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Synthesis, Structures, and Spectra of Cobalt(III) Complexes of the Novel Branched Cyclic Ligands 6-Methyl-6-(4-amino-2-azabutyl)-1-thia-4-azacycloheptane and *N*-(2-Aminoethyl)-3-methyl-3-(4-amino-2-thiabutyl)azetidone

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The preparation and properties of two cobalt(III) complexes, [Co(atac)(en)](NO₃)(ClO₄)₂ and [Co(amta)(en)]I₂Cl, are described, where atac is 6-methyl-6-(4-amino-2-azabutyl)-1-thia-4-azacycloheptane, amta is *N*-(2-aminoethyl)-3-methyl-3-(4-amino-2-thiabutyl)azetidone, and en is ethylenediamine. Both atac and amta arise from reaction between en and the benzenesulfonate of 2-methyl-2-(4-phthalimido-2-thiabutyl)-1,3-propanediol. The absolute configuration of one of the enantiomeric forms of [Co(amta)(en)]³⁺ ([Co(C₁₁H₂₉N₂S)]ClI₂) with Δ_{ε₅₂₅} = -2.61 M⁻¹ cm⁻¹ has been determined by single-crystal X-ray diffraction techniques (orthorhombic; space group P2₁2₁2₁; a = 11.657 (2), b = 11.670 (2) Å; c = 14.870 (2) Å; Z = 4; R = 0.036) and the complex shown to be Δ-[Co(amta)(en)]³⁺. The crystal structure of [Co(atac)(en)](NO₃)(ClO₄)₂ ([Co(C₁₁H₂₉H₂S)](NO₃)(ClO₄)₂) is also reported (monoclinic; space group P2₁/c; a = 9.054 (2), b = 17.561 (3), c = 14.506 (2) Å; β = 92.23 (1)°; Z = 4; R = 0.059). In each case the cobalt(III) ion is surrounded by five nitrogen donors (three from atac or amta; two from en) and the thioether atom. The effects of complexation of the strained four-membered azetidone and seven-membered 1,4-disubstituted cycloheptane rings manifest themselves in long Co-N bonds associated with the nitrogen donors of the strained rings (Co(1)-N(2) = 1.99 Å in [Co(amta)(en)]³⁺ and Co(1)-N(1) = 2.05 Å in [Co(atac)(en)]³⁺), shifts in the ligand field absorption spectra compared to those of other Co(N₃S)³⁺ cobalt(III) complexes, and unusual chemical shifts observed in the ¹³C NMR spectra.

Introduction

Neopentyl derivatives have been extensively employed as precursors for multidentate ligand syntheses. Recent examples of such syntheses include 1,1,1-tris(4-amino-2-thiabutyl)ethane (ten),² which resulted from reaction of 1,1,1-tris(mercaptomethyl)ethane with ethylene imine, and hexamine ligands such as 1,1,1-tris(4-amino-2-azabutyl)ethane (sen)³⁻⁵ and 1,1,1-tris(5-amino-2-azapentyl)ethane (stn),^{5,6} which result when the neopentyl derivative 1,1,1-tris(((tolylsulfonyl)oxy)methyl)ethane is permitted to react with an excess of the appropriate amine, ethylenediamine (en) or 1,3-propanediamine (tn), respectively. In each case the symmetrically substituted (N₃S₃ or N₆) ligands may be isolated. The synthetic procedure for the hexamine sen also results in the formation, through a competing intramolecular ring closure, of 6-methyl-6-(4-amino-2-azabutyl)-1,4-diazacycloheptane (L), which has been isolated and structurally characterized as the cobalt(III) complex [CoL(en)](ClO₄)₃.⁷ Other products arising from competing reactions have also been proposed.⁵

We have been interested in the synthesis of selectivity substituted neopentyl systems, possessing the potential for synthetic variations of the ratio of donor groups, as precursors to multidentate ligands. Specifically, we have been seeking a synthetic route to the ligand 1-(4-amino-2-thiabutyl)-1,1-bis(4-amino-2-azabutyl)ethane. This paper reports the isolation, spectral characteristics, and structures of cobalt(III) complexes of two products arising from the synthetic endeavours—one containing 6-methyl-6-(4-amino-2-azabutyl)-1-thia-4-azacycloheptane (atac) and the other possessing the substituted azetidone moiety *N*-(2-aminoethyl)-3-methyl-3-(4-amino-2-thiabutyl)azetidone (amta). Both products are proposed to arise through intramolecular ring-closure reactions.

Experimental Section

¹H NMR spectra were recorded with a Varian EM360 60-MHz spectrometer on external lock, sodium 3-(trimethylsilyl)propanesulfonate (NaTSP) or tetramethylsilane (Me₄Si) being the internal reference (s denotes a singlet, t a triplet, m a multiplet, and b a broad resonance). Fourier transform ¹³C[¹H] NMR spectra were recorded with a JEOL FX 100FT or a Bruker CXP-300 FT NMR spectrometer on external lock (D₂O) and 1,4-dioxane as internal reference (δ + 67.4 ppm downfield from Me₄Si). A complete assignment of the proton-decoupled ¹³C spectra was possible, employing the pulse sequence INEPT,⁸ which nulls resonances assigned to a quaternary carbon atom and provides a means of distinguishing between resonance due to methyl and methylene carbon atoms. Visible spectra were recorded with a Hewlett Packard 8450A UV/vis spectrophotometer attached to a Hewlett Packard 7225B plotter

and 8290/M flexible-disk drive (ε in M⁻¹ cm⁻¹). Circular dichroism (CD) spectra were recorded on a Jobin Yvon Dichrographe III. A solution of (+)₅₈₉-[Co(en)₃]Cl₃·NaCl·6H₂O was used as calibrant for the circular dichroism spectra. All evaporations were carried out with a Buchi evaporator under reduced pressure (<20 Torr) so that the solution temperature did not exceed 35 °C.

Syntheses. 2-Methyl-2-(bromomethyl)-1,3-propanediol was prepared as described previously.⁹ 2-Methyl-2-(mercapto-methyl)-1,3-propanediol was prepared by adaption of a previously described procedure.^{9,10} A solution of NaHS was prepared by reaction of sodium metal (3.5 g) in ethanol (75 mL), and H₂S as described.¹¹ Aliquots of the ethanolic NaHS solution (15 mL) were transferred to thick-walled glass tubes, each fitted with a Teflon tap and each containing 2-methyl-2-(bromomethyl)-1,3-propanediol (5 g). Five such tubes were prepared. The tubes and contents were degassed under vacuum after freezing in liquid N₂. After warming to room temperature, the tubes and contents were immersed in an oil bath and the bath was heated at 120 °C. A dense white precipitate of NaBr formed in each tube after 1 h, and heating was continued for a further 11 h. The reaction mixtures were permitted to cool to room temperature and the supernatant solutions separated and combined. The ethanol was removed under reduced pressure, and distillation of the resulting crude oil yielded a low-melting solid (8.4 g, 45%; bp 98–100 °C (0.1 Torr)). ¹H NMR (CDCl₃): δ 0.9 (CH₃, s, 3 H), 1.4 (SH, t, 1 H), 2.7 (CH₂SH, d, 2 H), 3.7 (CH₂OH, b, 6 H).

2-Methyl-2-(4-phthalimido-2-thiabutyl)-1,3-propanediol. 2-Methyl-2-(mercapto-methyl)-1,3-propanediol (14 g) was added under N₂ to a solution of sodium ethoxide (2.4 g of Na in 75 mL of ethanol); the mixture was heated under N₂ at 80 °C for 0.25 h and then cooled. A solution of *N*-(2-bromoethyl)phthalimide (26.1 g) in ethanol (75 mL) was added slowly, and the resulting yellow solution was heated and refluxed for 2 h under an atmosphere of N₂. The reaction mixture was allowed to cool to room temperature and filtered to remove solid NaBr. Ethanol was removed under reduced pressure, the residue suspended in water (200 mL), and the product extracted with CHCl₃ (2 × 100 mL). The combined organic extracts were evaporated, and the resulting clear oil crystallized from toluene on standing (17.5 g, 55%). Anal. Calcd for

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$C_{11}H_{17}NO_3S$: C, 58.22; H, 6.20; N, 4.53; S, 10.4. Found: C, 58.4; H, 6.2; N, 4.5; S, 9.4. 1H NMR ($CDCl_3$): δ 0.8 (CH_3 , s, 3 H), 2.9 (CH_2SCH_2 and OH , m, 6 H), 3.6 (CH_2OH , b, 4 H), 3.9 (CH_2N , t, 2 H), 7.8 (aromatic, m, 4 H).

The bis(benzenesulfonate) of 2-methyl-2-(4-phthalimido-2-thiabutyl)-1,3-propanediol was obtained by a synthetic route similar to that described previously.¹² The bis(benzenesulfonate) was obtained as a colorless oil that could not be induced to crystallize. 1H NMR ($CDCl_3$): δ 0.9 (CH_3 , s, 3 H), 2.5 (C_2CH_2S , s, 2 H), 2.7 (SCH_2CH_2 , t, 2 H), 3.8 (CH_2O and CH_2N , m, 6 H), 7.7 (aromatic, m, 14 H).

Preparation of $[Co(atac)(en)]^{3+}$ and $[Co(amta)(en)]^{3+}$. The bis(benzenesulfonate) of 2-methyl-2-(4-phthalimido-2-thiabutyl)-1,3-propanediol (30 g) was refluxed with a large excess of anhydrous ethylenediamine (en) (250 mL) for 18 h. Excess en was removed by distillation, and a solution of potassium hydroxide (6.3 g) in methanol (100 mL) was added to the cooled residue. A dense white precipitate of potassium benzenesulfonate formed. The reaction mixture was cooled overnight at 0 °C and then filtered; the organic solvent was evaporated by a rotary evaporator. A yellow oil was obtained. This crude oil was used directly in the subsequent reaction.

The crude ligand was dissolved in methanol (100 mL), and the mixture was added slowly to a solution of cobaltous bromide (16.5 g) dissolved in methanol (100 mL). Oxygen was bubbled through the solution for 4 h, during which time a brown solid was deposited. The resulting solution was added to a large volume of water (2 L) 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 to remove a minor purple band. Elution with 3 M HCl removed a major red-purple band. The eluate was evaporated to dryness to give a purple solid, which was redissolved in a large volume of water and rechromatographed on CM-Sephadex C-25 cation-exchange resin (Na^+ form), after being washed with water and 0.1 M NaCl to remove minor pink and purple bands. Elution with 0.3 M NaCl resulted in the separation of two red bands. These were collected separately on Dowex 50W-X2 cation-exchange resin, washed with 0.5 M HCl, and eluted with 3 M HCl. In each case a red solid was obtained upon evaporation of the solvent. The product obtained from the band eluted first was crystallized from water with NaI and subsequently identified as $[Co(amta)(en)]I_2Cl$ (2.9 g). Anal. Calcd for $[(C_{11}H_{29}N_5S)Co]ClI_2$: C, 21.6; H, 4.8; N, 11.4; S, 5.2. Found: C, 21.0; H, 4.6; N, 11.0; S, 4.2. Visible spectrum [λ_{max} , nm (ϵ_{max}) in H_2O]: 500 (229), 354 (336). 1H NMR: δ 1.3 (CH_3 , s, 3 H), 2.7–3.4 (CH_2 , m, 18 H). ^{13}C NMR: δ +69.9, +68.5, +66.6, +45.9, +44.8, +44.6, +43.8, +41.4, and +40.6 (CH_2), +36.4 (quaternary C), +23.9 (CH_3) in D_2O (Me_4Si).

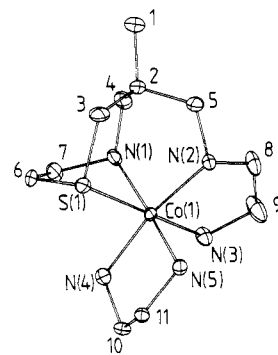
The product obtained from the band eluted second from the column was crystallized from water with $NaClO_4/NaNO_3$ and was subsequently identified as $[Co(atac)(en)](NO_3)(ClO_4)_2$ (3.7 g). (Caution! Perchlorate salts of metal complexes can be explosive and must be handled with care. Compounds should not be heated as solids.) Anal. Calcd for $[(C_{11}H_{29}N_5S)Co](NO_3)(ClO_4)_2$: C, 22.6; H, 5.0; N, 14.4; S 5.5. Found: C, 22.3; H, 5.0; N, 14.3; S, 5.0. Visible spectrum [λ_{max} , nm (ϵ_{max}) in H_2O]: 498 (206), 363 (297). 1H NMR (D_2O): δ 1.1 (CH_3 , s, 3 H), 2.7–3.4 (CH_2 , m, 18 H). ^{13}C NMR: δ +62.0, +58.2, +57.6, +57.4, +45.9, +45.5, +44.3, +44.0, and +38.7 (CH_2), +40.1 (quaternary C), +23.5 (CH_3) in D_2O (Me_4Si).

Resolution of $[Co(amta)(en)]I_2Cl$. The complex (0.10 g) was resolved into its enantiomeric forms through chromatography on CM-Sephadex cation-exchange resin (Na^+ form) employing an aqueous solution (0.15 M) of sodium (+)- s_{89} -tartrate as ion-pairing reagent. The column employed was packed to a height of 60 × 2.5 cm, and a flow rate of 0.5 mL/min was maintained. One pass down the column was sufficient for complete resolution. 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 crystallized to constant rotation from aqueous solutions containing sodium iodide. The first fraction eluted from the column gave $\Delta\epsilon_{525} = +2.62 M^{-1} cm^{-1}$ and $\Delta\epsilon_{370} = +0.25 M^{-1} cm^{-1}$. Anal. Calcd for $[(C_{11}H_{29}N_5S)Co]ClI_2$: C, 21.6; H, 4.8; N, 11.4. Found: C, 21.0; H, 4.6; N, 11.0. The second fraction gave $\Delta\epsilon_{525} = -2.61 M^{-1} cm^{-1}$ and $\Delta\epsilon_{370} = -0.25 M^{-1} cm^{-1}$. Anal. Found: C, 21.1; H, 4.7; N, 11.3.

X-ray Crystallography. Crystal data and the experimental conditions for data collection for $[Co(atac)(en)](NO_3)(ClO_4)_2$ and $[Co(amta)(en)]I_2Cl$ ($\Delta\epsilon_{525} = -2.62 M^{-1} cm^{-1}$) are given in Table I. Lorentz and polarization corrections using program SUSCAD¹³ and absorption correc-

Table I. Crystal Data

	$[Co(amta)(en)]I_2Cl$	$[Co(atac)(en)](NO_3)(ClO_4)_2$
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$
a, Å	11.657 (2)	9.054 (2)
b, Å	11.670 (2)	17.561 (3)
c, Å	14.870 (2)	14.506 (2)
β , deg		92.23 (1)
V, Å ³	2022.9	2233.2
D_{calcd} , g cm ⁻³	2.008	1.735
empirical formula	$C_{11}H_{29}ClCoI_2N_5S$	$C_{11}H_{29}Cl_2CoN_6O_{11}S$
fw	611.6	583.3
Z	4	4
F(000), e	1184	1208
abs coeff, cm ⁻¹	40.87	11.10
cryst color	red-orange	red-orange
dimens, mm	0.20 × 0.15 × 0.10	0.14 × 0.13 × 0.24
cryst habit	prismatic	prismatic
faces	$\pm\bar{1}11$, $\pm\bar{1}\bar{1}1$, $\pm 11\bar{2}$, ± 001	$\pm 0\bar{1}1$, ± 011 , ± 100
abs corr	numerical integration	
transmissn factor range	0.63, 0.71	0.78, 0.85
cryst degradation, %	<2	<2
temp, K	294	294
diffractometer		Enraf-Nonius CAD4-F
radiation		Mo K α , $\lambda = 0.71069$ Å
monochromator		graphite
scan mode	ω^{-2}/θ	ω^{-2}/θ
2 θ range, deg	1.0–50.0	1.0–50.0
no. of reflns measd	2044; $+h, +k, +l$	4511; $+h, +k, \pm l$
no. of reflns used ($I > 2.5\sigma(I)$)	1710	2129
R_{merg}		0.018
no. of variables	220	329
R	0.036	0.059
R_w	0.039	0.063
w [$=g/(\sigma^2(F_o) + kF_o^2)$]: g, k	0.45, 0.0034	2.66, 0.00039
shift/esd	<0.10	<0.4
residual extrema in	± 1.3	± 0.5
final diff map, e Å ⁻³		

Figure 1. ORTEP diagram of the $[Co(atac)(en)]^{3+}$ cation.

tions using program ABSORB¹⁴ were applied.

Structure Solution and Refinement. Direct methods were used to locate the heavier atoms, and all other atoms were located from subsequent difference Fourier maps. Hydrogen atoms were included at sites calculated by assuming tetrahedral geometry about carbon and nitrogen ($X-H = 0.97$ Å) with individual isotropic temperature factors while all nonhydrogen atoms were modeled anisotropically. The perchlorate anions in $[Co(atac)(en)](NO_3)(ClO_4)_2$ are both highly disordered, one by rotation with the chlorine stationary and the other by rotation and also displacement of the whole anion by about 1 Å. This disorder is probably responsible for the unusually large thermal motion found for some of the ligand atoms. Full-matrix least-squares refinement of all positional and thermal parameters converged (all shifts $<0.1\sigma$) with $R = 0.036$, $R_w = 0.039$,^{15a} and $w = 0.46/(\sigma^2(F_o) + 0.0034F_o^2)$ for $[Co(amta)(en)]I_2Cl$ and

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(15) (a) $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. (b) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

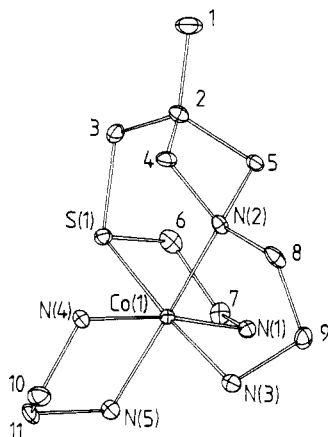


Figure 2. ORTEP diagram of the Δ -[Co(amta)(en)]³⁺ cation.

Table II. Positional Parameters ($\times 10^4$) for [Co(atac)(en)](NO₃)(ClO₄)₂

	x	y	z
Co(1)	2450 (1)	379 (1)	2193 (1)
S(1)	3142 (3)	-21 (1)	3653 (2)
N(1)	1353 (8)	1173 (4)	2977 (6)
N(2)	4126 (7)	1078 (4)	1962 (4)
N(3)	1628 (8)	786 (4)	979 (5)
N(4)	829 (8)	-379 (4)	2163 (5)
N(5)	3536 (7)	-421 (3)	1544 (4)
C(1)	4680 (19)	2141 (7)	4321 (9)
C(2)	3948 (15)	1541 (5)	3655 (7)
C(3)	4205 (15)	762 (6)	4134 (7)
C(4)	2352 (16)	1723 (6)	3465 (9)
C(5)	4763 (11)	1555 (6)	2751 (7)
C(6)	1385 (14)	168 (6)	4184 (7)
C(7)	442 (13)	737 (6)	3657 (8)
C(8)	3078 (12)	1568 (7)	1139 (8)
C(9)	2702 (16)	1278 (8)	540 (10)
C(10)	1159 (11)	-1024 (5)	1534 (7)
C(11)	2793 (11)	-1167 (4)	1653 (6)
N(6)	2487 (9)	-447 (5)	-1053 (5)
O(1)	3687 (7)	-400 (4)	-626 (4)
O(2)	2367 (9)	-700 (4)	-1851 (5)
O(3)	1345 (7)	-228 (4)	-657 (5)
Cl(1)	2928 (3)	3944 (1)	1997 (2)
O(4)	1631 (20)	4166 (11)	1506 (11)
O(5)	2988 (33)	3291 (14)	1390 (19)
O(6)	3894 (22)	4643 (12)	1811 (16)
O(7)	2674 (31)	3898 (11)	3004 (15)
O(4')	3726 (66)	4106 (33)	2775 (42)
O(5')	1895 (46)	3500 (25)	2492 (32)
O(6')	3820 (26)	3358 (12)	1699 (18)
O(7')	2039 (25)	4482 (14)	1463 (14)
O(4'')	3960 (73)	3375 (40)	2526 (52)
O(5'')	3714 (70)	3549 (32)	1168 (45)
O(6'')	4052 (38)	4572 (23)	2300 (29)
O(7'')	2029 (52)	3795 (23)	2829 (30)
Cl(2)	1152 (5)	-2439 (2)	4043 (4)
O(8)	1286 (22)	8319 (9)	3854 (15)
O(9)	2484 (22)	7171 (9)	4378 (15)
O(10)	435 (28)	7314 (13)	3151 (25)
O(11)	351 (27)	7616 (17)	4988 (19)
Cl(2')	1710 (16)	-2109 (8)	4582 (10)
O(8')	-23 (37)	7125 (18)	3698 (28)
O(9')	584 (57)	-1665 (24)	4302 (35)
O(10')	1747 (61)	-1952 (33)	3413 (43)
O(11')	2294 (38)	-1595 (19)	5338 (24)
O(12')	373 (60)	-2847 (29)	4579 (37)
O(13')	2730 (43)	7490 (24)	3800 (32)
O(14')	1616 (84)	7056 (27)	4721 (38)
O(15')	849 (67)	7006 (34)	2526 (48)

$R = 0.059$, $R_w = 0.063$, and $w = 2.66/(\sigma^2 F_o + 0.00039 F_o^2)$ for [Co(atac)(en)](NO₃)(ClO₄)₂. Maximum and minimum excursions in a final difference map were 1.3 (close to the I⁻ anions) and $-0.9 \text{ e } \text{\AA}^{-3}$ and 0.5 and $-0.4 \text{ e } \text{\AA}^{-3}$ for [Co(amta)(en)]I₂Cl and [Co(atac)(en)](NO₃)(ClO₄)₂, respectively.

Table III. Bond Lengths (\AA) and Angles (deg) for [Co(atac)(en)](NO₃)(ClO₄)₂

S(1)-Co(1)	2.235 (3)	N(1)-Co(1)	2.056 (6)
N(2)-Co(1)	1.989 (6)	N(3)-Co(1)	1.969 (7)
N(4)-Co(1)	1.981 (7)	N(5)-Co(1)	1.961 (6)
C(3)-S(1)	1.80 (1)	C(6)-S(1)	1.81 (1)
C(4)-N(1)	1.47 (2)	C(7)-N(1)	1.49 (1)
C(5)-N(2)	1.48 (1)	C(8)-N(2)	1.47 (1)
C(9)-N(3)	1.45 (1)	C(10)-N(4)	1.47 (1)
C(11)-N(5)	1.48 (1)	C(2)-C(1)	1.54 (2)
C(3)-C(2)	1.53 (2)	C(4)-C(2)	1.49 (2)
C(5)-C(2)	1.49 (2)	C(7)-C(6)	1.49 (2)
C(9)-C(8)	1.31 (2)	C(11)-C(10)	1.50 (1)
N(1)-Co(1)-S(1)	81.1 (2)	N(2)-Co(1)-S(1)	99.0 (2)
N(2)-Co(1)-N(1)	93.2 (3)	N(3)-Co(1)-S(1)	173.0 (2)
N(3)-Co(1)-N(1)	92.5 (3)	N(3)-Co(1)-N(2)	84.2 (3)
N(4)-Co(1)-S(1)	89.4 (2)	N(4)-Co(1)-N(1)	95.4 (3)
N(4)-Co(1)-N(2)	168.8 (3)	N(4)-Co(1)-N(3)	88.4 (3)
N(5)-Co(1)-S(1)	94.2 (2)	N(5)-Co(1)-N(1)	175.3 (3)
N(5)-Co(1)-N(2)	88.1 (3)	N(5)-Co(1)-N(3)	92.1 (3)
N(5)-Co(1)-N(4)	83.8 (3)	C(3)-S(1)-Co(1)	103.4 (3)
C(6)-S(1)-Co(1)	95.8 (4)	C(6)-S(1)-C(3)	99.8 (6)
C(4)-N(1)-Co(1)	113.2 (6)	C(7)-N(1)-Co(1)	106.6 (5)
C(7)-N(1)-C(4)	112.4 (8)	C(5)-N(2)-Co(1)	120.1 (5)
C(8)-N(2)-Co(1)	108.2 (5)	C(8)-N(2)-C(5)	109.6 (7)
C(9)-N(3)-Co(1)	110.3 (6)	C(10)-N(4)-Co(1)	111.2 (5)
C(11)-N(5)-Co(1)	110.3 (5)	C(3)-C(2)-C(1)	106.7 (9)
C(4)-C(2)-C(1)	110.6 (11)	C(4)-C(2)-C(3)	113.4 (9)
C(5)-C(2)-C(1)	106.9 (9e)	C(5)-C(2)-C(3)	108.4 (10)
C(5)-C(2)-C(4)	110.6 (9)	C(2)-C(3)-S(1)	116.5 (7)
C(2)-C(4)-N(1)	120.9 (8)	C(2)-C(5)-N(2)	115.7 (7)
C(7)-C(6)-S(1)	114.4 (6)	C(6)-C(7)-N(1)	109.9 (9)
C(9)-C(8)-N(2)	115.1 (10)	C(8)-C(9)-N(3)	114.5 (10)
C(11)-C(10)-N(4)	106.4 (7)	C(10)-C(11)-N(5)	106.9 (7)

Table IV. Positional Parameters ($\times 10^4$) for [Co(amta)(en)]I₂Cl

	x	y	z
Co(1)	7602 (1)	5900 (1)	1886 (1)
S(1)	8811 (2)	6188 (2)	711 (2)
N(1)	8953 (6)	6005 (7)	2660 (6)
N(2)	7245 (6)	7572 (7)	1959 (6)
N(3)	6659 (7)	5725 (7)	2968 (6)
N(4)	6235 (6)	5564 (7)	1134 (5)
N(5)	7856 (7)	4217 (7)	1785 (6)
C(1)	8164 (12)	9729 (10)	495 (9)
C(2)	8024 (8)	8526 (8)	882 (7)
C(3)	8669 (10)	7658 (9)	287 (6)
C(4)	6814 (9)	8132 (9)	1093 (7)
C(5)	8275 (8)	8392 (8)	1902 (6)
C(6)	10167 (8)	6302 (10)	1319 (8)
C(7)	10079 (8)	5746 (9)	2215 (7)
C(8)	6447 (9)	7738 (8)	2755 (7)
C(9)	6633 (9)	6843 (10)	3463 (6)
C(10)	6002 (9)	4305 (10)	1138 (8)
C(11)	7132 (9)	3754 (9)	1056 (7)
I(1)	8574 (1)	8765 (1)	7728 (0)
I(2)	9643 (1)	8105 (1)	4323 (0)
Cl(1)	6579 (2)	6015 (2)	9207 (1)

The absolute configuration of [Co(amta)(en)]³⁺ was established by refining the structure with all coordinates inverted; this converged with $R_w = 0.041$, confirming the adopted configuration at a confidence level of better than 99.5%.^{15b}

All calculations were performed by using the SHELX-76¹⁶ system of programs, and all scattering factors (neutral Co for Co(III)) and anomalous dispersion terms were taken from ref 17.

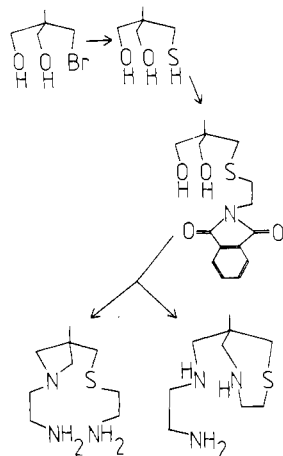
The atom-numbering schemes are given in Figures 1 and 2, and final atomic coordinates, bond lengths, and bond angles for both complexes are given in Tables II-V. Listings of observed and calculated structure factors, hydrogen atom coordinates and thermal parameters, close intermolecular contacts, and details of least-squares planes calculations (Tables S1-S9) are available as supplementary material.

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Table V. Bond Lengths (Å) and Valence Angles (deg) for [Co(amta)(en)]₂Cl

S(1)-Co(1)	2.267 (3)	C(8)-N(2)	1.516 (13)
N(1)-Co(1)	1.951 (8)	C(9)-N(3)	1.496 (13)
N(2)-Co(1)	1.996 (8)	C(10)-N(4)	1.492 (14)
N(3)-Co(1)	1.958 (8)	C(11)-N(5)	1.475 (13)
N(4)-Co(1)	1.983 (8)	C(2)-C(1)	1.524 (14)
N(5)-Co(1)	1.989 (8)	C(3)-C(2)	1.538 (13)
C(3)-S(1)	1.833 (11)	C(4)-C(2)	1.514 (13)
C(6)-S(1)	1.823 (11)	C(5)-C(2)	1.551 (13)
C(7)-N(1)	1.499 (12)	C(7)-C(6)	1.485 (15)
C(4)-N(2)	1.528 (13)	C(9)-C(8)	1.497 (15)
C(5)-N(2)	1.536 (11)	C(11)-C(10)	1.469 (15)
N(1)-Co(1)-S(1)	86.8 (2)	C(8)-N(2)-Co(1)	107.1 (6)
N(2)-Co(1)-S(1)	91.5 (2)	C(8)-N(2)-C(4)	113.7 (8)
N(2)-Co(1)-N(1)	94.2 (3)	C(8)-N(2)-C(5)	116.3 (7)
N(3)-Co(1)-S(1)	174.8 (3)	C(9)-N(3)-Co(1)	108.9 (6)
N(3)-Co(1)-N(1)	88.5 (3)	C(10)-N(4)-Co(1)	109.7 (6)
N(3)-Co(1)-N(2)	86.5 (3)	C(11)-N(5)-Co(1)	109.4 (6)
N(4)-Co(1)-S(1)	95.4 (2)	C(3)-C(2)-C(1)	109.6 (9)
N(4)-Co(1)-N(1)	172.2 (3)	C(4)-C(2)-C(1)	117.1 (9)
N(4)-Co(1)-N(2)	93.2 (3)	C(4)-C(2)-C(3)	111.9 (9)
N(4)-Co(1)-N(3)	89.5 (3)	C(5)-C(2)-C(1)	116.2 (9)
N(5)-Co(1)-S(1)	89.8 (3)	C(5)-C(2)-C(3)	113.8 (8)
N(5)-Co(1)-N(1)	89.2 (3)	C(5)-C(2)-C(4)	86.7 (7)
N(5)-Co(1)-N(2)	176.3 (3)	C(2)-C(3)-S(1)	117.5 (7)
N(5)-Co(1)-N(3)	92.5 (4)	C(2)-C(4)-N(2)	89.9 (7)
N(5)-Co(1)-N(4)	83.2(3)	C(2)-C(5)-N(2)	88.2 (7)
C(3)-S(1)-Co(1)	110.3 (3)	C(7)-C(6)-S(1)	110.6 (7)
C(6)-S(1)-Co(1)	99.6 (3)	C(6)-C(7)-N(1)	111.6 (8)
C(6)-S(1)-C(3)	100.4 (5)	C(9)-C(8)-N(2)	111.8 (8)
C(7)-N(1)-Co(1)	115.6 (6)	C(8)-C(9)-N(3)	105.3 (7)
C(4)-N(2)-Co(1)	116.1 (6)	C(11)-C(10)-N(4)	105.5 (8)
C(5)-N(2)-Co(1)	116.2 (6)	C(10)-C(11)-N(5)	106.9 (8)
C(5)-N(2)-C(4)	86.8 (7)		

**Figure 3.** Synthesis of amta and atac.

Results and Discussion

Syntheses and Complexes. The potentially quadridentate ligands 6-methyl-6-(4-amino-2-azabutyl)-1-thia-4-azacycloheptane (atac) and *N*-(2-aminoethyl)-3-methyl-3-(4-amino-2-thiabutyl)azetidino (amta) occur as major products in the reaction between the bis(benzenesulfonate) derivative of 2-methyl-2-(4-phthalimido-2-thiabutyl)-1,3-propanediol and ethylenediamine (en) (Figure 3). The crude reaction mixture contains residual en, which is difficult to remove completely.⁷ Reaction of this crude ligand mixture with cobalt (II) bromide and oxygen, in methanol, resulted, after separation by cation-exchange chromatography, in the isolation of [Co(atac)(en)]³⁺ and [Co(amta)(en)]³⁺. The complexes have been characterized by elemental analyses and ¹H and ¹³C NMR spectroscopy, and the structures have been confirmed by single-crystal X-ray structure analysis.

The formation of the quadridentate ligand atac in the synthesis is not unexpected, as the amine analogue 6-methyl-6-(4-amino-2-azabutyl)-1,4-diazacycloheptane (L) has been isolated previously from a similar synthesis.⁷ These seven-membered ring products

may form by nucleophilic attack of a primary amine on the carbon atom of a neighboring benzenesulfonated alcohol. Removal of the phthalimide protecting group is a prerequisite to the proposed intramolecular ring formation for the thioether analogue, and facile cleavage of this protecting group by amines has been reported.¹⁸ The analogous 6-methyl-6-(4-amino-2-thiabutyl)-1,4-diazacycloheptane product has not been observed in this work.

The formation of the azetidino ligand amta was unexpected. The azetidino forms part of a quadridentate ligand and may arise by an intramolecular nucleophilic attack of the secondary nitrogen of one 4-amino-2-azabutyl moiety on the carbon atom of a neighboring benzenesulfonate. The reaction is unusual in that formation of the four-membered ring competes with reactions leading to the 1,4-disubstituted cycloheptane ring, and the desired 1-(4-amino-2-thiabutyl)-1,1-bis(4-amino-2-azabutyl)ethane. Prolonged reaction time (48 h) has given no indication that the azetidino is formed as an intermediate. In contrast, the bidentate ligand 3-(aminomethyl)-3-methylazetidino (ama) has been isolated from reaction between 1,1,1-tris(((tolylsulfonyl)oxy)methyl)ethane and ammonia (100 °C, 60 atm, 12 h).¹⁹ Prolonged reaction (48 h) reportedly resulted in ring opening to give 1,1,1-tris(aminomethyl)ethane.¹⁹ Azetidino itself is stable to ring cleavage under strongly basic conditions, but ring opening does occur in dilute acid.²⁰

¹³C and ¹H NMR Spectra. The ¹³C NMR spectrum of [Co(atac)(en)]³⁺ exhibited 11 lines, evidence for the lack of symmetry in the molecule. The resonances at +23.5 and +40.1 ppm have been assigned as arising from methyl and quaternary carbon atoms, respectively.⁸ Four resonances at +62.0, +58.2, +57.6, and +57.4 ppm have been assigned to the methylene carbon atoms adjacent to secondary nitrogen centers,^{2,5,21,22} while resonances appearing at +45.4 and +38.7 ppm are assigned as arising from the methylene carbon atoms adjacent to the thioether.^{2,5,21,22} The more deshielded resonances (+62.0 and +45.4 ppm) may be assigned to the carbon atoms in the cysteamine portion of the strained 1-thia-4-azacycloheptane ring. Three resonances at +45.9, +44.3, and +44.0 ppm may be assigned as arising from methylene carbon atoms adjacent to the three primary amine donors.^{2,5,21,22}

For [Co(amta)(en)]³⁺ the ¹³C NMR spectrum also shows the influence of the highly strained azetidino ring, as well as the lack of symmetry in the molecule. The methylene carbon atoms of the azetidino display resonances at +69.9, +68.5, and +66.6 ppm. These chemical shifts indicate considerable deshielding of the carbon nuclei and are in a region usually associated with a methylene carbon adjacent to a tertiary nitrogen atom.²³ Resonances appearing at +23.9 and +36.4 ppm have been assigned as arising from the methyl and quaternary carbon atoms,⁸ respectively, while resonances observed at +45.9, +44.8, +44.6, and +43.8 ppm and at +40.6 and +41.4 ppm have been assigned as arising from methylene carbon atoms adjacent to primary amine and thioether donors, respectively.^{2,5,21,22} Tentatively, resonances appearing at +45.9 and +44.6 ppm for [Co(amta)(en)]³⁺ and +45.9 and +44.3 ppm for [Co(atac)(en)]³⁺ have been attributed to the methylene carbon atoms in the en ligand.

The proton spectra for both complexes are complicated. Both ¹H NMR spectra exhibit broad unresolved multiplets at 3 ppm with resonances assigned to the methyl protons observed at 1.3 ppm for [Co(amta)(en)]³⁺ and 1.1 ppm for [Co(atac)(en)]³⁺.

[Co(amta)(en)]³⁺ has cobalt and sulfur as chiral centers. Inspection of Dreiding models of the complex indicates that the configuration at the sulfur is predetermined by the configuration

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of the chelate rings of the complex. The sharp signals observed in the ^{13}C NMR spectrum imply that only one diastereoisomeric pair has been formed in the synthesis. Thus the configuration, Δ or Λ ,²⁴ of the five-membered rings about the cobalt atom predetermines the configuration at the sulfur atom. Assigning the free lone pair electrons of the coordinated sulfur atoms the lowest priority for the chirality sequence rules²⁵ requires the Δ configuration to have the sulfur atom in the *R* configuration, and equally, Λ requires the *S* configuration.

Description of Structures of [Co(atac)(en)](NO₃)(ClO₄)₂ and [Co(amta)(en)]Cl₂. An ORTEP²⁶ drawing of the cation [Co(atac)(en)]³⁺ with atom labels is shown in Figure 1. Intramolecular bond distances and bond angles with estimated standard deviations are listed in Table III. The structure consists of the complex cation, one nitrate, and two highly disordered perchlorate anions. There are numerous hydrogen bonds between the anions and the coordinated amine groups. The condensation in this case results in the formation of a quadridentate ligand. An ethylene bridge links the thioether sulfur to an amine nitrogen, resulting in the formation of the seven-membered ring. Considerable strain results from the formation of this ring; the Co(1)–N(1) distance of 2.056 (6) Å is one of the largest observed for a cobalt(III) amine complex. The Co(1)–S(1) bond is at the short end of the range and is evidently constrained by its attachment to N(1). The S(1)–C(6)–C(7)–N(1) torsion angle (16 (1)°) is close to being eclipsed. The strain is also evident at N(2) with a Co(1)–N(2)–C(5) angle of 120.1 (5)° observed. The structure of [CoL(en)]³⁺ displays a more severe flattening of the "ethylenediamine" chelate of the 1,4-diazacycloheptane ring (dihedral angle 8.0 (4)°),⁷ and in both molecules the neopentyl portion of the complex cation suffers similar severe strain. The effect of the larger sulfur atom in the atac ligand is reflected in the bond angles associated with the 1,4-disubstituted cycloheptane ring, with a C(2)–C(4)–N(1) bond angle of 120.9° in [Co(atac)(en)]³⁺ compared to 115.2° in [CoL(en)]³⁺.⁷ Similarly the S(1)–Co(1)–N(1) chelate bite angle (81.1°) is larger than that observed for the 1,4-diazacycloheptane analogue (76.4°)⁷ but smaller than that observed in [(en)₂Co(S(CH₃)CH₂CH₂NH₂)]³⁺ (86.8°), where the thioether is not constrained.²⁷

Atoms C(8) and C(9) show larger thermal motions in a direction perpendicular to the plane of the chelate ring. Attempts to locate two sites for these atoms were unsuccessful, suggesting that either a range of conformations exist or the ring is highly mobile. The disorder of these atoms results in an unreasonably short apparent C(8)–C(9) bond distance of 1.31 (2) Å.

Figure 2 shows the [Co(amta)(en)]³⁺ cations and the numbering system adopted. Intramolecular bond distances and bond angles with estimated standard deviations for [Co(amta)(en)]I₂Cl are listed in Table V. The cobalt(III) ion is surrounded by five nitrogen atoms and one sulfur atom. The formation of the azetidene ring is confirmed. The condensation has resulted in the formation of a quadridentate ligand with primary amine groups at each end and tertiary amine and thioether donor groups. The remaining two sites of the approximately octahedral structure are occupied by an ethylenediamine ligand. The chloride is hydrogen bonded to three amine groups N(1), N(3), and N(5), which form a face. All amine hydrogens are involved in exactly one hydrogen bond, to either chloride or the iodide anions. The bond lengths (1.51–1.55 Å) and angles (86.7–89.9°) within the azetidene ring reflect the considerable strain inherent in the formation of a four-membered ring. A least-squares plane through the four atoms of this ring shows that it is significantly puckered with all atoms lying 0.14–0.15 Å out of the plane. The longest cobalt–nitrogen

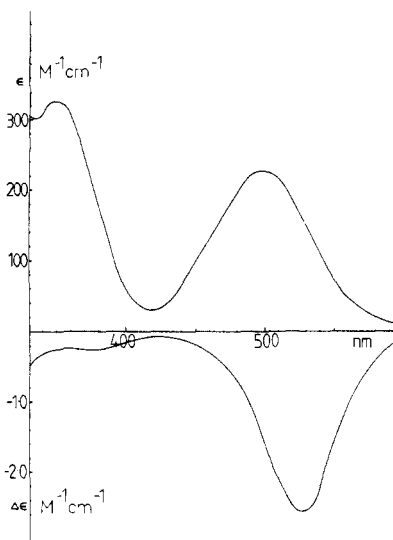


Figure 4. Circular dichroism and visible spectra of Δ -[Co(amta)(en)]I₂Cl.

bond is associated with the bond from the nitrogen of the azetidene ring to cobalt (1.99 Å) and is slightly longer than that observed in *mer*-[Co(ama)]³⁺ (1.98 Å).¹⁹ The chelate bite angles N(4)–Co–N(5) and N(1)–Co–S are quite normal for five-membered chelate rings, while that involving the azetidene, N(2)–Co–N(3), is slightly larger. The cobalt–sulfur distance is at the long end of the observed range, consistent with the previously reported observation that these distances increase as the constraints on the thioether decrease.²

For the $\Delta\epsilon_{525} = -2.62$ enantiomer, the absolute configuration is Δ in helical notation. The coordinated sulfur atom is therefore *R*, and the complex in Figure 2 is thus Δ -[Co(amta)(en)]³⁺.

Visible and Circular Dichroism Spectra. Both complexes in aqueous solution display visible absorption spectra characteristic of octahedrally coordinated cobalt(III) ions (Figure 4). For both [Co(atac)(en)]³⁺ and [Co(amta)(en)]³⁺ the ¹T_{1g} band is shifted to lower energy compared to that for similar [Co(N₅S)]³⁺ complexes, e.g., 487 nm (ϵ 177) for [(en)₂Co(S(CH₃)CH₂CH₂NH₂)]³⁺.²⁷ The ¹T_{2g} band appears in the spectra of both complexes as a well-defined shoulder on intense charge-transfer transitions arising from cobalt–nitrogen and cobalt–sulfur transitions. Whereas thiolato complexes such as [(en)₂Co(SCH₂CH₂NH₂)]²⁺ exhibit a shoulder at approximately 600 nm, arising from splitting of the ¹A_{1g} → ¹T_{1g} band,^{27–29} the thioether complexes [(en)₂Co(S(CH₃)CH₂CH₂NH₂)]³⁺, [Co(amta)(en)]³⁺, and [Co(atac)(en)]³⁺ do not display noticeable splitting. The possibility that a coordinated thioether provides a stronger ligand field than does a coordinated thiolate has been suggested as an explanation for this phenomenon.²⁷

The racemic [Co(amta)(en)]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 ($\Delta\epsilon_{525} = +2.62$) and a shoulder on the high-energy side at about 505 nm. A much smaller dichroism is associated with the second ligand field band, consistent with the magnetically nonallowed dipole transition for this T₂ state. Dichroism associated with sulfur–cobalt and nitrogen–cobalt charge-transfer transitions dominates the spectrum near 300 nm. In the region of the first ligand field band the circular dichroism is dominated by the E component, with a high-energy shoulder assigned to the A₁ → A₂ transition evident. The dichroism displayed by this complex is similar to that reported for other [CoN₅S]³⁺ complexes, e.g., for Λ -[(en)₂Co(S(CH₃)CH₂CH₂NH₂)]³⁺ $\Delta\epsilon_{497} = +3.22$ and $\Delta\epsilon_{384} = +0.06$.³⁰ Although

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the MCD for $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ displays a high-energy shoulder at about 460 nm, assigned to the $A_1 \rightarrow A_2$ transition, and a maximum at 487 nm, assigned to the $A_1 \rightarrow E$ transition, no splitting associated with the low-energy band is observed in the circular dichroism.³¹

The structural and spectroscopic implications of coordination of highly strained azetidone and 1,4-diazacycloheptane rings in CoN_6 complexes have been discussed and correlations between the average Co-N bond length and the position of the low-energy $^1T_{1g}$ band proposed.^{7,19} Similarly, it is possible to attribute the shift in λ_{max} of the low-energy $^1T_{1g}$ band for $[Co(amta)(en)]^{3+}$ and $[Co(atac)(en)]^{3+}$, compared to that observed for $[(en)Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$, in part to the presence of the strained chelate rings and to the subsequent effects on the Co-N and Co-S bond lengths in the former complexes. The spectral shifts are,

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however, not as marked as for the CoN_6 complexes, and a full examination of the effects of the incorporation of the thioether donor on the shifts in λ_{max} for the lowest energy $^1T_{1g}$ band must await the preparation of further examples of these types of complexes.

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Registry No. $[Co(amta)(en)]I_2Cl$, 108418-39-9; $[Co(atac)(en)]NO_3(ClO_4)_2$, 108418-41-3; $\Delta(-)-[Co(amta)(en)]I_2Cl$, 108507-66-0; $\Lambda(+)-[Co(amta)(en)]I_2Cl$, 108418-42-4; 2-methyl-2-(4-phthalimido-2-thiabutyl)-1,3-propanediol, 108418-43-5; 2-methyl-2-(bromomethyl)-1,3-propanediol, 2210-03-9; 2-methyl-2-(mercaptomethyl)-1,3-propanediol, 41988-08-3; *N*-(2-bromoethyl)phthalimide, 574-98-1; 2-methyl-2-(4-phthalimido-2-thiabutyl)-1,3-propanediol bis(benzenesulfonate), 108451-68-9.

Supplementary Material Available: Listings of thermal parameters and calculated hydrogen positions, close intermolecular contacts, and details of least-squares planes calculations (7 pages); listings of calculated and observed structure factors for both complexes (24 pages). Ordering information is given on any current masthead page.

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Layered Chlorotin Arsenate and Chlorotin Phosphate[†]

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The chlorotin arsenate and chlorotin phosphate $H[SnCl(OH)XO_4] \cdot 2H_2O$ ($X = As, P$) are layered compounds with intriguing intercalation properties. Directly intercalated are some derivatives of short-chain fatty acids (*N*-methylformamide, *N*-ethylformamide, *N*-ethylacetamide) and many primary, secondary, and tertiary amines. A tilted arrangement of the molecules with the alkyl chains radiating away from the surface is preferred. With short-chain alkylamines complete delamination of the crystals can occur. Long-chain alkylamines can be directly intercalated or adsorbed from diluted solutions. Alkylammonium derivatives can also be obtained by exchanging the protons by alkylammonium ions. The long-chain alkylamines or alkylammonium ions assume upright positions in the interlayer space. Preferentially, monolayers of perpendicular alkyl chains and bilayers of tilted alkyl chains (tilting angle $\sim 56^\circ$) are formed. Intercalation proceeds rapidly, and complete conversion into the guest-host structure is attained. The dehydrated forms of chlorotin arsenate and chlorotin phosphate maintain the capability of intercalating guest molecules up to dehydration temperatures of 300 °C.

Introduction

Phosphate and arsenate anions show a pronounced tendency to connect metal ions to layered host materials. Several types of layered compounds have been synthesized, and recent studies open new opportunities for utilizing them as molecular sieves and catalysts.^{1,2} Particular attraction is directed toward group IVA and group IVB (groups 4 and 14) compounds of the form $H_2-[M^V(XO_4)]_x \cdot xH_2O$ ($M^V = Zr, Ti, Hf, Ge, Sn; X = P, As$).³ A second, structurally different group comprises phosphates and arsenates $M^V OXO_4 \cdot xH_2O$, such as $VOPO_4 \cdot xH_2O$ ($x = 1, 2$), $VOAsO_4 \cdot xH_2O$ ($x = 2, 3$),⁴⁻¹⁰ $NbOPO_4 \cdot xH_2O$ ($x = 1, 3$),¹⁰⁻¹² and $VO(HPO_4) \cdot 0.5H_2O (= (VO)_2H_4P_2O_9)$.^{13,14} The alkaline-earth salts of monoalkyl phosphoric esters, for instance $CaPO_4CH_3 \cdot H_2O$, form a third group of layered phosphates.¹⁵

The structure of $VOPO_4 \cdot H_2O$ and $NbOPO_4 \cdot H_2O$ is composed of neutral $M^V O(H_2O)PO_4$ layers. The puckered $NbO(H_2O)PO_4$ layers consist of distorted $NbO_5(OH_2)$ octahedra connected in the equatorial planes by PO_4 tetrahedra.¹⁰ The additional water molecules of the higher hydrated forms are enclosed between the layers. $NbOPO_4 \cdot 3H_2O = [NbO(H_2O)PO_4] \cdot 2H_2O$ contains a monolayer of water molecules between the layers. Related are chlorotin phosphate $[SnCl(H_2O)PO_4] \cdot 2H_2O$ and chlorotin arsenate $[SnCl(H_2O)AsO_4] \cdot 2H_2O$. One proton in these compounds can be exchanged by metal ions, which may be expressed by the

formulas $H[SnCl(OH)PO_4] \cdot 2H_2O$ and $H[SnCl(OH)AsO_4] \cdot 2H_2O$.

Preparation and properties of the chlorotin arsenate have been reported by D emaret,¹⁶ who also described the intercalation of

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 (b) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA becomes groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)
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[†] Dedicated to Armin Weiss on the occasion of his 60th birthday.