1.716 (14), 1.791 (14), 1.695 (14), and 1.609 (14) Å, respectively] and contrast with the complex[10] *closo*-1,1,1,1-(MeCN)$_4$-1,2,4-CaC$_2$B$_{10}$H$_{12}$. In the latter structure the carbon atom that lies above the plane defined by four borons in the top belt interacts nearly symmetrically with the adjacent boron atoms [C(2)-B(3) and C(2)-B(7) distances are 1.519 (8) and 1.510 (7) Å, respectively] whereas the other carbon atom that lies below the plane interacts asymmetrically with the adjacent boron atoms [C(4)-B(3) and C(4)-B(5) distances are 1.645 (8) and 1.697 (7) Å, respectively].

It is interesting to note that complex **2** adopts a bent sandwich arrangement and is similar to that observed in the 7,8-dicarbollide samarium sandwich complex[1,2] and other cyclopentadienyl complexes of lanthanides.[11] The fact that the carborane ligand in **2** can be easily removed by an appropriate electrophilic reagent such as Eu^{2+} suggests that the bonding between the carborane ligands and the europium atom in **2** is quite ionic in character. We are currently extending our studies to neighboring lanthanides.

Acknowledgment. We thank the National Science Foundation (Grant CHE 88-06139) for the financial support of this work.

Supplementary Material Available: Tables of crystallographic data collection parameters, atom coordinates, bond distances and angles, anisotropic parameters, and torsion angles (7 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

---

(10) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 4962.

(11) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941 and references contained therein.

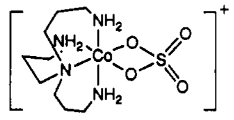
Department of Chemistry
and Biochemistry
University of California
Los Angeles, California 90024-1569

Rajesh Khattar
Carolyn B. Knobler
Stephen E. Johnson
M. Frederick Hawthorne*

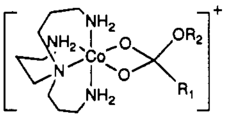
Received December 28, 1990

A Cobalt(III) Sulfato Chelate. Synthesis and Structure of [(trpn)Co(η^2-SO$_4$)]ClO$_4$·H$_2$O

We report here the synthesis and X-ray structure of I, a 4-membered sulfato complex of Co(III). Almost 30 years ago, Barraclough and Tobe[1] described a Co^{III}(η^2-SO$_4$) complex, but recently Buckingham et al.[2] showed that this compound is, in fact, a cobalt dimer with two sulfate bridges. Thus, complex I appears to be the first cobalt (III) compound of its kind.[3]



I



II

Our interest in [(trpn)Co(η^2-SO$_4$)]ClO$_4$·H$_2$O derived from the fact that I simulates, in charge and geometry, tetrahedral intermediate II postulated in cobalt-catalyzed ester hydrolyses.[4]

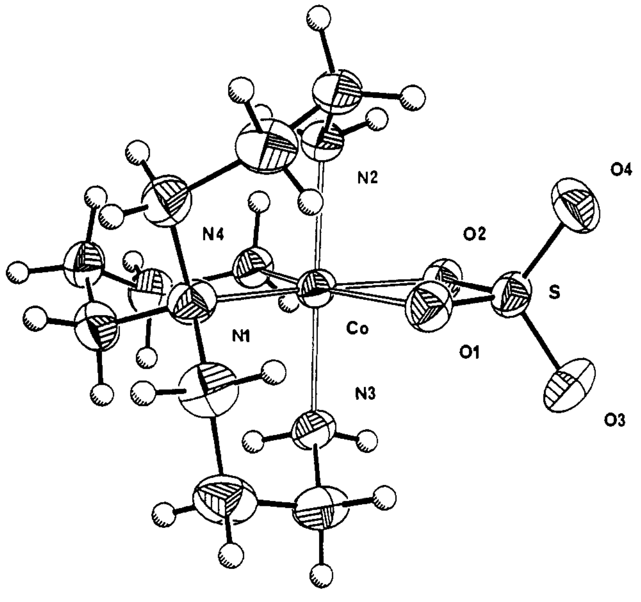


Figure 1. ORTEP representation of [(trpn)Co(η^2-SO$_4$)]ClO$_4$·H$_2$O complex at the 50% probability level. Selected bond lengths (Å) and interbond angles (deg): Co–O(1) = 1.974 (4), Co–O(2) = 1.950 (3), Co-N(1) = 1.983 (4), Co-N(2) = 1.977 (4), Co-N(3) = 1.971 (4), Co-N(4) = 1.949 (4), S-O(1) = 1.502 (3), S-O(2) = 1.517 (4), S-O(3) = 1.443 (4); S-O(4) = 1.441 (4); O(1)-Co-O(2) = 71.8 (1), O(1)-Co-N(1) = 98.3 (2), N-(1)-Co-N(4) = 100.3 (2), N(2)-Co-N(3) = 176.7 (2), O(1)-Co-N(4) = 161.4 (1), O(2)-Co-N(1) = 170.1 (2), Co-O(1)-S = 94.2 (2), Co-O(2)-S = 94.7 (2), O(1)-S-O(2) = 99.4 (2), O(1)-S-O(4) = 112.0 (2), O(2)-S-O(3) = 109.4 (2), O(3)-S-O(4) = 113.4 (2).

Consequently, an antibody based on protein-linked I might, in concert with [(trpn)Co(OH$_2$)$_2$]$^{3+}$, serve as a "metalloenzyme" toward sulfate, carboxylic, or carbonate esters.[5]

Compound I was synthesized by adding to water (500 mL) Co(ClO$_4$)$_2$·(H$_2$O)$_6$ (Strem, 18.9 g, 50 mmol) and trpn ligand[6] (9.4 g, 50 mmol) followed by NaHCO$_3$ (8.4 g, 100 mmol) and PbO$_2$ (26 g).[7] Stirring was carried out overnight, 70% HClO$_4$ was added slowly until pH 5 was reached, solids were removed by filtration, and the water was partially evaporated in vacuo to give [(trpn)Co(CO$_3$)]ClO$_4$·H$_2$O, in 75% yield after recrystallization from water. This substance (1.7 g, 4 mmol in 2 mL of water was mixed first with 70% HClO$_4$ (0.9 mL) and then with Na$_2$SO$_4$ (0.57 g, 4 mmol) in 20 mL of water. Partial stripping of water gave crude product, which, after recrystallization from water (82% yield), led to material having elemental analyses and spectral data[8] consistent with I. An X-ray structure was, however, required to definitely rule out a binuclear cobalt complex with bridging sulfates.

A perspective view of I is shown in Figure 1.[9] The Co(III)

---

(1) Barraclough, C. G.; Tobe, M. L. *J. Chem. Soc.* **1961**, 1993.

(2) Buckingham, D. A.; Clark, C. R.; Simpson, J.; Robinson, W. T. *Inorg. Chem.* **1988**, *27*, 3544.

(3) A Cambridge Data Base search revealed no entry for a Co^{III}(η^2-SO$_4$) moiety. Only few crystal structures have been reported for M(η^2-SO$_4$). (a) Ir(III): Fettinger, J. C.; Churchill, M. R.; Bernard, K. A.; Atwood, J. D. *J. Organomet. Chem.* **1988**, *340*, 377. (b) Mo(IV): Calhorda, M. J.; Carrondo, M. A. A. F. de C. T.; Dias, A. R.; Domingos, A. M. T. S.; Simoes, J. A. M.; Teixeira, C. *Organometallics* **1986**, *5*, 660. (c) Rh(III): Lucas, B. C.; Moody, D. C.; Ryan, R. R. *Cryst. Struct. Commun.* **1977**, *6*, 57. (d) Co(II): Benelli, C.; Di Vaira, M.; Noccioli, G.; Sacconi, L. *Inorg. Chem.* **1977**, *16*, 182. (e) Ru(II): Moody, D. C.; Ryan, R. R. *Cryst. Struct. Commun.* **1976**, *5*, 145. (f) Ru(II): Reed, J.; Soled, S. L.; Eisenberg, R. *Inorg. Chem.* **1974**, *13*, 3001.

(4) (A) Chin, J.; Banaszczyk, M. *J. Am. Chem. Soc.* **1989**, *111*, 2724. (b) Chin, J.; Zou, X. *J. Am. Chem. Soc.* **1984**, *106*, 3687.

(5) Iverson, B. L.; Lerner, R. A. *Science* **1989**, *243*, 1184.

(6) Chin, J.; Banaszczyk, M.; Jubian, V.; Zou, X. *J. Am. Chem. Soc.* **1989**, *111*, 186. The "trpn" stands for tris(3-aminopropyl)amine.

(7) Massoud, S. S.; Milburn, R. M. *Inorg. Chim. Acta* **1988**, *154*, 115.

(8) Anal. Calcd for C$_9$H$_{24}$N$_4$Co(SO$_4$)(ClO$_4$)·H$_2$O: C, 24.42; H, 5.46; N, 12.65; Cl, 8.01; S, 7.24. Found: C, 24.60; H, 5.51; N, 12.49; Cl, 7.87; S, 7.12. UV–vis [λ_{max}, (ϵ, nm M^{-1})]: 548 (91); 367 (120). ^{13}C NMR (D$_2$O; 1,4-dioxane at 67.6 ppm): δ 58.90, 56.47, 38.32, 37.72, 24.20, 21.76. FT-IR (KBr) SO$_4^{2-}$: ν_3 1251 (s), 1185 (s), 1152 (vs); ν_1 948 (s); ν_4 660 (s), 614 (m), 587 (m).

(9) Purple crystals of [(trpn)Co(η^2-SO$_4$)]ClO$_4$·H$_2$O are monoclinic, space group $P2_1/c$, with a = 8.753 (4) Å, b = 16.580 (7) Å, c = 12.510 (7) Å, β = 97.89 (4)°, v = 1798 (1) Å^3, d_{calcd} = 1.70 g/cm^3, Z = 4, MW = 460.77 and μ = 12.62 cm^{-1}. X-ray data were collected at 21 °C on a 0.3 × 0.3 × 0.35 mm crystal for 2670 independent reflections having 3° < 2θ < 45° on a Nicolet P3F four-circle diffractometer using graphite-monochromatized Mo Kα radiation. The positions of the heavy atoms were solved via the Patterson method, and the remaining non-hydrogen atoms were found by difference Fourier syntheses utilizing the SHELXTL program package. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final residuals were R = 0.051 (R_w = 0.062) for 2096 data with $I > 3\sigma(I)$.

0020-1669/91/1330-1972$02.50/0

ion adopts a distorted octahedral geometry with the following angles: N1–Co–N4 = 100.3°, N2–Co–N3 = 176.7°, and O1–Co–O2 = 71.8°. The large N1–Co–N4 angle, similar to that observed in $RuCl(\eta^2\text{-}SO_4)(NO)(PPh_3)_2$, reflects the strain in the contiguous four-membered ring.[10] A slightly deformed tetrahedral configuration was found for the sulfate ligand with O–S–O angles of 99.4, 109.4, 112.0, and 113.4°. The exocyclic S–O bonds are about 0.07 Å shorter than the endocyclic ones. "Short–long" trans effects are seen clearly: N4–Co (1.949 (4) Å) vs O1–Co (1.974 (4) Å); N1–Co (1.983 (4) Å) vs O2–Co (1.950 (3) Å). The two axial N–Co bonds are almost identical (1.971 (4) and 1.977 (4) Å). Finally, an interesting hydrogen-bonded network[11] exists between N4–H, water, and ClO_4^-. One is remained of the S_N1CB mechanism[12] in which hydroxide attacks an NH_2R coordinated to Co(III).

Hydrolysis of I was monitored by the absorbance decrease at 548 nm observed when a 10.2 mM aqueous solution of I was added to 0.2 M *N*-ethylmorpholine buffer (I = 1.0 M with $NaClO_4$) thermostated at 25.0 °C in a stopped-flow spectrophotometer. First-order rate constants of 0.19, 0.21, and 0.22 s^{-1} were obtained at pH values of 7.24, 7.89, and 8.20, respectively. This is about 65 times faster[2] than $[(en)_2Co(\mu\text{-}SO_4)]_2^{2+}$, where ring strain is not a factor, and almost 10 times faster than $[(trpn)Co(\eta^2\text{-}OAc)]^{2+}$. Binding of SO_4^{-2} to $[(trpn)Co(OH_2)_2]^{3+}$, followed from the 548-nm absorbance increase at pH 2.9 ([Co] = 5.04 mM; $NaClO_4$, I = 1.0 M; 0.023–0.24 M $NaSO_4$; 25°C), gave a second-order rate constant of 0.11 M^{-1} s^{-1}. *p*-Nitrophenyl sulfate, a weak ligand, was not hydrolyzed by $[(trpn)Co(OH_2)(OH)]^{2+}$.

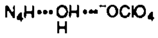
Acknowledgment. This work was supported by the National Institutes of Health and the Army Research Office. We also greatly appreciate the assistance of Professors K. S. Hagen and C. G. Trowbridge with the X-ray and stopped-flow analyses, respectively.

Supplementary Material Available: Details of the crystal structure determination for $[(trpn)Co(\eta^2\text{-}SO_4)]ClO_4{\cdot}H_2O$, including crystallographic experimental procedures, ORTEP drawings, and tables of crystal data (Table S1), atomic positional parameters (Table S2), bond distances (Table S3), bond angles (Table S4), anisotropic thermal parameters (Table S5), and hydrogen atom positions (Table S6) (10 pages); a listing of observed and calculated structure factors for $[(trpn)Co(\eta^2\text{-}SO_4)]ClO_4{\cdot}H_2O$ (7 pages). Ordering information is given on any current masthead page.

---

(10) Taura, T. *Inorg. Chim. Acta*, **1989**, *158*, 33.

(11) The following distances pertain to the hydrogen-bonded network



$$N_4H\cdots\underset{H}{O}H\cdots{}^{-}OClO_4$$

(see also Tables S2 and S6 and S6 of the supplementary data): N_4–O_w and O_w–O_p (2.856 Å); N_4H–O_w (1.941 Å); and O_wH–O_p (1.855 Å).

(12) Basolo, F.; Pearson, R. *Mechanisms of Inorganic Reactions*: John Wiley and Sons, Inc.: New York, 1967.

Department of Chemistry
Emory University
Atlanta, Georgia 30322

M. Banaszczyk
Jeng-Jong Lee
F. M. Menger*

Received January 29, 1991

A Triply Bonded Dirhenium Complex Containing a Nitrosyl Ligand

The reactions of nitric oxide with multiply bonded dimetal complexes can, like those with carbon monoxide and organic isocyanides, lead to cleavage of the metal–metal bond and the formation of products in which a metal–metal interaction is no longer present.[1,2] Examples include the conversions of $Mo_2X_4(PR_3)_4$ (X = Cl, Br; PR_3 = PEt_3, P-*n*-Bu_3, $PEtPh_2$) to $Mo(NO)_2X_2(PR_3)_2$,[3] $Mo_2(O\text{-}i\text{-}Pr)_6$ to $Mo_2(\mu\text{-}O\text{-}i\text{-}Pr)_2(O\text{-}i\text{-}Pr)_4(NO)_2$,[4] and $W_2(O\text{-}t\text{-}Bu)_6$ to $W(O\text{-}t\text{-}Bu)_3(NO)(py)$.[5] A few instances are also known where nitric oxide forms adducts with multiply bonded dimetal species, such as the case of the diruthenium complexes $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ and $Ru_2(\mu\text{-}N_3Ph_2)_4(NO)_2$.[6] Structure determinations on the carboxylate complexes where R = Et or CF_3 show that the Ru–Ru bonds are much longer and weaker than in the parent $Ru_2(\mu\text{-}O_2CR)_4$ compounds.[6,7] Quite different behavior is encountered with the nitrosonium cation NO^+, which we have found can serve as a one-electron oxidant in converting triply bonded dirhenium(II) species to their dirhenium(III,II) congeners.[8-10] We now describe a previously unreported reaction course in which NO^+ first behaves as a one-electron oxidant, followed by the incorporation of NO into the final reaction product without a net change in the metal–metal bond order.

Solutions of the dirhenium(II) complex $Re_2Cl_4(\mu\text{-}dmpm)_3$ (**1**; dmpm = $Me_2PCH_2PMe_2$) in 0.1 M *n*-Bu_4NPF_6/CH_2Cl_2 exhibit two one-electron oxidations at $E_{1/2}$ = +0.53 V and $E_{p,a}$ = +1.30 V vs Ag/AgCl.[11] The reversible oxidation can be accessed both electrochemically and chemically, the latter with the use of $NOPF_6$ as the oxidant. A mixture of **1** (0.10 g, 0.108 mmol) and $NOPF_6$ (0.023 g, 0.130 mmol) in 10 mL of dichloromethane was stirred at room temperature for 15 min, the purple solution evaporated to dryness, and ethanol added to the residue to afford the microcrystalline complex $[Re_2Cl_4(\mu\text{-}dmpm)_3]PF_6$ (**2**), yield 0.08 g (70%). Anal. Calcd for $C_{15}H_{42}Cl_4F_6P_7Re_2$: C, 16.88; H, 3.95. Found: C, 16.36; H, 4.14. The identity of **2** was further established by its electrochemical and spectroscopic properties.[12]

A different reaction product is obtained if **1** is reacted with $NOPF_6$ by using 1:2 molar proportions of these reagents. The reaction between **1** (0.21 g, 0.228 mmol) and $NOPF_6$ (0.080 g, 0.455 mmol) in dichloromethane (15 mL) for 4 h at room temperature led to a color change from red to purple to brown. The reaction mixture was filtered and evaporated to dryness and the residue treated with ethanol to give dark red-brown $Re_2Cl_5(dmpm)_2(NO)$ (**3**), yield 0.08 g (41%). Anal. Calcd for $C_{10}H_{28}Cl_5NOP_4Re_2$: C, 14.10; H, 3.29. Found: C, 14.62; H, 3.08. This same product was formed when acetone was used as the reaction solvent in place of dichloromethane and was also formed by the reaction of **2** with 1 equiv of $NOPF_6$ in dichloromethane.

The diamagnetic nitrosyl complex **3**, which is the first triply bonded dimetal species to contain a NO ligand, shows a single intense ν(NO) mode at 1750 cm^{-1} in its IR spectrum (Nujol mull). Its ^1H NMR spectrum (recorded in $CDCl_3$ at room temperature) exhibits a broad resonance (unresolved multiplet) at δ +4.13 (P–CH_2–P) and multiplets at δ +2.46, +2.00, and +1.60, in an intensity ratio of ca. 1:1:2, which are assigned to CH_3–P. The resonance at δ +1.60 is composed of two overlapping multiplets. Overall, these results indicate the presence of four inequivalent pairs of CH_3–P groups in the structure of **3**. The cyclic voltammograms of solutions of **3** in 0.1 M *n*-Bu_4NPF_6/CH_2Cl_2 show a

---

(1) Cotton, F. A.; Walton, R. A. *Muliple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(2) Walton, R. A. *ACS Symp. Ser.* **1981**, *No. 155*, 207.

(3) Nimry, T.; Urbancic, M. A.; Walton, R. A. *Inorg. Chem.* **1979**, *18*, 691.

(4) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 3354.

(5) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 116.

(6) Lindsay, A. J.; Wilkinson, G.; Montevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2723.

(7) Quelch, G. E.; Hillier, I. H.; Guest, M. F. *J. Chem. Soc., Dalton Trans.* **1990**, 3075.

(8) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.

(9) Dunbar, K. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 5.

(10) Costello, M. T.; Derringer, D. R.; Fanwick, P. E.; Price, A. C.; Rivera, M. I.; Scheiber, E.; Siurek, E. W., III; Walton, R. A. *Polyhedron* **1990**, *9*, 573.

(11) Anderson, L. B.; Cotton, F. A.; Falvello, L. R.; Harwood, W. S.; Lewis, D.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3637.

(12) Cyclic voltammogram (0.1 M *n*-$BuNPF_6/CH_2Cl_2$): $E_{1/2}$(red) = +0.54 V and $E_{p,a}$ = +1.28 V vs Ag/AgCl. IR spectrum (Nujol mull): 840 s cm^{-1} (ν(P–F) of PF_6^-). X-Band ESR spectrum (CH_2Cl_2 at −160 °C): $g \simeq 2.2$ (broad signal showing some hyperfine).

0020-1669/91/1330-1973$02.50/0