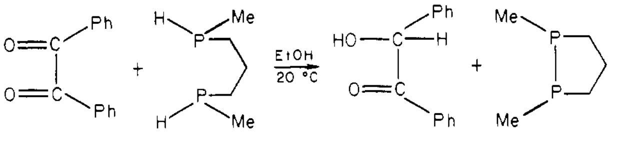
palladium complexes, $K = J_{AA'} + J_{BB'}$ becomes very large (~500 Hz) and the outer lines vanish. So, for the trans coupling constants an arbitrary value of 300 Hz was taken. Analysis of the $^{31}P\{^1H\}$ NMR spectrum of the other isomer (with an AA′BB′-type appearance) indicated P1 and P2 are chemically identical.

Clearly the steric conditions in **3a** encourage the formation of two additional five-membered chelate rings with the formation of the macrocyclic tetradentate ligand, [14]-tetraphos-1,4,8,11. The greater steric bulk of the phenyl groups in benzil in comparison to the methyl groups in biacetyl does not adversely affect the ring-closure reaction. The coupling of two six-membered chelate rings in **3a** over two three-carbon-atom bridges could not, however, be achieved.

If the free di(secondary phosphine) $HMeP(CH_2)_3PMeH$ (**1a**) is treated with benzil, a redox reaction occurs in which the main products are benzoin and 1,2-dimethyl-1,2-diphospholane[11,35] (eq 9).



(9)

1a

Ligand Displacement Reactions. One of the aims of the template synthesis of macrocyclic polydentate phosphine ligands was the preparation of the free ligand after displacement from the coordination sphere of palladium in **8–11**.

The extreme chelate effect of the tetradentate ligand stabilizes the complexes **8–11** with respect to displacement by monodentate ligands. However, because of its strong ligand field, we expected the cyanide ion to be able to displace the ligands.

Complex **9a** reacts rapidly with aqueous KCN, the macrocycle is broken up, and free $HMeP(CH_2)_2PMeH$ (**1**) is re-formed. By contrast **9b** reacts only slowly with cyanide. In the course of a few hours a mixture of uncharacterized complexes is formed. $HMeP(CH_2)_2PMeH$ (**1**) is only formed in traces. The complexes **10** and **11** are not destroyed by CN^- ions in aqueous or alcoholic solution.

Further experiments concerning ligand-exchange and ligand-replacement reactions on these complexes are currently investigated.

Acknowledgment. The Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen are thanked for financial support of this investigation. The authors wish to thank Prof. Dr. W. S. Sheldrick, Fachbereich Chemie, Universität Kaiserslautern, for collecting the crystallographic data. Dr. J. Hahn, Institut für Anorganische Chemie, Universität Köln, is thanked for measuring the ^{31}P NMR spectra of the compounds **10** and **11**. Prof. Dr. H. Harnisch and Dr. K. Gehrmann, Hoechst AG, and Prof. Dr. H. Hoffmann, Bayer AG, are thanked for generous gifts of chemicals.

Registry No. **1a**, 87137-74-4; **2**, 87137-65-3; **3a**, 87137-73-3; **3**, 81643-57-4; **4**, 87137-66-4; **5**, 87137-67-5; **6**, 87137-68-6; **7**, 87137-69-7; **8a**, 87137-70-0; **8b**, 87173-26-0; **9a**, 87173-24-8; **9b**, 87173-25-9; **10a**, 87137-71-1; **10b**, 87173-27-1; **10c**, 87173-28-2; **11a**, 87137-72-2; **11b**, 87173-29-3; **11c**, 87173-70-4.

Supplementary Material Available: Listings of thermal parameters and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221,
and the Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

Synthesis and Characterization of a S-Bonded Sulfenamide–Cobalt(III) Complex. Single-Crystal X-ray Structure of $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$. Kinetics of the NH_3OSO_3 Oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$

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Received January 4, 1983

Oxidation of (2-mercaptoethylamine-*N*,*S*)bis(ethylenediamine)cobalt(III) with excess hydroxylamine-*O*-sulfonic acid yields (2-aminoethanesulfenamido-*N*,*S*)bis(ethylenediamine)cobalt(III) in good yield. The mixed perchlorate/oxalate salt of this sulfenamide product has been characterized by single-crystal X-ray structural analysis. Crystals of $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$ are monoclinic, $P2_1/c$, with $a = 7.350$ (1) Å, $b = 17.290$ (5) Å, $c = 15.590$ (3) Å, $\beta = 100.76$ (2)°, and $Z = 4$. The structure was solved by direct methods and was refined to $R = 0.072$ based on 1715 reflections with $|F_o| > 4\sigma(|F_o|)$. Despite a somewhat short Co–S bond length of 2.250 (3) Å, the neutral S-bonded sulfenamide ligand does not induce a structural trans effect. The oxidation reaction follows the rate law $k_2[(en)_2Co(SCH_2CH_2NH_2)^{2+}][NH_3OSO_3]$ with $k_2 = a/(1 + b[H^+])$. At 25 °C, $\mu = 1.00$ M ($LiClO_4$ in aqueous media), $a = 3.2 \pm 0.1$ M^{-1} s^{-1} and $b = 16.4 \pm 0.6$ M^{-1}. The observed rate law is interpreted in terms of nucleophilic attack by the coordinated sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ on the N–O linkage of $NH_2OSO_3^-$. In this reaction the thiolato complex is as reactive a nucleophile as thiourea or triphenylphosphine.

Introduction

The chemistry of coordinated sulfur has been reviewed in detail, with special attention being given to the oxidation of thiols coordinated to cobalt(III).[3] These reactions (1) are facile, (2) often proceed via nucleophilic attack of the coordinated sulfur atom with concomitant atom or group transfer from the oxidant to the sulfur atom,[4] and (3) result in an oxidized ligand that is often considerably more stable than is the corresponding noncoordinated species. These generalizations are nicely illustrated by oxidations of the prototype thiolato cobalt(III) complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$

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(1) University of Cincinnati.

(2) Procter & Gamble.

(3) Deutsch, E.; Root, M. J.; Nosco, D. L. "Advances in Inorganic and Bioinorganic Reaction Mechanisms"; Sykes, A. G., Ed.; Academic Press: London, 1982; pp 269–389.

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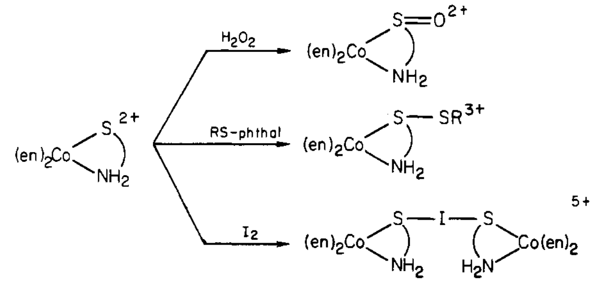
Table I. Visible-UV Spectrophotometric Parameters for Related Bis(ethylenediamine)cobalt(III) Complexes Containing N,S-Chelated Ligands

ligand	complex	λ_{max} $(\epsilon)^a$				ref
thiolato	$(en)_2Co(SCH_2CH_2NH_2)^{2+}$	600 (44) sh	482 (142)		282 (13800)	20
sulfenato	$(en)_2Co(S(O)CH_2CH_2NH_2)^{2+}$		470 (500)	365 (6700)	284 (3700)	6
sulfenyl iodide	$[(en)_2Co(SCH_2CH_2NH_2)]_2I^{5+}$		502 (838)		281 (31400)	8
disulfide	$(en)_2Co(S(SCH_3)CH_2CH_2NH_2)^{3+}$		489 (149)	343 (1710)	278 (7550)	7
sulfenamide	$(en)_2Co(S(NH_2)CH_2CH_2NH_2)^{3+}$		474 (212)		296 (6400)	*b*
sulfenamide	$(en)_2Co(S(NH(CH_3))CH_2CH_2NH_2)^{3+}$		474 (198)	310 (3580) sh	270 (5370)	*b*

[a] Wavelengths, λ, are in nm. Molar extinction coefficients, ε, given in parentheses, are in M^{-1} cm^{-1}. Spectra are recorded in dilute aqueous acid. [b] This work.

Scheme I



(Scheme I): reaction with H_2O_2 yields a coordinated sulfenic acid,[4-6] with *N*-thiophthalimides yields coordinated disulfides,[7] and with molecular iodine yields a coordinated sulfenyl iodide.[8]

In order to extend this type of group-transfer redox reaction to the synthesis of other coordinated sulfenyl ligands, we have investigated the oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by hydroxylamine-*O*-sulfonic acid, NH_3OSO_3. This compound is a rather good NH_2^+ donor[9] and has been used to aminate thiols (yielding sulfenamides, $RSNH_2$) and thioethers (yielding azasulfonium ions, $R_2SNH_2^+$). The reaction

$$(en)_2Co(SCH_2CH_2NH_2)^{2+} + NH_3OSO_3 \rightarrow (en)_2Co(S(NH_2)CH_2CH_2NH_2)^{3+} + HSO_4^- \quad (1)$$

does indeed occur, and in this paper we report on the kinetics of this process as well as on the structural characterization of the S-bonded sulfenamide product.

Experimental Section

Materials. All common laboratory chemicals were of reagent grade. Triply distilled water and doubly distilled perchloric acid (70–72%, G. F. Smith) were used in all kinetic experiments. Lithium perchlorate solutions were prepared by neutralizing Baker "Ultrex" lithium carbonate with perchloric acid as previously described.[10] Sephadex SP-C25 cation exchanger (sodium form) was prepared and stored as recommended by the manufacturer (Pharmacia). The perchlorate salt of (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) was prepared by a standard procedure[11] and recrystallized three times before use in kinetic experiments. Hydroxylamine-*O*-sulfonic acid (Aldrich) was used without further purification. *N*-Methylhydroxylamine-*O*-sulfonic acid was prepared by a literature procedure.[12]

(2-Aminoethanesulfenamido-*N,S*)bis(ethylenediamine)cobalt(III) Salts, $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)]X_3$ ($X = ClO_4^-$, SCN^-, and $C_2O_4^{2-}/ClO_4^-$). This complex was prepared by reaction of the thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with hydroxylamine-*O*-sulfonic acid. In a typical preparation, 10 g of $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ was dissolved in 300 mL of warm (35 °C) methanol and a stoichiometric amount (2.5 g) of NH_3OSO_3 was added. The color of the solution immediately changed from brown to yellow, and a yellow powder precipitated within minutes. This precipitate was removed by filtration and dissolved in about 50 mL of water. A solution of 0.5 M $Ba(ClO_4)_2$ was added dropwise until precipitation of $BaSO_4$ was complete. After removal of the $BaSO_4$ by filtration, the solution was concentrated by rotary evaporation until crystals just began to form. An equal volume of a saturated solution of $LiClO_4$ in ethanol was then added, and after the mixture was cooled to 4 °C, the recrystallized perchlorate salt was collected (yield ca. 40%). The thiocyanate salt was prepared by simple metathesis with KSCN. Neither the perchlorate salt nor the thiocyanate salt yielded crystals suitable for X-ray structural analysis. Similarly, small-scale preparations of a large number of other salts ($S_2O_6^{2-}$, PF_6^-, BF_4^-, $CH_2(COO)_2^{2-}$, etc.) failed to yield materials that were suitable for crystallographic analysis. Small but high-quality crystals were finally obtained by mixing equal amounts of saturated $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_3$ and saturated sodium oxalate aqueous solutions; the resulting material proved to be the mixed oxalate/perchlorate salt $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$. Visible–UV spectrophotometric parameters are reported in Table I. Anal. Calcd for $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_3\cdot H_2O$: Co, 10.11; S, 5.50; N, 14.42; Cl, 18.26. Found: Co, 9.96; S, 5.71; N, 14.21; Cl, 18.26.

(*N*-Methyl-2-aminoethanesulfenamido-*N,S*)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(S(NHCH_3)CH_2CH_2NH_2)](ClO_4)_3$. Reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with $CH_3NH_2OSO_3$ in methanol proceeds too slowly to be synthetically useful, but reaction in water (using a 10% molar excess of $CH_3NH_2OSO_3$) gives reasonable yields when the mixture is allowed to stand overnight at room temperature. Purification of the reaction mixture was effected by ion-exchange chromatography on Sephadex SP-C25, with the desired orange-brown product being eluted with 0.5 M $NaClO_4$ (pH 2). Rotary evaporation of this product band till incipient crystallization, followed by cooling at 4 °C overnight, yielded brown crystals of the desired perchlorate salt in ca. 50% yield. Visible–UV spectrophotometric parameters are reported in Table I. ^1H NMR (D_2O): δ 2.92 (s, CH_3), 3.33 (t, SCH_2), 2.80 (br m, NCH_2). Anal. Calcd for $[(en)_2Co(S(NHCH_3)CH_2CH_2NH_2)](ClO_4)_3$: C, 14.43; H, 4.47; N, 14.43; S, 5.50; Cl, 18.04. Found: C, 14.43; H, 4.78; N, 14.02; S, 5.50; Cl, 18.22.

Analyses and Procedures. Elemental analyses of solid samples were performed by Galbraith Laboratories, Inc., Knoxville, TN. Total cobalt analyses were performed by a modified Kitson Procedure.[13,14] Solutions of hydroxylamine-*O*-sulfonic acid used for kinetic experiments were analyzed iodometrically, using sodium thiosulfate titrant and starch indicator,[15] immediately before each series of experiments. Formal charges on complexes were inferred from the characteristics of their elution from Sephadex SP-C25 ion-exchange columns that had been calibrated with ions of known formal charge.

Equipment. Visible–UV spectra were recorded on a Cary 210 spectrophotometer at ambient temperature. Kinetic data were obtained

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Table II. Crystallographic Data for $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$

Crystal Properties

$a = 7.350$ (1) Å
$b = 17.290$ (5) Å
$c = 15.590$ (3) Å
$\beta = 100.76$ (2)°
crystal class: monoclinic
space group: $P2_1/c$ (No. 14)

fw = 532.32
$d_{calcd} = 1.82$ g/cm^3
$Z = 4$
$V = 1946.5$ (7) Å^3
$F(000) = 1092$

Data Collection

t: 22 °C
cryst dimens: 0.08 × 0.08 × 0.20 mm
λ(Mo K$\bar{\alpha}$): 0.71073 Å
μ(Mo K$\bar{\alpha}$): 13.2 cm^{-1}
Miller index range: $h,k,\pm l$
scan rate: variable; 4–29.2°/min
mode: ω–2θ scan
limiting sphere: $1.5° < 2\theta < 50°$
no. of unique reflcns measd: 3611
reflcns above bkgd ($|F_o| > 4\sigma(|F_o|)$): 1715

on a Cary 118B spectrophotometer equipped with a thermostated sample compartment that maintained temperature to ±0.1 C. X-ray measurements were made on a Syntex P2$_1$ diffractometer, equipped with a graphite monochromator and molybdenum target tube.

Kinetic Measurements and Calculations. All kinetic experiments were conducted in aqueous perchloric acid solutions maintained at constant 1.00 ± 0.01 M ionic strength with $LiClO_4$. Kinetics were monitored at the 282-nm ligand-to-metal charge-transfer band or the 600-nm shoulder in the visible–UV spectrum of the thiolato complex. Initial concentrations of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ were approximately 4×10^{-5} M for kinetics monitored at 282 nm and ca. 2×10^{-3} M for kinetics monitored at 600 nm. Pseudo-first-order concentration excesses of H_3NOSO_3 and H^+ over Co(III) were maintained at all times, and reactions were monitored for at least 4 half-lives. Values of the pseudo-first-order rate constant k_{obsd} and its associated standard deviation, $\sigma_{k_{obsd}}$, were obtained by nonlinear least-squares analysis[16] of OD_t–t data within the usual first-order rate expression. In calculations of second-order rate parameters and activation parameters, individual values of k_{obsd} were weighted as $(1/\sigma_{k_{obsd}})^2$. All reported errors are standard deviations.

Crystallographic Measurements and Calculations. An amber-colored, trapezoidal crystal of $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$ was mounted on the diffractometer. Unit cell parameters were derived by least-squares refinement of 16 carefully centered reflections. A summary of the crystallographic details is presented in Table II. During data collection, four standard reflections (500, 040, 004, and 22$\bar{1}$) were monitored after every 100 reflections to check crystal stability and account for long-term drift; the relative intensities of these standard reflections ranged from 0.99 to 1.07 with no systematic trend in the intensity variations. Due to the irregular shape of the crystal, ψ scans of 12 intense reflections within the range $50° \leq \chi \leq 75°$ were obtained in order to determine the extent of absorption by the crystal. Intensities observed during the scan varied less than 2% from the mean intensity of the scan, and thus no absorption corrections were applied to the intensity data. All calculations were performed on a Data General Eclipse computer using the SHELXTL[17] software.

Structure Solution and Refinement of $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$. The coordinates of the Co, Cl, and S atoms were obtained by direct methods. The remaining non-hydrogen atoms of the structure were located by difference Fourier techniques. The hydrogen atom locations were obtained from a difference density map computed after convergence of the least-squares refinement employing anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms bonded to O(9) (water) and N(1) were included at their (fixed) locations from the difference map. All other hydrogen atoms were included at their idealized positions, which were not refined. The isotropic thermal parameter for each hydrogen atom was assigned a value equal to 1.2 times the equivalent isotropic thermal parameter of the atom to which it is bonded. Final convergence of the refinement yielded $R = 0.072$ and $R_w = 0.075$. A final difference density map contained only small peaks (<0.7 e Å^{-3}) near the Co, S, Cl, and O atoms. Neutral-atom scattering curves were used for all atoms.[18] Corrections for anomalous dispersion were made for all non-hydrogen atoms.[18] The values of $10|F_o|$ and $10|F_c|$ are listed in Table A.[19]

Table III. Atom Coordinates (×10^4) for $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$[a,b]

atom	x	y	z
Co	−71 (2)	3665 (1)	−1748 (1)
Cl(1)	−3594 (4)	1449 (2)	6878 (2)
Cl(2)	3788 (5)	1412 (2)	−354 (2)
S	−2257 (4)	3868 (2)	−2944 (2)
O(1)	−5336 (14)	1495 (7)	6351 (7)
O(2)	−3514 (15)	1822 (7)	7666 (7)
O(3)	−3222 (20)	688 (8)	7037 (11)
O(4)	−2162 (15)	1733 (8)	6497 (7)
O(5)	5304 (22)	980 (9)	−417 (10)
O(6)	4311 (23)	2169 (9)	−579 (13)
O(7)	2357 (19)	1264 (10)	−1020 (10)
O(8)	3437 (29)	1468 (14)	413 (9)
O(9)	1824 (16)	−21 (7)	1174 (7)
O(10)	4892 (9)	5721 (4)	783 (4)
O(11)	2625 (8)	5013 (4)	29 (4)
N(1)	−1368 (13)	4005 (7)	−3829 (5)
N(2)	1536 (10)	3499 (4)	−599 (5)
N(3)	2091 (10)	4005 (5)	−2228 (5)
N(4)	435 (10)	2632 (5)	−2167 (5)
N(5)	−513 (10)	4739 (4)	−1397 (5)
N(6)	−2082 (11)	3225 (5)	−1202 (5)
C(11)	−1437 (14)	5242 (6)	−2116 (7)
C(12)	−3035 (14)	4782 (6)	−2625 (7)
C(13)	356 (14)	3328 (6)	48 (6)
C(14)	−1212 (14)	2835 (7)	−368 (7)
C(15)	1738 (16)	2697 (7)	−2781 (8)
C(16)	3082 (14)	3307 (7)	−2468 (8)
C(17)	4289 (12)	5207 (5)	240 (6)

[a] The estimated error in the last digit is given in parentheses. This form is used throughout. [b] The numbering scheme is shown in Figure 1.

Results

Characterization. The title complex is characterized by (1) its synthesis from $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and the known aminating agent NH_3OSO_3,[9] (2) elemental analysis of the perchlorate salt that gives an empirical composition in agreement with the proposed formulation, (3) cation-exchange elution characteristics that indicate a 3+ formal charge, (4) the visible–UV spectrophotometric parameters given in Table I, and (5) X-ray structural analysis of the mixed $ClO_4^-/C_2O_4^{2-}$ salt. The analogous complex derived from $CH_3NH_2OSO_3$ is characterized by the above methods, excluding X-ray structural analysis.

The data of Table I show that the visible–UV spectra of the sulfenamide complexes exhibit d–d bands typical of cobalt(III) complexes, as well as intense ligand-to-metal charge-transfer (LTMCT) bands in the near-UV region that characteristically arise from coordination of a sulfur to cobalt(III).[21] The complex tentatively formulated as $[(en)_2Co(S(CH_3NH)CH_2CH_2NH_2)]^{3+}$ also exhibits a shoulder at ca. 340 nm. Bands in this region of the spectrum are often observed for complexes containing a Co–S–X bonding array and have been attributed to a second LTMCT transition arises from inter-

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Table IV. Selected Bond Lengths and Angles for $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)]^{3+}$

Bond Lengths (Å)			
Co–S	2.250 (3)	Co–N(5)	1.980 (8)
Co–N(2)	1.974 (7)	Co–N(6)	1.990 (9)
Co–N(3)	1.968 (8)	S–N(1)	1.650 (10)
Co–N(4)	1.961 (8)	S–C(12)	1.782 (11)

Bond Angles (deg)			
S–Co–N(2)	171.3 (2)	N(2)–Co–N(5)	89.3 (3)
S–Co–N(3)	98.1 (2)	N(2)–Co–N(6)	85.5 (3)
S–Co–N(4)	91.0 (2)	N(3)–Co–N(4)	85.9 (3)
S–Co–N(5)	87.4 (2)	N(3)–Co–N(5)	90.6 (3)
S–Co–N(6)	86.7 (2)	N(3)–Co–N(6)	173.6 (3)
Co–S–C(12)	97.1 (3)	N(4)–Co–N(5)	175.9 (4)
Co–S–N(1)	112.5 (3)	N(4)–Co–N(6)	89.8 (4)
N(2)–Co–N(3)	90.0 (3)	N(5)–Co–N(6)	93.9 (3)
N(2)–Co–N(4)	92.9 (3)		

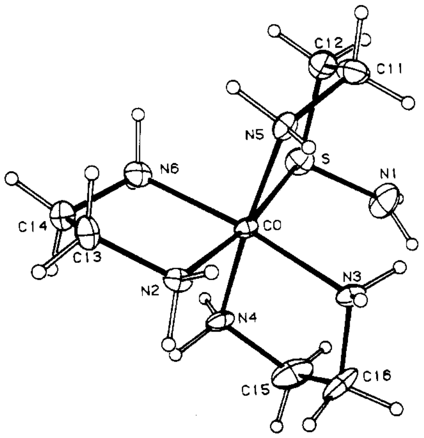

Figure 1. Perspective drawing of the $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)]^{3+}$ cation (30% probability ellipsoids). The hydrogen atoms are drawn artificially small for clarity.

action of lone electron pairs on S and X.[22]

Crystal Structure. Final crystallographic coordinates for the non-hydrogen atoms are given in Table III. Selected bond lengths and angles are presented in Table IV, while a complete listing of bond lengths, bond angles, and selected conformational angles is given in Table C.[19] Listings of anisotropic thermal parameters, possible hydrogen bonds, and hydrogen atom coordinates and temperature factors, appear in Tables D, E, and F, respectively.[19] A perspective drawing of the $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)]^{3+}$ cation is shown in Figure 1.

Kinetics. In the presence of pseudo-first-order excesses of NH_3OSO_3 and H^+, plots of ln $(OD_t - OD_\infty)$ vs. time are linear for at least 4 half-lives, indicating that the thiolato complex disappears by first-order kinetics. Values of the observed first-order rate parameters, k_{obsd}, as a function of $[NH_3OSO_3]$, $[H^+]$, temperature, monitoring wavelength, and presence of HSO_4^- are listed in Table B.[19] At constant $[H^+]$ plots of k_{obsd} vs. $[NH_3OSO_3]$ are linear with zero intercepts and thus $k_{obsd} = k_2[NH_3OSO_3]$. Values of k_2 are independent of the monitoring wavelength and the presence of 6.5×10^{-3} M HSO_4^-. Figure 2 shows that for the data at 25 °C, a plot of $1/k_2$ vs. $[H^+]$ is linear over the range $[H^+] = 0.010–1.00$ M. Thus

$$-d[\text{thiolato–Co}^{III}]/dt = k_2[NH_3OSO_3][\text{thiolato–Co}^{III}]$$

and

$$k_2 = a/(1 + b[H^+])$$

At 25 °C, $a = 3.2 \pm 0.1$ M^{-1} s^{-1} and $b = 16.4 \pm 0.6$ M^{-1}. At $[H^+] = 1.00$ M, the temperature dependence of k_2 over the range 14–45 °C is described by $\Delta H^* = 8.5 \pm 0.3$ kcal mol^{-1} and $\Delta S^* = -33 \pm 1$ eu.

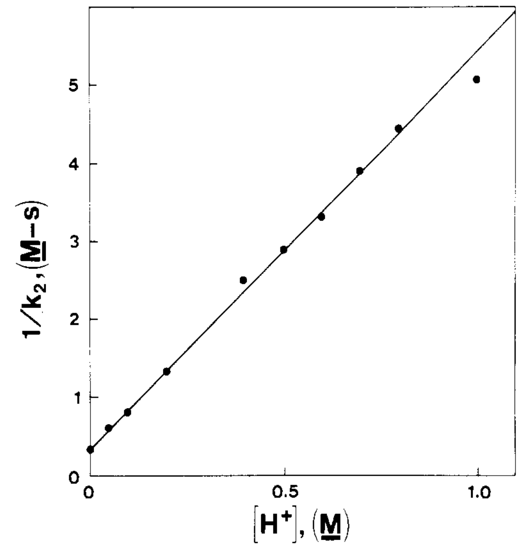

Figure 2. Plot of $1/k_2$ (M s) *vs.* $[H^+]$ (M) for the NH_3OSO_3 oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ (25 °C, μ = 1.00 M ($LiClO_4/HClO_4$)). Points at $[H^+]$ = 0.01, 0.10, 0.50, and 1.00 M represent averages of 6, 4, 4, and 10, respectively, independent determinations. The indicated line is arbitrarily drawn.

Discussion

Synthesis and Characterization. Hydroxylamine-*O*-sulfonic acid is a known[9] aminating reagent that readily transfers the NH_2^+ moiety to a variety of attacking nucleophiles. Since $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ contains a nucleophile coordinated sulfur atom,[4] reaction of this thiolato complex with hydroxylamine-*O*-sulfonic acid readily yields the NH_2^+ adduct $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)]^{3+}$ (eq 1). This NH_2^+ transfer reaction is also a redox reaction in that a coordinated thiolato ligand (RS^-) is oxidized to a sulfenamide ligand ($RSNH_2$). The identity of the S-bonded sulfenamide product is confirmed by single-crystal X-ray structural analysis of the mixed perchlorate/oxalate salt. Repeated attempts to obtain X-ray-quality single crystals of this material with other anions proved unsuccessful. Suitable crystals of the title complex presumably form because of stabilization derived from the intricate hydrogen-bonded network that involves amine and water protons and perchlorate, oxalate, and water oxygen atoms (Table E).

Reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with $CH_3NH_2OSO_3$ is much slower than is the reaction with NH_3OSO_3, presumably due to increased steric hindrance engendered by the additional methyl group. The resulting $[(en)_2Co(S(NHCH_3)CH_2CH_2NH_2)]^{3+}$ complex is also less stable than $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)]^{3+}$, undergoing very rapid Co–S bond fission in alkaline media.

The d–d transitions of the title complex and its sulfenato analogue $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ occur at approximately the same energy (474 and 470 nm; Table I), indicating that the S-bonded $RSNH_2$ and RSO^- ligands provide nearly the same ligand field strength. For complexes derived from $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$, both of these ligands provide stronger fields than do coordinated thiols (λ_{max} = 485 nm[23]) or coordinated disulfides (λ_{max} = 488–492 nm[22]). All three of the complexes $[(en)_2Co(S(X)CH_2CH_2NH_2)]^{n+}$, where X = O, NH_2^+, or $NHCH_3^+$, exhibit the characteristic sulfur-

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Table V. Rate and Activation Parameters Governing Reaction of Various Nucleophiles with Hydroxylamine-*O*-sulfonic Acid

nucleophile	k_n, M^{-1} s^{-1}	k_{nh}, M^{-1} s^{-1}	ΔH^*, kcal/mol	ΔS^*, eu	ref
$C_2H_5S^-$	32				30
$[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$	3.2	<0.02	8.5 ± 0.3^b	-33 ± 1^b	*a*
$(C_6H_5)_3P^d$	2.0		7.4 ± 0.2^c	-32 ± 1^c	28
$(NH_2)_2C{=}S$	1.6		7.4 ± 0.2^c	-32 ± 2^c	31
$S_2O_3^{2-}$	0.55		10.8 ± 0.1^c	-23 ± 1^c	31
I^-	0.069	0.023	11.6 ± 0.3^c	-24 ± 2^c	28
$(C_2H_5)_3N$	0.022				28
$HONH_2$	0.0014				30
OH^-	0.00005				30

[a] This work. [b] Activation parameters measured at $[H^+] = 1.00$ M and therefore describe essentially k_nK_a. [c] Activation parameters measured at low $[H^+]$ and therefore describe k_n. [d] Measured in 50% methanol.

to-cobalt charge-transfer transition in the UV, but only the sulfenato and *N*-methyl sulfenamide derivatives exhibit the near-UV band often observed for complexes containing a Co–S–X bonding array.[22] The origins of this near-UV band are not entirely clear but presumably involve interaction of lone pairs on the S and X atoms.[22] While both the sulfenamide and *N*-methyl sulfenamide complexes contain an appropriate lone pair on the pendant nitrogen atom, for the sulfenamide complex the predicted near-UV band appears to be too weak to be observed (Table I).

The coordinated RSO^- ligand of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ can be protonated to yield $[(en)_2Co(S(OH)CH_2CH_2NH_2)]^{3+}$, which has significantly different spectrophotometric properties from those of the unprotonated analogue.[24] However, attempts to deprotonate the title complex to yield $[(en)_2Co(S(NH)CH_2CH_2NH_2)]^{2+}$ led to rapid decomposition, and thus the spectrophotometric properties of this derivative could not be determined.

Crystal Structure. The structure consists of discrete cations, perchlorate and oxalate anions, and water molecules of hydration, all interconnected by strong hydrogen bonds (Table E). The first coordination sphere of the cationic complex has the same atom composition (5N, S) as does the parental thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$, confirming that NH_3OSO_3 oxidation of the thiolato complex occurs without Co–S bond fission. Both Δ(λλλ) (shown in Figure 1) and Λ(δδδ) isomers of the tris(chelate) cation occur in the crystal. All three of the five-atom chelate rings exhibit a half-chair conformation, with no anomalous variations in torsion angles or bond angles (Table C).

This structure is one of an extensive series involving the octahedral cobalt(III) complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and its derivatives.[3,6,7,20,25,26] Within this series it has been observed that the coordinated sulfur atom will cause a specific lengthening of the trans-situated nitrogen atom (structural trans effect, or STE) if the sulfur atom bears a formal negative charge. Complexes containing a coordinated sulfur atom bearing a zero formal charge do not exhibit a STE. Consistent with this generalization, the sulfur atom of the neutral S-bonded sulfenamide ligand of the title complex does not exert a detectable STE: average *cis*-Co–N = 1.975 (13) Å; *trans*-Co–N = 1.974 (7) Å. In this context of $[(en)_2Co(S(X)CH_2CH_2NH_2)]^{n+}$ structures, the Co–S bond length of the title complex (2.250 (3) Å) falls within the range of values observed for neutral disulfides and thioether ligands (2.272 (2)[7] and 2.267 (10)[20] Å, respectively) and for anionic sulfenato, thiolato, and sulfinato ligands (2.253 (1),[6] 2.226 (2),[25] and 2.191 (2)[26] Å, respectively).

Kinetics. Extensive studies,[27-31] especially by Krueger and co-workers, on the reactivity of hydroxylamine-*O*-sulfonic acid have shown that in acidic media both the protonated and unprotonated forms of this reagent can react with nucleophiles.

$$NH_3OSO_3 \overset{K_a}{=} NH_2OSO_3^- + H^+$$

$$\text{nuc} + NH_2OSO_3^- \xrightarrow{k_n} \text{products}$$

$$\text{nuc} + NH_3OSO_3 \xrightarrow{k_{nh}} \text{products}$$

This mechanism leads to the general rate law

$$\text{rate} = [\text{nuc}][\text{HOSA}]\left[\frac{k_n + k_{nh}[H^+]/K_a}{1 + [H^+]/K_a}\right]$$

where [HOSA] represents the total concentration of hydroxylamine-*O*-sulfonic acid in both protonated and unprotonated forms. If the term $k_{nh}[H^+]/K_a$ is much less than k_n, then this general rate law takes the form observed in this work for the reaction of hydroxylamine-*O*-sulfonic acid with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$:

$$\text{rate} = [(en)_2Co(SCH_2CH_2NH_2)^{2+}][\text{HOSA}]\left[\frac{a}{1 + b[H^+]}\right]$$

Thus, $b = 1/K_a$ and under the conditions of our studies (25 °C, $\mu = 1.00$ M ($LiClO_4$)) $1/b = K_a = 0.061 \pm 0.02$ M. This value is in good agreement with similarly derived acid dissociation constants reported by Krueger et al.[28] (0.055 M; 20 °C, $\mu = 0.1$ M ($NaOOCCH_3$)) and by Candlin and Wilkins[27] (0.033 M; 45 °C, $\mu = 1.0$ M ($NaClO_4$)), especially considering the different conditions employed in the three studies. The nonobservance of the $k_{nh}[H^+]/K_a$ numerator term in these studies implies that, even at $[H^+] = 1.0$ M, $k_{nh}[H^+]/K_a$ is less than 10% of the value of *a*; given the above derived value of K_a, this leads to the limit $k_{nh} < 0.02$ M^{-1} s^{-1} (25 °C). This limit is consistent with the observed value[29] of k_{nh} governing attack of I^- on H_3NOSO_3 ($k_{nh} = 0.023$ M^{-1} s^{-1}, 20 °C $\mu = 0.1$ M). Interestingly, while the anionic I^- reacts slightly more rapidly with $NH_2OSO_3^-$ than with NH_3OSO_3 ($k_n/k_{nh} = 3$),[28] the positive charge of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ favors reaction with $NH_2OSO_3^-$ by a considerably larger amount ($k_n/k_{nh} > 160$).

Rate and activation parameters describing the reaction of a variety of nucleophiles with hydroxylamine-*O*-sulfonic acid are given in Table V. These data show that $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is a reasonably good nucleophile toward hydroxylamine-*O*-sulfonic acid, being about as reactive as

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triphenylphosphine or thiourea. As expected, the coordinated thiolato sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is not as good a nucleophile as the noncoordinated thiolato sulfur atom of $C_2H_5S^-$, coordination to cobalt(III) reducing the nucleophilicity by about a factor of 10. However, this coordination-induced decrease in nucleophilicity toward hydroxylamine-*O*-sulfonic acid is much less than the comparable decrease in nucleophilicity towards CH_3I.[4] This observation implies that, for soft nucleophiles, cleavage of hydroxylamine-*O*-sulfonic acid is relatively insensitive to the nature of the attacking nucleophile. This implication is further supported by the small range of activation parameters observed for nucleophilic cleavage of hydroxylamine-*O*-sulfonic acid (Table V), indicating that for these soft nucleophiles it is primarily the energetics of N–O bond cleavage that dominate the activation process.

Acknowledgment. Financial support by the National Science Foundation, Grant No. CHE 79-26497, is gratefully acknowledged. We also thank L. C. Strickland, Procter & Gamble Co., for his assistance with the X-ray study.

Registry No. $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_3$, 87434-58-0; $[(en)_2Co(S(NH_2)CH_2CH_2NH_2)](ClO_4)_2(C_2O_4)_{1/2}\cdot H_2O$, 87434-62-6; $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$, 40330-50-5; $[(en)_2Co(S(NHCH_3)CH_2CH_2NH_2)](ClO_4)_3$, 87434-60-4; $HSCH_2CH_2NH_2$, 60-23-1; NH_3OSO_3, 2950-43-8; $CH_3NH_2OSO_3$, 3400-11-1.

Supplementary Material Available: Listings of $10|F_o|$ and $10|F_c|$ values (Table A), observed first-order rate parameters (Table B), bond lengths, bond angles, and torsion angles (Table C), anisotropic temperature factors (Table D), hydrogen-bond contact distances (Table E), and hydrogen atom coordinates and temperature factors (Table F) (18 pages). Ordering information is given on any current masthead page.

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Synthesis and Structures of Platinum(III) Complexes of α-Pyridone, $[X(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2X](NO_3)_2\cdot nH_2O$ ($X^- = Cl^-, NO_2^-, Br^-$)

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Received March 22, 1983

Oxidative addition of the head-to-tail platinum(II) dimer *cis*-$[Pt(NH_3)_2(C_5H_4NO)]_2^{2+}$, where C_5H_4NO is the α-pyridonate anion, with nitric acid in the presence of an excess of NO_2^-, Cl^-, or Br^- leads to crystalline platinum(III) dimers of general formula $[X(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2X](NO_3)_2\cdot nH_2O$ (**1**, **2**, and **6**, respectively). The structures of all three cations are composed of two *cis*-diammineplatinum(III) units linked in a head-to-tail fashion by two bridging α-pyridonate groups and capped on the Pt–Pt bond axis by the anionic X^- ligand. The Pt–Pt bond lengths [2.582 (1)–2.547 (1) Å] vary as $X^- = Br^- \sim NO_2^- > Cl^- > NO_3^-$, a statistically valid (30σ) trend that parallels the known trans-influence series for these ligands. The axial ligand–platinum bonds are elongated by ~0.15 Å from "normal" values, revealing the metal–metal bond itself to have a strong trans influence. Compound **1** ($X^- = NO_2^-$) is monoclinic, space group $C2/c$, with $a = 32.184$ (5) Å, $b = 8.712$ (2) Å, $c = 18.500$ (4) Å, $\beta = 124.20$ (2)°, $V = 4290$ Å^3, and $Z = 8$; **2** ($X^- = Cl^-$) is monoclinic, space group $P2_1/n$, with $a = 8.656$ (1) Å, $b = 25.728$ (3) Å, $c = 10.203$ (2) Å, $\beta = 113.45$ (2)°, $V = 2084$ Å^3, and $Z = 4$; **6** ($X^- = Br^-$) is monoclinic, space group $I2/c$, with $a = 27.059$ (5) Å, $b = 8.597$ (3) Å, $c = 18.789$ (3) Å, $\beta = 90.48$ (1)°, $V = 4371$ Å^3, and $Z = 8$.

Introduction

Until recently there have been only a few reports of binuclear compounds of platinum(III) that contain metal–metal bonds.[1-7] Consequently, the chemistry of platinum(III) complexes remains largely unexplored. Among the more thoroughly investigated examples of these compounds are the binuclear *cis*-diammineplatinum(III) complexes of α-pyridone, $[(X)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(X)]^{n+}$.[3,4] These compounds, which contain α-pyridonate ligands that bridge the Pt–Pt bond in either a head-to-head or a head-to-tail fashion, can be prepared from chemical or electrochemical oxidation of the corresponding platinum(II) dimer, $[(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2]^{2+}$.[3] Structural studies have shown that the Pt–Pt distance in the α-pyridonate-bridged complexes decreases by an average of 0.3 Å upon metal–metal bond formation. Electrochemical studies of this process show that, in the case of the head-to-tail isomer, the platinum–platinum bond is formed through a concerted two-electron charge-transfer process.[3] Metal–metal bond formation in the corresponding head-to-head isomer has also been studied in detail.[3,8] In both cases, the binuclear platinum(III) complexes contain neutral or anionic ligands (X) that occupy positions trans to the Pt–Pt bond, and consequently these complexes are structurally similar to a variety of isoelectronic rhodium(II) dimers.[9]

In a preliminary structural report,[4] it was shown that the axial ligands, X ($X = NO_2^-, NO_3^-$), in the head-to-tail α-pyridonate-bridged platinum(III) complexes are capable of influencing the platinum–platinum bond distance. While this effect has been the subject of numerous structural and theoretical studies in the case of the tetrakis(μ-carboxylato)dirhodium(II) complexes $[Rh_2(O_2CR)_4L_2]$,[9,10] the details of the

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