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Crystal Structure Determination of a (μ-Amido)(μ-hydroxo)(μ-superoxo)dicobalt(III) Complex from the Werner Collection

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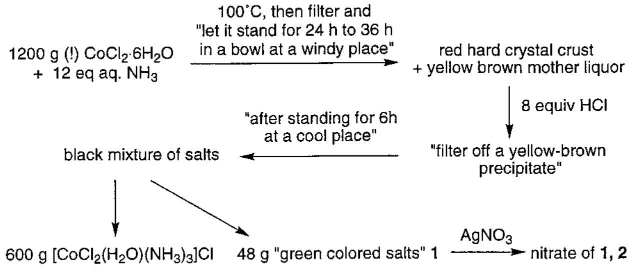
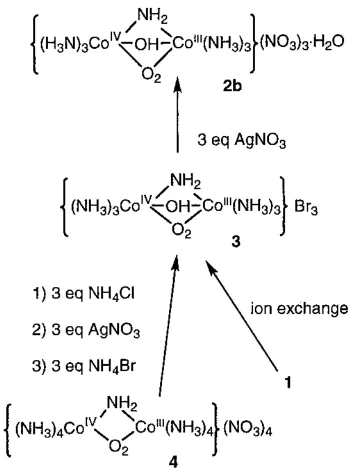
Introduction

The study of dinuclear cobalt complexes began as early as the middle of the 19th century.[1,2] Reaction of dioxygen with polyamminecobalt(II) salts yielded brown "oxykobaltiake"[3] and green "anhydrooxykobaltiake" compounds.[4] At the turn of the 20th century, one of us described these species respectively as deriving from the addition product of one molecule of O_2 either to two pentaamminecobalt(II) units[5] or to one pentaammine-cobalt(II) and one pentaamminecobalt(III) unit.[6] The nature of the O−O bond in the resulting dinuclear cobalt complexes was the subject of much controversy. X-ray diffraction and vibrational and EPR spectroscopic studies eventually allowed the distinction to be made between superoxo and peroxo ligands. Several dicobalt(III) complexes with a superoxo ion as the only bridging unit were crystallographically characterized,[7−11] and other superoxo-bridged dicobalt complexes had either an additional μ-amido[12,13] or a μ-hydroxo[14] bridge. In these doubly bridged dicobalt complexes, the resulting five-membered rings were almost flat.

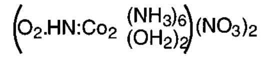
Scheme 1. Werner's Description[16] of the Synthesis of Melanochloride Following Vortmann's Notes[15]



Scheme 2. Werner's Description of the Synthesis of **2b** from **4** or by Counterion Exchange from **1**[5]



In the late 1890's, an attempt was made to repeat an earlier synthesis[15] of melanochloride. The procedure, outlined in Scheme 1, yielded a mixture that contained a new green salt, **1**. Since the elemental analysis of **1** could not be explained, the chloride was exchanged for nitrate to afford salt **2**, which crystallized "nach einiger Zeit ... in grossen Blättern" (after some time ... in the form of large sheets).[16] The nitrate compound **2** was initially characterized as an "ozoimidohexammindikobalt nitrate", **2a**.[17] Subsequent work led to the reassignment of **2** as



$$\left(O_2.HN:Co_2\begin{matrix}(NH_3)_6\\(OH_2)_2\end{matrix}\right)(NO_3)_2$$

2a

the μ-amido-ol-peroxo-$Co^{III}Co^{IV}$ salt **2b** based on elemental analysis and reactivity.[5,18] The bromide analogue **3** could be synthesized either from the octaammine dicobalt nitrate **4** or by anion exchange from the chloride salt **1**, a byproduct of the melanochloride synthesis (Scheme 2).

In the present work, we have reinvestigated the chemical nature of **2** by modern crystallographic methods using crystals from the Werner collection at the University of Zürich, probably synthesized around 1909. The result afforded a new chemical motif described herein.

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Table 1. Crystallographic Data for $[Co_2(\mu\text{-}OH)(\mu\text{-}O_2)(\mu\text{-}NH_2)(NH_3)_6](NO_3)_3 \cdot 1.25H_2O$ (**2**)

empirical formula	$Co_2H_{23.5}N_{10}O_{13.25}$
fw	493.61
cryst size	0.2 × 0.2 × 0.05 mm^3
crystal color, shape	brown, hexagonal shaped plate
wavelength	Mo Kα, 0.710 73 Å
temp	188(2) K
cryst syst, space group	monoclinic, $P2_1/n$
unit cell dimensions	$a = 14.1508(9)$ Å $b = 8.8313(6)$ Å, $\beta = 115.530(1)°$ $c = 15.1098(10)$ Å
vol	1703.9(2) Å^3
Z, calcd density	4, 1.910 Mg/m^3
absorption coeff	2.036 mm^{-1}
θ range for data collection	1.65−28.28°
reflns collected/unique	10433/3963 [$R_{int} = 0.0567$]
absorption correction	SADABS
max and min transmission	1.000000 and 0.868332
data/restraints/parameters	3963/35/275
S on F^2/obsd reflns [$I > 2\sigma(I)$]	0.967/2540
final R indices [$I > 2\sigma(I)$]^{a,b}	$R = 0.0497$, wR$^2 = 0.1082$
largest diff peak and hole	0.713 and −0.544 e/Å^3

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR^2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Experimental Section

The X-ray crystal structure determination was carried out on a Bruker (formerly Siemens) CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710$ 73 Å) controlled by a Pentium-based PC running the SMART software package.[19] Single crystals were mounted at room temperature on the ends of glass fibers in Paratone N oil, and data were collected for 20 s per frame at 188 K in a stream of cold dinitrogen maintained by a Bruker LT-2A nitrogen cryostat. Data collection and reduction protocols are described in detail elsewhere.[20] The structure was solved by direct methods and refined using the SHELXL97 software package.[21] The disorder of the μ-amido and μ-hydroxo units was confirmed by replacing the mixed arrangement with either two oxygen or two nitrogen atoms, which yielded either unreasonably large or small thermal parameters, respectively. Hydrogen atoms were assigned idealized locations (ammine ligands) or located and refined (water molecules). The latter thermal parameters were restrained at 1.5 times the U_{eq} value of the pertinent atom. Empirical absorption corrections were applied by using SADABS.[22] Relevant crystallographic information is reported in Table 1.

Results and Discussion

The structure of **2** is depicted in Figure 1, and selected geometric information is listed in Table 2. Two Co(III) ions at a distance of 2.776(1) Å are bridged by hydroxo, amido, and superoxo anions. The oxygen−oxygen bond distance of 1.340(4) Å is well within the reported range (1.26−1.36 Å) reported for superoxide ions bridging two Co(III) centers.[23] The cation has almost perfect C_{2v} symmetry, the deviations from the best planes through N2−Co1−O3−O4−Co2−N6, N1−Co1−O1A−Co2−N4, and N3−Co1−N7A−Co2−N5 being less than 0.02 Å. The individual metal ions have slightly distorted octahedral coordination environments, with bond angles ranging from 80.3(1)° to 94.4(2)°. These values and the Co−N and Co−O bond lengths are in good agreement with the results of numerous octahedral cobalt(III) structures.[11,24,25] The amido and the hydroxo bridge are indistinguishable and were refined as a 1:1 disordered pair. The coordination spheres of the cobalt atoms are each completed by three terminally coordinated ammonia molecules. One of the three nitrate anions in the crystal lattice has disordered oxygen atoms. In addition, a fully occupied and a one-quarter occupied water were located.

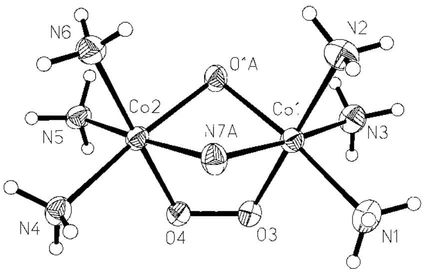

Figure 1. ORTEP plot of the cation in $[Co_2(\mu\text{-}OH)(\mu\text{-}O_2)(\mu\text{-}NH_2)(NH_3)_6](NO_3)_3 \cdot 1.25H_2O$ (**2**). Atoms are shown with 50% probability thermal ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg)[a]

Co1/2−N7A/ O1A/N7B/O1B[b]	1.922(4)	O3−Co1−N1	88.36(15)
Co1−O3	1.872(3)	N1−Co1−N2	91.00(17)
Co2−O4	1.887(3)	O3−Co1−N3	89.65(15)
O3−O4	1.340(4)	N1−Co1−N3	92.41(17)
Co1−N1	1.965(4)	N2−Co1−N3	91.39(17)
Co1−N2	1.968(4)	O4−Co2−N5	89.11(14)
Co1−N3	1.968(4)	N6−Co2−N5	90.54(16)
Co2−N4	1.964(4)	O4−Co2−N4	88.98(14)
Co2−N5	1.963(4)	N6−Co2−N4	92.03(16)
Co2−N6	1.947(4)	N5−Co2−N4	91.42(16)
Co1−Co2	2.7664(9)	Co1−O3−O4	112.8(2)
Co1−N7A/O1A/ N7B/O1B−Co2[b]	92.0(2)	Co2−O4−O3	111.8(2)

[a] Numbers in parentheses represent estimated standard deviations in the last digit(s) listed. [b] N7A and O1A as well as N7B and O1B are constrained to be on the same positions, respectively. Therefore, their distances to the cobalt atoms are the same.

The X-ray results clearly confirm the chemical nature of **2** as described in 1910 with the exception of the metal and O_2^- oxidation states. To the best of our knowledge, this species is the first crystallographically characterized dinuclear transition metal complex having all three μ-hydroxo, μ-amido, and μ-superoxo bridging ligands. The maintenance of the sample stability and crystallinity over nearly a century is also noteworthy.

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Supporting Information Available: A crystallographic information file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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