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The First Oxygen-Bonded Sulfenate Ion: Crystal and Molecular Structures of Bis(ethylenediamine)(2-pyridinesulfenato-*O*)cobalt(III) and Bis(ethylenediamine)(2-pyridinesulfinato-*O*)cobalt(III)

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The first O-bonded sulfenate species $[Co(en)_2(py\text{-}SO\text{-}O)]^{2+}$ has been synthesized by isomerization of its S-bonded linkage isomer, $[Co(en)_2(pyridine\text{-}2\text{-}sulfenate\text{-}S]^{2+}$. The sulfenate ion in both forms is stabilized by coordination to the electropositive cobalt(III) ion. The driving force for the formation of the O-bonded sulfenate linkage isomer comes from the four to five membered ring expansion which accompanies the rearrangement. Crystal structures of the green O-sulfenate confirm the formulation and reveal varying amounts of a cocrystallized O-bonded sulfinate diastereomer. The cations have essentially identical structures except for the extra oxygen in the O-sulfinate. Differences in packing of cations and perchlorates give rise to two different structural types for the salts, corresponding to sulfenate-rich and sulfinate-rich phases.

Introduction

Stable sulfenic acids and their salts are rare species.[1−3] They are especially reactive, undergoing electrophilic and nucleophilic processes including disproportionation. For example, a sulfenic acid can react with itself leading to a range of products including thiosufinate, thiolsulfonate, disulfide, monomeric sulfinate and sulfonate,[1−4] and disulfide plus H_2O_2.[5,6]

Efforts to stabilize organic sulfenate focus on reducing the sulfur nucleophilicity, either electronically or sterically. Coordination to a metal ion through sulfur also greatly stabilizes the species.[7−13] Since the work of George and Watkins,[7] several such S-bonded species have been isolated and characterized, mainly derivatives of the kinetically inert Co(III) but also Ir(II), Rh(III), and Ni(II).[14−16] We were the first to crystallographically characterize such a complex,[8] while demonstrating the optical stability of the bound sulfur center. Herein, we report the first oxygen-bonded metal-stabilized sulfenate, also characterized crystallographically.[17]

Pyridine-2-thiol (py-SH) can be chelated to Co(III) through nitrogen and sulfur to form a relatively stable four-membered ring. The brown $[Co(en)_2(py\text{-}S)]^{2+}$ complex is typical.[14] We reasoned that stepwise oxidation of this complex using H_2O_2 would yield, sequentially, the S-bonded sulfenate and S-

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(1) Allison, W. S. *Acc. Chem. Res.* **1976**, *9*, 293.
(2) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 205.
(3) Patai, S. *The Chemistry of Sulfenic Acids and their Derivatives*; Wiley: Chichester, U.K., 1990.
(4) Davis, F. A.; Billmers, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 7016.
(5) Davis, F. A.; Jenkins, R. H., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 7967.
(6) Gainsford, G. J.; Jackson, W. G.; Sargeson, A. M. Results to be published.
(7) George, T. A.; Watkins, D. D. *Inorg. Chem.* **1973**, *12*, 398.
(8) Jackson, W. G., Sargeson, A. M.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1976**, *835*, 934.
(9) Deutsch, E.; Root, M. J.; Nosco, D. L. In *Advances in Inorganic and Bioorganic Mechanisms*; Sykes, A. G., Ed.; Academic Press: New York, 1983; Vol. 3, p 269.
(10) Lydon, J. D.; Deutsch, E. *Inorg. Chem.* **1982**, *21*, 3180.
(11) Konno, T.; Okamoto, K.-I.; Einaga, H.; Hidaka, J. *Chem. Lett.* **1983**, 969.
(12) Mäcke, H.; Houlding, V.; Adamson, A. W. *J. Am. Chem. Soc.* **1980**, *102*, 6888.
(13) Adzamli, I. K.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 1366.
(14) Kita, M.; Yamanari, K.; Shimura, Y. *Chem. Lett.* **1983**, 141.
(15) Kita, M.; Yamanari, K.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3272.
(16) Font, I.; Buonomo, R.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1993**, *32*, 5897.
(17) Jackson, W. G.; Rahman, A. F. M. M. Paper presented at the IC'92 Conference (Royal Australian Chemical Institute), Monash University, Dec 1992; *Abs. IC'92* **1992**, TI, p 48.

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bonded sulfinate, and each of these species, if isolated, might be induced to thermally rearrange to their O-bonded linkage isomers which would increase the ring size to the more favorable five-membered ring. [There are precedents for linkage isomerization reactions accompanied by ring expansion or ring contraction.][18−20] These expectations have now been realized, and this work deals with the sulfenate rearrangement.

Results and Discussion

The brown complex $[Co(en)_2(py\text{-}S)](ClO_4)_2$ was subjected to controlled oxidation in aqueous H_2O_2 and the orange product crystallized with H_2ZnCl_4 or $NaClO_4$. This material was characterized as the S-bonded sulfenate species, $[Co(en)_2(py\text{-}SO\text{-}S)]ZnCl_4$, from microanalysis and its characteristic UV−vis spectrum (intense 360 nm absorption),[7−9] and it was shown to be the expected mixture of two diastereomers[7,8,15] from its ^{13}C NMR spectrum in D_2O and ^1H NMR in D_2O and $Me_2SO\text{-}d_6$ (1.3:1; kinetic distribution). The diastereomers have been separated by fractional crystallization, and slow inversion at sulfur (which is usual)[18] is again demonstrated by the resistance to epimerization. Both $ZnCl_4^{2-}$ and ClO_4^- salts but especially the latter quickly develop a deep olive green color in the solid state under light. In Me_2SO solution, the orange compound turns into the green material over a period of about an hour, and this rearrangement is also catalyzed by light. The reaction is substantially slower in the dark.

In water, the S-bonded sulfenate complex behaves differently. Comparable amounts of thiolato and O-bonded sulfinato complexes result when the orange S-bonded sulfenate complex was warmed in dilute aqueous acid under normal laboratory lighting, suggesting disproportionation through O-atom transfer. It appears the S- rather than O-sulfinate arises from S- to O-rearrangement; the other disproportionation (thiolato) product is stable under the conditions. In the absence of light and air, the S-sulfenate undergoes a slow reduction to the thiol complex (∼50%); the other product (∼50%) is the isomerized, green O-sulfenate, and there was no evidence for the expected coproduct, the sulfinate complex, O- or S-bonded, a fact presently not understood.

In a separate experiment, the green O-sulfenate complex was indeed oxidized slowly in water by air, to give O-bonded sulfinate as a mixture (2:1; equilibrium distribution) of the two diastereoisomers (which have been separated), and the aerial oxidation is catalyzed by sunlight. The same oxidation is effected much more rapidly using acidic H_2O_2, but the product isomer ratio is different (1:1; kinetic distribution).

The green product from the rearrangement in Me_2SO was shown to be identical to that derived by photochemical rearrangement in the solid state, and was crystallized using ClO_4^- or $ZnCl_4^{2-}$ as counteranions. The "green" absorption band at 610 nm in the visible spectrum suggested a weak ligand field for the sulfur moiety, comparable to that of I^-. The persistence of a strong 368 nm absorption in the UV−vis spectrum, albeit less intense, and the mode of synthesis suggested that the green material was a linkage isomer of the S-bonded sulfenate.[9] The single-crystal X-ray structures were undertaken on perchlorate salts of several samples of the green O-sulfenate, **1**, **2**, and **3**, and as well, on the major diastereomer of the O-bonded sulfinate, **4**.

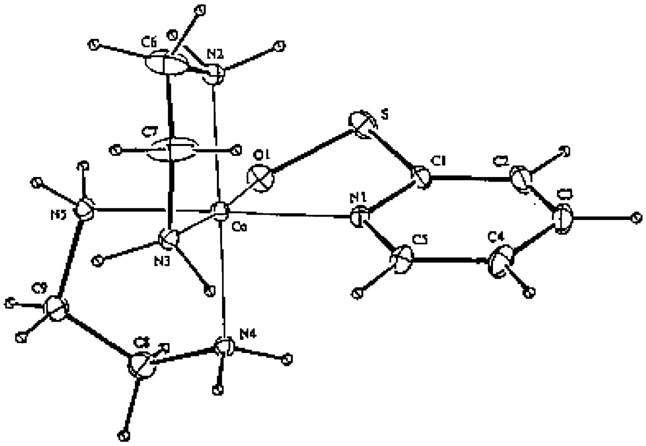

Figure 1. ORTEP diagram for the sulfenate complex (the Δ isomer is arbitrarily displayed).

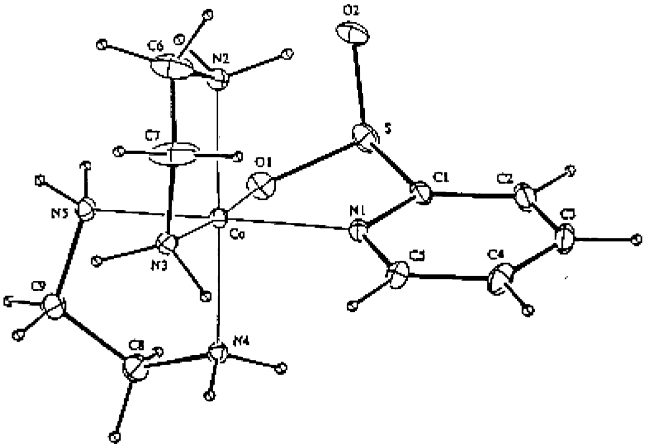

Figure 2. ORTEP diagram for one of the diastereomeric sulfinate complexes (the Δ isomer is arbitrarily displayed).

Compounds **1** and **2** have clearly similar cell dimensions and are essentially isostructural (Figure 1). Both contain the O-bonded sulfenate moiety, but one has a second oxygen with an occupancy of ca. 0.21 bonded to the sulfur in positions consistent with O-bonded sulfinate. Compound **3** has different cell dimensions, a different overall structure, and 0.83 occupancy for the second oxygen. It seemed likely that this structure would be related to that of the pure O-bonded sulfinate, and this was found to be the case (compound **4**, Figure 2; see ahead). This is an example of at least partial solid solution (or cocrystallization) between sulfenate and sulfinate end members, with each structure being able to accommodate at least ca. 20% of the other without significant distortion. What occurs outside these ranges is unknown, but it could involve either other structural types or merely a mixture of the present two. The cation

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(18) Jackson, W. G.; Sargeson, A. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, p 273.

(19) Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1988**, *27*, 1068.

(20) Gainsford, G. J.; Jackson, W. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1982**, *104*, 137.

maintains essentially the same geometry in all four structures (except for the variable content of the second oxygen). There is evidence of minor disorder in the ethylenediamine molecules, with the C−C bond being somewhat shortened in most cases, indicating that the carbon coordinates represent the average of two positions located normal to the C−C bond.

Because the structural parameters were very similar for the two cocrystallized species, compounds **2**−**3** ranging in composition from 20% to 80% O-sulfenate "impurity", we undertook the structure of the perchlorate salt of one of the two red O-sulfinate diastereomers. From the NMR spectra of the green and two red materials, we knew which pure diastereomer to choose, **4**. The structural result was very similar, except for the now 100% oxygen occupancy of one of the two S positions, the same position as that observed in the cocrystallized material. It is tempting to suggest from these results that the spacial requirements of an oxygen on sulfur are similar to that for an electron lone pair.

We have encountered the cocrystallization phenomenon previously.[6,21] One example is the Co(III) complex of diastereomeric sulfinamides derived from (*R*)-cysteine;[21] in that structure, the two cations each have an S−O group, but the oxygens differ in their orientation. These two molecules appear to be able to cocrystallize in any proportion. In the other example,[6] the cocrystallized species have −S−NH− and S−N(CH_3)− groups; again, any ratio appears to be possible. We have been unable to separate mixtures of the present O-bonded sulfenate and O-bonded sulfinate by changing the counterions, to $ZnCl_4^{2-}$ or NO_3^-. ClO_4^- for example and fractionally crystallizing the mixture, although this has been a successful strategy used previously.[21]

For the cocrystallized materials, we were curious to know if the O-sulfinate formed stereoselectively by solid state oxidation in the crystal or resulted merely from selective crystallization from preformed sulfinate. Control experiments using mixtures of the essentially pure green O-bonded sulfenate admixed with, first, one pure O-bonded sulfinate diastereomer, and second, a mixture of the two diastereomers, when crystallized, always produced crystalline crops which appeared to be microscopically homogeneous, but which contained (NMR) only the one (and same) O-bonded sulfenate isomer. Thus, it seems the green substance milks the O-bonded sulfinate isomer mixture of just the one epimeric form, and we presume the other isomer has the "wrong oxygen orientation" to allow it to cocrystallize with the O-bonded sulfenate. In further control experiments, we established that the O-bonded sulfinate impurity in the green O-bonded sulfenate compound was not formed in the solid state; it was present in the synthesized material. It was difficult to avoid entirely because we discovered that the O-bonded sulfenate is photochemically oxidized readily to the O-bonded sulfinate (vide supra), and thus, appreciable amounts can form during the recrystallization process unless due care is taken.

Several S-bonded sulfenates have now been characterized crystallographically,[8,9,22,23] but the complex reported herein is the first bonded through oxygen.[24] Clearly, the intrinsically unstable sulfenates are stabilized by metal ion coordination through either sulfur or oxygen. The S-bonded sulfenate has been likened to a sulfoxide,[18] and the structural analogy extended to the O-bonded isomer would be a sulfenate ester. These organic species are both relatively unreactive compared to the parent sulfenic acid or its anion, and this is also true of the linkage isomeric metal ion complexes; coordination to Co(III) reduces the nucleophilicity of sulfur.[9]

While O-bonded sulfenates were not known previously, it now seems that there is not an overwhelming preference for one bonding mode over the other, so that factors such as ring strain can come into play. This has been discussed previously in connection with O- and S-bonded sulfinate.[18,25]

Experimental Section

All chemicals were analytical or an equivalent grade. ^{13}C and ^{1}H NMR spectra were recorded on a Varian Unity Plus 400 MHz instrument at 25 °C. Solvents used were Me_2SO-d_6 with the central peak of the CD_3 septet as the reference (^{13}C, δ 39.37; ^{1}H, δ 2.50 ppm relative to $SiMe_4$). Product distributions were measured generally by ^{13}C NMR, but the aromatic region of the ^{1}H NMR also provided good resolution of individual species. Full visible absorption spectra were obtained with use of an HP 8452A diode-array spectrophotometer. Cation exchange media used were Dowex 50W×2 (H^+ form, 200−400 mesh; Biorad) and SP-Sephadex C25 (Na^+ form; Pharmacia). New compounds were analyzed by the Australian Microanalytical Service located in the Research School of Chemistry, ANU.

[Co(en)$_2$(py-S)](ClO$_4$)$_2$ was synthesized by the published method[14] by the anaerobic redox reaction between $Co(ClO_4)_2{\cdot}6H_2O$ (1 equiv), ethylenediamine (2 equiv) and (2-pyridyl)disulfide (0.5 equiv) in ethanol. It was purified by IEC on Dowex by elution with 2 M HCl, and the resultant Cl^- salt was recrystallized twice from water as the perchlorate. ^{1}H NMR (Me_2SO-d_6): δ 8.20 (d, 1H, CH), 7.73 (t, 1H, CH), 7.04 (t, 1H, CH), 6.98 (d, 1H, CH), 5.47 (2H, NH), 5.15 (1H, NH), 5.05 (1H, NH), 4.62 (1H, NH), 4.54 (2H, NH), 4.15 (1H, NH), 2.63(m, 8H, NH) ppm. ^{13}C NMR (Me_2SO-d_6): 175.67 (1C, CS), 149.14 (1C, CH), 137.80 (1C, CH), 125.99 (1C, CH), 118.11 (1C, CH), 45.59 (1C, CH_2), 45.01 (2C, CH_2), 44.41 (1C, CH_2).

[Co(en)$_2$(py-SO-*S*)](ClO$_4$)$_2$ was prepared from the parent thiolate (3.0 g) in water (60 mL) containing 3 M HCl (10 mL) by oxidation with H_2O_2 (30%, 3 mL), added dropwise over 2 min. After 10 min, "H_2ZnCl_4" (1 mL; 2 M $ZnCl_2$ in 5 M HCl) and *i*-PrOH (300 mL) were added to the now orange solution. The resultant precipitate was recrystallized twice from water as the $ZnCl_4^{2-}$ and also ClO_4^- salts using H_2ZnCl_4 or $NaClO_4$ (5 M) as precipitants. Yield: 2.2 g, 72% ($ZnCl_4^{2-}$). The orange needles were collected, washed with ethanol and ether, and air-dried.

Two diastereomers, isomer ratio ca. 65:35. ^{13}C NMR (D_2O). Major isomer: δ 172.5 (1C, CS), 153.3 (1C, CH), 145.1 (1C, CH), 132.0 (1C, CH), 129.2 (1C, CH), 47.6 (1C, CH_2), 47.0 (2C, CH_2),

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[21] Gainsford, G. J.; Jackson, W. G.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1981**, 875.

[22] Okamoto, K.-I.; Konno, T.; Einaga, H.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 393.

[23] Adzamli, I. K.; Libson, K.; Lydon, J. D.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 303.

[24] The chiral S center is lost in the S- to O-bonded sulfenate rearrangement.

[25] Jackson, W. G.; Jurisson, S. S.; O'Leary, M. A. *Inorg. Chem.* **1993**, *32*, 445.

Table 1. Bond Lengths and Bond and Torsional Angles for Compound **1**, $Co(C_5H_4NSO_{1.00})(C_2H_8N_2)_2(ClO_4)_2$

Interatomic Distances[a] (Å)

Co−O1	1.890(2)	N1−C1	1.352(4)	C1−S	1.741(4)	N4−C8	1.465(5)	Cl1−O41	1.427(3)
Co−N1	1.961(3)	C1−C2	1.379(5)	S−O1	1.592(3)	C8−C9	1.428(6)	Cl2−O12	1.430(3)
Co−N2	1.967(3)	C2−C3	1.371(7)	S−O2	1.439(37)	C9−N5	1.484(5)	Cl2−O22	1.399(3)
Co−N3	1.977(3)	C3−C4	1.373(7)	N2−C6	1.475(5)	Cl1−O11	1.412(4)	Cl2−O32	1.443(4)
Co−N4	1.947(3)	C4−C5	1.376(6)	C6−C7	1.392(7)	Cl1−O21	1.419(3)	Cl2−O42	1.389(4)
Co−N5	1.958(3)	C5−N1	1.351(5)	C7−N3	1.492(5)	Cl1−O31	1.441(3)		

Interatomic Angles[a] (deg)

O1−Co−N1	87.1(1)	N2−Co−N5	93.4(1)	C1−C2−C3	118.4(4)	O21−Cl1−O31	108.0(2)
O1−Co−N2	92.0(1)	N3−Co−N4	95.1(1)	C2−C3−C4	119.7(4)	O21−Cl1−O41	110.8(3)
O1−Co−N3	175.3(1)	N3−Co−N5	91.7(1)	C3−C4−C5	119.4(4)	O31−Cl1−O41	107.7(2)
O1−Co−N4	88.0(1)	N4−Co−N5	85.8(1)	C4−C5−N1	121.8(4)	O12−Cl2−O22	111.1(2)
O1−Co−N5	85.0(1)	O1−S−O2	105.5(18)	N2−C6−C7	111.7(4)	O12−Cl2−O32	105.2(2)
N1−Co−N2	91.4(1)	C1−S−O1	99.7(1)	C6−C7−N3	112.2(4)	O12−Cl2−O42	113.5(3)
N1−Co−N3	96.4(1)	C1−S−O2	114.7(16)	N4−C8−C9	110.8(3)	O22−Cl2−O32	107.0(3)
N1−Co−N4	89.4(1)	C5−N1−C1	117.8(3)	C8−C9−N5	110.5(4)	O22−Cl2−O42	113.4(3)
N1−Co−N5	170.9(1)	N1−C1−S	115.3(2)	O11−Cl1−O21	109.4(2)	O32−Cl2−O42	105.9(3)
N2−Co−N3	84.8(1)	S−C1−C2	122.0(3)	O11−Cl1−O31	110.1(2)		
N2−Co−N4	179.3(1)	N1−C1−C2	122.7(4)	O11−Cl1−O41	110.9(2)		

Torsional Angles[a] (deg)

O1−S−C1−N1	−19.9(3)	C5−N1−C1−S	178.1(3)	N1−C1−C2−C3	−0.6(6)	N2−C6−C7−N3	−38.2(7)
O1−S−C1−C2	160.8(3)	C5−N1−C1−C2	−2.6(5)	C1−C2−C3−C4	2.2(6)	N4−C8−C9−N5	42.1(6)
O2−S−C1−N1	92.2(19)	C1−N1−C5−C4	4.3(6)	C2−C3−C4−C5	−0.6(7)		
O2−S−C1−C2	−87.1(19)	S−C1−C2−C3	178.6(3)	C3−C4−C5−N1	−2.7(7)		

[a] ESD in parentheses.

Table 2. Bond Lengths and Bond and Torsional Angles for Compound **2**, $Co(C_5H_4NSO_{1.21})(C_2H_8N_2)_2(ClO_4)_2$

Interatomic Distances[a] (Å)

Co−O1	1.903(3)	N1−C1	1.356(5)	C1−S	1.750(5)	N4−C8	1.463(6)	Cl1−O41	1.429(4)
Co−N1	1.958(3)	C1−C2	1.373(6)	S−O1	1.558(3)	C8−C9	1.433(7)	Cl2−O12	1.430(4)
Co−N2	1.971(3)	C2−C3	1.371(8)	S−O2	1.429(16)	C9−N5	1.477(6)	Cl2−O22	1.396(4)
Co−N3	1.979(3)	C3−C4	1.382(8)	N2−C6	1.471(6)	Cl1−O11	1.412(4)	Cl2−O32	1.432(4)
Co−N4	1.951(3)	C4−C5	1.374(6)	C6−C7	1.394(8)	Cl1−O21	1.419(3)	Cl2−O42	1.388(4)
Co−N5	1.960(3)	C5−N1	1.343(6)	C7−N3	1.477(6)	Cl1−O31	1.443(3)		

Interatomic Angles[a] (deg)

O1−Co−N1	86.6(1)	N2−Co−N5	93.4(1)	C1−C2−C3	119.0(5)	O21−Cl1−O31	107.9(2)
O1−Co−N2	92.2(1)	N3−Co−N4	95.1(1)	C2−C3−C4	118.9(4)	O21−Cl1−O41	110.6(3)
O1−Co−N3	175.7(1)	N3−Co−N5	91.7(1)	C3−C4−C5	119.5(5)	O31−Cl1−O41	107.6(2)
O1−Co−N4	87.7(1)	N4−Co−N5	85.9(1)	C4−C5−N1	122.0(5)	O12−Cl2−O22	110.4(3)
O1−Co−N5	85.3(1)	O1−S−O2	107.3(7)	N2−C6−C7	112.4(4)	O12−Cl2−O32	105.4(3)
N1−Co−N2	91.5(1)	C1−S−O1	99.1(2)	C6−C7−N3	113.8(5)	O12−Cl2−O42	113.9(3)
N1−Co−N3	96.6(1)	C1−S−O2	112.8(7)	N4−C8−C9	111.1(4)	O22−Cl2−O32	107.6(3)
N1−Co−N4	89.2(1)	C5−N1−C1	117.9(3)	C8−C9−N5	110.7(4)	O22−Cl2−O42	112.7(3)
N1−Co−N5	170.8(1)	N1−C1−S	115.8(3)	O11−Cl1−O21	109.4(2)	O32−Cl2−O42	106.2(4)
N2−Co−N3	84.9(1)	S−C1−C2	121.7(4)	O11−Cl1−O31	110.5(3)		
N2−Co−N4	179.3(1)	N1−C1−C2	122.5(4)	O11−Cl1−O41	110.8(3)		

Torsional Angles[a] (deg)

O1−S−C1−N1	−19.9(3)	C5−N1−C1−S	178.5(3)	N1−C1−C2−C3	−1.9(7)	N2−C6−C7−N3	−32.9(9)
O1−S−C1−C2	160.0(4)	C5−N1−C1−C2	−1.5(6)	C1−C2−C3−C4	3.4(8)	N4−C8−C9−N5	41.3(7)
O2−S−C1−N1	93.3(8)	C1−N1−C5−C4	3.4(7)	C2−C3−C4−C5	−1.5(8)		
O2−S−C1−C2	−86.8(8)	S−C1−C2−C3	178.1(4)	C3−C4−C5−N1	−2.0(8)		

[a] ESD in parentheses.

46.4 (1C, CH_2) ppm. Minor isomer: δ 172.4 (1C, CS), 153.5 (1C, CH), 144.9 (1C, CH), 132.1 (1C, CH), 129.4 (1C, CH), 47.8 (1C, CH_2), 47.1 (2C, CH_2), 46.5 (1C, CH_2), 46.3 (1C, CH_2) ppm.

[Co(en)$_2$(py-SO$_2$-*S*)]ZnCl$_4$ was prepared as described for the sulfenate but allowing a 30 min reaction time. The yellow-orange product was worked up as for the sulfenate to afford 2.3 g (70%) of the pure $ZnCl_4^{2-}$ salt.

[Co(en)$_2$(py-SO-*O*)](ClO$_4$)$_2$ and [Co(en)$_2$(py-SO-*O*)]ZnCl$_4$. [Co(en)$_2$ py-SO-*S*)]ZnCl$_4$ (2.0 g, 3.9 mmol) was dissolved in DMSO (10 mL) and purged with nitrogen for 10 min. The solution was then either stirred at 20 °C for 4 h or left in the sun for 10−15 min whence the orange solution became green. This was poured into ethanol/ether (3:1 v/v) with constant stirring to precipitate a green solid which after settling was separated by decantation. The product was purified by column chromatography on Dowex (Na^+form) or SP-Sephadex (Na^+-form), using as eluant $NaClO_4$, 1.0 or 0.25 M, respectively. The eluate was reduced to near dryness by rotary evaporation at <40 °C or by fridge drying. Green crystals deposited after 48 h at 5 °C. The product was collected, washed with ethanol and ether, and air-dried. This material was recrystallized from water using "H_2ZnCl_4" to afford green needles.

Anal. Calcd for $CoC_9H_{20}N_5OSZnCl_4$: C, 21.09; H, 3.93; N, 13.67; S, 6.26. Found: C, 20.30; H, 4.11; N, 13.47; S, 5.28%.

This green complex is not very stable in solution and tends to cocrystallize with thiolato as well as O-bonded sulfinate complexes in varying proportions.

^1H NMR (Me$_2$SO-d_6): δ 8.10 (d, 1H, CH), 7.70 (t, 1H, CH), 7.42 (d, 1H, CH), 7.15 (t, 1H, CH), 5.70 (1H, NH), 5.50 (1H, NH),

Table 3. Bond Lengths and Bond and Torsional Angles for Compound **3**, $Co(C_5H_4NSO_{1.83})(C_2H_8N_2)_2(ClO_4)_2$

Interatomic Distances[a] (Å)

Co−O1	1.913(3)	N1−C1	1.354(7)	C1−S	1.800(6)	N4−C8	1.479(7)	Cl1−O41	1.415(6)
Co−N1	1.957(4)	C1−C2	1.378(8)	S−O1	1.534(4)	C8−C9	1.523(8)	Cl2−O12	1.425(5)
Co−N2	1.959(4)	C2−C3	1.381(10)	S−O2	1.472(5)	C9−N5	1.482(7)	Cl2−O22	1.426(4)
Co−N3	1.971(4)	C3−C4	1.378(10)	N2−C6	1.471(7)	Cl1−O11	1.379(5)	Cl2−O32	1.413(5)
Co−N4	1.944(4)	C4−C5	1.372(8)	C6−C7	1.421(9)	Cl1−O21	1.424(6)	Cl2−O42	1.401(6)
Co−N5	1.943(4)	C5−N1	1.348(7)	C7−N3	1.479(8)	Cl1−O31	1.431(5)		

Interatomic Angles[a] (deg)

O1−Co−N1	85.6(2)	N2−Co−N5	91.8(2)	C1−C2−C3	118.1(6)	O21−Cl1−O31	108.1(4)
O1−Co−N2	91.7(2)	N3−Co−N4	95.5(2)	C2−C3−C4	119.3(6)	O21−Cl1−O41	108.5(5)
O1−Co−N3	176.9(2)	N3−Co−N5	91.2(2)	C3−C4−C5	119.6(6)	O31−Cl1−O41	108.5(4)
O1−Co−N4	87.5(2)	N4−Co−N5	85.3(2)	C4−C5−N1	122.4(6)	O12−Cl2−O22	110.3(3)
O1−Co−N5	87.9(2)	O1−S−O2	110.0(3)	N2−C6−C7	111.5(5)	O12−Cl2−O32	109.1(3)
N1−Co−N2	92.6(2)	C1−S−O1	97.1(2)	C6−C7−N3	111.1(6)	O12−Cl2−O42	110.1(3)
N1−Co−N3	95.5(2)	C1−S−O2	105.2(3)	N4−C8−C9	105.8(5)	O22−Cl2−O32	108.9(3)
N1−Co−N4	90.2(2)	C5−N1−C1	117.3(5)	C8−C9−N5	105.8(4)	O22−Cl2−O42	107.9(3)
N1−Co−N5	172.3(2)	N1−C1−S	115.9(4)	O11−Cl1−O21	109.2(4)	O32−Cl2−O42	110.5(4)
N2−Co−N3	85.3(2)	S−C1−C2	120.7(5)	O11−Cl1−O31	112.0(4)		
N2−Co−N4	177.0(2)	N1−C1−C2	123.4(5)	O11−Cl1−O41	110.5(4)		

Torsional Angles[a] (deg)

O1−S−C1−N1	−17.1(4)	C5−N1−C1−S	175.7(4)	N1−C1−C2−C3	1.5(9)	N2−C6−C7−N3	−39.6(9)
O1−S−C1−C2	161.1(5)	C5−N1−C1−C2	−2.5(8)	C1−C2−C3−C4	0.8(10)	N4−C8−C9−N5	51.2(5)
O2−S−C1−N1	95.9(5)	C1−N1−C5−C4	1.2(9)	C2−C3−C4−C5	−2.0(10)		
O2−S−C1−C2	−85.8(5)	S−C1−C2−C3	−176.6(5)	C3−C4−C5−N1	1.0(10)		

[a] ESD in parentheses.

Table 4. Bond Lengths and Bond and Torsional Angles for Compound **4**, $Co(C_5H_4NSO_{2.00})(C_2H_8N_2)_2(ClO_4)_2$

Co−O1	1.903(2)	N1−C1	1.348(3)	C1−S	1.819(3)	Co−N3	1.960(2)	C3−C4	1.383(5)	N2−C6	1.486(3)		
Co−N1	1.959(2)	C1−C2	1.377(4)	S−O1	1.545(2)	Co−N4	1.950(2)	C4−C5	1.378(4)	C6−C7	1.492(4)		
Co−N2	1.969(2)	C2−C3	1.391(4)	S−O2	1.487(2)	Co−N5	1.945(2)	C5−N1	1.351(3)	C7−N3	1.492(3)		

N4−C8	1.481(3)	Cl1−O41	1.420(2)	Cl1−O11	1.403(2)	Cl2−O32	1.416(2)
C8−C9	1.508(4)	Cl2−O12	1.433(2)	Cl1−O21	1.431(2)	Cl2−O42	1.421(3)
C9−N5	1.493(3)	Cl2−O22	1.425(2)	Cl1−O31	1.434(2)		

O1−Co−N1	85.6(1)	N2−Co−N5	91.8(1)	C1−C2−C3	118.8(3)	O21−Cl1−O31	109.0(2)
O1−Co−N2	92.3(1)	N3−Co−N4	95.1(1)	C2−C3−C4	118.5(3)	O21−Cl1−O41	109.7(2)
O1−Co−N3	177.4(1)	N3−Co−N5	91.6(1	C3−C4−C5	119.5(3)	O31−Cl1−O41	108.6(1)
O1−Co−N4	87.4(1)	N4−Co−N5	85.6(1	C4−C5−N1	122.4(3)	O12−Cl2−O22	111.2(1)
O1−Co−N5	87.6(1)	O1−S−O2	110.7(1	N2−C6−C7	107.7(2)	O12−Cl2−O32	109.0(2)
N1−Co−N2	92.6(1)	C1−S−O1	96.1(1)	C6−C7−N3	107.2(2)	O12−Cl2−O42	109.5(2)
N1−Co−N3	95.3(1)	C1−S−O2	103.6(1)	N4−C8−C9	106.4(2)	O22−Cl2−O32	109.0(1)
N1−Co−N4	90.0(1)	C5−N1−C1	117.6(2)	C8−C9−N5	106.2(2)	O22−Cl2−O42	107.2(2)
N1−Co−N5	172.0(1)	N1−C1−S	115.8(2)	O11−Cl1−O21	109.0(2)	O32−Cl2−O42	110.8(2)
N2−Co−N3	85.2(1)	S−C1−C2	121.0(2)	O11−Cl1−O31	111.2(2)		
N2−Co−N4	177.3(1)	N1−C1−C2	123.1(2)	O11−Cl1−O41	109.3(2)		

O1−S−C1−N1	−17.4(2)	C5−N1−C1−S	176.6(2)	N1−C1−C2−C3	0.7(4)	N2−C6−C7−N3	−48.9(3)
O1−S−C1−C2	160.3(2)	C5−N1−C1−C2	−1.1(4)	C1−C2−C3−C4	0.5(4)	N4−C8−C9−N5	50.9(3)
O2−S−C1−N1	95.7(2)	C1−N1−C5−C4	0.2(4)	C2−C3−C4−C5	−1.3(4)		
O2−S−C1−C2	−86.7(2)	S−C1−C2−C3	−176.8(2)	C3−C4−C5−N1	1.0(4)		

[a] ESD in parentheses.

5.45 (1H, NH), 5.25 (1H, NH), 4.80 (1H, NH), 4.70 (1H, NH), 4.25 (1H, NH), 4.10 (1H, NH), 2.60 (m, 8H, CH_2) ppm. ^{13}C NMR (Me_2SO-*d*$_6$): δ 180.0 (1C, CS), 150.6 (1C, CH), 136.7 (1C, CH), 119.7 (1C, CH), 115.7 (1C, CH), 45.35 (1C, CH_2), 44.6 (1C, CH_2), 43.9 (1C, CH_2), 43.3 (1C, CH_2) ppm.

[Co(en)$_2$(py-SO$_2$-*O*)]ZnCl$_4$. [Co(en)$_2$(py-SO$_2$-*S*)]ZnCl$_4$ (2.0 g, 3.9 mmol) was dissolved in water (50 mL) and then heated at 40 °C for 6 h or left in the sun for 3 h. The brown-yellow solution which had become red was then rotary evaporated to 10 mL. "H_2ZnCl_4" (1 mL) was added and the mixture left at 5 °C for 2 h. The resulting red crystals of [Co(en)$_2$(py-SO$_2$-*O*)]ZnCl$_4$ were collected, washed with ethanol and ether, and air-dried. Yield: 1.8 g (90%). The red sulfinate was further purified by ion-exchange chomatography on a Dowex 50W-X2 (Na^+ form; 200−400 mesh) column using 1 M HCL as eluant to give a single red band. Diastereomer separation was noticeable by segmenting the band into several portions: front, middle, and rear. The eluates were reduced to dryness, and then, each was dissolved in a minimum of water. Crystals were readily obtained from concentrated aqueous solution with H_2ZnCl_4 or $HClO_4$ as precipitants (5 °C, 6 h). The red crystalline fractions were filtered, washed with ethanol and ether, and air-dried.

Anal. Calcd for $C_9H_{20}N_5CoSO_{10}Cl_2$: C, 20.78; H, 3.88; N, 13.46; S, 6.16. Found: C, 21.43; H, 4.08; N, 13.97; S, 6.14%.

^1H NMR (Me_2SO-*d*$_6$), more soluble isomer: δ 8.68 (d, 1H, CH), 8.35 (t, 1H, CH), 8.14 (d, 1H, CH), 7.90 (t, 1H, CH), 5.98 (1H, NH), 5.70 (1H, NH), 5.63 (1H, NH), 5.42 (1H, NH), 5.20 (1H, NH), 4.85 (1H, NH), 4.45 (1H, NH), 4.20 (1H, NH), 2.65 (m, 8H, CH_2) ppm.

^{13}C NMR (Me_2SO-*d*$_6$): 176.6 (1C, CS), 152.0 (1C, CH), 142.0 (1C, CH), 127.7 (1C, CH), 123.7 (1C, CH), 45.4 (2C, CH_2), 44.8 (1C, CH_2), 43.1 (1C, CH_2) ppm.

^{1}H NMR (Me$_2$SO-d_6), less soluble isomer: δ 8.51 (d, 1H, CH), 8.30 (t, 1H, CH), 8.11 (d, 1H, CH), 7.85 (t, 1H, CH), 5.98 (1H, NH), 5.70 (1H, NH), 5.63 (1H, NH), 5.42 (1H, NH), 5.20 (1H, NH), 4.85 (1H, NH), 4.45 (1H, NH), 4.20 (1H, NH), 2.65 (m, 8H, CH$_2$) ppm.

^{13}C NMR (Me$_2$SO-d_6): 176.7 (1C, CS), 151.8 (1C, CH), 141.6 (1C, CH), 127.4 (1C, CH), 123.5 (1C, CH), 45.1 (1C, CH$_2$), 45.0 (1C, CH$_2$), 44.3 (1C, CH$_2$), 44.1 (1C, CH$_2$) ppm.

Crystallography

Crystal Data for 1. Co(C$_5$H$_4$NSO$_{1.00}$)(C$_2$H$_8$N$_2$)$_2$(ClO$_4$)$_2$, M = 505.3, triclinic, space group $P\bar{1}$, a = 9.231(2) Å, b = 9.383(2) Å, c = 11.253(3) Å, α = 75.73(2)°, β = 84.80(2)°, γ = 84.92(2)°, V = 938.5(4) Å^3, D_c = 1.79 g cm^{-3}, Z = 2, μ_{Mo} = 13.58 cm^{-1}. Crystal size 0.11 mm by 0.17 mm by 0.24 mm, 2θ_{max} = 50°, min and max transmission factors 0.73 and 0.84. The number of reflections was 2901 considered observed out of 3284 unique data, with R_{merge} = 0.007 for 189 pairs of equivalent h01 reflections. Final residuals R, R_w were 0.039, 0.062.

Crystal Data for 2. Co(C$_5$H$_4$NSO$_{1.21}$)(C$_2$H$_8$N$_2$)$_2$(ClO$_4$)$_2$, M = 507.4, triclinic, space group $P\bar{1}$, a = 9.216(3) Å, b = 9.374(3) Å, c = 11.283(4) Å, α = 75.83(3)°, β = 85.15(3)°, γ = 85.21(3)°, V = 939.7(6) Å^3, D_c = 1.79 g cm^{-3}, Z = 2, μ_{Mo} = 13.57 cm^{-1}. Crystal size 0.11 mm by 0.12 mm by 0.15 mm, 2θ_{max} = 50°, min and max transmission factors 0.81 and 0.86. The number of reflections was 2734 considered observed out of 3291 unique data, with R_{merge} = 0.010 for 195 pairs of equivalent 0kl reflections. Final residuals R, R_w were 0.042, 0.059.

Crystal Data for 3. Co(C$_5$H$_4$NSO$_{1.83}$)(C$_2$H$_8$N$_2$)$_2$(ClO$_4$)$_2$, M = 517.5, triclinic, space group $P\bar{1}$, a = 8.684(5) Å, b = 9.362(5) Å, c = 11.787(6) Å, α = 96.43(3)°, β = 98.71(3)°, γ = 94.58(3)°, V = 936.7(8) Å^3, D_c = 1.83 g cm^{-3}, Z = 2, μ_{Mo} = 13.66 cm^{-1}. Crystal size 0.04 mm by 0.10 mm by 0.13 mm, 2θ_{max} = 50°, min and max transmission factors 0.84 and 0.93. The number of reflections was 2495 considered observed out of 3280 unique data, with R_{merge} = 0.016 for 140 pairs of equivalent hk0 reflections. Final residuals R, R_w were 0.053, 0.065.

Crystal Data for 4. Co(C$_5$H$_4$NSO$_{2.00}$)(C$_2$H$_8$N$_2$)$_2$(ClO$_4$)$_2$, M = 520.2, triclinic, space group $P\bar{1}$, a = 8.611(3) Å, b = 9.370(3) Å, c = 11.786(4) Å, α = 96.57(2)°, β = 98.44(2)°, γ = 94.23(2)°, V 930.6(5) Å^3, D_c = 1.86 g cm^{-3}, Z = 2, μ_{Mo} = 13.76 cm^{-1}. Crystal size 0.11 mm by 0.20 mm by 0.25 mm, 2θ_{max} = 50°, min and max transmission factors 0.77 and 0.83. The number of reflections was 2875 considered observed out of 3248 unique data, with R_{merge} = 0.010 for 198 pairs of equivalent h0l reflections. Final residuals R, R_w were 0.027, 0.044.

Structure Determination. Reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromatized molybdenum radiation (λ 0.7107 Å). Data were correct for absorption using the method of De Meulenaer and Tompa.[26] Reflections with $I > 3\sigma(I)$ were considered observed. The structures were determined by direct phasing and Fourier methods. Hydrogen atoms were included in calculated positions and were assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full matrix least squares. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\sum w\Delta^2/\sum wF_o{}^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from *International Tables for X-ray Crystallography*.[27] Structure solution was by MULTAN80,[28] and refinement used BLOCKLS, a local version of ORFLS.[29] ORTEP−II[30] running on a Macintosh IIcx was used for the structural diagrams (Figures 1 and 2), and an IBM 3090 computer was used for calculations.

All four compounds are racemates, belonging to achiral point groups. In the figures, we arbitrarily show the Δ form. Tables of bond lengths, and bond and torsional angles, for each of the four structures are given in Tables 1−4. Crystallographic files in CIF format for compounds **1**, **2**, **3**, and **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 191559−191562, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44−1223−336033. E-mail: deposit@ccdc.cam.ac.uk. Internet: http//www.ccdc.cam.ac.uk.) These files are also available as Supporting Information.

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Supporting Information Available: Tables of atomic and thermal parameters (Tables 1S−4S) and crystallographic material in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) De Meulenaer, J.; Tompa, M. *Acta Crystallogr.* **1965**, *19*, 1014.

(27) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Ed.; Kynoch Press: Birmingham, 1974; Vol. 4.

(28) Main, P. *MULTAN80*; University of York: York, England, 1980.

(29) Busing, W. R.; Martin, K. O.; Levy, H. A. *ORFLS*; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

(30) Johnson, C. K. *ORTEP-II*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.