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Alkaline Hydrolysis of Bridged and Monodentate Sulfato Complexes of Cobalt(III). X-ray Structure of $[Co(en)_2(OS(O)_2O)]_2ZnCl_4 \cdot H_2O$ Containing *cis*-Bis(μ-sulfato) Bridges

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The previously described four-membered sulfato chelate $[Co(en)_2(O_2SO_2)]^+$ has been shown to contain *cis*-bis(μ-sulfato) bridges. The crystal structure of $[Co(en)_2(OS(O)_2O)]_2ZnCl_4 \cdot H_2O$ is reported (monoclinic, $C2/c$, a = 19.329 (8) Å, b = 13.832 (3) Å, c = 11.221 (3) Å, β = 122.12 (2)°, Z = 4). Hydrolysis leads to the *cis*-$[Co(en)_2(OSO_3)(OH_2)]^+$ cation in acidic solution ($[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $k = (7 \pm 1) \times 10^{-5}$ s^{-1}, I = 1.0 M (NaCl), 25 °C) and to *cis*-$[Co(en)_2(OSO_3)(OH)]$ in alkaline solution ($k_{OH} = 1.85 \times 10^2$ mol^{-1} dm^3 s^{-1}, I = 1.0 M (NaCl), 25 °C). Subsequent alkaline hydrolysis of *cis*-$[Co(en)_2(OSO_3)(OH)]$ follows the rate law $k_{obsd} = k_0 + k_{OH}[OH^-]$ with $k_0 = 4.1 \times 10^{-3}$ s^{-1} and k_{OH} = 0.22 mol^{-1} dm^3 s^{-1} (I = 1.0 M ($NaClO_4$), 25 °C) and results in *cis*-$[Co(en)_2(OH)_2]^+$ and SO_4^{2-}.

Introduction

During our investigations into the mechanisms of chelate ring opening and closing in cobalt(III) complexes we have had cause to reexamine the supposed four-membered sulfato chelate $[Co(en)_2(O_2SO_2)]X$ ($X = Br^-, ClO_4^-$) described many years ago by Barraclough and Tobe[1] and used in a subsequent kinetic investigation by Barraclough and Murray.[2] Barraclough and Tobe[1] describe its preparation by heating the solid intermediate aqua monodentate $[Co(en)_2(OH_2)(OSO_3)]Br \cdot H_2O$ or $[Co(en)_2(OH_2)(OSO_3)]ClO_4$ at 100 °C for 24 h. The bromide salt $[Co(en)_2(O_2SO_2)]Br$ could be recrystallized from cold water and converted by metathesis to the corresponding perchlorate salt. The purple-red product has a distinctive absorption at about 600 nm, and the bromide salt was reported to have a molecular weight and conductivity characteristic of a 1:1 electrolyte. Its infrared spectrum, however, could not be distinguished from that expected for bridging sulfate.

In this report we characterize by X-ray analysis this chelated complex as containing *cis*-bis(μ-sulfato) groups within the dimeric cation $[Co(en)_2(OS(O)_2O)]_2^{2+}$. We also report its hydrolysis under alkaline conditions as well as the hydrolysis of the cis-monodentate species $[Co(en)_2(OH)(OSO_3)]$ since these aspects were not considered by Barraclough and Murray.[2]

Experimental Section

Preparations. *cis*-$[Co(en)_2(OH_2)(OSO_3)]X$ ($X = OAc^-, ClO_4^-$). *trans*-$[Co(en)_2(OH_2)_2](ClO_4)_3$[3] (20.54 g, 40 mmol) and $Li_2SO_4 \cdot H_2O$ (7.68 g, 60 mmol) in water (50 cm^3) was maintained at ~50 °C for 16 h. The red-purple solution was then diluted with water (25 cm^3) and loaded onto a short column (7 × 7 cm) of Dowex 50W-X2 cation-exchange resin in the lutidinium form (column preparation: H^+ form treated with NaCl/NaOH, Na^+ form treated with 2 M lutidine acetate). When the column was washed with water, a small violet band was removed (anionic or uncharged) and red-purple $[Co(en)_2(OH_2)(OSO_3)]^+$ was then eluted with lutidine acetate (2 mol dm^{-3}). This fraction was quickly reduced to almost dryness (rotavaporation, 45 °C), the residue transferred to a beaker with a minimum volume of water, and this solution cooled in ice. When the beaker was scratched, the acetate salt ($X = OAc^-$) began to crystallize and this was aided by small additions of MeOH. The fine red crystals (3.5 g) were collected, washed with MeOH and Et_2O, and dried in air. Anal. Calcd for $[Co(en)_2(OH_2)(OSO_3)](CH_3CO_2)$: C, 20.46; H, 6.01; N, 15.91. Found: C, 19.78; H, 6.09; N, 15.63. ^1H NMR (90 MHz, D_2O, ppm from NaTPS): 1.6 (3), OAc^-; 2.2–2.4 (4), ethylenediamine CH; 2.5–2.8 (4), ethylenediamine CH; 5.55 (4), NH; 5.8 (4), NH. Addition of $NaClO_4$ to a concentrated aqueous solution of the acetate salt resulted in red needles of $[Co(en)_2(OH_2)(OSO_3)]ClO_4$. This was easily recrystallized from warm water by the addition of $NaClO_4$. Anal. Calcd: C, 12.23; H, 4.62; N, 14.27; S, 8.17. Found: C, 11.93, H, 4.64; N, 14.11; S, 7.99. Visible spectrum (λ_{max}, nm (absorptivity, mol^{-1} dm^3 cm^{-1}): in water at pH 3.05, 502 (102), 363 (77); in water at pH 7.56, 512 (94), 365 (70). The bromide salt was similarly prepared by the addition of NaBr.

Dimeric $[Co(en)_2(OS(O)_2O)]_2Br_2 \cdot 2H_2O$ and $[Co(en)_2(OS(O)_2O)]_2ZnCl_4 \cdot H_2O$. $[Co(en)_2(OH_2)(OSO_3)]ClO_4$ was heated at 110 °C in vacuo (10^{-2} mmHg) for 5 h. (*Caution!*) The red color rapidly deepened to purple, and a mass loss corresponding to one H_2O occurred. This material was ground with 1.1 mol equiv of tetraphenylarsenic(V) chloride in a small amount of water, the mixture filtered, and a concentrated aqueous solution of NaBr added dropwise to the cooled filtrate. Purple $[Co(en)_2(OS(O)_2O)]_2Br_2 \cdot 2H_2O$ deposited. This material was recrystallized by rapid solution in warm water and cooling. Anal. Calcd: C, 12.31; H, 5.16; N, 14.36; S, 8.21; Br, 20.48. Found: C, 12.11; H, 4.72; N, 14.38; S, 8.18; Br, 21.16. Visible spectrum (λ, nm (absorptivity, mol^{-1} dm^3 cm^{-1})): 503 (220), 370 (73). Crystals suitable for X-ray analysis were prepared by adding $ZnCl_2$ to an aqueous acidic (dilute HCl) solution of the bromide salt and cooling in an ice bath, followed by a similar recrystallization. The $ZnCl_4^{2-}$ salt is more soluble in water than the Br^- salt; the ClO_4^- salt is almost insoluble in water.[1]

Kinetic Data. Rate data were obtained with a Cary 219 spectrophotometer with the cell compartment thermostated at 25.0 °C. Solutions of $[Co(en)_2(OS(O)_2O)]_2Br_2 \cdot 2H_2O$ in water were kept in an ice–water bath and were used within 2 h; solutions of $[Co(en)_2(H_2O)(OSO_3)]ClO_4$ were made up in 1.0 M $NaClO_4$.

Data Collection and Reduction. Crystals of $[Co(en)_2(OS(O)_2O)]_2ZnCl_4 \cdot H_2O$ were grown as described above, and a red-purple plate was selected and used for data collection. Precession photography using Cu Kα radiation showed a *C*-centered monoclinic unit cell with absences consistent with the space group *Cc* or $C2/c$. Success of the refinement confirmed the space group as $C2/c$ (No. 15).[4] Relevant details of the crystal, data collections, and refinements are summarized in Table I. Data were processed and analytical absorption corrections applied by using programs from the SHELXTL package.[5]

Structure Solution and Refinement. The structure was solved by direct methods using the TREF option of the program SHELXS-86.[6] This showed the Zn atom on the special position 0, *y*, $^1/_4$ (Wyckoff symmetry position type e)[5] consistent with $Z = 4$, together with the Co, both Cl atoms, the S atom, and two of the sulfate oxygens. The remaining non-hydrogen atoms were found by least-squares refinement and difference Fourier cycles using the program SHELX-76.[7] A difference map at this stage showed a high peak, ~4.5 e Å^{-3}, also lying on the 2-fold axis, and this was assigned to the oxygen atom of a water molecule of crystallization. The presence of a solvent molecule was expected from the analytical data, and its inclusion improved the agreement between the observed and calculated crystal densities.

Refinement continued by including the hydrogen atoms of the ethylenediamine ligands as fixed contributions to F_c (r_{E-H} = 0.98 Å) with

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Table I. Crystal Data, Data Collection, and Refinement of $[Co(en)_2(OS(O)_2O)]_2ZnCl_4 \cdot H_2O$

Crystal Data

formula: $C_8H_{34}O_9N_8S_2Cl_4Co_2Zn$
fw: 775.59
cryst syst: monoclinic
space group: $C2/c$ (No. 15)[4]
$a = 19.329$ (8) Å
$b = 13.832$ (3) Å
$c = 11.221$ (3) Å
$\beta = 122.12$ (2)°
$V = 2541$ (1) Å^3
$D_{calcd} = 2.03$ g cm^{-3}
$D_{measd} = 1.98$ g cm^{-3} (flotation)
$Z = 4$
$F(000) = 1303.9$
cryst size: 0.42 × 0.11 × 0.08 mm
μ(Mo Kα) = 29.36 cm^{-1}

Data Collection and Refinement

diffractometer: Nicolet P3
temp: 233 ± 5 K
radiation: Mo Kα ($\lambda = 0.71069$ Å)
monochromator: graphite
scan type: θ–2θ
scan speed: 4.88° min^{-1}
data limits: $4 < 2\theta < 45°$
reflns measd: $h,k,\pm l$
total no. of reflns collected: 1688
abs corr: analytical[a]
transmission: 0.8119 (max), 0.7135 (min)
cryst decay: <1%[b]
no. of unique data: 1376 ($I > 2\sigma(I)$)
$R_{merg} = 0.03$
no. of variables: 154
$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.042$
$R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o| = 0.043$
$w = 3.1101/(\sigma^2F + 0.000257F^2)$

[a] See ref 7. [b] Standard reflections (600), (0,10,0), and (0,0,10) measured after every 100 reflections.

Table II. Final Positional and Equivalent Thermal Parameters for $[Co(en)_2(OS(O)_2O)]_2 \cdot ZnCl_4 \cdot H_2O$

atom	x/a	y/b	z/c	U_{eq},[a] Å^2
Zn(1)	0.0000	−0.2330 (1)	0.2500	0.0195
Cl(1)	−0.1006 (1)	−0.3285 (1)	0.0837 (2)	0.0224
Cl(2)	−0.0622 (1)	−0.1300 (1)	0.3237 (2)	0.0261
Co(1)	0.2307 (1)	−0.3420 (1)	0.1357 (1)	0.0119
S(1)	0.1968 (1)	−0.3609 (1)	−0.1716 (2)	0.0121
O(1)	0.2466 (3)	−0.3806 (3)	−0.0155 (4)	0.013
O(2)	0.1194 (3)	−0.4109 (3)	−0.2358 (4)	0.019
O(3)	0.1817 (3)	−0.2531 (3)	−0.1909 (4)	0.012
O(4)	0.2459 (3)	−0.3905 (3)	−0.2285 (4)	0.015
N(1)	0.1387 (3)	−0.2534 (4)	0.0243 (6)	0.014
N(2)	0.1474 (3)	−0.4403 (4)	0.0758 (6)	0.020
C(1)	0.0590 (4)	−0.3057 (5)	−0.0527 (7)	0.017
C(2)	0.0670 (4)	−0.3946 (5)	0.0310 (8)	0.028
N(3)	0.2329 (3)	−0.3098 (4)	0.3065 (5)	0.015
N(4)	0.3194 (3)	−0.4316 (4)	0.2511 (5)	0.018
C(3)	0.2818 (5)	−0.3842 (5)	0.4178 (7)	0.024
C(4)	0.3533 (4)	−0.4106 (5)	0.4029 (7)	0.027
O(5)	0.0000	−0.9177 (7)	0.2500	0.123

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i \cdot a_j$.

fixed isotropic temperature factors. Scattering factors for the Zn and Co atoms and corrections for anomalous dispersion were taken from the usual compilation.[8] The non-hydrogen atoms were refined anisotropically, and a weighting scheme based on counting statistics was introduced. Refinement of this model converged with $R = 0.042$ and $R_w = 0.043$. A final difference Fourier synthesis showed a number of peaks in the range 0.7–0.8 e Å^{-3} in the vicinity of the Zn and Cl atoms of the anion, but they were too close (<1.0 Å) to be of chemical significance. Other high peaks were found close to the solvate oxygen, which may be due to hydrogen atoms, but these were not refined.

Positional parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms of $[Co(en)_2(OS(O)_2O)]_2ZnCl_4 \cdot H_2O$ are given in Table II with selected interatomic distances and angles in Table III. Data deposited as supplementary material include listings of the anisotropic thermal parameters (Table S1), positional and thermal parameters for the calculated hydrogen atoms (Table S2), observed and calculated structure factors (Table S3), and equations of selected least-squares planes (Table S4).[9]

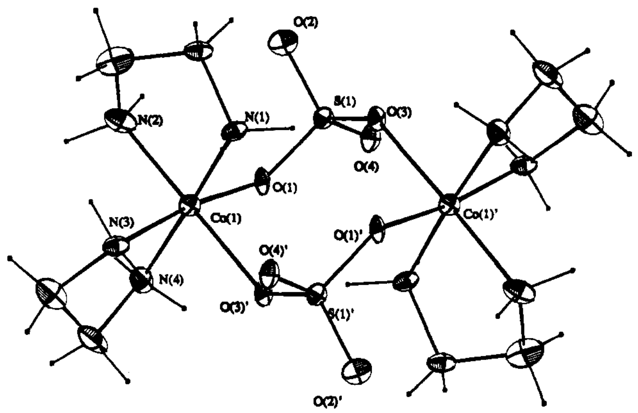

Figure 1. View of the $[Co(en)_2(OS(O)_2O)]_2^{2+}$ cation showing the atom-numbering scheme for the unique portion of the molecule. Thermal ellipsoids are drawn at the 50% probability level.

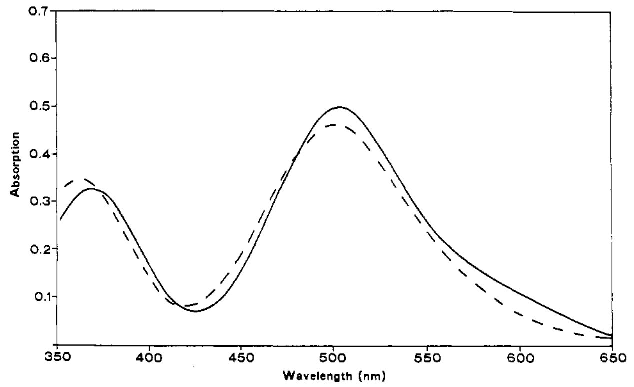

Figure 2. Visible spectra (—) of a 4.53×10^{-3} mol dm^{-3} solution of $[Co(en)_2(OS(O)_2O)]_2Br_2 \cdot 2H_2O$ in water at pH ~3 and (--) of the same solution after 16 h at pH ~3, when it represents *cis*-$[Co(en)_2(OH_2)(OSO_3)]^+$.

Results and Discussion

The major result of this study is that a simple four-membered sulfato chelate of cobalt(III) has yet to be described, although the related thiosulfato chelate (S,O-coordination) is known.[15]

Syntheses. The Barraclough and Tobe preparation of $[Co(en)_2(OH_2)(OSO_3)]Br$ involved the treatment of *trans*-$[Co(en)_2Cl_2]Cl$ with concentrated H_2SO_4, followed by aquation of the resulting $[Co(en)_2(OSO_3)_2]^-$ intermediate and slow crystallization in the presence of LiBr at 0 °C over 3 days.[1] In our hands this procedure gave low yields of an impure product and was not very satisfactory, although the correct material was obtained following recrystallization. Our synthesis gives much higher yields and follows that used in preparing the cis and trans monodentate oxalato complexes.[10] Treatment of the readily obtainable[3] *trans*-$[Co(en)_2(H_2O)_2](ClO_4)_3$ with Li_2SO_4 at 50 °C overnight resulted in largely $[Co(en)_2(OH_2)(OSO_3)]^+$, which was readily isolated by ion-exchange chromatography. Elution with lutidinium (or pyridinium) acetate at pH ~4 separated the required red 1+ complex from other minor products. Chromatography gave no indication of separate trans and cis 1+ bands (as was found in the oxalato preparation[10]), and the isolated $[Co(en)_2(OH_2)(OSO_3)](OAc)$ product is tentatively assigned the cis configuration. Its visible spectrum resembles that for *cis*-$[Co(en)_2(OH_2)(OC_2O_3)]^+$ and is very different from that found for *trans*-$[Co(en)_2(OH_2)(OC_2O_3)]^+$;[11] trans isomers of this type invariably have asymmetric absorptions in the vicinity of 540–550

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Table III. Bond Lengths and Angles for $[Co(en)_2(OS(O)_2O)]_2ZnCl_4{\cdot}H_2O$

	Bond Lengths (Å)		
Co(1)–O(1)	1.954 (4)	S(1)–O(4)	1.455 (4)
Co(1)–O(3)[a]	1.966 (4)	N(1)–C(1)	1.492 (8)
Co(1)–N(1)	1.965 (5)	N(2)–C(2)	1.494 (9)
Co(1)–N(2)	1.935 (5)	C(1)–C(2)	1.505 (10)
Co(1)–N(3)	1.945 (5)	N(3)–C(3)	1.502 (8)
Co(1)–N(4)	1.947 (5)	N(4)–C(4)	1.492 (8)
S(1)–O(1)	1.508 (4)	C(3)–C(4)	1.522 (10)
S(1)–O(2)	1.446 (5)	Zn(1)–Cl(1)	2.269 (2)
S(1)–O(3)	1.513 (4)	Zn(1)–Cl(2)	2.284 (2)
	Bond Angles (deg)		
O(1)–Co(1)–N(1)	97.2 (2)	O(1)–S(1)–O(2)	110.1 (3)
O(1)–Co(1)–N(2)	89.6 (2)	O(1)–S(1)–O(3)	107.5 (2)
O(1)–Co(1)–N(3)	170.8 (2)	O(1)–S(1)–O(4)	107.2 (3)
O(1)–Co(1)–N(4)	85.0 (2)	O(2)–S(1)–O(3)	109.3 (3)
O(1)–Co(1)–O(3)	87.1 (2)	O(2)–S(1)–O(4)	113.0 (3)
O(3)–Co(1)–N(1)	96.8 (2)	O(3)–S(1)–O(4)	109.6 (2)
O(3)–Co(1)–N(2)	176.4 (2)	Co(1)–O(1)–S(1)	131.4 (3)
O(3)–Co(1)–N(3)	88.5 (2)	Co(1)–N(1)–C(1)	111.9 (4)
O(3)–Co(1)–N(4)	84.9 (2)	Co(1)–N(2)–C(2)	110.1 (4)
N(1)–Co(1)–N(2)	85.0 (2)	N(1)–C(1)–C(2)	107.6 (5)
N(1)–Co(1)–N(3)	91.3 (2)	N(2)–C(2)–C(1)	107.4 (5)
N(1)–Co(1)–N(4)	177.2 (2)	Co(1)–N(3)–C(3)	109.7 (4)
N(2)–Co(1)–N(3)	94.6 (2)	Co(1)–N(4)–C(4)	109.4 (4)
N(2)–Co(1)–N(4)	93.4 (2)	N(3)–C(3)–C(4)	106.3 (6)
N(3)–Co(1)–N(4)	86.6 (2)	N(4)–C(4)–C(3)	107.4 (6)
		Cl(1)–Zn(1)–Cl(2)	106.0 (1)

[a] Symmetry transformations: $^1/_2 - x$, $^1/_2 - y$, $-z$.

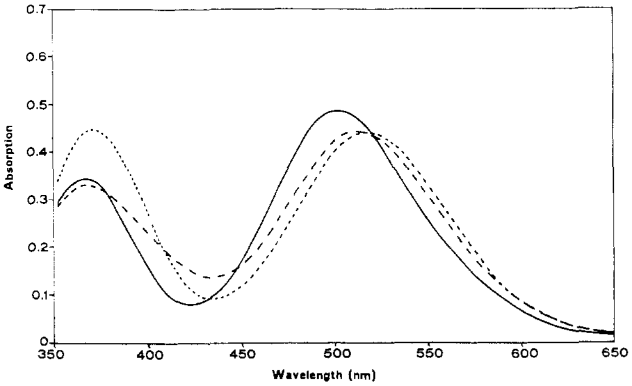

Figure 3. Visible spectra (—) of a 9.54×10^{-3} mol dm^{-3} aqueous solution of *cis*-$[Co(en)_2(OH_2)(OSO_3)]ClO_4$, (– –) of the same solution recorded immediately after adjustment to pH 7.56, when it represents *cis*-$[Co(en)_2(OH)(OSO_3)]$, and (- - -) of this solution after adjustment to pH ~13, when it represents the hydrolysis product *cis*-$[Co(en)_2(OH)_2]^+$ (path length 2 cm).

nm with about half the molar extinction coefficients of their corresponding cis isomers. Also, hydrolysis of $[Co(en)_2(OH_2)(OSO_3)]ClO_4$ in strong alkali immediately gives *cis*-$[Co(en)_2(OH)_2]^+$,[12] and hydrolysis of the cis-bridged species in acid solution gives a spectrum identical with that found for the isolated product (comparisons in Figures 2 and 3). Both reactions are likely to give structurally retentive products, especially the reaction in acid. Thus, there seems to be little doubt that the isolated product is *cis*-$[Co(en)_2(OH_2)(OSO_3)]Y$ ($Y = OAc^-$, Br^-, ClO_4^-). The bromide and perchlorate salts were obtained by adding LiBr and $NaClO_4$, respectively, to the very soluble acetate salt, and all three salts gave identical visible spectra (λ_{max} 502 nm, ϵ 102 mol^{-1} dm^3 cm^{-1}; Figure 3), which are essentially the same as that reported by Barraclough and Tobe.[1]

The bridged *cis*-$[Co(en)_2(OS(O)_2O)]_2^{2+}$ ion, previously described as the four-membered chelate,[1] could in our hands only be prepared by heating (at ~60 °C under the heat lamp was sufficient) the perchlorate salt of the monodentate sulfato complex $[Co(en)_2(OH_2)(OSO_3)]ClO_4$. Overnight pyrolysis at 120 °C of the acetate or bromide salts did not lead to the same product, although Barraclough and Tobe reported success for their bromide salt.[1] Thus, the acetate salt showed little color change on heating and lacked the increased absorption at 580–620 nm that characterizes the bridged species. Its aqueous solution did however give a small OD decrease at 600 nm on standing ($t_{1/2} \approx 50$ min). The bromide salt turned deep red-purple on heating and gave a product that was very soluble in water. Its absorption spectrum had λ_{max} at 528 nm and high extinctions below 400 nm. There was no characteristic absorption at 580–620 nm. Subsequent spectral changes included a large OD decrease at 350 nm. This could result from aquation of coordinated Br^- in a *cis*- or *trans*-$[Co(en)_2(OSO_3)Br]$ product, or from opening up of the long-sought-after four-membered chelate $[Co(en)_2(O_2SO_2)]^+$. Apparently the product of this composition reported earlier by Duff[13] is an aqua–sulfato complex that has properties similar to those given above.[1] But perhaps these aspects warrant careful reexamination.

The almost insoluble $[Co(en)_2(OS(O)_2O)]_2(ClO_4)_2$ product produced by pyrolyzing $[Co(en)_2(OH_2)(OSO_3)]ClO_4$ was readily converted with $(C_6H_5)_4AsCl$ to the very soluble purple chloride salt, from which the less soluble Br^- salt was easily obtained. Visible spectra of the various salts $[Co(en)_2(OS(O)_2O)]_2X$ ($X = Br_2{\cdot}2H_2O$, $(ClO_4)_2$, $ZnCl_4{\cdot}H_2O$) were indistinguishable and have a characteristic shoulder in the 580–630-nm region ($\epsilon_{600} = 26$ mol^{-1} dm^3 cm^{-1}). Our spectrum and the subsequent changes in it correspond to those already reported.[1,2]

Crystal Structure of $[Co(en)_2(OS(O)_2O)]_2ZnCl_4{\cdot}H_2O$. The structure consists of independent $[Co(en)_2(OS(O)_2O)_2Co(en)_2]^{2+}$ cations, $ZnCl_4^{2-}$ anions, and water molecules. The structure of the $[Co(en)_2(\mu\text{-}OS(O)_2O)_2Co(en)_2]^{2+}$ cation is shown in Figure 1. Coordination about the two cobalt atoms is distorted-octahedral with the ethylenediamine ligands adopting $\lambda\lambda$ and $\delta\delta$ conformations in the centrosymmetrically related halves of the dimeric cation. The mean Co–N(en) bond distance, 1.95 (1) Å, is unremarkable. The cobalt atoms are bridged by a pair of sulfato ligands such that O(1) of one sulfato ligand binds to Co(1) with O(3) binding to Co(1)′ via the symmetry transformation $^1/_2 - x$, $^1/_2 - y$, $-z$. Hence, the $Co(en)_2OSO_3$ fragment completely defines the cation unit in the structure. The O atoms of the sulfato bridges occupy cis positions on each Co atom.

The geometry of the bridging sulfato deviates little from the expected tetrahedral with O–S–O angles in the range 107.5–113.0°. There are, however, significant differences between the exocyclic (average 1.450 (4) Å) and endocyclic (average 1.510 (2) Å) S–O bond distances. A similar variation has been reported for the μ-SO_4,NH_2 complex,[14] and this was ascribed to variations in bond order between the free and coordinated S–O bonds. Interestingly, the more highly strained chelated thiosulfato complex $[Co(en)_2S_2O_3]ClO_4$[15] shows the reverse effect. The central eight-membered Co(–O–S–O–)$_2$Co ring system in the present molecule is puckered, with the Co(1), S(1), Co(1)′, and S(1)′ atoms strictly coplanar, while the O(1) and O(3) atoms are displaced to opposite sides of the plane by 0.611 (6) and 0.343 (5) Å, respectively.

Hydrolysis Kinetics. (a) Bridged Complex. Hydrolysis was followed by monitoring the decrease in OD at 600 nm in the absence of added electrolyte ($I = 0.01$ M, pH ~3), in 1.0 M NaCl at pH ~4, and in 1.0 and 0.1 M HCl ($I = 1.0$ M (NaCl)). Figure 2 gives the spectra of the reactant and the product after 16 h. Good first-order data were obtained, and the rate constants 9.3×10^{-5}, 7.1×10^{-5}, 7.4×10^{-5}, and 7.4×10^{-5} s^{-1} respectively are to be compared with values in the range $(6.5–9.7) \times 10^{-5}$ s^{-1} reported by Barraclough and Murray[2] at lower acidities and ionic strengths. The absence of an acid-catalyzed pathway up to 1.0 mol dm^{-3} [H^+] contrasts with the rapid acid-catalyzed ring-

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Table IV. Rate Data for the Alkaline Hydrolysis of the Cis-Bridged Complex Ion $[Co(en)_2(OS(O)_2O)]_2^{2+}$ (25.0 °C, I = 1.0 M (NaCl))[a]

pH[b]	$10^5[OH^-]$,[c] mol dm^{-3}	10^3k_{obsd}, s^{-1}	$10^{-2}k_{obsd}/[OH^-]$, mol^{-1} dm^3 s^{-1}
9.12	2.24	40.8	1.82
8.87	1.29	23.9	1.85
8.54	0.59	12.2	2.07
8.22	0.28	3.38	1.21

[a] [Co] = 5.0×10^{-3} mol dm^{-3}. [b] 0.1 mol dm^{-3} TRIS buffers (I = 1.0 M (NaCl)). [c] Calculated by using pK_w = 13.77 in 1.0 mol dm^{-3} NaCl.

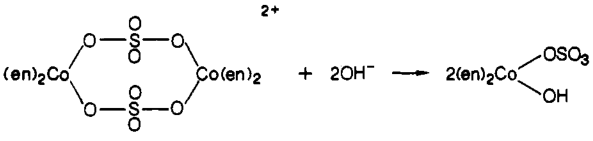
Table V. Comparisons of Rate Data for the Alkaline Hydrolysis of Sulfato, Carbonato, and Phosphato Complexes of Cobalt(III) (25 °C, I = 1.0 M)

	k_{OH}, mol^{-1} dm^3 s^{-1}	ref
$[Co(en)_2(OS(O)_2O)]_2^{2+}$	1.85×10^2	this work
$[Co(en)_2(O_2CO)]^+$ (chelate)	3.2×10^{-3}	18
$[Co(en)_2(O_2PO_2)]$ (chelate)	1.6×10^{-2}	21
$[Co(en)_2(OH)(OSO_3)]$	0.22	this work
$[Co(en)_2(OH)(OCO_2)]$	4.7×10^{-5}	18
$[Co(en)_2(OH)(OPO_3)]^-$	$\sim 1 \times 10^{-6}$	17d[a]

[a] Calculated from activation energy data and rates measured at higher temperatures.

opening reactions of bidentate carbonate[16] and phosphate.[17b]

An OD increase at 575 nm was used to follow hydrolysis under alkaline conditions with *cis*-$[Co(en)_2(OH)(OSO_3)]$ resulting (eq 1). The cis configuration was confirmed by quenching to pH

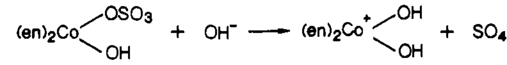


(1)

~3 after 6 half-lives, when the visible spectrum was indistinguishable from that for isolated *cis*-$[Co(en)_2(OH_2)(OSO_3)]ClO_4$.

Rate data are given in Table IV. A first order in $[OH^-]$ dependence is observed over the limited pH range 8.22–9.12, $k_{obsd} = k_{OH}[OH^-]$, with $k_{OH} = 1.85 \times 10^2$ mol^{-1} dm^3 s^{-1} at 25 °C and I = 1.0 M (NaCl). This rather rapid reaction is to be compared with the much slower opening of bidentate carbonate and phosphate chelates in alkaline solution; Table V gives comparative data. It is likely that Co–O bond fission is involved, as it is for the carbonato[18] and phosphato[19] chelates, but this has not been established.

(b) Monodentate Complex. Hydrolysis of *cis*-$[Co(en)_2(OH)(OSO_3)]$ in strongly alkaline solution gives rise to *cis*-$[Co(en)_2(OH)_2]^+$ (eq 2). This was shown by the extinctions and



$$(en)_2Co(OSO_3)(OH) + OH^- \longrightarrow (en)_2Co^+(OH)(OH) + SO_4^{2-} \quad (2)$$

band positions of the product (Figure 3; ϵ_{518} = 92 mol^{-1} dm^3 cm^{-1}, ϵ_{371} = 94 mol^{-1} dm^3 cm^{-1}). Authentic *cis*-$[Co(en)_2(OH)_2]^+$ has ϵ_{520} = 94 mol^{-1} dm^3 cm^{-1} and ϵ_{370} = 101 mol^{-1} dm^3 cm^{-1}, and *trans*-$[Co(en)_2(OH)_2]^+$ has $\epsilon_{520} = \epsilon_{370}$ = 50 mol^{-1} dm^3 cm^{-1}, in 1 M electrolyte.[12] In less alkaline solution subsequent cis → trans isomerization in the immediate product complicates the kinetics and it cannot be stated with certainty that the k_0 term (see below) results entirely in *cis*-$[Co(en)_2(OH)_2]^+$. However, spectral evidence suggests this to be the case.

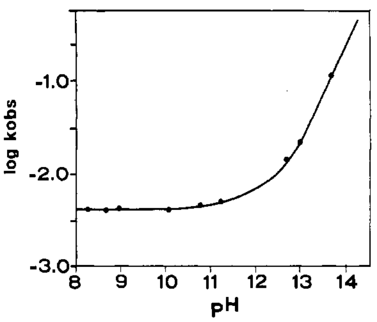


Figure 4. Plot of log k_{obsd} vs pH for the alkaline hydrolysis of *cis*-$[Co(en)_2(OH)(OSO_3)]$ at 25.0 °C and I = 1.0 M ($NaClO_4$).

Table VI. Rate Data for the Alkaline Hydrolysis of *cis*-$[Co(en)_2(OH)(OSO_3)]$ (I = 1.0 M ($NaClO_4$), 25.0 °C)

pH[a]	$[OH^-]$, mol dm^{-3}	k_{obsd}, s^{-1}	pH[a]	$[OH^-]$, mol dm^{-3}	k_{obsd}, s^{-1}
	0.5	0.112	9.85	1.20×10^{-4}	4.08×10^{-3}
	0.1	2.17×10^{-2}	8.73	9.12×10^{-6}	4.28×10^{-3}
	0.05	1.50×10^{-2}	8.43	4.57×10^{-6}	4.05×10^{-3}
11.04	1.86×10^{-3}	5.00×10^{-3}	8.07	2.00×10^{-6}	4.11×10^{-3}
10.56	6.17×10^{-4}	4.33×10^{-3}			

[a] $[OH^-]$ was calculated by using pK_w = 13.77. TRIS and NEt_3 buffers (0.1 mol dm^{-3}) were used to maintain pH.

Rate data were collected at 380 nm, where isomerization in the product can readily be allowed for (following the large OD increase this results in a small OD decrease), and data are given in Table VI. Figure 4 clearly depicts a rate law of the form

$$k_{obsd} = k_0 + k_{OH}[OH^-]$$

with $k_0 = 4.1 \times 10^{-3}$ s^{-1} and k_{OH} = 0.22 mol^{-1} dm^3 s^{-1} at 25 °C and I = 1.0 M ($NaClO_4$). The previously measured pK_a for the aqua complex (6.3 at 0 °C and 1 mol dm^{-3} $NaClO_4$)[2] ensures that the reactant is in the hydroxo form under such pH conditions. Comparisons show that k_{OH} is some 4 times greater than that for monodentate sulfate in $[Co(NH_3)_5(OSO_3)]^+$ ($k_{OH} = 4.9 \times 10^{-2}$ mol^{-1} dm^3 s^{-1})[20] and that the enhanced rate for the bridged sulfato complex compared to those for $[Co(en)_2(O_2CO)]^+$ and $[Co(en)_2(O_2PO_2)]$ (factors of 5×10^4 and $\sim 1 \times 10^4$ respectively are involved; Table V) is paralleled in the hydrolysis of the corresponding monodentate complexes (5×10^3 and 2×10^5, respectively). Comparisons of k_0 for hydrolysis of the monodentate aqua ($\sim 1 \times 10^{-4}$ s^{-1} at 45.8 °C[2]) and hydroxo (4.1×10^{-3} s^{-1} at 25.0 °C) complexes implies that the cis-hydroxo ligand has an enhanced labilizing effect for aquation. This is anticipated and has received discussion elsewhere.[17d]

Acknowledgment. We wish to thank Professor G. M. Sheldrick for useful discussions regarding the structure solution.

Supplementary Material Available: Thermal parameters (Table S1), final positional and thermal parameters of calculated hydrogen atoms (Table S2), and least-squares planes[9] and distances of atoms (Å) from the planes for $[CoSO_4(en)_2]_2ZnCl_4{\cdot}H_2O$ (Table S4) (3 pages); observed and calculated structure factors (Table S3) (8 pages). Ordering information is given on any current masthead page.

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(21) Lincoln and Stranks[17a] quote a rate constant of 1.75 mol^{-1} dm^3 s^{-1} for the OH^--catalyzed ring-opening reaction, but this value is incorrect. We (unpublished data) obtain a value of 1.6×10^{-2} mol^{-1} dm^3 s^{-1} over the $[OH^-]$ range 1.0–0.05 mol dm^{-3}, and Hay and Bembi (*Inorg. Chim. Acta* **1983**, *78*, 143) give the same value (but this was incorrectly ascribed to subsequent hydrolysis of the monodentate comomplex).