small quantity of an unidentified orange liquid was produced along with **1**. This liquid cosublimed with **1** at 40–70 °C, below the sublimation temperature of pure **1**. Combining the reactants in a 3:2 ratio[6c] (in ether or THF) produced a green-brown, ether-soluble solid from which **1** could be sublimed above 90 °C. The light green **1** melted at 124–126 °C and showed high thermal stability (dec pt >250 °C).[7] It was very soluble in ethereal solvents, and moderately soluble in hydrocarbons. While easily separated from Et_2O or THF, **1** could not be separated from coordinated tetraglyme or pyridine by sublimation.[5a] A strong bidentate ligand, $Me_2N(CH_2)_2NMe_2$ (TMEDA), reacted instantly with **1** to form a blue solid,[8] which was sublimed at 60–80 °C from the $Ba(HFTB)_2$ residue.

The X-ray analysis[9] of **1** shows (Figure 1) Ba to be located on a 2-fold axis so that only one of the $Cu(HFTB)_3^-$ anions is crystallographically unique. The $\{Cu^{II}O_3\}$ chromophore is three-coordinate, Y shaped, and planar (maximum deviation from a least-squares plane is 0.008 Å). Its dihedral angle with the $\{CuO_3\}$ plane related by the 2-fold axis is 56.8°, and with the O(1)–Ba–O(2) plane, it is 165.8°. While a three-coordinate planar geometry is common for $\{Cu^IX_3\}$,[10] the only other known compound[11] with a similar Cu(II) geometry is $[(PFTB)Cu_2(OCMe_3)_3]_2$. The Cu–O distances to the HFTB ligands that are also coordinated to Ba are short (1.889 (6) and 1.878 (7) Å), but similar to those in mononuclear copper(II) alkoxides[2d] (1.865–1.892 Å) and a monomeric copper(II) siloxide complex[2a] (1.835–1.861 Å). The Cu–O distance (1.781 (7) Å) to the unshared HFTB ligand is shorter. Comparable distances in $[(PFTB)Cu_2(OCMe_3)_3]_2$ are 1.865 (4), 1.867 (4), and 1.798 (5) Å. The Ba^{2+} cation is coordinated (Figure 2) to four oxygens (2.636–2.644 Å) and eight fluorines (2.94–3.14 Å). The monomeric structure of **1** (intermolecular Ba···F = 5.12 Å, Ba···O = 7.80 Å, and Cu···Cu = 8.77 Å) helps to explain its unusually low sublimation temperature.

The copper perfluoro-*tert*-butoxide **2** and its etherates [**2**·nOEt$_2$] were prepared from a reaction between $Ba(PFTB)_2$ and $CuCl_2$ (1:1 mole ratio).[13] The etherates with $n = 2$ to $n = 4$ were liquids, and the $n = 1$ etherate was a solid. The elemental analyses were consistent with the formulas $Cu_4(PFTB)_7$ and $Cu_4(PFTB)_7(OEt_2)_n$, implying a mixed-valence copper(I/II) alkoxide. Spontaneous reduction to Cu(I) is not unreasonable as it was previously observed in the reaction of $CuCl_2$ with salts of other bulky ligands such as $LiN(SiMe_3)_2$.[14] However, an X-ray powder pattern of the solids from the hydrolysis[15] of **2** shows no evidence for Cu_2O. While the mass spectrum of **2** shows no evidence for chloro or oxo ligands, the presence of a fluoro ligand or some other unusual arrangement, with all Cu atoms in the +2 oxidation state, cannot be ruled out.

Acknowledgment. We thank John Callahan (NRL) for assistance with the mass spectrum and ONR for financial support.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic displacement coefficients, and hydrogen atom coordinates (6 pages); a table of structure factors (11 pages). Ordering information is given on any current masthead page.

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(7) Anal. Found (calcd) for $Ba[Cu(HFTB)_3]_2$: C, 21.26 (21.34); H, 1.05 (1.34); Cu 9.31 (9.41); Ba, 9.81 (10.17). NMR: ^1H (C_6D_6) δ −1.05 ($\upsilon_{1/2}$ = 370 Hz), −11.41 ($\upsilon_{1/2}$ = 780); ^{19}F ($CFCl_3$ ref) δ −51.0 ($\upsilon_{1/2} \approx$ 1800 Hz), −56.8, −60.2 ($\upsilon_{1/2} \approx$ 2500). ESR: (Et_2O) g = 2.21, 4.36; −196 °C, $g_\perp$ = 2.14, $g_\parallel$ = 2.51. UV/vis [λ, nm (ε)]: 270 (4300), 360 (7500), 755 (240), 875 (170), 980 (100).

(8) Anal. Found: C, 30.41; H, 3.75; F, 43.61; Cu, 11.98; consistent with $Cu(HFTB)_2(TMEDA)_{0.9}$ (TMEDA loss on sublimation?). Mp: 137–140 °C. Dec pt: 145–158 °C. NMR (C_6D_6): ^1H δ −5.45 ($\upsilon_{1/2}$ = 350 Hz); ^{19}F δ −45.6 ($\upsilon_{1/2}$ = 3400 Hz). ESR (C_6D_6, −196 °C); $g_\perp$ = 2.06, $g_\parallel$ = 2.33.

(9) **1** crystallizes in space group $C2/c$ with the following unit cell parameters: a = 23.843 (12) Å, b = 18.324 (8) Å, c = 10.998 (6) Å, β = 116.97°, V = 4282 (4) Å^3, Z = 4, d_{calc} = 2.09 g/cm^3, and μ = 20.8 cm^{-1}. An irregular green translucent crystal was sealed in a glass capillary and a total of 3112 ($3.5 < 2\theta < 45°$, $0 \le h \le 25$, $0 \le k \le 19$, $-11 \le l \le 10$) data were collected (2825 unique, R_{int} = 1.02% for equivalents) on a computer-controlled diffractometer (four-circle Nicolet R3m/V with Mo Kα radiation, λ = 0.71073 Å, and incident beam monochromator) at −35 °C. Corrections were applied for Lorentz, polarization, and absorption effects. The structure was solved by direct methods with the aid of the program SHELXTL[12] and refined with a full-matrix least-squares refinements[12] with restraints on C–F and next-nearest-neighbor F–F distances. The fluorine atoms are not well-defined, and the HFTB ligand not coordinated to Ba was treated as a disorder with respect to methyl group position. Occupancy was refined to $^1/_5$, $^2/_5$, and $^2/_5$, and the corresponding CF_3 group occupancies were $^4/_5$, $^3/_5$, and $^3/_5$, respectively, for the three sites. Final R values for the 2355 data with $F_o > 3\sigma(|F_o|)$ were R = 0.064 and R_w = 0.080. The 341 parameters refined include the coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogens were placed in calculated positions.

(10) (a) Sorrel, T. N.; Malachowski, M. R.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 3250. (b) Kappenstein, C.; Hugel, R. P. *Inorg. Chem.* **1977**, *16*, 250. (c) Sorrel, T. N.; Malachowski, M. R. *Inorg. Chem.* **1983**, *22*, 1883.

(11) George, C. F.; Purdy, A. P. Unpublished results.

(12) Sheldrick, G. M. SHELXTL80. *An integrated system for Solving, Refining, and Displaying Crystal Structures from Diffraction Data.* University of Gottingen, Federal Republic of Germany, 1980.

(13) A mixture of $Ba(PFTB)_2$[2i] (2.08 g, 3.42 mmol), $CuCl_2$ (0.471 g, 3.50 mmol), and Et_2O (25 mL) was stirred at 75 °C for 40 h, and the pale yellow mixture was filtered (residue 0.76 g). As the ether was vacuum evaporated at 0 °C, an off-white solid formed, which turned to a green liquid as more ether was removed. Repeated distillation with mild warming of the pot (heat gun) and the receiving flask at 0 °C allowed ether to be removed slowly,[5a] distilling green etherates (90% yield from first distillation) and ultimately a thermochromic orange crystalline material (**2**). Anal. Found (calcd) for $Cu_4(PFTB)_7(OEt_2)_4$: C, 24.04 (24.07); H, 1.44 (1.84); Cu, 11.12 (11.58); F, 54.11 (54.51). Found (calcd) for $Cu_4(PFTB)_7(OEt_2)$: C, 19.50 (19.48); H, 0.55 (0.51). Found (calcd) for $Cu_4(PFTB)_7$: C, 17.55 (17.71); H, 0 (0); Cu, 13.37 (13.38); F, 62.99 (63.02). $Cu_4(PFTB)_7(OEt_2)_2$ was identified by NMR integration ($C_6H_5CF_3$ internal standard). Data for **2** are as follows. Mp: 68–71 °C. NMR: ^{19}F δ −1.6 ($\upsilon_{1/2} \approx$ 2500 Hz), −51.7 (line width increased and intensity decreased with increased amount of Et_2O); ^1H (of etherates) CH_3 position variable, observed from δ 6 to 25. ESR: (C_6D_6) −196 °C, $g_\perp$ = 2.08, $g_\parallel$ = 2.63. UV/vis [λ, nm (ε)]: 360 (8400), 780 (230), 910 (180), 1050 (165). Test for chloride ($AgNO_3$) was negative. MS (of etherate): *m/e* 831 (12%), $Cu_2(PFTB)_3^+$; *m/e* 615 (16), $Cu_2(PFTB)_2F^+$; *m/e* 596 (29), $Cu_2(PFTB)_2^+$; *m/e* 380 (32), $Cu_2(PFTB)F^+$; *m/e* 361 (64), $Cu_2(PFTB)^+$; *m/e* 372 (70), $Cu(PFTB)(OEt_2)^+$; peaks from additional loss of CF_2 or CF_3. All attempts to solve the crystal structure were unsuccessful.

(14) Burger, H.; Wannagat, U. *Monatsh. Chem.* **1964**, *95*, 1099.

(15) Dried at 140 °C under vacuum.

(16) Part of this work was performed while a NRC-NRL research associate.

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Synthesis and Structural Characterization of the Europium Sandwich $[1,1\text{-}(THF)_2\text{-}commo\text{-}1,1'\text{-}Eu(1,2,4\text{-}EuC_2B_{10}H_{12})_2]^{2-}$

Recent work from our laboratory has focused attention on the carborane complexes of the lanthanide elements, and we have recently reported representative dicarbollide complexes of Yb and Sm.[1,2] In this communication, we report the synthesis and

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(1) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 4458.

(2) Manning, M. J.; Knobler, C. B.; Khattar, R.; Hawthorne, M. F. *Inorg. Chem.*, in press.

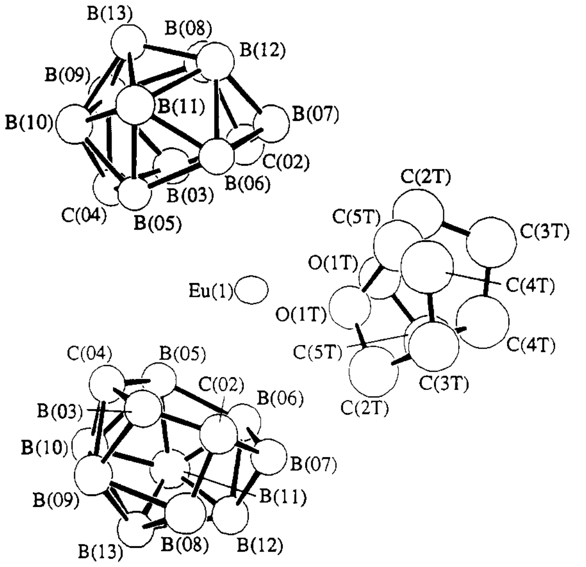

Figure 1. Molecular structure of $[1,1\text{-}(THF)_2\text{-}\mathit{commo}\text{-}1,1'\text{-}Eu(1,2,4\text{-}EuC_2B_{10}H_{12})_2]^{2-}$. All hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Eu(1)–O(1T), 2.63 (1); Eu(1)–C(2), 2.89 (1); Eu(1)–B(3), 3.09 (2); Eu(1)–C(4), 3.20 (1); Eu(1)–B(5), 2.98 (2); Eu(1)–B(6), 2.99 (2); C(2)–B(3), 1.45 (2); C(2)–B(7), 1.55 (2); C(4)–B(3), 1.60 (2); C(4)–B(5), 1.64 (2). Selected bond angles (deg): B(13)–Eu(1)–B(13), 127.4 (3); O(1T)–Eu(1)–O(1T), 74.8 (3); B(13)–Eu(1)–O(1T), 109.9 (3) and 111.3 (3).

structural characterization of a novel europium sandwich complex. To our knowledge, it represents the first structurally chracterized example of a lanthanide sandwich complex containing $[\mathit{nido}\text{-}7,9\text{-}C_2B_{10}H_{12}]^{2-}$ ligands.

The interaction of $Na_2[nido\text{-}7,9\text{-}C_2B_{10}H_{12}]$[3] (0.66 g, 4.58 mmol) with $EuI_2(THF)_2$ (2.5 g, 4.55 mmol) in THF at room temperature affords a light yellow complex that is insoluble in THF but soluble in MeCN. Recrystallization of this complex from MeCN/Et_2O gives orange crystals. An X-ray diffraction study showed[4] this species to be a polymeric complex with the composition $[Eu(C_2B_{10}H_{12})(MeCN)_3]_n$ (**1**). Complex **1** is isostructural with the recently reported strontium complex $[\mathit{closo}\text{-}1,1,1\text{-}(MeCN)_3\text{-}1,2,4\text{-}SrC_2B_{10}H_{12}]_n$.[5] The complete structural characterization of complex **1** will be published elsewhere. Complex **1** (1.1 g, 2.15 mmol) reacts further with $Na_2[\mathit{nido}\text{-}7,9\text{-}C_2B_{10}H_{12}]$ (0.265 g, 1.84 mmol) in THF to afford an orange complex that is soluble in THF and MeCN. Metathesis of this complex with Et_4NCl followed by recrystallization from THF/MeCN/Et_2O gives orange crystals, which an X-ray diffraction study showed to be a monomeric complex with the formulation $[Eu(C_2B_{10}H_{12})_2(THF)_2][NEt_4]_2$ (**2**).[6] The sodium salt of **2**, $Na_2[Eu(C_2B_{10}H_{12})_2(THF)_2]$, reacts with 1 molar equiv of $EuI_2(THF)_2$ to afford the THF derivative of **1**. As expected, complex **2** can be directly obtained from the addition of a THF solution of $EuI_2(THF)_2$ (1.1 g, 2 mmol) to a THF solution of $Na_2[\mathit{nido}\text{-}7,9\text{-}C_2B_{10}H_{12}]$ (0.64 g, 4.44 mmol) followed by metathesis with Et_4NCl. Interestingly, reaction of a half-equiv of $EuCl_3$ with $Na_2[\mathit{nido}\text{-}7,9\text{-}C_2B_{10}H_{12}]$ with subsequent reduction of Eu(III) results, as well, in the formation of **2**. Furthermore, we have observed that the disproportionation reaction of **1** with 1 molar equiv of NaC_5Me_5 in THF followed by metathesis with Et_4NCl also affords crystalline **2**.

A view of the molecular structure[7] of **2** is illustrated in Figure 1, along with some important interatomic distances and angles. The europium atom is sandwiched by two carborane ligands. The remainder of the coordination sphere about the europium is completed by two THF ligands. The dianion **2** has a 2-fold axis that passes through europium and relates one carboranyl and one THF ligand to the two other ligands. The Eu–carborane B and C distances range from 2.89 to 3.20 Å, while the Eu–O(THF) distance is 2.63 (1) Å. The angles around europium that involve the two apical boron atoms B(13), 127.4 (3)°, and the two THF oxygen atoms O(1T), 74.8 (3)°, are very similar to those found previously for the 7,8-dicarbollide samarium sandwich complex $[3,3\text{-}(THF)_2\text{-}\mathit{commo}\text{-}3,3'\text{-}Sm(3,1,2\text{-}SmC_2B_9H_{11})_2][PPN]$.[1,2] In the present case the B(13)–Eu(1)–O(1T) angles are 109.9 (3) and 111.3 (3)° and thus the coordination geometry about the europium atom in **2** can be best viewed as distorted tetrahedron.

The C_2B_{10} moiety in **2** can be compared with that observed in other metallacarborane complexes. The interatomic distance B(3)···B(8) in **2** is 2.14 (2) Å, very similar to 2.166 Å found in the complex[8] $\mathit{closo}\text{-}1,1\text{-}(PPh_3)_2\text{-}1\text{-}H\text{-}1,2,4\text{-}RhC_2B_{10}H_{12}$ (**3**) but longer than the 2.082 Å found in the complex[9] $\mathit{closo}\text{-}1\text{-}(\eta\text{-}C_5H_5)\text{-}1,2,4\text{-}CoC_2B_{10}H_{12}$. The B(9)···C(2) distance is 2.65 (2) Å, somewhat shorter than 2.72 Å found in complex[8] **3**. The C(2)···B(12) distance is 2.83 (2) Å, nearly the same as 2.841 Å reported for complex[8] **3**, while the B(3)···B(10) distance, 2.91 (2) Å, is nearly identical with 2.938 Å found in this same complex.[8] In complex **2**, the four boron atoms in the top belt (bonding face) of the carborane cage are coplanar (within 0.002 Å) with C(2) lying above (0.205 Å) and C(4) lying below (0.191 Å) this plane. The five boron atoms of the bottom belt are coplanar (within 0.06 Å). The planes defined by the top and the bottom belts are nearly parallel (4.6° between their normals). Both the carbon atoms C(2) and C(4) interact asymmetrically with the adjacent boron atoms in the top belt [C(2)–B(3), C(2)–B(7), C(4)–B(3), and C(4)–B(5) distances are 1.45 (2), 1.55 (2), 1.60 (2), and 1.64 (2) Å, respectively]. These interactions are shorter than those found in the complex[5] $[\mathit{closo}\text{-}1,1,1\text{-}(MeCN)_3\text{-}1,2,4\text{-}SrC_2B_{10}H_{12}]_n$ [C(2)–B(3), C(2)–B(7), C(4)–B(3), and C(4)–B(5) distances are

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(3) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1976**, *15*, 2872.

(4) Khattar, R.; Johnson, S. E.; Hawthorne, M. F. Unpublished results.

(5) Khattar, R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1990**, *29*, 2191.

(6) Data for **2** are as follows. FAB MS (*m/e*, fragment): found, 845.010, M^+; calcd, 845.140, M^+. ^{11}B NMR (THF-d_8, 20 °C, chemical shifts referenced to external $BF_3{\cdot}OEt_2$ (in ppm), peaks upfield of the reference designated as negative, areas given in parentheses): −9.49 (1), $^1J_{BH}$ = 128 Hz; −0.60 (4), $^1J_{BH}$ = 149 Hz; 3.44 (2), $^1J_{BH}$ = 145 Hz; 9.95 (1), $^1J_{BH}$ = 154 Hz; 29.1 (1), $^1J_{BH}$ = 158 Hz.

(7) Crystal data: $C_{28}H_{80}B_{20}O_2N_2Eu$, monoclinic, $I2/c$, a = 18.571 (7) Å, b = 9.396 (3) Å, and c = 27.813 (10) Å, β = 103.38 (1)°, V = 4721 Å^3, and Z = 4 (anion located on a 2-fold axis). Other data: μ(Mo Kα) = 13.6 cm^{-1}, D(calcd) = 1.2 g cm^{-3}, T = 298 K, λ = 0.7107 Å, orange plate specimen, crystal size 0.05 × 0.22 × 0.4 mm. An orange crystal obtained from a THF/MeCN/Et_2O solution was sealed in a capillary on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of this department. Systematic absences were found for hkl reflections for which $h + k + l \neq 2n$ and for $h0l$ reflections for which $l \neq 2n$. Unit cell parameters were determined from a least-squares fit of 17 accurately centered reflections ($4.4 < 2\theta < 13.5°$). Data were collected at 298 K in the θ–2θ scan mode. Three intense reflections (31$\bar{4}$, 202, 01$\bar{1}$) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay and fluctuated a maximum of ±4.5%, during the course of the experiment (60.5 h). Of the 1499 unique reflections measured, 1201 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; ABSCOR, a locally written ψ-scan-based absorption correction calculation; ORTEP (Johnson). Atoms were located by use of heavy-atom methods. All calculations were performed on the VAX 3100 computer of the J. D. McCullough Crystallographic Laboratory. With the exception of Eu, refined anisotropically, all non-hydrogen atoms were refined isotropically (122 parameters). All carboranyl H atoms were included in located positions. All methyl and methylene H atoms were included in calculated positions in structure factor calculations, C–H = 1.0 Å, with an assigned u value of 0.06 (carboranyl), 0.10 (THF), or 0.09, 0.10, or 0.11 Å^2 (cation). H parameters were not refined. Scattering factors for H were obtained from Stewart et al. (Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175) and for other atoms were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV. Anomalous dispersion terms were applied to the scattering of Eu. The largest peak on a final difference electron density map was 1 e Å^{-3}. The final discrepancy index was R = 0.050, R_w = 0.059, and GOF = 1.89.

(8) Hewes, J. D.; Knobler, C. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 206.

(9) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1974**, *13*, 1411.

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-$CaC_2B_{10}H_{12}$. 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.

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[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.

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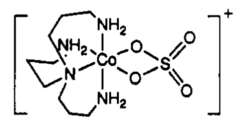
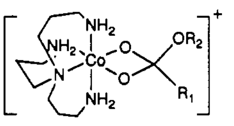
A Cobalt(III) Sulfato Chelate. Synthesis and Structure of $[(trpn)Co(\eta^2\text{-}SO_4)]ClO_4 \cdot H_2O$

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 $Co^{III}(\eta^2\text{-}SO_4)$ 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 $[(trpn)Co(\eta^2\text{-}SO_4)]ClO_4 \cdot H_2O$ derived from the fact that I simulates, in charge and geometry, tetrahedral intermediate II postulated in cobalt-catalyzed ester hydrolyses.[4] 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]

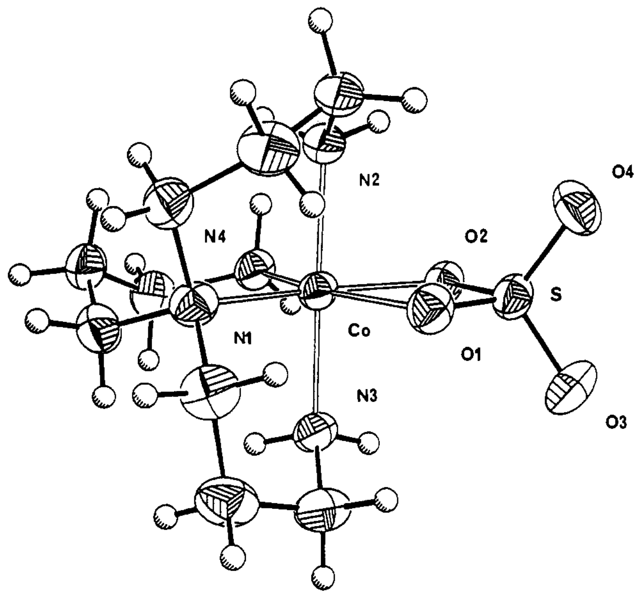


Figure 1. ORTEP representation of $[(trpn)Co(\eta^2\text{-}SO_4)]ClO_4 \cdot H_2O$ complex at the 50% probability level. Selected bond lengths (Å) and interbond angles (deg): Co–O(1) = 1.974 (4), Co–O(2) = 1.950 (3), Co-N(1) = 1.983 (4), Co-N(2) = 1.977 (4), Co-N(3) = 1.971 (4), Co-N(4) = 1.949 (4), 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).

Compound I was synthesized by adding to water (500 mL) $Co(ClO_4)_2 \cdot (H_2O)_6$ (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 $[(trpn)Co(CO_3)]ClO_4 \cdot H_2O$, 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_2SO_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)

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[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 $Co^{III}(\eta^2\text{-}SO_4)$ moiety. Only few crystal structures have been reported for $M(\eta^2\text{-}SO_4)$. (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 $C_9H_{24}N_4Co(SO_4)(ClO_4) \cdot H_2O$: 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_2O; 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 $[(trpn)Co(\eta^2\text{-}SO_4)]ClO_4 \cdot H_2O$ are monoclinic, space group $P2_1/c$, with $a = 8.753$ (4) Å, $b = 16.580$ (7) Å, $c = 12.510$ (7) Å, $\beta = 97.89$ (4)°, $v = 1798$ (1) Å^3, $d_{calcd} = 1.70$ g/cm^3, $Z = 4$, MW = 460.77 and $\mu = 12.62$ 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 $3° < 2\theta < 45°$ 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 $I > 3\sigma(I)$.

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