In view of the above considerations, the arrangement of the 2,3,2-tet ligand in the title complex appears to be relatively strain free and to lead to strong Cu(II)–ligand overlap. Closure of the 2,3,2-tet ligand with a $-(CH_2)_3-$ bridge yields a 2,3,2,3 macrocyclic tetraamine whose metal complexes contain linked 5,6,5,6 arrangements of chelate rings. Cu(cyclam)$^{2+}$ and Cu(tet-a)$^{2+}$ are examples of such systems. These and related macrocyclic complexes exhibit exceptional stability (log $K \sim 28$)[12,26] and blue-shifted ligand field bands. In Cu(cyclam)$^{2+}$, the Cu–N distances, N–Cu–N angles, planarity of the CuN_4 chromophores, and configurations of the chelate rings closely resemble those of the title complex (Table V). The relatively high stability of the Cu(2,3,2-tet)$^{2+}$ complex is consistent with its close structural relationship to the Cu(cyclam)$^{2+}$ complex.

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Registry No. Cu(2,3,2-tet)$(ClO_4)_2$, 72331-56-7.

Supplementary Material Available: A listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Aromatic Thiolato Complex (2-Mercaptoaniline-*N*,*S*)bis(ethylenediamine)cobalt(III). Crystal Structure of $[(en)_2Co(SC_6H_4NH_2)](ClO_4)Cl$

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The aromatic thiolato complex $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ may be synthesized by reduction of $[o\text{-}C_6H_4(NH_2)S-]_2$ with an ethylenediamine–cobalt(II) mixture in a water–tetrahydrofuran solvent system. This complex is shown to undergo the same oxidation, alkylation, and adduct formation reactions characteristic of the aliphatic thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. The visible–UV spectrophotometric parameters of the aliphatic and aromatic analogues, and those of their derivatives, are compared and discussed. The title complex crystallizes in space group $P2_1/n$ with $a = 9.904$ (1) Å, $b = 7.5045$ (8) Å, $c = 23.308$ (2) Å, $\beta = 92.693$ (8)°, and $Z = 4$. A total of 2543 unique reflections measured with an automated diffractometer were used to refine the crystal structure to a conventional R factor of 0.035. The cobalt atom is octahedrally coordinated by five nitrogen atoms and the sulfur atom of the *o*-mercaptoaniline ligand, all six ligand–metal bond lengths being equivalent to the analogous bond lengths observed in $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. The cobalt(III) coordination sphere therefore appears to be structurally indifferent to the distinction between aromatic and aliphatic thiolato ligands. The best current estimate of the thiolato-induced structural trans effect is 0.044 (2) Å.

Introduction

The 1-equiv reduction of an organic disulfide (or diselenide) by a labile metal(II) center to yield an inert thiolato– (or selenolato–) metal(III) complex has proven to be an important and useful synthetic route to the general class of robust metal–chalcogen complexes.[3-9]

$$2M^{II} + RXXR \rightarrow 2M^{III}\text{–}XR \qquad (1)$$

$$X = S, Se$$

We have been particularly interested in chelated (thiolato)bis(ethylenediamine)cobalt(III) complexes as advantageous substrates on which to base investigations of the sulfur-induced structural trans effect,[10-12] the properties and reactivity of coordinated sulfur,[10-15] and the ability of sulfur to mediate inner-sphere electron transfer.[6,16,17] These complexes are readily prepared in aqueous media by reaction 1 when RSH is an *aliphatic* thiol containing a suitable chelate functionality, e.g.

$$4en + 2Co^{2+}(aq) + [H_2NCH_2CH_2S-]_2 \rightarrow 2[(en)_2Co(SCH_2CH_2NH_2)]^{2+} \qquad (1a)$$

However, this preparation is not nearly so straightforward when RSH is an *aromatic* chelating thiol (e.g., $o\text{-}C_6H_4(NH_2)SH$ rather than $NH_2CH_2CH_2SH$), and until this study the preparation of an aromatic (thiolato)bis(ethylenediamine)cobalt(III) complex by eq 1 had not succeeded. The difficulties encountered in applying eq 1a to aromatic systems could arise from the undoubtedly complicated, multistep, redox

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Table I. Crystal Data and Experimental Parameters

A. Crystal Data

formula	$CoC_{10}H_{22}Cl_2N_5O_4S$	a	9.904 (1) Å	d(obsd)	1.66 (2) g cm^{-3}
fw	438.27	b	7.5045 (8) Å	d(calcd)	1.68 g cm^{-3}
V	1730.4 (3) Å^3	c	23.308 (2) Å	space group	$P2_1/n$
Z	4	β	92.693 (8)°	μ(Mo Kα)	14.8 cm^{-1}

B. Experimental Parameters

radiation	Mo Kα, $\bar{\lambda}$(Kα) = 0.710 73 Å, graphite monochromator	scan range	−1.0° from Kα_1 to +1.1° from Kα_2
temp	22 °C	bkgd counting	stationary counts for half of scan time at each end of scan
receiving aperture	circular, 4-mm diameter, 20 cm from crystal	2θ (max)	50°
		data collected	3065
scan rate	variable, 2–8° min^{-1}	data with $F_o^2 > 3\sigma(F_o^2)$	2543

mechanism[3,18] that underlies the simple stoichiometry of eq 1 or from some peculiar characteristic or instability of the aromatic thiolato–cobalt(III) product. In order to decide between these hypotheses, and also hopefully to prepare and characterize an aromatic (thiolato)bis(ethylenediamine)cobalt(III) complex for use in our structural and mechanistic investigations, we undertook the research described herein. In this study we have focused on the synthesis and characterization of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$, the aromatic analogue of the prototype aliphatic thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$.

Experimental Section

General Data. Visible–UV spectra were recorded on a Beckman ACTA III spectrophotometer at ambient temperature, and ^1H NMR spectra were obtained by using a Varian T-60 instrument (t ca. 37 °C). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Sephadex SP-C50 cation-exchange resin was obtained from Pharmacia Fine Chemicals and was prepared and stored as recommended by the manufacturer. All common laboratory chemicals were of reagent grade. The reactions of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ with CH_3I and Hg^{2+} were conducted, and spectrophotometrically monitored, as previously described[13,15] for $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$.

2,2′-Diaminodiphenyl Disulfide. This material was prepared by air oxidation of 2-aminothiophenol (Aldrich) in 60/40 ethanol/water. The yellow crystalline product was recrystallized from aqueous ethanol; mp 91–93 °C.

(2-Mercaptoaniline-*N*,*S*)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(SC_6H_4NH_2)](ClO_4)_2$. To a stirred, deaerated solution of $Co(ClO_4)_2 \cdot 6H_2O$ (58.4 g, 0.16 mol) in 100 mL of tetrahydrofuran and 60 mL of water was added 98% ethylenediamine (28.5 mL, 0.4 mol). To the resultant warm (ca. 50 °C) solution was immediately added 2,2′-diaminodiphenyl disulfide (20 g, 0.08 mol) and the entire mixture stirred for ca. 20 min under a nitrogen atmosphere. After that time, 60% $HClO_4$ (ca. 100 mL) was added, and then the mixture was allowed to stand overnight at ca. 4 °C. The resulting crude product was collected and recrystallized by dissolving it in water at room temperature, filtering, adding concentrated $HClO_4$ to incipient precipitation, and cooling to induce crystallization. The green-brown product needles were collected, washed with water and ethanol, and dried in a vacuum desiccator. The homogeneity of this product was confirmed by ion-exchange chromatography on Sephadex SP using 0.25 M $NaClO_4$ as eluant; yield of recrystallized product 34 g (42%). Anal. Calcd for $C_{10}H_{22}N_5SCo(ClO_4)_2$: C, 23.92; H, 4.41; N, 13.94; S, 6.38; Co, 11.72. Found: C, 24.22; H, 4.66; N, 13.89; S, 6.31; Co, 11.97.

(2-Sulfenatoaniline-*N*,*S*)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(S(O)C_6H_4NH_2)](ClO_4)_2$, Solutions. Dilute solutions of this complex were prepared by H_2O_2 oxidation of 10^{-3}–10^{-4} M solutions of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$. In one case, the resultant reaction mixture was purified by ion exchange on Sephadex SP using 0.25 M $NaClO_4$ as eluant, and the UV spectrum of the product was determined in 0.01 M $HClO_4$.

(2-Sulfinatoaniline-*N*,*S*)bis(ethylenediamine)cobalt(III) Salts, $[(en)_2Co(S(O)_2C_6H_4NH_2)]X_2$, $X^- = ClO_4^-$, SCN^-. This complex was prepared by oxidation of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ with excess H_2O_2. In a typical preparation, 10 g of $[(en)_2Co(SC_6H_4NH_2)](ClO_4)_2$ was slurried in 50 mL of 12% $HClO_4$, and then 30 mL of 30% H_2O_2 was added to the actively stirred solution. The color of this mixture immediately changed from brown to red-orange, the remaining solid dissolved, and the solution became warm. Within 1 h, the stirred solution turned deep yellow and a precipitate formed. After a total of 90 min, the mixture was allowed to stand overnight at ca. 4 °C. The orange product was collected, recrystallized from 1 M $HClO_4$ by addition of saturated aqueous $NaClO_4$, washed with successive portions of water and ethanol, and dried in a vacuum desiccator; yield of recrystallized product 8 g (80%). The thiocyanate salt, as the monohydrate, was obtained by metathesis with NaSCN. Anal. Calcd for $C_{12}H_{24}N_7S_3CoO_3$: C, 30.70; H, 5.15; N, 20.88; S, 20.49; Co, 12.55. Found: C, 30.72; H, 5.00; N, 21.19; S, 20.49; Co, 12.12.

Collection and Reduction of X-ray Data. In order to avoid the disorder problems frequently encountered with perchlorate ions, we attempted to prepare the chloride salt of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ by dissolving an excess of NaCl in a concentrated solution of $[(en)_2Co(SC_6H_4NH)](ClO_4)$. Within about 30 min, crystals clearly different from those of the perchlorate salt began to form. One of these crystals, a nearly rectangular prism of approximate dimensions 0.5 × 0.2 × 0.1 mm, was mounted in a glass capillary with its long dimension approximately parallel to the capillary axis. Initial centering of reflections, generation of possible unit-cell vectors, and assignment of indices were carried out on a Syntex P2$_1$ diffractometer by standard procedures which have been described.[19] Interaxial angles were suggestive of monoclinic symmetry; the identity of the symmetry axis was confirmed by axial rotation photographs. Strong reflections with $30° \leq 2\theta \leq 35°$ were identified by collection of all data within these limits at a scan rate of 29.3°/min in 2θ. Refined cell parameters were based upon the setting angles of 15 of these reflections. Profiles of ω and 2θ scans of several representative reflections showed peaks of normal breadths and only slight asymmetry. The density was determined by flotation in $CCl_4/CHBr_3$ solutions. Crystal data are summarized in part A of Table I. Intensity data were collected by the 2θ–θ scan technique in bisecting geometry. Other experimental parameters are tabulated in part B of Table I. No reflections were strong enough to exceed the valid range of the coincidence correction. Four standard reflections were monitored after every 50 data. The intensity of these reflections showed only random variations no greater than ±2% from their mean values; hence no corrections for varying standards were necessary. Examination of the data set revealed systematic absences ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$) indicative of space group $P2_1/n$.[20]

Data were processed by previously described methods.[21] Because of the close spacing of reflections along c, 16 reflections showed asymmetric background counts arising from overlap with adjacent reflections. These reflections were routinely picked up by the data-processing program and were manually corrected for overlap on the basis of the 96-step peak profiles recorded by the diffractometer. The p factor in the expression for the standard deviation of the observed intensities[22] was given a value of 0.05. Sample calculations showed

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Table II. Visible–UV Spectrophotometric Parameters for *N,S* Bis(ethylenediamine)cobalt(III) Complexes Containing Chelated Thiolato, Sulfenato, and Sulfinato Ligands[a, b]

complex	λ_{max} (ϵ)					
		Thiolato Complexes				
$[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$	600 (44), sh	482 (142)			282 (13 800)	
$[(en)_2Co(SC_6H_4NH_2)]^{2+}$	580 (80), sh	470 (170), sh	400 (240)	350 (300), sh	279 (19 400)	260 (14 600), sh
		Sulfenato Complexes[c]				
$[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$		470 (500)		365 (6700)	284 (3700)	
$[(en)_2Co(S(O)C_6H_4NH_2)]^{2+}$		475 (800), sh		375 (6000)	285 (4400)	
		Sulfinato Complexes				
$[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$		432 (220)			288 (14 800)	
$[(en)_2Co(S(O)_2C_6H_4NH_2)]^{2+}$		430 (250)			285 (13 400)	

[a] Wavelengths, λ, of maxima (max) and shoulders (sh) are in nm. Molar extinction coefficients, ε, given in parentheses, are in M^{-1} cm^{-1}. Spectra are recorded in dilute aqueous perchloric acid. [b] Parameters for the aromatic complexes come from this work. Parameters for the aliphatic complexes come from ref 12. [c] The sulfenato complexes are unstable in solution, and therefore the reported extinction coefficients have relatively large uncertainties. Reported parameters were obtained by generating the sulfenato complexes in situ.

that neglect of an absorption correction introduced a maximum error of 4% in any structure factor, with most errors being much smaller. Hence no correction was made for absorption.

Structure Solution and Refinement. The structure was solved by use of the MULTAN system of direct-methods programs.[23] Intensity statistics were consistent with expectations for a centrosymmetric structure. Phasing, based upon the 250 reflections with normalized structure factors (E's) ≥ 1.75, yielded one set of phases whose figures of merit were clearly superior to those of all other phase sets. An E map based upon these phases yielded the positions of all nonhydrogen atoms of the cation with the exception of three atoms of one ethylenediamine ligand. The remaining atoms were located by difference Fourier syntheses.[24] At this point, it became clear that we were dealing with crystals of the mixed chloride/perchlorate salt rather than with the chloride salt as had originally been assumed. Two cycles of isotropic refinement of all nonhydrogen atoms yielded discrepancy factors $R_1 = 0.099$ and $R_2 = 0.147$.[25] An additional cycle with anisotropic thermal parameters reduced these values to 0.054 and 0.088. A difference Fourier map at this point clearly revealed peaks, ranging in height from 1.1 to 1.9 e/Å^3, attributable to the 22 hydrogen atoms. All other peaks ≥ 1.2 e/Å^3 in height were interpretable as arising from residual thermal motion of Co or Cl(1). In the final least-squares refinement, all hydrogen atoms were included at fixed idealized positions (C–H = 0.95 Å, trigonal or tetrahedral angles as appropriate). This refinement coverged to discrepancy factors $R_1 = 0.035$ and $R_2 = 0.053$, with a maximum parameter shift of 1.5 standard deviations for the perchlorate oxygen atoms and 0.4σ for all other atoms.

In all structure factor calculations, atomic scattering factors (including anomalous terms for Co and Cl) were taken from ref 26. The final standard deviation of an observation of unit weight was 1.64. Calculation of structure factors for the data with $F_o^2 \leq 3\sigma(F_o^2)$ showed nine reflections with $F_c^2 > 3\sigma(F_o^2)$; of these, only one had a $\Delta F/\sigma$ value >5.

Results

Characterization. In addition to the X-ray structure analysis described below, the $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ complex is characterized by (1) the synthetic route used for its preparation, (2) elemental analysis of the isolated perchlorate salt (see the Experimental Section) which gives an empirical composition in agreement with the proposed formulation, (3) its cation-exchange elution characteristics which are consistent with the assigned 2+ formal charge, (4) its ^{1}H NMR spectrum[28] which confirms the presence of aromatic, as well as aliphatic, C–H and N–H bonds, and (5) its visible–UV spectrophotometric parameters which are given in Table II. With regard to the latter, the spectrum includes d–d bands characteristic of cobalt(III) complexes, an intense ligand-to-metal charge-transfer (LTMCT) band at 279 nm which is diagnostic[5,15] for sulfur bonded to cobalt(III), and a shoulder at ca. 600 nm which is apparently characteristic[15,29] for cobalt(III) complexes containing five ammine nitrogen atoms and one thiolato sulfur atom in the primary coordination sphere.

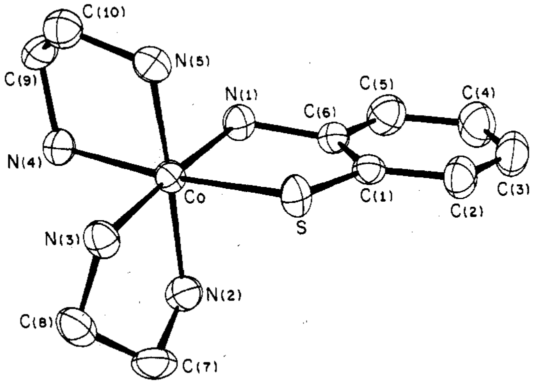

Figure 1. Perspective view of the $[(en)_2Co(SC_4H_4NH_2)]^{2+}$ cation. The ellipsoids represent 50% probability. Hydrogen atoms have been omitted for clarity.

Crystal Structure. Final atomic positional and thermal parameters, and their associated estimated standard deviations, for nonhydrogen atoms are listed in Table III. Bond distances and angles involving nonhydrogen atoms are given in Tables IV and V, respectively. Potential hydrogen-bonding contacts are given in Table VI. Tables of hydrogen atom parameters, principal amplitudes of thermal motion, and observed and calculated structure factors are available.[27] Figure 1 shows a perspective view of the $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ cation.

This structure consists of discrete cationic complexes, chloride anions, and perchlorate anions with only weak hydrogen bonds bridging the ions. The perchlorate anion is well-behaved in that none of the thermal parameters describing the oxygen atoms are excessively large. The cobalt(III) center is six-coordinate (five nitrogen atoms and the sulfur atom of the mercaptoaniline ligand) in an approximately octahedral configuration. There are two types of nitrogen atoms cis to

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(27) Supplementary material.

(28) ^{1}H NMR in dimethyl-d_6 sulfoxide; peak positions (δ) relative to internal tetramethylsilane: aromatic C–H, multiplet at 7.0–7.6; aliphatic C–H, multiplet at 2.4–3.1 partially obscured by solvent; aromatic N–H, broad singlet at 6.2; aliphatic N–H, multiplet at 4.0–5.0.

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Table III. Atomic Positional and Thermal Parameters[b] for Nonhydrogen Atoms of $[\mathrm{Co(en)_2(C_6H_4NH_2S)}](\mathrm{ClO_4})\mathrm{Cl}$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.32887 (4)[a]	0.47010 (6)	0.11389 (2)	1.98 (2)	1.86 (2)	1.61 (2)	0.22 (1)	0.42 (1)	0.04 (1)
Cl(1)[c]	−0.36305 (11)	0.25714 (14)	0.43048 (4)	4.12 (5)	3.24 (4)	2.96 (4)	−1.07 (3)	−0.98 (3)	0.60 (3)
Cl(2)	0.24845 (10)	0.47641 (12)	0.29924 (4)	3.95 (4)	2.35 (4)	2.20 (4)	0.28 (3)	0.89 (3)	−0.25 (3)
S	0.50583 (9)	0.34363 (13)	0.07284 (4)	2.56 (4)	3.18 (4)	1.71 (4)	0.81 (3)	0.71 (3)	0.10 (3)
O(1)	−0.4595 (4)	0.3451 (5)	0.3952 (2)	5.96 (21)	6.33 (21)	7.02 (23)	0.00 (16)	−2.00 (17)	2.00 (18)
O(2)	−0.2857 (5)	0.3703 (6)	0.4669 (1)	9.13 (25)	8.16 (24)	3.61 (16)	−5.39 (20)	−0.75 (16)	−0.57 (16)
O(3)	−0.4319 (5)	0.1303 (6)	0.4637 (2)	11.76 (32)	7.26 (24)	5.54 (20)	−6.07 (22)	−1.90 (20)	3.03 (18)
O(4)	−0.2749 (5)	0.1720 (8)	0.3910 (3)	7.08 (26)	11.87 (38)	12.44 (39)	1.36 (28)	2.53 (26)	−5.67 (33)
N(1)	0.3929 (3)	0.3578 (4)	0.1862 (1)	2.12 (12)	2.51 (12)	1.76 (11)	0.35 (9)	0.51 (9)	−0.03 (9)
N(2)	0.4366 (3)	0.6855 (4)	0.1321 (1)	2.46 (13)	2.36 (12)	3.10 (14)	−0.11 (10)	0.47 (10)	−0.06 (10)
N(3)	0.2722 (3)	0.5950 (4)	0.0423 (1)	2.93 (13)	2.66 (13)	2.23 (12)	0.36 (11)	0.30 (10)	0.41 (10)
N(4)	0.1651 (3)	0.5572 (4)	0.1534 (1)	2.07 (11)	2.20 (12)	2.74 (13)	0.16 (9)	0.42 (10)	−0.04 (10)
N(5)	0.2164 (3)	0.2630 (4)	0.0933 (1)	2.78 (13)	2.08 (12)	2.06 (12)	0.07 (10)	0.12 (10)	−0.23 (9)
C(1)	0.5937 (3)	0.2737 (4)	0.1365 (1)	2.23 (13)	1.85 (13)	2.21 (14)	−0.02 (11)	0.47 (11)	0.09 (11)
C(2)	0.7227 (4)	0.1968 (5)	0.1371 (2)	2.43 (15)	3.22 (17)	3.30 (17)	0.76 (13)	0.78 (13)	0.21 (14)
C(3)	0.7837 (4)	0.1406 (6)	0.1873 (2)	2.38 (16)	4.12 (20)	4.25 (20)	0.78 (14)	0.23 (14)	0.59 (16)
C(4)	0.7223 (4)	0.1633 (6)	0.2390 (2)	2.82 (17)	4.33 (20)	3.25 (18)	0.46 (14)	−0.39 (14)	0.86 (15)
C(5)	0.5942 (4)	0.2394 (5)	0.2395 (2)	2.55 (15)	3.17 (17)	2.50 (16)	−0.12 (12)	0.21 (12)	0.13 (13)
C(6)	0.5318 (3)	0.2929 (4)	0.1882 (1)	1.93 (13)	1.77 (12)	2.32 (14)	0.01 (10)	0.38 (10)	0.12 (11)
C(7)	0.4401 (4)	0.8017 (5)	0.0802 (2)	3.78 (18)	2.34 (15)	3.86 (19)	−0.53 (14)	1.38 (15)	0.44 (14)
C(8)	0.3037 (4)	0.7884 (5)	0.0495 (2)	4.01 (18)	2.49 (16)	3.17 (17)	0.78 (14)	1.02 (14)	0.88 (14)
C(9)	0.0692 (4)	0.4049 (5)	0.1592 (2)	2.21 (14)	2.66 (15)	3.08 (16)	−0.12 (12)	0.75 (12)	0.03 (13)
C(10)	0.0726 (4)	0.2938 (5)	0.1053 (2)	2.62 (15)	2.69 (15)	2.82 (16)	−0.17 (12)	−0.06 (12)	−0.32 (13)

[a] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [c] The chlorine atom of the perchlorate ion is designated Cl(1); the chloride ion is Cl(2).

Table IV. Bond Lengths (Å)

Co–S	2.246 (1)	N(2)–C(7)	1.494 (5)
Co–N(1)	1.964 (3)	N(3)–C(8)	1.492 (5)
Co–N(2)	1.972 (3)	N(4)–C(9)	1.496 (5)
Co–N(3)	1.972 (3)	N(5)–C(10)	1.482 (5)
Co–N(4)	2.011 (3)	C(7)–C(8)	1.502 (6)
Co–N(5)	1.959 (3)	C(9)–C(10)	1.509 (5)
S–C(1)	1.764 (4)	C(2)–C(3)	1.359 (6)
N(1)–C(6)	1.458 (4)	C(3)–C(4)	1.385 (6)
C(1)–C(2)	1.402 (5)	C(4)–C(5)	1.392 (6)
C(1)–C(6)	1.386 (5)	C(5)–C(6)	1.378 (5)
Cl(1)–O(1)	1.396 (4)	Cl(1)–O(3)	1.422 (4)
Cl(1)–O(2)	1.402 (3)	Cl(1)–O(4)	1.447 (5)

Table V. Bond Angles (Deg)

(a) Metal Coordination Sphere			
S–Co–N(1)	87.54 (8)	N(1)–Co–N(5)	91.52 (12)
S–Co–N(2)	90.75 (9)	N(2)–Co–N(3)	85.56 (13)
S–Co–N(3)	92.13 (9)	N(2)–Co–N(4)	94.29 (12)
S–Co–N(4)	173.91 (9)	N(2)–Co–N(5)	177.31 (12)
S–Co–N(5)	90.39 (9)	N(3)–Co–N(4)	91.66 (12)
N(1)–Co–N(2)	90.96 (12)	N(3)–Co–N(5)	91.97 (12)
N(1)–Co–N(3)	176.50 (12)	N(4)–Co–N(5)	84.72 (12)
N(1)–Co–N(4)	88.96 (12)		
(b) 2-Mercaptoaniline Ligand			
Co–S–C(1)	97.56 (11)	C(2)–C(3)–C(4)	121.1 (4)
Co–N(1)–C(6)	115.9 (2)	C(3)–C(4)–C(5)	119.6 (4)
S–C(1)–C(2)	123.0 (3)	C(4)–C(5)–C(6)	119.0 (3)
S–C(1)–C(6)	118.7 (3)	C(5)–C(6)–C(1)	121.7 (3)
C(2)–C(1)–C(6)	118.3 (3)	N(1)–C(6)–C(1)	117.5 (3)
C(1)–C(2)–C(3)	120.3 (4)	N(1)–C(6)–C(5)	120.6 (3)
(c) Ethylenediamine Ligands			
Co–N(2)–C(7)	109.7 (2)	N(2)–C(7)–(18)	107.0 (3)
Co–N(3)–C(8)	108.5 (2)	N(3)–C(8)–C(7)	107.3 (3)
Co–N(4)–C(9)	108.8 (2)	N(4)–C(9)–C(10)	107.9 (3)
Co–N(5)–C(10)	111.7 (2)	N(5)–C(10)–C(9)	107.6 (3)
(d) Perchlorate Anion			
O(1)–Cl(1)–O(2)	114.2 (3)	O(2)–Cl(1)–O(3)	109.8 (2)
O(1)–Cl(1)–O(3)	107.7 (3)	O(2)–Cl(1)–O(4)	108.9 (3)
O(1)–Cl(1)–O(4)	104.5 (3)	O(3)–Cl(1)–O(4)	111.7 (4)

Table VI. Possible Hydrogen-Bonding Interactions[a]

atoms	dist, Å	angle, deg
S···H2N3$^{\mathrm{II}}$ [b]	2.80	139
Cl(2)···H1N1$^{\mathrm{III}}$	2.29	163
Cl(2)···H2N2$^{\mathrm{IV}}$	2.43	154
Cl(2)···H2N1$^{\mathrm{I}}$	2.43	136
Cl(2)···H1N5$^{\mathrm{III}}$	2.44	151
Cl(2)···H2N4$^{\mathrm{I}}$	2.75	138
O(1)···H1N4$^{\mathrm{V}}$	2.24	157
O(2)···H2N5$^{\mathrm{VI}}$	2.17	167

[a] Interactions listed are A–H···B interactions for which the H···B distance is shorter by at least 0.25 Å than the sums of the Pauling–van der Waals radii and for which the A–H···B angle is at least 130°. [b] Symmetry transformations are as follows: (I) x, y, z; (II) $1-x, 1-y, -z$; (III) $^1/_2-x, {}^1/_2+y, {}^1/_2-z$; (IV) $^1/_2-x, -{}^1/_2+y, {}^1/_2-z$; (V) $-{}^1/_2-x, -{}^1/_2+y, {}^1/_2-z$; (VI) $-{}^1/_2+x, {}^1/_2-y, {}^1/_2+z$.

the coordinated sulfur atom: the single aniline nitrogen atom N(5) and the three ethylenediamine nitrogen atoms N(1)–N(3). The Co–N bond length for the unique aniline nitrogen atom (1.963 (3) Å) falls within the range spanned by the other three cis Co–N bond lengths (1.959 (3)–1.972 (3) Å), and thus the four cis Co–N bond lengths can be considered to be equivalent. The trans Co–N bond length (2.011 (3) Å) is significantly longer than the average of the four cis Co–N bond lengths (1.967 (3) Å), giving rise to a ground-state structural trans effect (STE) of 0.044 (4) Å. The two ethylenediamine chelate rings of $[(\mathrm{en})_2\mathrm{Co}(\mathrm{SC_6H_4NH_2})]^{2+}$ adopt a $\lambda\delta$ configuration, as do the two en rings of $[(\mathrm{en})_2\mathrm{Co}(\mathrm{S(O)CH_2CH_2NH_2})]^{2+}$,[12] but in contrast to the en rings of $[(\mathrm{en})_2\mathrm{Co}(\mathrm{S(O)_2CH_2CH_2NH_2})]^{2+}$ [11] and $[(\mathrm{en})_2\mathrm{Co}(\mathrm{SCH_2CH_2NH_2})]^{2+}$ [10] which adopt a $\lambda\lambda$ configuration. The five-membered mercaptoaniline chelate ring is not planar; the four atoms Co, S, C(1), and C(6) are coplanar to within ca. 0.05 Å, but N(1) is 0.28 Å out of this plane. The six carbon atoms of the phenyl ring are coplanar to within 0.012 Å, but the S and N(1) atoms deviate from this plane by 0.025 and 0.137 Å, respectively.

Discussion

Synthesis and Properties. The preparation of $[(\mathrm{en})_2\mathrm{Co}(\mathrm{SCH_2CH_2NH_2})]^{2+}$ by eq 1a proceeds in essentially quantitative yield in aqueous solution.[6,9,30] However, [*o*-C$_6$H$_4$-

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$(NH_2)S-]_2$ cannot be directly substituted for $[NH_2CH_2CH_2S-]_2$ in this procedure because the aromatic compound is essentially insoluble in water. Our approach to circumventing this difficulty has been to conduct the preparation in solvent systems that dissolve all the starting materials; we have primarily used mixtures of water and polar organic solvents (e.g., alcohols, ketones, ethers, *N,N*-dimethylformamide, etc.). None of these solvent systems are totally satisfactory in that they all lead to a mixture of products, the desired $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ often being a minor component. It is hypothesized that the addition of polar organic solvents to the aqueous reaction medium adversely affects the several cobalt(II)–ligand equilibria that are necessary for the two inner-sphere electron transfers which underlie the desired reaction stoichiometry (eq 1). However, it was found that a 60/40 mixture of tetrahydrofuran and water consistently leads to at least a 50% yield of the desired $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ product and that, through the use of crystallization and ion-exchange chromatographic purification techniques, this material can be obtained in high purity.

The perchlorate salt of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ is stable in the solid state (over desiccant, in the dark), but aqueous solutions suffer decomposition over a period of days. While the conditions governing this decomposition were not investigated, it is clear that $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ is significantly less stable than the aliphatic analogue $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. In general, $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ undergoes the same gamut of reactions observed for $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$: (1) oxidation of the coordinated thiol to a S-bonded sulfenic acid by a stoichiometric amount of H_2O_2[12]

$$(en)_2Co(SC_6H_4NH_2)^{2+} + H_2O_2 \rightarrow (en)_2Co(S(O)C_6H_4NH_2)^{2+} + H_2O \quad (2)$$

(the sulfenato derivative is characterized by the distinctive charge-transfer band at 370 nm (Table II) which is diagnostic[12] for this class of complexes), (2) further oxidation of the S-bonded sulfenic acid to the S-bonded sulfinic acid[11,12]

$$(en)_2Co(S(O)C_6H_4NH_2)^{2+} + H_2O_2 \rightarrow (en)_2Co(S(O)_2C_6H_4NH_2)^{2+} + H_2O \quad (3)$$

(3) reaction with alkyl halides to yield a S-bonded thioether[13]

$$(en)_2Co(SC_6H_4NH_2)^{2+} + CH_3I \rightarrow (en)_2Co(S(CH_3)C_6H_4NH_2)^{3+} + I^- \quad (4)$$

and (4) reaction with soft-metal centers to yield sulfur-bridged adducts[15]

$$(en)_2Co(SC_6H_4NH_2)^{2+} + Hg^{2+} \rightarrow (en)_2Co(S(Hg)C_6H_4NH_2)^{4+} \quad (5)$$

However, the aromatic sulfur atom of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ is apparently a weaker Brønsted base than the aliphatic sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ since the latter can be protonated in concentrated HCl[29] while the former cannot. This observation is consistent with the fact that aromatic thiols are stronger Brønsted acids than aliphatic thiols.

The spectra of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ and its sulfenato and sulfinato derivatives (Table II) are generally similar to the spectra of the aliphatic analogues. The LMCT band in the spectrum of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ (279 nm) tails into the visible region, causing the 470-nm d–d band to appear as a shoulder rather than a peak and giving this complex its unusual green-brown color. The *o*-phenylene moiety contributes a peak at 260 nm and presumably enhances the extinction coefficients of the aromatic derivatives relative to the aliphatic complexes. The presence of a peak at 400 nm in the spectrum of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ is somewhat surprising since none of the other five N,S aromatic or aliphatic complexes exhibit this transition. The shoulder at 350 nm is assigned as the expected $^1A_{1g} \rightarrow {}^1T_{2g}$ d–d transition for cobalt(III), this transition usually being obscured by the tail of the Co–S LMCT band (when $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is protonated, the LMCT band shifts sufficiently for the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition to be observed at ca. 345 nm[29]). Observation of the characteristic[5,15] LMCT band at ca. 280 nm for the three complexes $[(en)_2Co(SC_6H_4NH_2)]^{2+}$, $[(en)_2Co(S(O)C_6H_4NH_2)]^{2+}$, and $[(en)_2Co(S(O)_2C_6H_4NH_2)]^{2+}$ implies that the Co–S bond remains intact through this series.

Table VII. Selected Bond Lengths (Å) for the Complexes $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ and $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ [a]

bond	$[(en)_2Co(SC_6H_4NH_2)]^{2+}$	$[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$
trans Co–N	2.011 (3)	2.001 (5)
av cis Co–N[b]	1.967 (3)	1.955 (7)
STE[c]	0.044 (4)	0.046 (8)
Co–S	2.246 (1)	2.226 (2)
S–C	1.764 (4)	1.818 (8)

[a] Data for the aromatic complex come from this work. Data for the aliphatic complex come from ref 12. [b] Estimated error computed as $[(r_i - r_{av})^2/(n^2 - n)]^{1/2}$. [c] Estimated error computed as $[(\sigma_{cis})^2 + (\sigma_{trans})^2]^{1/2}$.

Structural Characterization. Table VII compares selected bond lengths for the analogous aromatic and aliphatic thiolato complexes $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ and $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. All six analogous ligand–metal bond lengths for the two complexes are essentially the same, and indeed the sulfur-induced elongation of the trans Co–N bond (the STE) is the same for both complexes. The cobalt(III) coordination sphere therefore appears to be structurally indifferent to the distinction between aromatic and aliphatic thiolato ligands. Three other measurements of the thiolato-induced STE have been reported: in $[(en)_2Co(SCH_2COO)]^+$ the STE is 0.043 (5) Å,[10] while in anhydrous and hydrated forms of $[(en)_2Co(SCH_2CH(COO)NH_2)]^+$ the STE is reported as 0.049 (6) and 0.039 (8) Å. Thus, five independent determinations of this parameter fall within a 0.01-Å range and consequently appear to define a structural phenomenon characteristic of thiolato–cobalt(III) complexes. The average of these five determinations is 0.044 (2) Å, and this may be taken as the best current estimate of the thiolato-induced STE.

While the S–C bond length of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is typical for a paraffinic C–S bond (taken as 1.81 (1) Å[32]), the S–C bond length of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ is significantly shorter and falls in the region characteristic of a "partial double bond" (e.g., the C–S bond length in thiophene is 1.73 (1) Å[32]). Likewise, as expected,[32] the aniline N–C bond length (1.458 (4) Å) is somewhat shorter than the average ethylenediamine N–C bond lengths in $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ (1.491 (3) Å). These structural parameters may reflect the incipient "noninnocent" ligand character of *o*-mercaptoaniline;[33] the potential ability of *o*-mercaptoaniline to delocalize charge density could account for many of the difficulties encountered in preparing $[(en)_2Co(SC_6H_4NH_2)]^{2+}$ and for some of the anomalous properties of this complex.

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Registry No. $[(en)_2Co(SC_6H_4NH_2)](ClO_4)_2$, 72905-17-0; $[(en)_2Co(S(O)C_6H_4NH_2)](ClO_4)_2$, 72893-80-2; $[(en)_2Co(S(O)_2C_6H_4NH_2)](ClO_4)_2$, 72893-82-4; $[(en)_2Co(S(O)_2C_6H_4NH_2)](SCN)_2$, 72893-84-6; 2,2′-diaminodiphenyl disulfide, 1141-88-4; $[(en)_2Co(SC_6H_4NH_2)](ClO_4)Cl$, 72905-18-1.

Supplementary Material Available: Listings of structure factor amplitudes, hydrogen atom positional parameters, and principal root-mean-square amplitudes of thermal motion (11 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of (Octaethylporphinato)iron(III) Perchlorate. Anomalous Magnetic Properties and Structural Aspects

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The crystal structure of (octaethylporphinato)iron(III) perchlorate has been determined by the X-ray method. The compound crystallizes in the monoclinic space group $P2_1/a$ with four molecules in a unit cell of dimensions $a = 18.87$ (1) Å, $b = 14.20$ (5) Å, $c = 13.64$ (1) Å, and $\beta = 106.05$ (6)°. The crystal structure is composed of dimers of the complex; the two iron porphyrins have a "face-to-face" contact with a closest approach of 3.56 Å between the meso carbon and the pyrrolic α-carbon on the different porphyrins. This dimerization is explained by weak π–π^* interactions. Weak (π-pyrrolyl)iron interactions were also noted between the approached complexes. The perchlorate anion has C_{3v} symmetry. $Fe \rightarrow (O_1\text{–}Cl)$ π^* back-bonding seems to cause a longer Cl–O$_1$ bond (1.515 Å) relative to the other three Cl–O bonds. The porphinato core is planar within 0.04 Å. The average Fe–N and Fe–OClO$_3$ distances are determined as 1.994 (10) and 2.067 (9) Å, respectively. The iron atom is displaced by 0.26 Å out of the plane defined by the four porphinato nitrogen atoms. The overall geometric parameters give a good indication that the complex has an intermediate-spin state ($S = {}^3/_2$) in comparison with high- or low-spin iron porphyrins. The temperature-dependent magnetic moment revealed the iron atom to be in the $S = {}^3/_2$ state only. The structural details are discussed with its anomalous magnetic properties from other physical measurements.

Introduction

Ferricytochrome *c′*, a heme enzyme, isolated from photosynthetic and denitrifying bacteria, has been shown to have unusual chemical and physical properties.[1] Maltempo has suggested that the anomalous magnetic property arises from the electronic configurations of heme iron at the ground state of quantum mechanical admixtures of an intermediate-spin state ($S = {}^3/_2$) and of a high-spin state ($S = {}^5/_2$), coupled via a spin–orbit interaction.[1]

Few intermediate-spin or mixed-spin synthetic heme complexes have received much attention[2-4,6] since the synthesis and magnetic properties of (octaethylporphinato)iron(III) perchlorate, $(OEP)Fe^{III}ClO_4$, were reported.[2,3] The unusual magnetic moments of these complexes were interpreted in terms of a thermal admixture of the high-spin ($S = {}^5/_2$) and low-spin ($S = {}^1/_2$) states.[3] Recently, Dolphin et al.[2] have reported that $(OEP)Fe^{III}ClO_4$ is of an intermediate-spin state on the basis of Mössbauer spectra and magnetic susceptibility at various temperatures. The structure of heme centers has been discussed in relation to the function and mechanism of heme proteins.[5b] A number of molecular structures of iron porphyrins have been reported.[5,8-10] Scheidt et al. have reported the crystal structure of the ferric perchlorate complex of tetraphenylporphine, $(TPP)Fe^{III}ClO_4 \cdot {}^1/_2C_8H_{10}$[6a,b] and interpreted it in terms of the $S = {}^3/_2$ state and the quantum mechanically mixed $S = {}^3/_2, {}^5/_2$ state, respectively. In this paper, we describe the crystal structure of $(OEP)Fe^{III}ClO_4$, its geometry, and its temperature-dependent magnetic moment.

Experimental Section

Crystal Structure. $(OEP)Fe^{III}ClO_4$ was prepared by refluxing a benzene solution of $(OEP)Fe^{III}Cl$ and $AgClO_4$.[3] Dark brown platelike crystals were obtained by recrystallization from benzene solution. Preliminary X-ray data showed that the crystal is monoclinic and the space group is $P2_1/a$ from the systematic absences of $h0l$ for h odd and $0k0$ for k odd. The unit cell dimensions are $a = 18.87$ (1) Å, $b = 14.20$ (5) Å, $c = 13.64$ (1) Å, and $\beta = 106.05$ (6)°, from Weissenberg photographs calibrated by Ge standard power lines, respectively. The calculated density, with the assumption of four molecules in a unit cell, is 1.300 g/cm^3. The observed density was

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