5)	9350 (3)
C(1)	3223 (4)	2643 (6)	12780 (3)
C(2)	3005 (3)	2527 (5)	11888 (3)
C(3)	3853 (3)	2787 (5)	11649 (3)
C(4)	2642 (3)	1058 (5)	11682 (3)
C(5)	2297 (3)	3625 (5)	11552 (3)
C(6)	3689 (4)	4773 (5)	10406 (3)
C(7)	3235 (3)	−310 (6)	10469 (3)
C(8)	897 (3)	3067 (7)	10538 (3)
C(9)	3309 (3)	4853 (5)	9530 (3)
C(10)	3037 (4)	−275 (5)	9590 (3)
C(11)	531 (3)	3005 (7)	9679 (3)
C(12)	2231 (4)	3780 (6)	8425 (3)
C(13)	2358 (3)	1138 (5)	8441 (3)
C(14)	927 (3)	2284 (6)	8499 (3)
C(15)	1755 (3)	2415 (5)	8211 (3)
N(5)	1407 (3)	2376 (5)	7323 (3)
O(1)	1283 (3)	3451 (5)	6964 (2)
O(2)	1218 (3)	1234 (5)	7024 (2)
Zn(1)	4754 (1)	2237 (1)	7727 (1)
Cl(1)	4777 (1)	2137 (2)	9015 (1)
Cl(2)	3356 (1)	2519 (1)	6996 (1)
Cl(3)	5299 (1)	306 (1)	7295 (1)
Cl(4)	5655 (1)	3949 (2)	7489 (1)
Cl(5)	3305 (1)	1634 (2)	4846 (1)
Cl(5′)	1067 (24)	5860 (40)	9374 (22)
O(3)	4342 (5)	4289 (7)	5709 (4)
O(3′)	3998 (13)	3856 (21)	4912 (13)

[a] Primes indicate minor contributors to disordered species. Occupancies: Cl(5) and O(3), 0.87 (2); Cl(5′) and O(3′), 0.13 (2).

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Table IV. Bond Lengths (Å) for $[Co(N_4S_2)]Cl(ClO_4)_2$

S(1)–Co(1)	2.205 (2)	S(2)–Co(1)	2.218 (2)
N(1)–Co(1)	1.985 (5)	N(2)–Co(1)	1.979 (5)
N(3)–Co(1)	1.975 (5)	N(4)–Co(1)	1.993 (5)
C(3)–S(1)	1.805 (7)	C(6)–S(1)	1.805 (7)
C(4)–S(2)	1.829 (6)	C(7)–S(2)	1.811 (7)
C(5)–N(1)	1.499 (8)	C(8)–N(1)	1.498 (7)
C(11)–N(2)	1.472 (8)	C(10)–N(3)	1.472 (8)
C(9)–N(4)	1.486 (8)	C(2)–C(1)	1.549 (9)
C(3)–C(2)	1.519 (9)	C(4)–C(2)	1.563 (8)
C(5)–C(2)	1.518 (9)	C(9)–C(6)	1.500 (10)
C(10)–C(7)	1.528 (9)	C(11)–C(8)	1.493 (9)
O(1)–Cl(1)	1.419 (5)	O(2)–Cl(1)	1.421 (5)
O(3)–Cl(1)	1.425 (6)	O(4)–Cl(1)	1.411 (6)

Table V. Bond Angles (deg) for $[Co(N_4S_2)]Cl(ClO_4)_2$

S(2)–Co(1)–S(1)	90.5 (1)	N(1)–Co(1)–S(1)	95.6 (1)
N(1)–Co(1)–S(2)	87.7 (1)	N(2)–Co(1)–S(1)	175.8 (2)
N(2)–Co(1)–S(2)	93.7 (2)	N(2)–Co(1)–N(1)	84.6 (2)
N(3)–Co(1)–S(1)	88.2 (1)	N(3)–Co(1)–S(2)	87.8 (1)
N(3)–Co(1)–N(1)	174.1 (2)	N(3)–Co(1)–N(2)	91.9 (2)
N(4)–Co(1)–S(1)	86.6 (1)	N(4)–Co(1)–S(2)	176.6 (1)
N(4)–Co(1)–N(1)	94.3 (2)	N(4)–Co(1)–N(2)	89.2 (2)
N(4)–Co(1)–N(3)	90.5 (2)	C(3)–S(1)–Co(1)	106.6 (2)
C(6)–S(1)–Co(1)	100.1 (2)	C(6)–S(1)–C(3)	104.9 (3)
C(4)–S(2)–Co(1)	106.2 (2)	C(7)–S(2)–Co(1)	97.8 (2)
C(7)–S(2)–C(4)	105.0 (3)	C(5)–N(1)–Co(1)	120.4 (4)
C(8)–N(1)–Co(1)	109.7 (4)	C(8)–N(1)–C(5)	110.0 (4)
C(11)–N(2)–Co(1)	108.2 (4)	C(10)–N(3)–Co(1)	113.1 (4)
C(9)–N(4)–Co(1)	113.5 (4)	C(3)–C(2)–C(1)	107.6 (5)
C(4)–C(2)–C(1)	105.5 (5)	C(4)–C(2)–C(3)	112.1 (5)
C(5)–C(2)–C(1)	107.7 (5)	C(5)–C(2)–C(3)	111.5 (5)
C(5)–C(2)–C(4)	112.0 (5)	C(2)–C(3)–S(1)	111.7 (4)
C(2)–C(4)–S(2)	112.8 (4)	C(2)–C(5)–N(1)	116.5 (5)
C(9)–C(6)–S(1)	108.6 (5)	C(10)–C(7)–S(2)	104.5 (4)
C(11)–C(8)–N(1)	108.3 (5)	C(6)–C(9)–N(4)	108.0 (5)
C(7)–C(10)–N(3)	109.1 (5)	C(8)–C(11)–N(2)	106.4 (5)
O(2)–Cl(1)–O(1)	107.3 (3)	O(3)–Cl(1)–O(1)	111.4 (4)
O(3)–Cl(1)–O(2)	109.2 (4)	O(4)–Cl(1)–O(1)	109.8 (4)
O(4)–Cl(1)–O(2)	111.0 (4)	O(4)–Cl(1)–O(3)	108.1 (3)

Table VI. Bond Lengths (Å) for $[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$

S(1)–Co(1)	2.219 (1)	S(2)–Co(1)	2.209 (1)
N(1)–Co(1)	2.042 (4)	N(2)–Co(1)	1.999 (4)
N(3)–Co(1)	1.998 (4)	N(4)–Co(1)	1.992 (4)
C(3)–S(1)	1.800 (6)	C(6)–S(1)	1.810 (5)
C(4)–S(2)	1.800 (5)	C(7)–S(2)	1.800 (6)
C(5)–N(1)	1.530 (6)	C(8)–N(1)	1.497 (6)
C(9)–N(2)	1.492 (7)	C(12)–N(2)	1.502 (7)
C(10)–N(3)	1.509 (6)	C(13)–N(3)	1.496 (6)
C(11)–N(4)	1.486 (8)	C(14)–N(4)	1.469 (7)
C(2)–C(1)	1.537 (7)	C(3)–C(2)	1.518 (8)
C(4)–C(2)	1.531 (6)	C(5)–C(2)	1.534 (7)
C(9)–C(6)	1.516 (7)	C(10)–C(7)	1.512 (7)
C(11)–C(8)	1.484 (8)	C(15)–C(12)	1.509 (7)
C(15)–C(13)	1.538 (7)	C(15)–C(14)	1.519 (8)
N(5)–C(15)	1.529 (6)	O(1)–N(5)	1.204 (6)
O(2)–N(5)	1.222 (6)	Cl(1)–Zn(1)	2.281 (2)
Cl(2)–Zn(1)	2.250 (1)	Cl(3)–Zn(1)	2.261 (1)
Cl(4)–Zn(1)	2.280 (2)	O(3′)–O(3)	1.438 (23)

icosane as NON_4S_2sar, it being understood that the second trigonal cap contains a methyl group as dictated by the synthetic procedures. The presence of different capping groups is reflected by the prefix X, i.e., XN_4S_2sar (X = NO, AM, CL, H); the prefixes are those described in a previous publication concerning the nomenclature employed for similar hexaaza-encapsulated complexes.[17] The amine-capped ligand therefore becomes AMN_4S_2-sar; protonation of the NH_2– cap is described by the suffix H, e.g., $[Co(AMN_4S_2sarH)]^{4+}$.[17] With this nomenclature the ligand 1-methyl-8-nitro-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]-icosane becomes NON_3S_3sar, in contrast to the previous abbreviation;[6] the previously reported hexadentate ligand ten[6] becomes N_3S_3.

Syntheses and Complexes. The potentially hexadentate ligand 5-methyl-5-(4-amino-2-azabutyl)-3,7-dithianonane-1,9-diamine, N_4S_2, was synthesized from reaction between 2-aminoethanethiol and 1,1,1-tris(((tolylsulfonyl)oxy)methyl)ethane and subsequent reaction of the product with 1,2-diaminoethane. The mixture of products which results reflects the statistical consequences of this synthetic approach. After reaction with a cobalt(II) salt and oxygen in methanol, the red solid obtained after preliminary chromatographic purification was determined to be a mixture of two products (Scheme I). Separation of these complexes, subsequently shown to be $[Co(N_4S_2)]^{3+}$ and $[Co(N_3S_3)]^{3+}$,[6] was accomplished on a small scale after elution on Sephadex cation-exchange column with a dilute aqueous solution

Table VII. Bond Angles (deg) for $[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$

S(2)–Co(1)–S(1)	93.5 (0)	N(1)–Co(1)–S(1)	94.0 (1)
N(1)–Co(1)–S(2)	89.9 (1)	N(2)–Co(1)–S(1)	86.4 (1)
N(2)–Co(1)–S(2)	176.7 (1)	N(2)–Co(1)–N(1)	93.4 (2)
N(3)–Co(1)–S(1)	88.4 (1)	N(3)–Co(1)–S(2)	86.3 (1)
N(3)–Co(1)–N(1)	175.6 (2)	N(3)–Co(1)–N(2)	90.4 (2)
N(4)–Co(1)–S(1)	176.1 (1)	N(4)–Co(1)–S(2)	90.2 (1)
N(4)–Co(1)–N(1)	84.8 (2)	N(4)–Co(1)–N(2)	89.9 (2)
N(4)–Co(1)–N(3)	93.0 (2)	C(3)–S(1)–Co(1)	109.2 (2)
C(6)–S(1)–Co(1)	96.1 (2)	C(6)–S(1)–C(3)	105.9 (2)
C(4)–S(2)–Co(1)	108.0 (2)	C(7)–S(2)–Co(1)	96.3 (2)
C(7)–S(2)–C(4)	106.3 (2)	C(5)–N(1)–Co(1)	118.1 (3)
C(8)–N(1)–Co(1)	105.0 (3)	C(8)–N(1)–C(5)	111.6 (4)
C(9)–N(2)–Co(1)	114.9 (3)	C(12)–N(2)–Co(1)	115.9 (3)
C(12)–N(2)–C(9)	110.2 (5)	C(10)–N(3)–Co(1)	114.0 (3)
C(13)–N(3)–Co(1)	116.3 (3)	C(13)–N(3)–C(10)	109.3 (3)
C(11)–N(4)–Co(1)	109.2 (3)	C(14)–N(4)–Co(1)	117.6 (3)
C(14)–N(4)–C(11)	111.3 (4)	C(3)–C(2)–C(1)	107.6 (4)
C(4)–C(2)–C(1)	106.3 (4)	C(4)–C(2)–C(3)	112.5 (4)
C(5)–C(2)–C(1)	107.0 (4)	C(5)–C(2)–C(3)	112.0 (4)
C(5)–C(2)–C(4)	111.0 (4)	C(2)–C(3)–S(1)	116.6 (3)
C(2)–C(4)–S(2)	118.1 (3)	C(2)–C(5)–N(1)	119.2 (4)
C(9)–C(6)–S(1)	104.5 (3)	C(10)–C(7)–S(2)	103.7 (3)
C(11)–C(8)–N(1)	106.5 (5)	C(6)–C(9)–N(2)	110.5 (5)
C(7)–C(10)–N(3)	111.3 (4)	C(8)–C(11)–N(4)	108.3 (4)
C(15)–C(12)–N(2)	112.6 (4)	C(15)–C(13)–N(3)	111.4 (4)
C(15)–C(14)–N(4)	112.6 (4)	C(13)–C(15)–C(12)	113.6 (4)
C(14)–C(15)–C(12)	113.4 (5)	C(14)–C(15)–C(13)	111.3 (4)
N(5)–C(15)–C(12)	107.4 (4)	N(5)–C(15)–C(13)	106.3 (4)
N(5)–C(15)–C(14)	104.0 (3)	O(1)–N(5)–C(15)	119.4 (4)
O(2)–N(5)–C(15)	116.8 (4)	O(2)–N(5)–O(1)	123.7 (4)
Cl(2)–Zn(1)–Cl(1)	109.9 (1)	Cl(3)–Zn(1)–Cl(1)	113.5 (1)
Cl(3)–Zn(1)–Cl(2)	107.5 (1)	Cl(4)–Zn(1)–Cl(1)	111.6 (1)
Cl(4)–Zn(1)–Cl(2)	111.2 (1)	Cl(4)–Zn(1)–Cl(3)	102.9 (1)

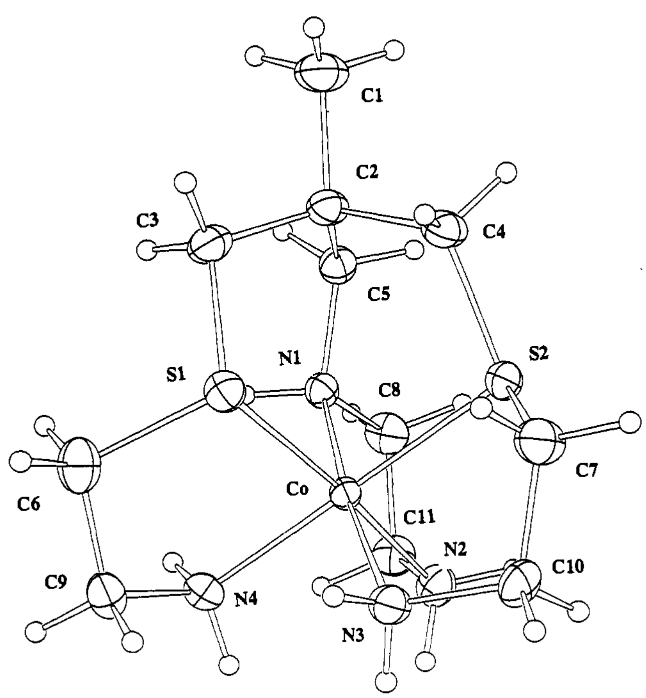


Figure 1. ORTEP plot of the complex cation of $[Co(N_4S_2)]Cl(ClO_4)_2$, giving the crystallographic atom numbering. Probability ellipsoids of 30% are shown.

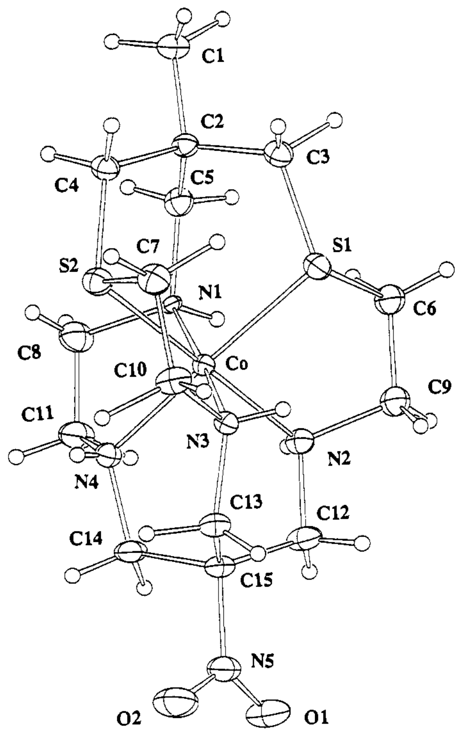
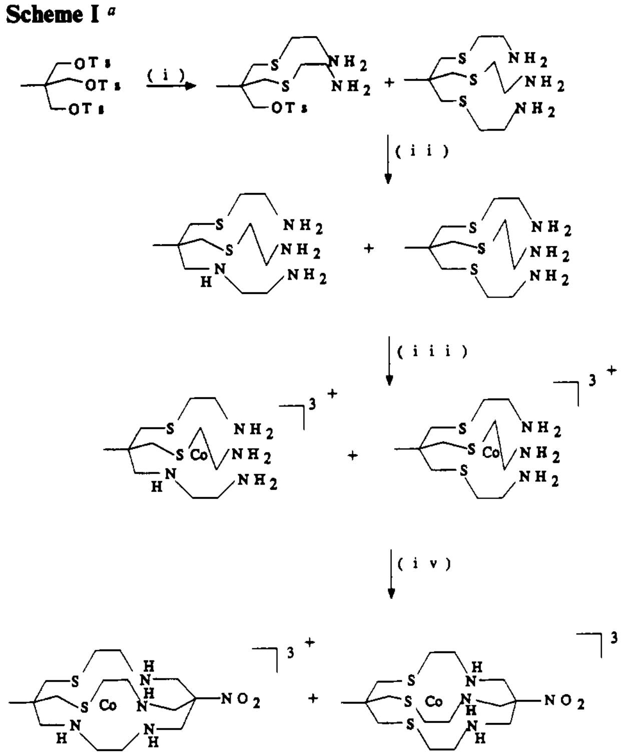


Figure 2. ORTEP plot of the complex cation of $[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$, giving the crystallographic atom numbering. Probability ellipsoids of 30% are shown.

Scheme I [a]



[a] Key: (i) $NaSCH_2CH_2NH_2$, EtOH, Δ; (ii) en, Δ; (iii) $CoCl_2$, O_2, MeOH; (iv) CH_3NO_2, HCHO, Na_2CO_3.

of sodium citrate. Alternatively, reaction of the mixture of complexes with nitromethane and formaldehyde in the presence of base, chemistry which has been extensively investigated and shown to result in encapsulated complexes,[2–6] resulted in the nitro-capped species $[Co(NON_4S_2sar)]^{3+}$ and the previously observed $[Co(NON_3S_3sar)]^{3+}$.[6] The mixture of products was readily separated chromatographically with Sephadex cation-exchange resin. Reduction of the apical nitro group to a protonated amine, and subsequent reactions to produce the chloro- and proteo-capped cages, as well as reactions resulting in the AZA-capped complex, were achieved as described for many similar complexes,[3,4,6,11,19] although in some cases more forcing conditions were required. The free ligand 1-amino-8-methyl-6,10-dithia-3,13,16,19-tetraazabicyclo[6.6.6]icosane (AMN_4S_2sar) was isolated after reaction of the metal complex, as cobalt(II), with cyanide ion in aqueous solution.[19,20]

The cobalt(III) complexes have been characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy. The nature of two of the complexes was further confirmed by single-crystal X-ray structure analysis.

Discussion of the Structures. The structure of $[Co(N_4S_2)]Cl(ClO_4)_2$ (the complex isolated from the second band eluted in the resolution) consists of the complex cation, two perchlorate anions, and a Cl^- anion. Weak hydrogen bonds connect all H(amine) atoms with O(perchlorate) atoms or the chloride anion. The conformation of the complex cation is described as lel_3[21] since the C–C vectors of the N–C–C–S chelate rings are parallel to the pseudo-C_3 axis of the complex. The cap atoms approximately eclipse the sulfur atoms to which they are bonded. For the $\Delta\epsilon_{475} = -6.27$ enantiomer, the absolute configuration is Δ in helical notation.[21] The coordinated sulfur atoms are *S*, as is the coordinated secondary amine nitrogen atom.[21]

The structure of $[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$ consists of the complex cation, a tetrachlorozincate anion, a chloride anion, and a water molecule. There are hydrogen bonds between all H(amine) and H(water) atoms and Cl(tetrachlorozincate), Cl^-, or O(water) atoms, some of which are quite strong. The conformation of the complex cation is also lel_3, and each of the caps eclipses the adjacent atoms. Thus the caps are staggered with respect to each other and the conformation is similar to that observed for other macrobicyclic complexes with 3 N 3 S or 6 N coordination spheres.[2,6,19] The presence of dissimilar bonds in the caps of both $[Co(N_4S_2)]Cl(ClO_4)_2$ and $[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$ results in a tilting of these caps with respect to the pseudo-C_3 axis of these complexes.

Average Co–S bond lengths in the two structures are similar (2.212 and 2.214 Å) and are similar to those in a pendant arm sulfur–nitrogen encapsulated complex of cobalt(III) (2.215 Å)[19] and $[Co(AZAN_3S_3sar)]^{3+}$ (2.226 (1) Å).[6] They are at the short end of the range for Co–S(thioether) bonds.[22,23] There are significant differences in the Co–N bond lengths for the two structures. Those in the half-capped species, $[Co(N_4S_2)]Cl(ClO_4)_2$, average 1.983 Å, slightly longer than those in the relatively strain-free complex $[Co(NH_3)_6]^{3+}$ (1.973 (1) Å).[24] In the fully encapsulated complex, $[Co(NON_4S_2sar)](ZnCl_4)Cl\cdot H_2O$, the Co–N bond lengths are longer, averaging 2.008 Å. The bond adjacent to the two S atoms is one of the longest Co–N bonds observed [2.042 (4) Å].[25] Evidently, the encapsulation imposes stresses on the bond, tending to make it more similar to the adjacent Co–S bonds.

^{13}C NMR Spectra. The ^{13}C NMR spectra of these complexes display resonances typical of this type of sulfur–nitrogen ligand and exhibit clearly the lack of symmetry in the molecules. In the case of the half-capped species $[Co(N_4S_2)]^{3+}$, the resonances at ~−22 ppm are typical of that for a methylene adjacent to a primary amine bound to cobalt(III).[4,6,19,26] For the encapsulated complexes, the resonances assigned to methylene carbon atoms

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Table VIII. Ligand Field Spectra of Co(III) Encapsulated Complexes and Related Chromophores[a]

ligand	donors	$E(^1A_{1g} \rightarrow {^1T_{1g}})$[b]	$E(^1A_{1g} \rightarrow {^1T_{2g}})$[b]	$10Dq$[b]	B[b]	ref
sen	6 N	21 400	29 400	22 710	587	45
sep	6 N	21 200	29 400	22 450	607	3
$diAMN_6sar$	6 N	21 050	29 100	22 300	594	4
$AZAMEN_6sar$	6 N	21 300	29 250	22 600	583	43
$AMMEN_6sarH$	6 N	21 200	29 000	22 510	571	43
NH_3	6 N	21 200	29 550	22 410	620	44
en	6 N	21 500	29 600	22 800	596	44
tacn	6 N	21 850	30 100	23 170	607	c
N_4S_2	4 N 2 S	20 800	27 950	22 140	516	c
$AZAN_4S_2sar$	4 N 2 S	20 450	27 500	21 770	509	c
AMN_4S_2sarH	4 N 2 S	20 450	27 700	21 750	526	c
NON_4S_2sar	4 N 2 S	20 450	27 700	21 750	526	c
CLN_4S_2sar	4 N 2 S	20 450	27 700	21 750	526	c
HN_4S_2sar	4 N 2 S	20 490	27 550	21 810	510	c
N_3S_3	3 N 3 S	20 650	27 150	22 000	462	6, c
$AZAN_3S_3sar$	3 N 3 S	20 450	26 800	21 790	451	43
AMN_3S_3sarH	3 N 3 S	20 500	27 150	21 840	475	6, c
NON_3S_3sar	3 N 3 S	20 450	27 050	21 790	471	6, c

[a] Values of $10Dq$ and B were calculated from solution data (reported in the references) using expressions (2) given in the text of this work. [b] All units are in cm^{-1}. [c] This work.

adjacent to the coordinated thioether (~−27 ppm) and secondary amines (~−12 ppm) are as observed previously.[6,19,26] As well, the resonance positions of quaternary carbon atoms bound to NO_2 (+20.5 ppm), NH_3^+ (−10.3 ppm), Cl (−5.7 ppm), and H (−29.9 ppm) capping groups are in accord with previous observations.[4,6,19,26]

Visible Spectra. The visible absorption spectra of these complexes are indicative of octahedrally coordinated low-spin cobalt(III) ions, with two d–d absorption bands corresponding to the spin-allowed $^1A_{1g} \rightarrow {^1T_{1g}}$ and $^1A_{1g} \rightarrow {^1T_{2g}}$ transitions. Alteration of the substituent on the cap has little effect on position of the band maxima of the d–d absorption bands in the encapsulated complexes, an observation made previously for the hexaamine encapsulated complexes.[27] The band maxima of the $^1A_{1g} \rightarrow {^1T_{1g}}$ and $^1A_{1g} \rightarrow {^1T_{2g}}$ transitions for the complexes examined in this study, along with those of related systems, are given in Table VIII.

At this point, it is appropriate to make some comment on the determination of octahedral ligand field parameters for low-spin Co(III) complexes. In the absence of complete d^6 ligand field calculations, it has been customary[28-30] to approximate the transition energies associated with the $^1T_{1g}$ and $^1T_{2g}$ excited states with the following diagonal energy expressions in order to evaluate the ligand field parameters B, C, and Dq:

$$E(^1A_{1g} \rightarrow {^1T_{1g}}) = 10Dq - C$$

$$E(^1A_{1g} \rightarrow {^1T_{2g}}) = 10Dq - C + 16B \qquad (1)$$

From the above expressions, the value of the Racah B parameter is easily determined from the difference of $16B$ between the two transition energies. In order to evaluate Dq, the assumption $C \approx 4B$ is usually made.[30]

A detailed low-temperature, single-crystal spectroscopy study of $[Co(NH_3)_6]^{3+}$ has been reported,[31] where the spin-forbidden $^1A_{1g} \rightarrow {^3T_{1g}}$ and $^1A_{1g} \rightarrow {^3T_{2g}}$ transitions were also observed. Since the $^1T_{1g}$, $^1T_{2g}$, $^3T_{1g}$, and $^3T_{2g}$ states all arise from the $(t_{2g})^5(e_g)^1$ configuration, it was possible to determine all three octahedral ligand field parameters uniquely as $B = 619$, $C = 3656$, and $Dq = 2400$ cm^{-1}. However, the value of B is approximately 20% larger than the value of 516 cm^{-1} calculated using the diagonal energy expressions above. The difference is significant and highlights the fact that the diagonal energy expressions are inadequate when appreciable configuration interaction occurs. As a further example to illustrate this point, we have carried out complete d^6 ligand field calculations, employing CAMMAG,[32] for $[Co(en)_3]^{3+}$ based on the reported band positions for both singlet and triplet spin states observed in the low-temperature single-crystal spectrum.[29] The best fit values were found to be $B = 605$, $C = 3595$, and $Dq = 2360$ cm^{-1}. Here again the agreement is poor since B is approximately 20% larger than the value of 503 cm^{-1} calculated from the diagonal energy expressions above. Furthermore, the C/B ratios for $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ are both 5.9, indicating that $C \approx 6B$ is a far better approximation for $[CoN_6]^{3+}$ type complexes than $C \approx 4B$. The poor approximation of $C = 4B$ for Co(III) complexes has been previously pointed out in relation to $Co(NH_3)_{6-x}(CN)_x^{(3-x)+}$ complexes.[33]

In the absence of complete d^6 ligand field calculations, a better approximation for the spin-allowed $^1A_{1g} \rightarrow {^1T_{1g}}$ and $^1A_{1g} \rightarrow {^1T_{2g}}$ and spin-forbidden $^1A_{1g} \rightarrow {^3T_{1g}}$ and $^1A_{1g} \rightarrow {^3T_{2g}}$ transition energies are the following perturbation expressions which have been corrected for configuration interaction:[34]

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

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

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

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

Without the observation of the spin-forbidden bands, a unique determination of B, C, and Dq is not possible. However, we have found that the above energy expressions for the two spin-allowed transitions give good agreement (within 5%) with those obtained from complete ligand field calculations when $C \sim 6B$. For example, using the band maxima of approximately 21 800 and 30 050 cm^{-1} observed in the low-temperature single-crystal

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Table IX. Rotational Strengths of the $^1A_{1g} \rightarrow {}^1T_{1g}$ Transition in Λ-$[Co(N_{6-n}S_n)]^{3+}$ Complexes

ligand	donors	λ_{max}[a]	$\Delta\epsilon_{max}$[b]	ref
en	6 N	490	+1.89	3
		430	-0.17	
sen	6 N	502	+0.42	3
		450	-1.05	
sep	6 N	461	-2.37	3
AZAMEN$_6$sar	6 N	463	-3.10	3
(en)$_2$(aet)	5 N S	498	+3.22	36
N$_4$S$_2$	4 N 2 S	475	+6.36	*c*
aeaps	4 N 2 S	520	+7.0	35
AZAN$_3$S$_3$sar	3 N 3 S	480	+10.9	6
atch	3 N 3 S	480	+11.9	26
N$_3$S$_3$	3 N 3 S	470	+12.4	6

[a] Expressed in nm. [b] M^{-1} cm^{-1}. [c] This work.

spectrum of $[Co(NH_3)]^{3+}$,[31] expressions (2) give $B = 607$ and $Dq = 2311$ cm^{-1}, in good agreement with $B = 619$ and $Dq = 2400$ cm^{-1} obtained from the complete d^6 calculation. Similarly, from the reported band maxima at 21 350 and 29 400 cm^{-1} for $[Co(en)_3]^{3+}$,[29] expressions (2) result in $B = 592$ and $Dq = 2264$ cm^{-1}, again in good agreement with $B = 605$ and $Dq = 2360$ cm^{-1} obtained from the complete d^6 calculation.

As a consequence of the above findings, the values of B and $10Dq$ listed in Table VIII were determined using expressions (2) with the Racah C parameter set to $6B$. As the number of thioether donors increases through the series 6 N, 4 N 2 S, and 3 N 3 S, there is a corresponding reduction in the Racah B parameter, approximately 100 cm^{-1} between 6 N and 3 N 3 S end members, the result of increased covalency as the nitrogen donors are replaced by thioethers. There is some indication of a linear dependence of B on the number of thioether ligands, since B is reduced between 40 and 50 cm^{-1} for every thioether donor. The relationship between $10Dq$ and the number of thioether donors is not so clear since although $10Dq$ decreases between 500 and 1000 cm^{-1} from 6 N to 4 N 2 S coordination, there is negligible change from 4 N 2 S to 3 N 3 S coordination.

Circular Dichroism. The racemic $[Co(N_4S_2)]^{3+}$ ion has been resolved into its chiral forms through ion-exchange chromatography and with an aqueous solution of sodium $(+)_{589}$-tartrate as an ion-pairing reagent. The enantiomer eluted first from the column displayed a positive circular dichroism associated with the $^1T_{1g}$ band ($\Delta\epsilon_{475} = +6.36$) and a much smaller dichroism associated with second ligand field band ($\Delta\epsilon_{358} = -1.95$) consistent with the magnetic dipole forbidden transition to the $^1T_{2g}$ state. The observed CD in terms of $\Delta\epsilon_{max}$ for the $^1T_{1g}$ band is given for Λ-$[Co(N_4S_2)]^{3+}$ and a number of related complexes of varying N and S donor ratios in Table IX.

In the octahedral approximation, the first-order rotational strengths for the orbital components of the $^1T_{1g}$ state cancel and hence no net rotational strength is predicted. The residual CD observed in solution for these and other optically active Co(III) complexes[2,3,6,26,35,36] results from low-symmetry splitting, second- and higher-order rotational strengths, and vibronically (Hertzberg–Teller) induced rotational strength. In the case of trigonal tris-chelate complexes, Shinada[37] showed that the net second-order rotational strength was nonvanishing, the sign of which was related to the sign of the trigonal field splitting parameter K as well as the odd parity ligand-field potential of $T_{2u}(z)$ symmetry.

For saturated trigonal tris-chelate complexes, Peacock[38,39] has shown that the sign of the rotational strength $R(E)$ of the $T_1(E)$ component can be predicted from the smaller twist angle between the upper and lower trigonally displaced sets of ligands. The twist angle (ω) is defined to be positive if the sense of rotation from the upper to lower set of ligands is clockwise; otherwise it is negative. A negative value of ω correlates with a positive rotational strength $R(E)$ for the $T_1(E)$ component. Interestingly, $R(E)$ is positive for all trigonally compressed geometries and negative for all elongated geometries.[38,40] For trigonally compressed geometries, the trigonal field splitting parameter K is negative and the $T_1(E)$ component lies to lower energy.

On the basis of the crystal structure of $(+)_{510}$-[Co(AZAN$_3$S$_3$sar)](ZnCl$_4$)Cl,[6] the Λ-Co(N$_3$S$_3$) chromophore has an overall trigonally compressed geometry with a negative ω value of $\sim 59°$. Accordingly, this should give rise to a positive value for $R(E)$ with the $T_1(E)$ component lying to lower energy. Ligand field calculations using the angular overlap model[34] confirm this energy order and indicate that the trigonal splitting of the $^1T_{1g}$ state is less than 100 cm^{-1}. The net positive CD ($\Delta\epsilon_{max} = +10.9$) observed in solution[6] for Λ-[Co(AZAN$_3$S$_3$sar)]$^{3+}$ can therefore be attributed to the dominant rotational strength of the $T_1(E)$ component. A positive CD ($\Delta\epsilon_{max} = +6.36$) is also observed for $[Co(N_4S_2)]^{3+}$ containing the Λ-Co(4 N 2 S) chromophore, but for this complex the analysis is complicated by the presence of additional low-symmetry distortions. The positive CD observed for these complexes contrasts with the hexaaza cage analogues such as Λ-[Co(AZAMEsar)]$^{3+}$ and Λ-[Co(sep)]$^{3+}$, where the net rotational strength in solution (Table IX) was negative and attributed to the dominance of the rotational strength of the higher lying $T_1(A_2)$ component, resulting from the step-wise capping of Λ-$[Co(en)_3]^{3+}$.[3] The introduction of thioether groups in these complexes apparently leads to an enhancement in positive rotational strength for the Λ-configurations.

From an examination of the $\Delta\epsilon_{max}$ values given in Table IX for a number of Λ-Co(N$_{6-n}$S$_n$) complexes, there is a clear indication that the net positive rotational strength increases with increasing number of thioether donors. This is consistent with a static coupling model as the rotational strength to second order of perturbation involves terms of the following form:

$$\sum_{\Gamma_u\gamma_u} \frac{\langle \Gamma_\gamma | V_u | \Gamma_u \gamma_u \rangle \langle \Gamma_u \gamma_u | \mathbf{P} | \Gamma' \gamma' \rangle}{\Delta E(\Gamma, \Gamma_u)}$$

Here V_u is the odd parity ligand field potential, **P** is the electric dipole operator, $\Gamma\gamma$ and $\Gamma'\gamma'$ are the ground and excited even parity ligand field states, and ΔE is the energy difference between the odd parity charge-transfer state Γ_u and the ground-state Γ.[37] As the number of thioether donors increases, the contribution of the above terms to the rotational strength increases due to the larger number of charge-transfer states Γ_u associated with the thioether donors, as well as a smaller energy difference ΔE due to the lower energy of thioether–Co(III) charge-transfer transitions. In addition, the increased CD with increasing number of thioether donors is also consistent with the dynamic coupling model[41] as thioether donors are more polarizable than nitrogen donors and hence will give rise to greater rotational strength.

Supplementary Material Available: Listings of full crystal data (Table S1), thermal parameters (Tables S2 and S6), hydrogen positional and thermal parameters (Tables S3 and S7), torsion angles (deg) (Tables S4 and S8), and close intermolecular contacts (Tables S5 and S9) and the circular dichroism spectra of [Co(N$_4$S$_2$)]Cl(ClO$_4$)$_2$ (Figure 3) (11 pages). Ordering information is given on any current masthead page.

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