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Encapsulated Metal Ions: Synthesis, Structure, and Spectra of Nitrogen-Sulfur Ligand Atom Cages Containing Cobalt(III) and Cobalt(II)

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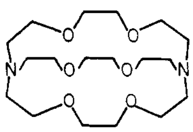
The cobalt(III) complex of the hexadentate ligand 4,4′,4″-ethylidynetris(3-thiabutan-1-amine) reacts with formaldehyde and ammonia to form the encapsulated-metal complex [(1-methyl-3,13,16-trithia-6,8,10,19-tetraazabicyclo[6.6.6]eicosane)cobalt(III)](3+). Analogous capping strategy with nitromethane and formaldehyde yields [(1-methyl-8-nitro-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]eicosane)cobalt(III)](3+). This nitro-substituted encapsulated-metal complex is readily reduced to an amino-substituted cage complex. The macrobicyclic nature and absolute configuration of the aza-capped complex has been established by an X-ray crystallographic analysis of the $(+)_{510}$-[Co(azacapten)]$ZnCl_4$·Cl complex. An X-ray crystallographic analysis of the corresponding racemic complex indicates that the structure is disordered between the two enantiomers in the crystal. The catoptric forms of the aza-capped complex display a strikingly large dichroism associated with the first ligand field band, with $\Delta\epsilon_{480} = -10.3\ M^{-1}\ cm^{-1}$ for one of the enantiomers. The chiral cobalt(III) cage may be reduced to a chiral cobalt(II) complex and reoxidized by O_2 with complex retention of chirality. Hydrogen peroxide is produced in this reaction. The reaction of O_2 with the cobalt(II) complex is also rapid, with $k_{O_2} = 290\ (\pm 30)\ M^{-1}\ s^{-1}$ at 25 °C ($\mu = 0.2$).

Introduction

Macrobicyclic ligands that encapsulate cations within a cagelike environment have been classified generally as cryptates (**1**).[2-6] The polyether cryptate ligands have shown remarkable selectivity toward alkali and alkaline-earth cations, but the encapsulation of transition metal ions within these ligands has been achieved unambiguously in only a few instances.[6] Encapsulation of transition-metal ions with nitrogen or sulfur donor ligands must, however, be inherently more likely, and some examples have already been reported (**2**, **3**).[7-12] These examples probably use uncoordinated nucleophiles on bound ligands to capture electrophilic reagents and complete the cage.



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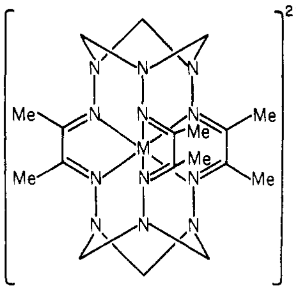

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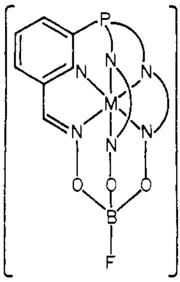

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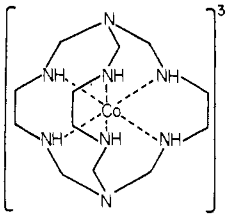
A macrobicyclic ligand with six saturated nitrogen donors has been synthesized recently by a metal-assisted condensation reaction using tris(ethane-1,2-diamine)cobalt(III) ion with formaldehyde and ammonia.[13,14] The complex so formed [(1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane)cobalt(III)](3+) has been given the trivial name $[Co(sepulchrate)]^{3+}$ (**4**).[13] Apart from the six nitrogen donor atoms, there are two aza caps, which are not bonded to the metal ion. In this chemistry, deprotonation of the bound NH_2 groups in the parent $[Co(en)_3]^{3+}$ ion provides the nucleophiles for the condensation of formaldehyde and the resulting imines are subsequently captured by the nucleophilic NH_3 to complete the cage.



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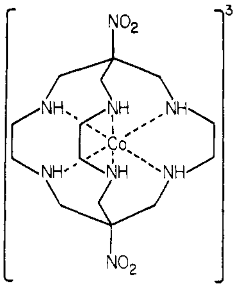

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A similar synthesis involving $[Co(en)_3]^{3-}$, CH_2O, and CH_3NO_2 in basic conditions yields an analogous complex with nitromethyl caps in place of the aza caps (**5**).[15] This condensation occurs by a similar route, and the efficiency of the process arises presumably from the intramolecularity of the reaction. Ring closure in such organic bicyclic ring systems of this size would be inhibited by large entropy effects. This problem is reduced markedly by the presence of the metal ion,

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which reduces the large ring synthesis to a series of optimal five- or six-membered ring syntheses.[16]

There is an obvious need to expand the variety of donor atoms in such cage molecules, and this paper reports a new hexadentate ligand containing sulfur and nitrogen donor atoms, the cobalt(III) complex, the capping syntheses, resolution into chiral forms, reactions, and the crystal and molecular structure of one of the chiral forms of the capped complex.

Experimental Section

^{1}H NMR spectra were recorded with a JEOL Minimar 100-MHz spectrometer on external lock and with sodium 4,4-dimethyl-4-silapentanesulfonate (DSS) or tetramethylsilane (Me_4Si) as internal references. Fourier transform $^{13}C\{^1H\}$ NMR spectra (δ) were recorded with a JEOL FX 60 spectrometer using an external lock (D_2O) and 1,4-dioxane as the internal reference (δ +66.6 downfield from Me_4Si). Visible spectra (ϵ in M^{-1} cm^{-1}) were recorded with a Cary 118C spectrophotometer, and infrared spectra were recorded with a Perkin-Elmer Model 457 IR spectrophotometer with KBr plates. Rotatory dispersion and circular dichroism spectra were recorded with a Perkin-Elmer P22 spectropolarimeter and a Jasco Model ORD/UV-5 with a Sproul Scientific SS 20 CD modification, respectively. All evaporations were conducted in a Buchi rotary evaporator under reduced pressure (~20 mmHg) so that the temperature of the solution did not exceed 25 °C.

1,1,1-Tris(mercaptomethyl)ethane was prepared from 1,1,1-tris(bromomethyl)ethane as described previously.[17]

4,4′,4″-Ethylidynetris(3-thiabutan-1-amine) (ten). 1,1,1-Tris(mercaptomethyl)ethane (6 g) was added dropwise with stirring to ethylenimine (4.6 g). Cautious heating initiated a gentle reflux, and the mercaptan was added at such a rate to maintain the solution at reflux. The mixture was stirred for 2 h after completion of the addition. Excess ethylenimine was removed under reduced pressure, leaving a viscous yellow oil, yield 10 g. ^{1}H NMR: δ 1.02 (CH_3, singlet, 3 H), 1.50 (NH_2, singlet, 6 H), 2.8 ($-CH_2-$, multiplet, 18 H) in $CDCl_3$(Me_4Si).

$[Co(ten)]Cl_2 \cdot ClO_4 \cdot H_2O$. The ligand ten (10 g) was dissolved in methanol (25 mL) and added to a methanolic solution (75 mL) of cobaltous acetate (11.25 g). Oxygen was bubbled through the solution for 5 h, during which time the initially brown solution became yellow and a yellow solid was deposited. The resulting methanolic solution was added to a large volume of water and filtered. The filtrate was sorbed on Dowex 50W-X2 cation-exchange resin (H^+ form, 200–400 mesh) and washed with water and 1 M HCl. Elution with 3 M HCl removed a major red component, and the eluate was evaporated to give a red solid, which was redissolved in a large volume of water and rechromatographed on Sephadex C-25 cation-exchange resin (Na^+ form), after being washed with water and with 0.1 M NaCl. This eluant removed a minor pink fraction, and the column was then eluted with 0.2 M NaCl to remove the major red component, which 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 $NaClO_4$ (13.5 g). Anal. Calcd for $CoC_{11}H_{29}N_3S_3Cl_3O_5$: C, 24.33; H, 5.39; N, 7.74; S, 17.71; Co, 10.85; Cl, 19.59. Found: C, 24.5; H, 5.4; N, 7.5; S, 17.6; Co, 10.7; Cl, 19.8. Visible spectrum (λ_{max} (ϵ_{max}), in H_2O): 484 nm (574), 367 nm (676). ^{1}H NMR: δ 1.4 (CH_3, singlet, 3 H), 3.3 (–CH–, multiplet, 18 H) in D_2O. ^{13}C NMR: δ +44.5, +41.9, +39.5 ($-CH_2-$), +28.0 (CH_3) in D_2O (Me_4Si).

$[Co(azacapten)](ClO_4)_3 \cdot 2H_2O$. $[Co(ten)]Cl_2 \cdot ClO_4$ (3.5 g) was dissolved in water (100 mL) along with lithium carbonate (6 g). To this solution were added separately, dropwise over approximately 3 h, aqueous solutions (200 mL) of 28% ammonia (20 g) and 37% formaldehyde solution (73 g). At the completion of the addition, the deep red reaction mixture was stirred for 1 h, filtered, and the pH adjusted to 4 with concentrated HCl. The solution was diluted to 2 L, sorbed on Dowex 50W-X2 cation-exchange resin (H^+ form, 200–400 mesh), and washed with water and 1 M HCl. Elution with 3 M HCl removed a major red fraction, which was evaporated to dryness. The red solid obtained was dissolved in a large volume of water, sorbed on Sephadex C-25 cation-exchange resin (Na^+ form), and washed with water and 0.1 M NaCl solution to remove minor pink and brown fractions, which were discarded. The column was then eluted with 0.2 M NaCl to remove a major red fraction, which was collected on Dowex 50W-X2 cation-exchange resin, eluted with 3 M HCl, and evaporated to dryness. The complex was crystallized from water as dark red needles with use of $NaClO_4$ (1.5 g). Anal. Calcd for $CoC_{14}H_{34}N_4S_3Cl_3O_{14}$: C, 22.60; H, 4.62; N 7.53; S, 12.93; Co, 7.92; Cl, 14.29. Found: C, 22.7; H, 4.6; N, 7.4; S, 13.2; Co, 8.0; Cl, 14.5. Visible spectrum (λ_{max} (ϵ_{max}), in H_2O) 489 nm (831), 373 nm (965). ^{1}H NMR: δ 1.4 (CH_3, singlet, 3 H), 3.5 ($-CH_2-$, multiplet, 24 H) in D_2O. ^{13}C NMR: δ + 67.5, +53.5, +41.0, +39.2 ($-CH_2-$), +42.10 (apical C), +27.5 (CH_3) in D_2O (Me_4Si).

$[Co(NO_2capten)]Cl_2 \cdot ClO_4 \cdot {}^3/_2H_2O$. $[Co(ten)]Cl_2 \cdot ClO_4$ (1.5 g) was dissolved in water (100 mL), and to this solution were added nitromethane (0.69 g) and 37% formaldehyde solution (6 g). Sodium carbonate (0.24 g) was added, and the dark purple reaction mixture was stirred for 4 h at 22 °C. then acetic acid was added to adjust the pH to 3, and after dilution the red solution was sorbed on Dowex 50W-X2 cation-exchange resin (H^+ form, 200–400 mesh). After the column was washed with water and 1 M HCl to remove a minor pink fraction, a major red band was eluted with 3 M HCl. The solution was evaporated to dryness, and the red solid was dissolved in a large volume of water, sorbed on Sephadex C-25 cation-exchange resin (Na^+ form), and washed with water and 0.1 M NaCl. Elution with 0.2 M NaCl solution removed one major red band, which was collected on Dowex 50W-X2 cation-exchange resin. Elution with 3 M HCl and evaporation gave the red complex as the chloride salt from which the perchlorate was crystallized with use of water and $NaClO_4$ (1.3 g). Anal. Calcd for $CoC_{15}H_{33}N_4S_3Cl_3O_{7.5}$: C, 27.67; H, 5.12; N, 8.61; S, 14.77; Co, 9.05; Cl, 16.34. Found: C, 27.9; H, 5.1; N, 8.6; S, 14.3; Co, 9.0; Cl, 16.4. Visible spectrum (λ_{max} (ϵ_{max}), in H_2O): 489 nm (735), 368 nm (789). ^{1}H NMR: δ 1.4 (CH_3, singlet, 3 H), 3.3 ($-CH_2-$, multiplet, 24 H) in D_2O. ^{13}C NMR: δ +87.4 ($C-NO_2$); +55.3, +52.3, +40.5, +38.7 ($-CH_2-$), +42.3 (apical C), +27.6 (CH_3) in D_2O (Me_4Si).

$[Co(NH_2capten)HCl]Cl_3 \cdot {}^5/_2H_2O$. $[Co(NO_2capten)]Cl_2 \cdot ClO_4$ was reduced to $[Co(NH_2capten)HCl]^{2+}$ with use of zinc and hydrochloric acid under a nitrogen atmosphere. After oxidization of the complex with hydrogen peroxide solution the complex was crystallized as a hygroscopic red solid from hydrochloric acid. Anal. Calcd for $CoC_{15}H_{38}N_4S_3Cl_4O_{2.5}$: C, 29.46; H, 6.27; N, 9.16; S, 15.73; Co, 9.64; Cl, 23.19. Found: C, 29.1; H, 6.1; N, 9.2; S, 16.0; Co, 9.6; Cl, 24.1. Visible spectrum (λ_{max} (ϵ_{max}), in H_2O): 489 nm (774), 369 nm (848). ^{1}H NMR δ 1.4 (CH_3, singlet, 3 H), 3.2 ($-CH_2-$, multiplet, 24 H) in D_2O. ^{13}C NMR: δ +55.7 ($C-NH_3^+$), +54.9 +52.9, +40.9, +38.3 ($-CH_2-$), +42.6 (apical C), +27.6 (CH_3) in D_2O (Me_4Si).

Resolution of $[Co(azacapten)](ClO_4)_3$. The complex (0.5 g) was resolved into its enantiomeric forms by upward-flow chromatography on Sephadex C-25 cation-exchange resin (Na^+ form) with sodium $(+)_{589}$-antimonyltartrate (0.2 M) as eluant. The column employed was a Pharmacia SR 25 column (70 × 3.5 cm). A flow rate of 2 cm^3 min^{-1} was maintained with a peristaltic pump in a closed circuit. The initial single red band separated into two bands after two cycles on the column. The fractions were eluted from the column and freed of eluant after sorption on Dowex 50W-X2 resin and washing with 0.5 M HCl. Elution of the derivative forms with 3 M HCl and evaporation resulted in red solids. The enantiomers were converted to their respective perchlorate salts in water with use of stoichiometric amounts of $AgClO_4$. Removal of AgCl and evaporation allowed the perchlorates to crystallize. The enantiomers were recrystallized from water to constant rotation. The first fraction eluted from the column gave $[M]_{510} = -23\,200°$ M^{-1} m^{-1} and $[M]_{450} = +23\,200°$ M^{-1} m^{-1} with $\Delta\epsilon_{480} = -10.3$ M^{-1} cm^{-1} and $\Delta\epsilon_{360} = +2.83$ M^{-1} cm^{-1}. Anal. Calcd for $CoC_{14}H_{34}N_4S_5Cl_3O_{14}$: C, 22.60; H, 4.62; N, 7.53. Found: C, 22.9; H, 4.7; N, 7.5. The second fraction gave $[M]_{510} = +23\,800°$ M^{-1} m^{-1} and $[M]_{450} = -24\,100°$ M^{-1} m^{-1} with $\Delta\epsilon_{480} = +10.9$ M^{-1} cm^{-1} and $\Delta\epsilon_{360} = -3.01$ M^{-1} cm^{-1}. Anal. Calcd for $CoC_{14}H_{34}N_4S_3Cl_3O_{14}$: C, 22.60; H, 4.62; N, 7.53. Found: C, 22.9; H, 4.4; N, 7.5.

Resolution of $Co(ten)Cl_2 \cdot ClO_4 \cdot H_2O$. This complex was resolved into its enantiomeric forms as described above for the capped complex. The enantiomers were crystallized from water with $NaClO_4$ to constant rotation. The first fraction eluted from the column gave $[M]_{510} = +19\,900°$ M^{-1} m^{-1} and $[M]_{430} = -30\,400°$ M^{-1} m^{-1} with $\Delta\epsilon_{470} = +12.4$ M^{-1} cm^{-1} and $\Delta\epsilon_{360} = -4.47$ M^{-1} cm^{-1}. Anal. Calcd for $C_{11}H_{29}N_2S_2CoCl_3O_5$: C, 24.33; H, 5.39; N, 7.74. Found: C, 24.6; H, 5.1; N, 7.8. The second fraction gave $[M]_{510} = -19\,700°$ M^{-1} m^{-1}

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Table I. Crystal Data for $[Co(azacapten)](S_2O_6)_{1.5}\cdot 4H_2O$ and $(+)_{510}$-$[Co(azacapten)]ZnCl_4\cdot Cl$

	$[Co(azacapten)]$-$(S_2O_6)_{1.5}\cdot 4H_2O$	$(+)_{510}$-$[Co(azacapten)]$-$ZnCl_4\cdot Cl$
	(A) Crystal Data	
cryst system	monoclinic	cubic
space group	$P2_1/c$ (No. 14)	$P2_13$ (No. 198)
a, Å	15.547 (9)	13.370 (1)
b, Å	10.516 (6)	
c, Å	17.23 (1)	
β, deg	90.8 (2)	
V, Å^3	2816.7	2390.0
D_{obsd}, g cm^{-3}	1.68 (2)	1.82 (2)
D_{calcd}, g cm^{-3}	1.694	1.801
empirical formula	$C_{14}H_{38}CoN_4O_{13}S_6$	$C_{14}H_{30}Cl_5CoN_4S_3Zn$
fw	721.9	648.0
Z	4	4
μ, cm^{-1}	10.42	24.84
$F(000)$, electrons	1496	1330
color	red	red
habit	plates	octahedral
dimens, mm	0.15 × 0.20 × 0.05	0.15 × 0.30 × 0.30
transmission factors	0.95, 0.87	0.75, 0.60
T, °C	21	21
	(B) Data Collection	
diffractometer	STOE, two-circle, Weissenberg geometry	
radiation	Mo Kα (λ 0.710 69 Å)	
monochromator	graphite	
mode	ω scan	
2θ range, deg	0–50.0	0–55.0
reflctns measd	$+h, +k, \pm l$	$+h, +k, +l$
levels collected	$h0l$–$h7l$	$0kl$–$14kl$
total reflctns measd	3516 total, 2754 independent	2877 total, 1025 independent
data averaging $R(I)$	3.0%	3.2%

and $[M]_{430} = +31\,000°$ M^{-1} m^{-1} with $\Delta\epsilon_{470} = -12.1$ M^{-1} m^{-1} and $\Delta\epsilon_{360} = +4.31$ M^{-1} cm^{-1}. Anal. Calcd for $C_{11}H_{29}N_3S_3CoCl_3O_5$: C, 24.33; H, 5.39; N, 7.74. Found: C, 24.2; H, 5.3; N, 7.8.

$(+)_{510}$-$[Co(azacapten)]^{2+}$. An aqueous solution of $(-)_{510}$-$[Co(azacapten)](ClO_4)_3$, $[M]_{510} = -23\,200°$ M^{-1} m^{-1}, was reduced with zinc amalgam under nitrogen to a purple solution of $(+)_{510}$-$[Co(azacapten)]^{2+}$. Visible spectrum (λ_{max} (ϵ_{max}), in H_2O): 500 nm (124), 550 s (104); $[M]_{510} = +1140°$ M^{-1} m^{-1}, $[M]_{450} = +4650°$ M^{-1} m^{-1}. This solution was reacted with excess O_2 to regenerate the Co(III) state, whence $[M]_{510} = -23\,000°$ M^{-1} m^{-1}.

X-ray Crystallography. Crystal data and the experimental conditions for data collection for racemic $[Co(azacapten)](S_2O_6)_{1.5}\cdot 4H_2O$ and $(+)_{510}$-$[Co(azacapten)]ZnCl_4\cdot Cl$ are given in Table I.

Solution and Refinement of the Structure of Racemic $[Co(azacapten)](S_2O_6)_{1.5}\cdot 4H_2O$.[18] The structure was solved by heavy-atom method and confirmed by direct methods. All nonhydrogen atoms of the complex and dithionate ions were located and included to give $R = 0.23$. At this stage a second coordination sphere was located about the cobalt, and it was noticed that some of the atoms in the initial coordination sphere had excessively large thermal parameters. A disordered model corresponding to occupation of the same site by both enantiomers gave good agreement, and the group multiplicity parameter refined to 0.64 (1). In this model the cobalt and the carbon atoms of the ethane cap and of the cysteamine chelate rings as well as the nitrogen of the amine cap are shared by both enantiomers on the site. The oxygens of both dithionate ions and two of the four water molecules are also disordered, and their group multiplicity parameter refined to 0.66 (2). It was evident that the disorder in cations and anions was correlated, and the parameter for all disorder was fixed at 0.65 for the last cycles of refinement. All parameters were refined with use of blocked-matrix least-squares techniques with the final refinement sequence organized in blocks, which enabled all parameters to interact. Only the cobalt and sulfur atoms were refined anisotropically. Individual layer scale factors were adjusted during the isotropic phase of the refinement, which also employed unit weights. The weighting scheme was later refined and converged at $w =$

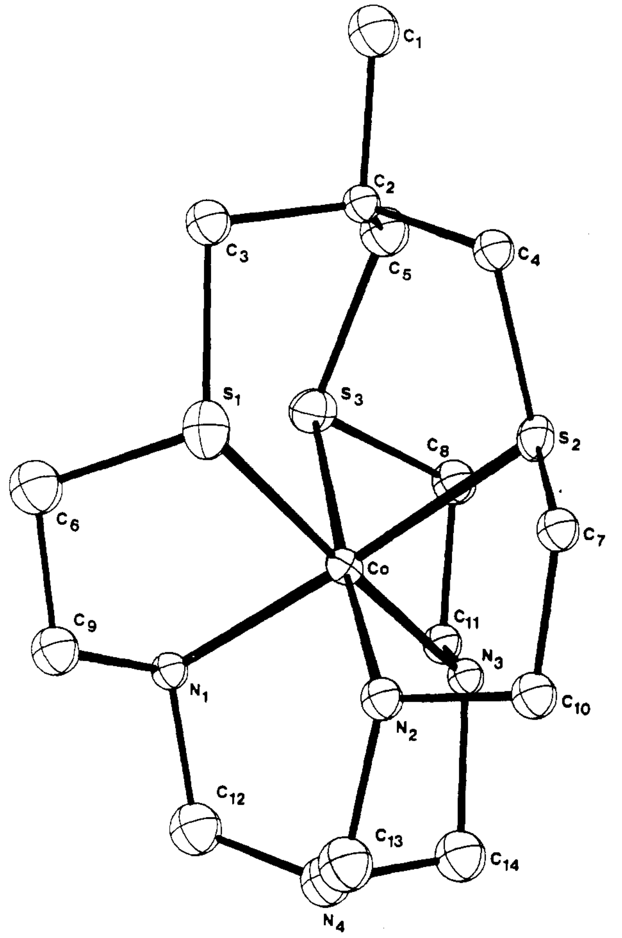

Figure 1. Projection perpendicular to the threefold axis of the racemic $[Co(azacapten)]^{3+}$ ion. Ellipsoids enclose 50% probabilities.

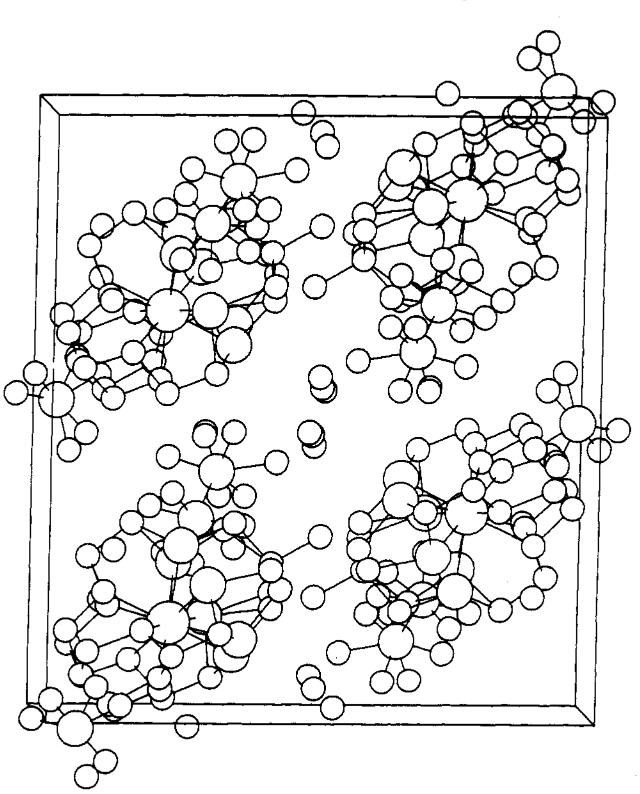

Figure 2. Cell packing and disorder for $[Co(azacapten)]^{3+}$, viewed down the y axis.

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(18) Programs used include those for local data reduction (AUPTP), structure solution and refinement (SHELX by G. M. Sheldrick), and thermal ellipsoid plots (ORTEP by C. K. Johnson).

Table II. Atomic Positional Parameters ($\times 10^4$) for [Co(azacapten)]$(S_2O_6)_{1.5}\cdot 4H_2O$ (Standard Deviations in Parentheses)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	2214 (2)	4502 (3)	3333 (2)	C(3*)	3229 (40)	3499 (71)	1823 (35)
S(1)	3469 (6)	5496 (12)	3572 (5)	C(4*)	4116 (38)	3237 (69)	3125 (34)
S(2)	2925 (8)	2730 (11)	3278 (6)	C(5*)	4026 (40)	5462 (78)	2430 (37)
S(3)	2409 (6)	4774 (10)	2056 (5)	C(12*)	1123 (38)	5579 (74)	4663 (34)
S(1*)[a]	2333 (11)	3186 (19)	2364 (9)	C(13*)	692 (38)	3550 (65)	4254 (31)
S(2*)	2868 (11)	5967 (19)	2661 (10)	C(14*)	317 (36)	5271 (65)	3437 (32)
S(3*)	3404 (12)	3788 (19)	3875 (11)	O(1)	1178 (19)	9701 (30)	4554 (17)
S(4)	395 (6)	9212 (9)	4960 (5)	O(2)	631 (20)	8908 (28)	5774 (17)
S(5)	2833 (8)	44 (9)	1766 (6)	O(3)	−37 (27)	8356 (40)	4504 (22)
S(6)	3246 (8)	8638 (9)	1036 (5)	O(4)	3668 (31)	762 (44)	1855 (27)
N(1)	1124 (19)	3701 (31)	3064 (16)	O(5)	2364 (21)	895 (29)	1317 (16)
N(2)	1672 (19)	6177 (29)	3407 (16)	O(6)	2266 (24)	−574 (36)	2336 (21)
N(3)	2092 (18)	4179 (30)	4459 (16)	O(7)	3781 (20)	−2116 (32)	1460 (16)
N(4)	619 (14)	4906 (24)	4183 (12)	O(8)	3520 (23)	−702 (32)	371 (18)
N(1*)	2022 (31)	5639 (54)	4212 (27)	O(9)	2377 (21)	−2022 (28)	812 (17)
N(2*)	1550 (34)	3108 (53)	3986 (29)	O(10)	2768 (17)	9545 (28)	5226 (15)
N(3*)	1003 (36)	4982 (57)	2809 (31)	O(11)	1086 (11)	7361 (15)	2041 (9)
C(1)	4964 (16)	3844 (27)	1923 (14)	O(12)	1073 (13)	1019 (17)	3060 (11)
C(2)	4077 (16)	4019 (24)	2369 (14)	O(13)	4857 (26)	1719 (40)	331 (23)
C(3)	4115 (32)	2766 (49)	2877 (28)	O(1*)	748 (33)	9267 (48)	4258 (27)
C(4)	4205 (31)	5276 (53)	2755 (28)	O(2*)	−376 (36)	8265 (54)	4822 (33)
C(5)	3390 (25)	4083 (41)	1705 (21)	O(3*)	952 (39)	9261 (59)	5503 (36)
C(6)	3064 (16)	7069 (24)	3426 (13)	O(4*)	3516 (37)	386 (59)	2228 (33)
C(7)	3061 (17)	2436 (28)	4305 (15)	O(5*)	2800 (39)	9534 (62)	2520 (33)
C(8)	1532 (16)	3711 (24)	1715 (13)	O(6*)	1978 (58)	171 (83)	1550 (51)
C(9)	2195 (15)	7098 (24)	3798 (13)	O(7*)	4313 (61)	9124 (81)	861 (48)
C(10)	2190 (17)	2841 (27)	4642 (14)	O(8*)	3012 (37)	8807 (54)	381 (32)
C(11)	739 (17)	3975 (25)	2258 (15)	O(9*)	3331 (54)	7524 (79)	1458 (44)
C(12)	400 (32)	3931 (51)	3689 (29)	O(10*)	4654 (34)	5986 (53)	149 (31)
C(13)	685 (28)	6162 (46)	3756 (25)	O(13*)	5074 (56)	9039 (86)	−531 (50)
C(14)	1262 (30)	4662 (54)	4782 (26)				

[a] Minor contributors are denoted by an asterisk (multiplier 0.35).

Table III. Interatomic Distances (A) for Racemic [Co(azacapten)]$(S_2O_6)_{1.5}\cdot 4H_2O$[a]

Co–S(1)	2.24 (1)	N(2)–C(13)	1.50 (6)
Co–S(2)	2.17 (1)	N(3)–C(14)	1.59 (6)
Co–S(3)	2.24 (1)	C(12)–N(4)	1.51 (5)
Co–N(1)	1.96 (3)	C(13)–N(4)	1.45 (5)
Co–N(2)	1.98 (3)	C(14)–N(4)	1.37 (6)
Co–N(3)	1.94 (3)	$S(4)^{II}$–S(4)	2.07 (2)
C(1)–C(2)	1.59 (4)	S(4)–O(1)	1.50 (3)
C(2)–C(3)	1.49 (6)	S(4)–O(2)	1.48 (3)
C(2)–C(4)	1.58 (6)	S(4)–O(3)	1.37 (4)
C(2)–C(5)	1.56 (5)	S(5)–S(6)	2.05 (1)
C(3)–S(1)	1.84 (5)	S(5)–O(4)	1.51 (5)
C(4)–S(2)	1.96 (5)	S(5)–O(5)	1.38 (3)
C(5)–S(3)	1.80 (4)	S(5)–O(6)	1.48 (4)
S(1)–C(6)	1.79 (3)	S(6)–O(7)	1.36 (3)
S(2)–C(7)	1.81 (3)	S(6)–O(8)	1.41 (3)
S(3)–C(8)	1.85 (3)	S(6)–O(9)	1.56 (3)
C(6)–C(9)	1.51 (3)	N(1)–O(11)	2.80
C(7)–C(10)	1.54 (5)	N(3A)–O(11)	2.84
C(8)–C(11)	1.58 (4)	N(3)–O(12)	2.82
C(9)–N(1)	1.43 (4)	N(2A)–O(12)	2.81
C(10)–N(2)	1.45 (4)	$N(2)^{I}$–O(8)	3.14
C(11)–N(3)	1.53 (4)	$N(1A)^{I}$–O(8A)	2.59
N(1)–C(12)	1.66 (5)		

[a] Symmetry: I, *x*, $1/2 - y$, $1/2 + z$; II, $-x$, $-y$, $-z$.

Table IV. Bond Angles (Deg) for Racemic $[Co(azacapten)]^{3+}(S_2O_6)_{1.5}\cdot 4H_2O$

S(1)–Co–S(3)	89.6 (4)	C(3)–C(2)–C(4)	118 (3)
S(1)–Co–N(1)	86.7 (9)	C(2)–C(3)–S(1)	112 (3)
S(1)–Co–N(2)	89.7 (9)	C(3)–S(1)–C(6)	103 (2)
N(1)–Co–N(3)	91.7 (13)	S(1)–C(6)–C(9)	106 (2)
Co–S(1)–C(3)	110 (2)	C(6)–C(9)–N(1)	107 (2)
Co–S(1)–C(6)	95.9 (9)	C(9)–N(1)–C(12)	111 (3)
Co–N(1)–C(9)	114 (2)	N(1)–C(12)–N(4)	105 (3)
Co–N(1)–C(12)	115 (2)	C(12)–N(4)–C(13)	117 (3)
C(1)–C(2)–C(3)	98 (3)		

$1.98(\sigma^2(F) + 0.00171F^2)$. The final *R* was 0.0897 on *F* for 1149 nonzero reflections, and R_w was 0.0875 ($R_w = \sum w^{1/2}(F_o - F_c)/\sum(F_o)$). The largest residuals, 0.7 e A^{-3}, in the final difference map are located near the anions and disordered water molecules.

All scattering factors (Co(I) for (Co(III)) were taken from ref 19. A thermal ellipsoid plot of the cation is shown in Figure 1, and Figure 2 depicts the cell packing and disorder. Final atomic coordinates of the cation are given in Table II. Tables III and IV contain the important molecular geometry. So that the absolute configuration of the complex and better molecular geometry would be obtained, the structure of the resolved complex was undertaken.

Solution and Refinement of the Structure of $(+)_{510}$-[Co(azacapten)]$ZnCl_4\cdot Cl$.[18] The positions of the cobalt and zinc atoms were determined from a three-dimensional Patterson synthesis. Inclusion of these atoms gave and *R* value of 0.49, and all other nonhydrogen atoms could be located from a weighted difference map. The *R* value with nonhydrogen atoms refined isotropically was 0.092. Anisotropic refinement of all atoms resulted in location of the hydrogen atoms, and these were included and refined, initially with a group thermal parameter and finally independently to give $R = 0.0271$. All parameters were refined with use of full-matrix least-squares techniques. A weighting scheme was applied and refined to give $w = 2.59/(\sigma^2(F) + 0.00014F^2)$. The final *R* for 956 nonzero reflections was 0.0268, and R_w was 0.0271. All shifts of positional and thermal parameters were less than 0.1σ in the final cycle. The largest peak in the final difference map was 0.36 e Å^{-3}.

So that the absolute configuration could be established, the mirror image of the structure was also refined at the last cycle. The *R* value for the refined inverted image was 0.0412, which with Hamilton's significance test[20] establishes the configuration as that originally refined, to a significance level of much better than 0.005. All scattering factors (Co(I) for Co(III) and Zn(0) for Zn(II)) were taken from ref 19. The final least-squares parameters are given in Table V, and Tables VI and VII list the crystal geometry. Figure 3 is a projection down the threefold axis, and Figure 4 shows the molecular perpendicular to this axis.

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(19) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, p 99.

(20) Hamilton, W. C. Acta Crystallogr. **1965**, *18*, 502.

Table V. Final Least-Squares Positional Parameters[a] for $(+)_{510}$-[Co(azacapten)]$ZnCl_4$·Cl (Standard Deviations in Parentheses)

atom	*x*	*y*	*z*
Co	69394 (3)	69394 (3)	69394 (3)
Zn	29826 (3)	29826 (3)	29826 (3)
Cl(1)	18425 (8)	21568 (7)	31398 (8)
Cl(2)	39626 (8)	39626 (8)	39626 (8)
Cl(3)	9240 (11)	9420 (11)	9420 (11)
S(1)	63620 (6)	80055 (7)	80800 (7)
N(1)	5959 (2)	5928 (2)	7464 (2)
N(2)	5667 (2)	5667 (2)	5667 (2)
C(1)	9089 (3)	9089 (3)	9089 (3)
C(2)	8422 (3)	8422 (3)	8422 (3)
C(3)	7367 (3)	8470 (3)	8860 (3)
C(4)	5720 (3)	7092 (4)	8857 (3)
C(5)	5209 (3)	6409 (4)	8125 (4)
C(6)	5475 (3)	5302 (3)	6661 (3)

[a] Co, Zn, Cl, and S ×10^5, others ×10^4.

Table VI. Interatomic Distances (Å) for $(+)_{510}$-[Co(azacapten)]$ZnCl_4$·Cl

Co-S(1)	2.226 (1)	C(4)-C(5)	1.504 (6)
Co-N(1)	2.009 (3)	C(5)-N(1)	1.483 (5)
C(1)-C(2)	1.544 (10)	Zn-Cl(1)	2.276 (1)
C(2)-C(3)	1.529 (4)	Zn-Cl(2)	2.269 (2)
C(3)-S(1)	1.814 (4)	Cl(3)-N(1)^{I} [a]	3.286
S(1)-C(4)	1.819 (4)	Cl(3)-H(10)^{I}	2.624

[a] Symmetry operation I: $^1/_2 + x$, $^1/_2 - y$, $1 - y$.

Table VII. Bond and Torsion Angles (Deg) for $(+)_{510}$-[Co(azacapten)]$ZnCl_4$·Cl

S(1)-Co-N(1)	88.0 (1)	S(1)-C(4)-C(5)	104.5 (3)
S(1)-Co-S(1)^{II} [a]	91.2 (0)	C(4)-C(5)-N(1)	110.1 (3)
N(1)-Co-N(1)^{II}	91.3 (1)	C(5)-N(1)-C(6)	112.0 (3)
Co-S(1)-C(3)	111.1 (1)	N(1)-C(6)-N(2)	113.1 (3)
Co-S(1)-C(4)	97.2 (2)	C(6)-N(2)-C(6)^{II}	114.7 (2)
Co-S(1)-C(5)	111.0 (3)	C(1)-C(2)-C(3)-S(1)	166.2 (3)
Co-N(1)-C(6)	113.9 (2)	C(2)-C(3)-S(1)-C(4)	126.0 (3)
C(1)-C(2)-C(3)	106.5 (3)	C(3)-S(1)-C(4)-C(5)	−156.5 (3)
C(3)-C(2)-C(3)^{II}	112.3 (3)	S(1)-C(4)-C(5)-N(1)	60.0 (4)
C(2)-C(3)-S(1)	116.5 (3)	C(4)-C(5)-N(1)-C(6)	−185.2 (4)
C(3)-S(1)-C(4)	104.7 (2)	C(5)-N(1)-C(6)-N(2)	116.2 (4)

[a] Symmetry operation II: *z*, *x*, *y*.

Kinetic Experiments. All solutions were flushed with nitrogen for at least 3 h before each kinetic run and mixed in a stopped-flow apparatus that has been flushed with nitrogen as well. The kinetics of the oxidation of $[Co(azacapten)]^{2+}$ with O_2 was followed spectrophotometrically at 340 or 300 nm. Solutions of $[Co(azacapten)]^{2+}$ in 0.2 M NaCl were made in situ by reducing solutions of [Co(azacapten)]$(ClO_4)_3$ with Zn powder or amalgamated Zn. Solutions of O_2 were made by mixing O_2-saturated water with O_2-free aqueous NaCl-HCl solutions. The concentrations of $[Co(azacapten)]^{2+}$ in the reactant solutions were determined spectrophotometrically at 340 nm after complete oxidation to $[Co(azacapten)]^{3+}$ with excess O_2. Concentrations of H_2O_2 formed in the reaction solutions were determined iodometrically.[21] For pseudo-first-order conditions with excess O_2 or Co(II) a rate law of the form $-d[O_2]/dt = -{}^1/_2 d[Co(azacapten)^{2+}]/dt = k_{ox}[Co(azacapten)^{2+}][O_2]$ was obtained, with $k_{ox} = 290\ (\pm 30)\ M^{-1}\ s^{-1}$. The second-order rate constant was found to be independent of $[H^+]$ for $10^{-3} < [H^+] < 10^{-1}$ M. The stoichiometry of the reaction was given by

$$2[Co(azacapten)]^{2+} + O_2 + 2H^+ \rightarrow 2[Co(azacapten)]^{3+} + H_2O_2$$

Results and Discussion

Syntheses and Complexes. The potentially hexadentate ligand 4,4′,4″-ethylidynetris(3-thiabutan-1-amine) (ten) was synthesized by the reaction between ethylenimine and 1,1,1-tris(mercaptomethyl)ethane.[22] Nucleophilic attack by sulfur on the three-membered imine ring with consequent ring opening provides a facile high-yield route to the desired 2-thiaethan-1-amine linkage.

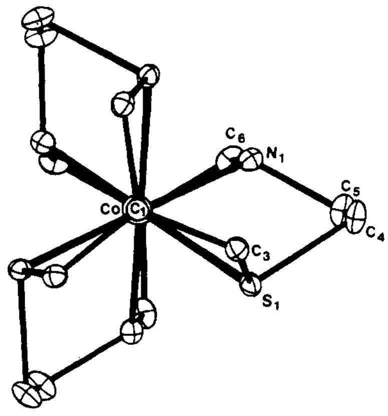

Figure 3. Projection down the threefold axis of the $(+)_{510}$-$[Co(azacapten)]^{3+}$ ion. Ellipsoids enclose 50% probabilities.

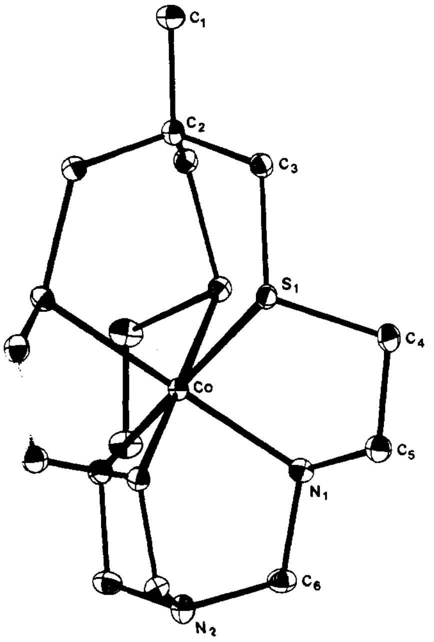

Figure 4. Projection perpendicular to the threefold axis of the $(+)_{510}$-$[Co(azacapten)]^{3+}$ ion. Ellipsoids enclose 50% probabilities.

Oxidation of a mixture of cobalt(II) acetate and the hexadentate ligand ten, by O_2, in methanol gave $[Co(ten)]^{3+}$, where the ligand was bound to the cobalt(III) ion by all six donor atoms.

Encapsulation of the cobalt(III) ion was effected by condensing the $[Co(ten)]^{3+}$ complex with formaldehyde and ammonia.[14] The cage complex formed in this reaction, [(1-methyl-3,13,16-trithia-6,8,10,19-tetraazabicyclo[6.6.6]eicosane)cobalt(III)](3+), was given the trivial name $[Co(azacapten)]^{3+}$. The analogous capping reaction with nitromethane and formaldehyde[15] resulted in the nitromethyl-capped complex [(1-methyl-8-nitro-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]eicosane)cobalt(III)](3+), $[Co(NO_2capten)]^{3+}$. The nitro group was reduced with zinc and hydrochloric acid to produce, after reaction with oxygen, the protonated aminomethyl-capped complex $[Co(NH_3capten)]^{4+}$. These reactions are shown in Figure 5. All complexes were characterized by elemental analyses and ^1H and ^{13}C NMR spectroscopy. The macrobicyclic nature of the $[Co(azacapten)]^{3+}$ complex was

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(21) Vogel, A. I. "A Text-Book of Quantitative Inorganic Analysis", 3rd ed.; Longmans, Green and Co.: New York, 1961; p 363.

(22) Searle, G.; Larsen, E. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 143.

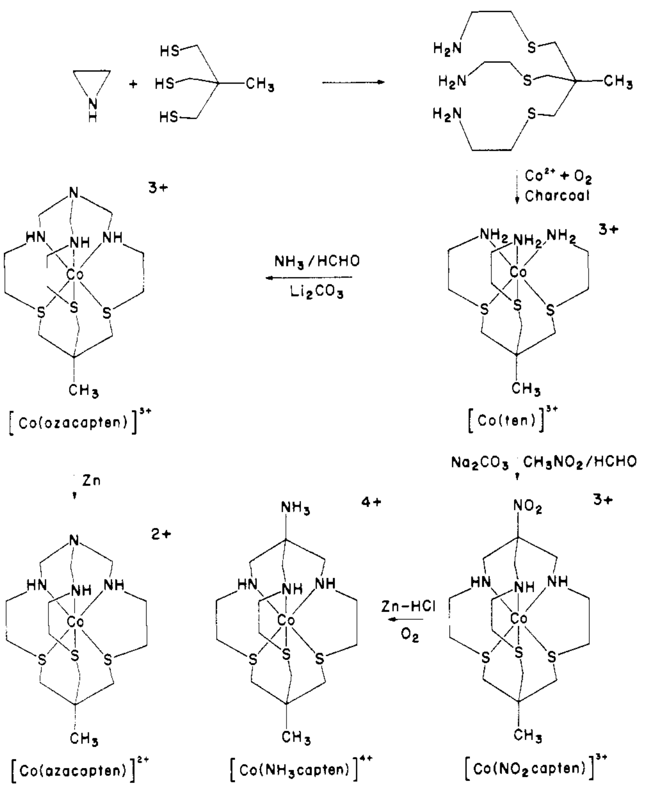

Figure 5. Synthesis and encapsulation reactions of $[Co(ten)]^{3+}$.

confirmed by a single-crystal X-ray structure analysis (Figures 1–4).

^1H and ^{13}C NMR Spectra. The ^{13}C NMR spectra of all these complexes reflect the anticipated C_3 symmetry for the complexes in solution. The $[Co(ten)]^{3+}$ complex displays three signals of equal intensity in the ^{13}C spectrum at +44.5, +41.9, and +39.5 ppm and a signal of lower intensity at higher field, +28.0 ppm (relative to Me_4Si). Partially decoupled spectra confirmed these signals as arising from three methene carbon atoms and a methyl carbon atom, respectively. From studies of the ^{13}C NMR spectra of a number of multidentate cobalt(III) complexes with nitrogen and sulfur donor atoms[23] the resonances at +44.5, +41.9, and +39.5 ppm have been assigned as arising from three types of methene carbon atoms, those adjacent to the nitrogen, those in the cap, and those adjacent to thioether. The ^{13}C NMR spectrum of $[Co(ten)]^{3+}$ is also a clear indication of the high symmetry of the ion. Not only does the ^{13}C spectrum indicate a hexadentate role for the ligand but it also implies that all three chiral sulfur centers have the same chirality and that, on the average at least, all the chelate conformations of the three strands of the ligands are identical. The aza-capped complex displays methene carbon resonances at +67.5, +53.5, +41.0, and +39.2 ppm. The resonances at +67.5, and +53.5 ppm have been assigned to the carbon atoms adjacent to the apical nitrogen atom and the coordinated secondary amine in the cysteamine fragment, respectively. In the ^{13}C NMR spectrum of the $[Co(sepulchrate)]^{3+}$ complex, the resonance assigned to the carbon atoms adjacent to the cap appears at +66.9 ppm while the carbon atoms in the ethan-1,2-diamine fragment result in signals at +53.4 ppm.[13,14] The ^{13}C spectra of the nitromethyl- and aminomethyl-capped complexes also display two pairs of methene carbon resonances associated with the carbon atoms adjacent to the nitrogen and sulfur donors in the cysteamine fragment. The $[Co(NO_2capten)]^{3+}$ complex displays a low-field resonance at +87.4 ppm, associated with the nitromethyl carbon atoms, and this signal is shifted to higher field, +55.7 ppm, on reduction of the electron-withdrawing nitro group to the aminomethyl-capped complex. The ^{13}C NMR spectra of all these capped complexes exhibit a low-intensity resonance at ~+42.0 ppm, which has been assigned to the apical carbon atom in the ten fragment.

The proton spectra for all complexes are complicated. The methene protons in the caps display AB doublet pairs, and a more complex pattern is observed for the protons in the cysteamine fragment.

The $[Co(ten)]^{3+}$ ion has cobalt and the three sulfur centers as chiral elements, leading potentially to three diastereoisomeric pairs. Both ^1H and ^{13}C NMR spectra, however, imply that only one diastereoisomeric pair has been formed in the synthesis, but it is not clear if the sharp signals observed are due to one of the conforms "lel" or "ob"[24] or to rapid interchange between the "lel" and "ob" conformations. In this hexadentate molecule the packing of the ligand strands about the metal ion is tight so that inversion at one sulfur atom leads to prohibitive nonbonding contacts between the inverted chelate and its neighbor. Moreover, inversion at a sulfur center generates an unstable envelope configuration of the cobalt cysteamine chelate. The configuration Δ or Λ of the three cysteamine residues about the cobalt atom therefore predetermines what the configuration at the three sulfur atoms will be. Assigning the free lone pair of electrons on the coordinated sulfur atom the lowest priority for the chirality sequence rules[25] requires the Λ configuration to have all three sulfur centers in the *R* configuration.

Similar arguments apply to the capped species except that the cobalt, sulfur, and coordinated nitrogen centers are all chiral and the number of apparent isomeric possibilities has increased. It is clear, however, from the ^{13}C NMR spectra especially, that only one diasteroisomer has been produced in each capping synthesis, namely, that where all the nitrogen and sulfur centers each have the same configuration (e.g. Co-Λ,S-*RRR*,N-*SSS*).

Discussion of the Structures. The racemic dithionate structure establishes the molecular connectivity, but the accuracy is limited by disorder and detailed discussion of the molecular geometry is inappropriate. The structure is held together by a number of hydrogen bonds, but very few are associated with the complex cation. These include strong hydrogen bonds between two of the amine groups and the two undisordered water molecules. These molecules appear to associate equally with either enantiomer, and this probably explains their lack of disorder. There is also an association between the third amine and one of the dithionate anions with similar-strength bonds between each enantiomer and its associated contributor to the dithionate disorder. This inability of the structure to distinguish between the enantiomers enables the observed disorder to occur. Other cases of racemic disorder of this type are unknown to us, and for this reason both structures are reported.

The resolved complex lies (Figures 3 and 4) on a symmetry site with the threefold axis passing through the cobalt atom and the "capping" atoms. The cysteamine rings adopt the lel conformation, as in the dithionate salt. Both salts have their cations in the same overall conformation with their capping groups almost, but not exactly, staggered. The conformation closely resembles that observed in $[Co^{III}(sepulchrate)]Cl_3 \cdot H_2O$,[13] which has trimetheneamino caps at both ends of the molecule. The detailed geometry of these caps agrees to within

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[23] Gahan, L. R.; Hammershøi, A.; Sargeson, A. M., unpublished observations.

[24] "Tentative Proposals for Nomenclature of Absolute Configurations Concerned with Six Coordinate Complexes Based on the Octahedron", *Inorg. Chem.* **1970**, *9*, 1.

[25] IUPAC Commission on Nomenclature of Organic Chemistry. *Pure Appl. Chem.* **1976**, *45*, 26.

5° in torsion angles and 1° in bond angles for these caps in both the sepulchrate[13] and azacapten cage structures. The effect of substitution of the thioether atoms is to increase the torsion angle at the central carbon–carbon bond from 54.6° in sepulchrate to 60.0° in the sulfur cage complex. All bond lengths have values to be expected from the structure of $[Co(sepulchrate)]^{3+}$ including a lengthened Co^{III}–N(1) at 2.009 (3) Å and a shortened N(2)–C(6) at 1.438 (5) Å compared to those of other cobalt(III) amine complexes. The alteration in carbon–nitrogen bond lengths going from nitrogen (cap)–carbon to carbon–nitrogen (cysteamine fragment) to nitrogen (cysteamine fragment)–carbon up the chain, toward the thioether donors, is also seen in the structure of $[Co(sepulchrate)]^{3+}$. We ascribe this effect to an increased component of sp^2 hybridization at the capping nitrogen, which has a C–N(cap)–C angle of 114.7° halfway between the ideal sp^3 and sp^2 angles. The cobalt–sulfur distance is at the short end of the range for cobalt(III) thioether bonds. The value of 2.226 (1) Å is less than that in $[Co(daes)_2]^{3+}$[26] (2.246 (1) Å, daes is $((NH_2CH_2CH_2-)_2S)$) and in $[Co(S,S\text{-elem})]^{+}$[27] (2.267 Å, elem is $(CH_3SCH_2CH_2CH(CO_2)CH_2NHCH_2-)_2$). In these structures, all with nitrogen trans to sulfur, the cobalt–sulfur bond lengths tend upwards as the constraints connecting sulfur to the metal decrease.

There is only one notable close contact in the structure due to a hydrogen bond between Cl(3) and the amine hydrogen (Table VI).

For the $(+)_{510}$-[Co(azacapten)]$ZnCl_4$·Cl complex the absolute configuration is the same as for Λ-(*S*)-$[Co(sepulchrate)]^{3+}$, which is formed from Λ-$[Co(en)_3]^{3+}$. Thus the complex in Figures 3 and 4 is Λ-$(+)_{510}$-$[Co(azacepten)]^{3+}$. The absolute configuration of the tris(cysteamine)cobalt(III) core is Λ(δδδ) in IUPAC helical notation.[24] The $CH_3C(-CH_2S-)_3$ cap is λ and the $N(-CH_2NH-)_3$ cap is δ in this notation[24] so that the absolute configuration can be denoted as $(+)_{510}\Lambda(\delta\delta\delta)\lambda_{(S\ cap)}\delta_{(N\ cap)}$.

Visible, Rotatory Dispersion, and Circular Dichroism Spectra. The visible absorption spectra of all these complexes are indicative of octahedrally coordinated cobalt(III) ions and similar to those observed previously for the cobalt(III) hexaamine cage complexes.[13] The influence of the charge-transfer component of the coordinated thioether groups on the visible spectra of these sulfur–nitrogen complexes is seen from the magnitude of the molar absorptivities for the two low-energy absorption bands for the $[Co(ten)]^{3+}$ complex and the cage complexes derived from this hexadentate. This effect has been observed previously for ligands containing thioether atoms coordinated to cobalt(III).[28–31]

The visible absorption, rotatory dispersion, and circular dichroism curves for the $(+)_{510}$-$[Co(ten)]^{3+}$ and $(+)_{510}$-$[Co(azacapten)]^{3+}$ complexes are shown in Figures 6 and 7. The circular dichroism of these complexes shows a strikingly large dichroism associated with the first ligand field band, with $\Delta\epsilon_{480} = +12.4\ M^{-1}\ cm^{-1}$ and $\Delta\epsilon_{480} = +10.9\ M^{-1}\ cm^{-1}$, respectively. The magnitude of the dichroism for the second ligand field band is lower in each case, consistent with the magnetically nonallowed dipole transition for this basically T_2 state. This band is overlapped by an intense charge-transfer transition at higher energy. For the Λ-(*S*)-$[Co(sepulchrate)]^{3+}$ complex, the sign of the net rotatory strength for the first ligand field transition is reversed over that of the parent Λ-$[Co(en)_3]^{3+}$ complex, and the $A_1 \rightarrow A_2(-)$ transition dominates the $A_1 \rightarrow E(+)$ transition.[32] In the case of the Λ-$[Co(azacapten)]^{3+}$ complex, which has C_3 symmetry, the relative rotary strengths are reversed over the situation observed in the $[Co(sepulchrate)]^{3+}$ molecule[13] and the transition corresponding to the E component in D_3 symmetry dominates.

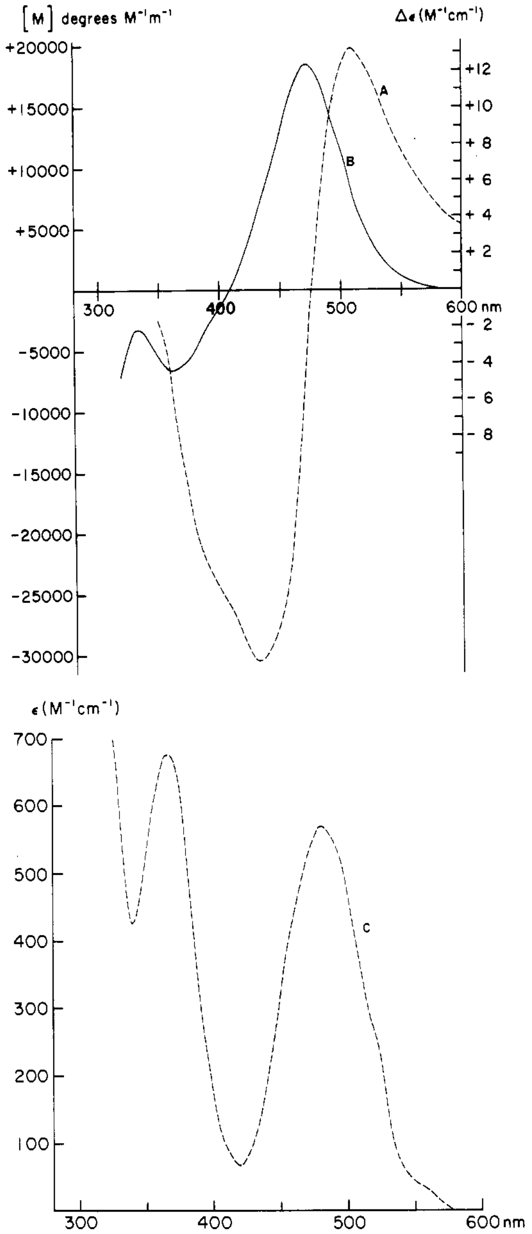

Figure 6. Rotatory dispersion (A), circular dichroism (B), and visible absorption (C) spectra of $(+)_{510}$-(Co(ten)]Cl_2·ClO_4.

When $(+)_{510}$-[Co(ten)]Cl_2·ClO_4 is capped with formaldehyde and ammonia, the $(+)_{510}$-$[Co(azacapten)](ClO_4)_3$ complex is isolated in high optical purity. On the basis of comparisons of the circular dichroism spectra exhibited by the two complexes, the absolute configuration of $(+)_{510}$-$[Co(ten)]^{3+}$ may be assigned as Λ.

Reduction of an aqueous solution of $(-)_{510}$-$[Co^{III}(azacapten)]^{3+}$ with zinc amalgam under a nitrogen atmosphere results in an extremely oxygen-sensitivie purple solution of $(+)_{510}$-$[Co^{II}(azacapten)]^{2+}$. The visible absorption and rotatory dispersion spectra of an aqueous solution of this cobalt(II) complex are shown in Figure 8. Reaction of this purple solution with oxygen results in the reproduction of the visible

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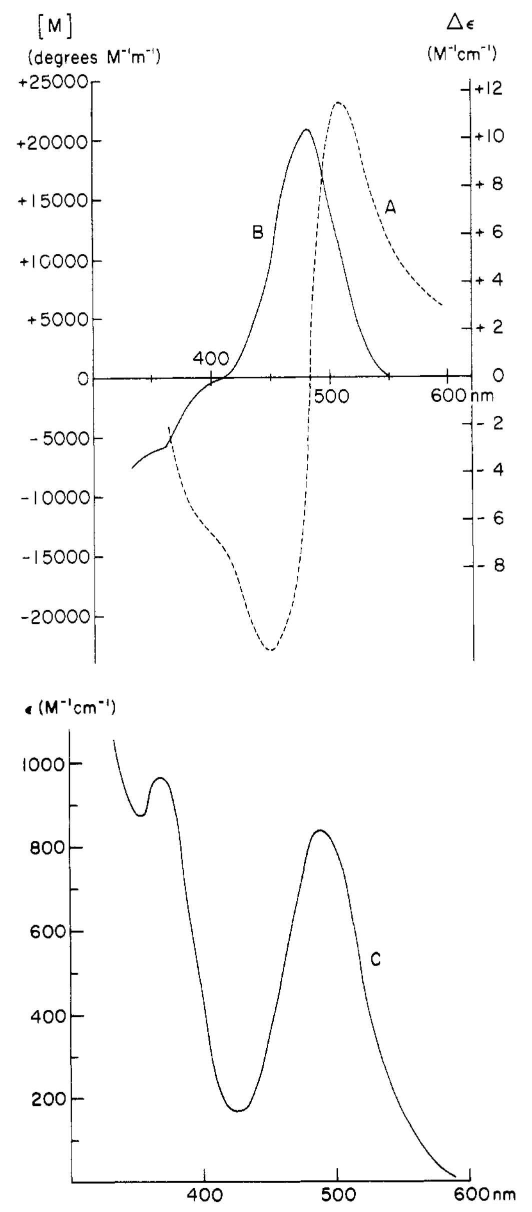

Figure 7. Rotatory dispersion (A), circular dichroism (B), and visible absorption (C) spectra of $(+)_{510}$-[Co(azacapten)]$(ClO_4)_3$.

absorption and rotatory dispersion spectra of the corresponding red cobalt(III) complex quantitatively. No evidence for oxidation of the coordinated thioether atoms was obtained. This is consistent with known chemistry of coordinated thioether complexes of cobalt(III).[33]

The stability of the $[Co^{II}(azacapten)]^{2+}$ complex to racemiziation is extraordinary. Cobalt(II) complexes are usually labile, exchanging their ligands on a microsecond scale. However, it has been found previously that no exchange with $^{60}Co^{2+}(aq)$ took place in 24 h at 25 °C with $[Co^{II}(sepulchrate)]^{2+}$.[13] These cage complexes presumably prevent the dissociation of the metal ion by the tight packing of the ligand. The necessity of inverting all seven chiral centers synchronously in order to racemize these cage complexes accounts for the observed chiral stability.

Reactions of the $[Co^{II}(azacapten)]^{2+}$ Complex with Oxygen. The $[Co^{II}(azacapten)]^{2+}$ complex reacts quantitatively with O_2 to give H_2O_2 and the cobalt(III) cage. The reaction is fast (k_2 = 290 M^{-1} s^{-1} at 25 °C) and is unusual for a cobalt(II) complex, although typical of the cage chemistry. Usually cobalt(II) amine complexes react with O_2 to give cobalt(III) peroxy dimers. However, the tight packing of the ligand around the metal ion in these cages ensures that formation of peroxy dimers is not possible, and coordination of O_2 to the metal ion seems to be excluded. This implies an outer-sphere redox process for this reaction that is considerably more rapid for the sulfur–nitrogen cage than for the hexaamine cages where, for example, k_2 = 44 M^{-1} s^{-1} for the reaction of $[Co^{II}(sepulchrate)]^{2+}$ with O_2,[13] even though the redox potential for the sulfur cage is less negative than that for the $[Co^{II}(sepulchrate)]^{2+}$ ion.

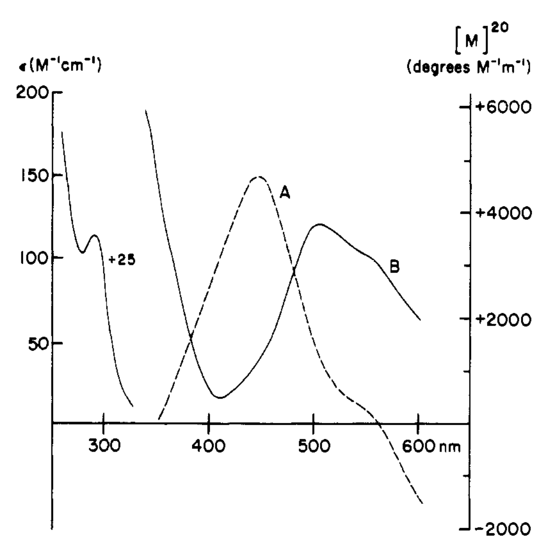

Figure 8. Rotatory dispersion (A) and visible absorption (B) spectra of $(+)_{510}$-$[Co(azacapten)]^{2+}$ obtained by reducing an aqueous solution of $(-)_{510}$-$[Co(azacapten)]^{3+}$ with zinc amalgam under nitrogen.

Separation of the oxidized complex from the H_2O_2 allows the latter to be titrated with I_2. Approximately 30% of the expected H_2O_2 was lost by decomposition of H_2O_2 on the Dowex ion-exchange resin used for the separation. The experiment implies that the cage is not oxidized to a hydroperoxide derivative but that electron transfer occurs by an outer-sphere process. Certainly oxidation of the sulfur atoms to sulfoxide or sulfone can be excluded. However, a more tenuous association of O_2 with a lone pair of electrons on the sulfur atom cannot be excluded as the route to the relatively efficient outer-sphere redox process. The electron-transfer reactions of the sulfur–nitrogen cages are currently being investigated,[34] in conjunction with an electrochemical investigation of the redox properties of these cages.[35]

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Registry No. [Co(azacapten)]$(S_2O_6)_{1.5}\cdot 4H_2O$, 81505-67-1; $(+)_{510}$-[Co(azacapten)]$ZnCl_4\cdot Cl$, 81600-14-8; [Co(ten)]$Cl_2\cdot ClO_4$, 81600-16-0; [Co(azacapten)]$(ClO_4)_3$, 81570-79-8; [Co(NO_2capten)]$Cl_2\cdot ClO_4$, 81505-69-3; [Co(NH_2capten)HCl]Cl_3, 81505-70-6; $(-)_{510}$-[Co(azacapten)]$(ClO_4)_3$, 81505-72-8; $(+)_{510}$-[Co(azacapten)]$(ClO_4)_3$, 81570-17-4; $(+)_{510}$-[Co(ten)]$Cl_2\cdot ClO_4$, 81505-74-0; $(-)_{510}$-[Co(ten)]$Cl_2\cdot ClO_4$, 81570-81-2; $(+)_{510}$-$[Co(azacapten)]^{2+}$, 81505-75-1; ten, 81505-76-2; 1,1,1-tris(mercaptomethyl)ethane, 6156-22-5; ethylenimine, 151-56-4; formaldehyde, 50-00-0; ammonia, 7664-41-7; nitromethane, 75-52-5.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal parameters (16 pages). Ordering information is given on any current masthead page.

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