

Original Research

The Unexpected Synthesis of a New (μ_2 -hydroxo- μ_2 -peroxo) Dicobalt Complex

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Abstract

The compound, [cis-dichloro-(tris-2-amino(ethylamine))cobalt(III)]chloride hydrate, [cis-Cl₂-(tren)Co(III)Cl]·H₂O, a conglomerate crystallizing in $P2_1$ with $Z = 4$ ($Z' = 2$), has been used as a precursor in the synthesis of a new dicobalt(III) peroxo complex: [(μ_2 -hydroxo)(μ_2 -peroxo)bis(tris-2-amino(ethylamine))di-cobalt(III)] tris(triiodide) dihydrate. This material crystallizes, without disorder, in space group $P2_12_12_1$ with $Z = 4$ ($Z' = 2$), thus making it, unambiguously, an example of a conglomerate. Its cell constants are 11.1416(2), 16.0553(3), 20.7699(3) Å, $V = 3715.36(11)$ Å³, measured at 100K, with an R-factor of 3.69% and a Flack parameter of -0.012(7). There are no phase transitions induced by warming the crystals to 296K. It is obtained from an aqueous NH₄I solution in two different ways, described below.



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Keywords

μ -hydroxo- μ -peroxo dicobalt compounds; tris(2-aminoethyl)amine cobalt species; iodides; tri-iodides; kryptoracemates; conglomerates

1. Introduction

The Cambridge Structural Database, or CSD [1], has 100 examples of μ -peroxo di-cobalt compounds with a wide variety of different ligands. Of these, five crystallize in Sohncke space groups and all are disordered to different degrees. Moreover, the referenced set contains eighteen examples of (μ_2 -hydroxo)(μ_2 -peroxo) complexes, none of which crystallize in a Sohncke space group.

Bernal [2] studied complex cations of the type $[(\text{NH}_3)_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{5+}$, as prepared by Werner [3] and Werner & Mylius [4], who postulated that the above formula implies two different cobalt ions with valences of +3 and +4 and a (μ -peroxo)(O_2^{2-}) bridge system; however, other structures can be imagined where the two cobalt ions are +3 each and the two oxygen atoms are forming a μ -superoxo (O_2^-) bridge system, which is a free radical. Given the results of the esr experiment [2], it is quite reasonable to suggest that the relevant O-O moiety should be classified as a superoxide bridge, given the observed g-value of 2.025 which is typical of free radicals. This observation should be contrasted with the values normally associated with a variety of relevant, paramagnetic, cobalt complexes that Collman [5] discussed in detail (see especially Table 2 [5]).

In retrospect, it is remarkable that despite the fact that the theory of Coordination Chemistry was enunciated in 1893, at which time there were considerable misgivings as to its validity, Werner had a very good grasp of what the chemical composition of the complexes were no matter what their proper electronic descriptions were, for such formulations were completely beyond the chemical theories of those days. Interestingly, dinuclear cobalt complexes were under investigation by Fremy as early as 1852 [6]. Several of these substances have been, and still are, rather controversial because the precise assignment of the nature of the O-O bridge is debatable, particularly those that are paramagnetic. (Readers are referred to a paper by Spingler [7] which gives a very thorough and compact history up through that time). Finally, note that since the year 2000, the structures of 52 μ -peroxo-dicobalt compounds have been determined, of which 9 contain also an additional OH bridge, i.e., [GUVSIZ, HULXES, MANYIM, PIVGIM, PIVGOS, RUCJUW, RUVJUO, UMIJEH, XAWWEA (CSD, [1]). Given the colors described for these complexes (orange, red, green, brown, black), this suggests that each of them requires detailed studies by a variety of techniques for proper formulation, because of the electronic changes introduced by the broad range of the ligands surrounding the cobalt species.

2. Materials and Methods

All the chemicals were of analytical reagent grade and were obtained from Sigma Aldrich, Fisher Scientific or VWR, and used without purification.

2.1 Synthesis of the Metal Complexes

Synthesis of the precursor [cis-Cl₂Co(III)(tren)]Cl·H₂O:

The first precursor cis-dinitro(tris-2-amino(ethylamine))cobalt(III) chloride, [cis-(NO₂)₂Co(tren)]Cl, was prepared following the process of Uprety [8]. A crystal from this preparation was mounted on the X-ray diffractometer and the cell dimensions were determined to match the existing material. Then this material was used to prepare the 2nd precursor, cis-dichloro(tris-2-amino(ethylamine))cobalt(III) chloride hydrate, [cis-Cl₂Co(tren)]Cl·H₂O, by adding 30% HCl to the previous complex, again following the preparation of Uprety [8]. To verify we had the desired starting material, we determined the space group and cell constants of this material and found that the structure was known and in the CSD [1] as **LIHPIE**.

Synthesis of **(1)**, [(μ₂-hydroxo)(μ₂-peroxo)di-cobalt(III)(tren)] tris(triiodide)·2H₂O:

The 2nd precursor above, [cis-Cl₂Co(tren)]Cl·H₂O, was used to make the product [(μ₂-hydroxo)(μ₂-peroxo)di-cobalt(III)(tren)] tris(triiodide)·2H₂O (**1**) by the following procedure (which was intended to make the simple iodide from the chloride with composition [cis-Cl₂Co(tren)] : 0.5 g of ([Co(tren)cisCl₂]Cl·H₂O was dissolved in a minimum amount of warm deionized water in a 50 mL beaker. 0.22 g of NH₄I was dissolved in a minimum amount of warm deionized water in a separate 50 mL beaker. The NH₄I solution was slowly poured into the [Co(tren)cisCl₂]Cl·H₂O solution. A wine-like red color was observed as the two solutions were mixed. The solution was left to heat at low temperature for about 15 minutes with continuous stirring, then left to slowly crystallize. Very dark wine-red crystals of **(1)** were collected.

2.2 X-Ray Diffraction Data Collection and Processing for (1)

A suitable crystal of **(1)** was mounted on a Bruker-AXS SMART APEX II CCD diffractometer at 100(1)K. Cell dimensions and intensities were all collected with CuKα radiation (λ = 1.54178 Å). Data processing, Lorentz-polarization, and face-indexed numerical absorption corrections were performed using SAINT, APEX, and SADABS computer programs [9-13] (see Table 1). The structure was solved by direct methods and refined by full-matrix least-squares methods on F², using the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. All H atoms were found in electron-density difference maps and allowed to ride on their respective C, N or O atoms. The methylene H atoms were then placed in geometrically idealized positions and constrained to ride on their parent C atoms with C—H distances of 0.99 Å; the N—H distances were fixed at 0.86 Å and the O—H distances were fixed at 0.84 Å. All of the above had U_{iso}(H) = 1.2U_{eq}(C) or 1.2U_{eq}(N) and U_{iso}(H) = 1.5U_{eq}(O). The crystallographic data have been deposited with the Cambridge Crystallographic Data Center. The deposition number for **(1)** is: 1977410 for the 100K structure.

3. Results and Discussion

3.1 The Structure of [(μ₂-hydroxo)(μ₂-peroxo)di-cobalt(III)(tren)] tris(triiodide)·2H₂O

Compound **(1)**: The structure was solved to yield a di-cobalt(III)(tren) species connected together by μ₂-hydroxo⁻¹ and μ₂-peroxo⁻² bridges. There are three (I₃⁻) counterions as required by electro-neutrality, and two waters of crystallization (see Figure 1). Details of the structure of the μ-hydroxo-μ-peroxo complex **(1)** are presented in Table 1.

As mentioned above, the addition of NH_4I to a solution of the precursor was intended to provide the simple iodide salt of the cis-dichloro(tren) species. Given our unexpected result, and in an effort to determine the origin of the peroxide, we reacted the same starting materials while purging all of the solutions continuously with dry N_2 gas. The results of this experiment are that the color of the solution, after heating as above, remained a visible purple color (still under N_2 atmosphere), and not the wine-red color observed previously after heating. When the solution was then exposed to air with stirring and heating, it turned wine-red within two to three minutes, indicating that it had incorporated O_2 from the air. Equally good-quality crystals of **(1)** were obtained from this preparation, sharing the same space group and cell constants as those of **(1)**, and shown in Figure 1. Thus, it seems reasonable to postulate that the reaction in this case is a simple redox reaction wherein I^- is oxidized to I_2 (and thence to form the I_3^- anion), while air O_2 is reduced to the peroxide anion O_2^{2-} , generating the observed bridged structure.

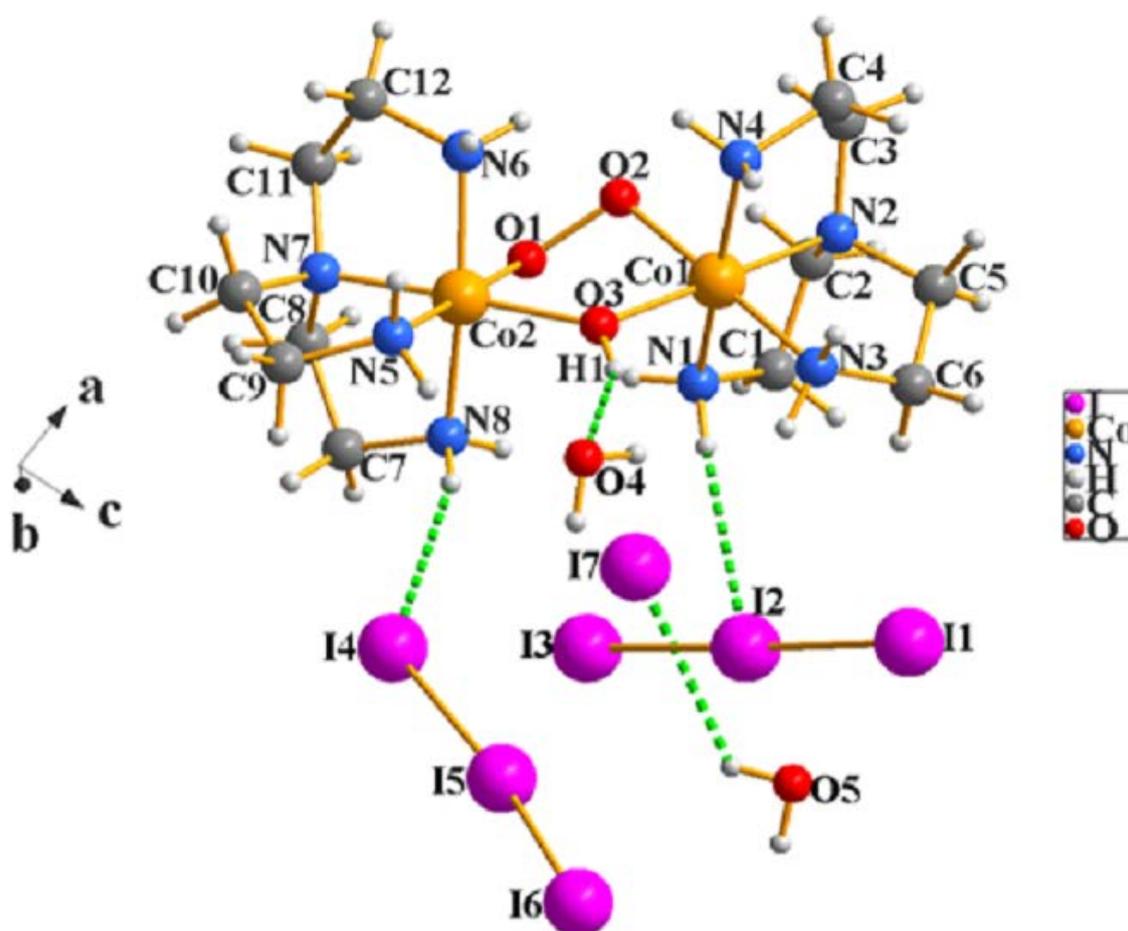


Figure 1 The conglomerate μ_2 -hydroxo⁻¹ μ_2 -peroxo²⁻ trenCo complex is shown here. The two trenCo moieties do not match in their absolute configurations. The entire cation is at a general position of the Sohncke space group $P2_12_12_1$. For an overlay of the left and right trenCo moieties, see Figure 2 below.

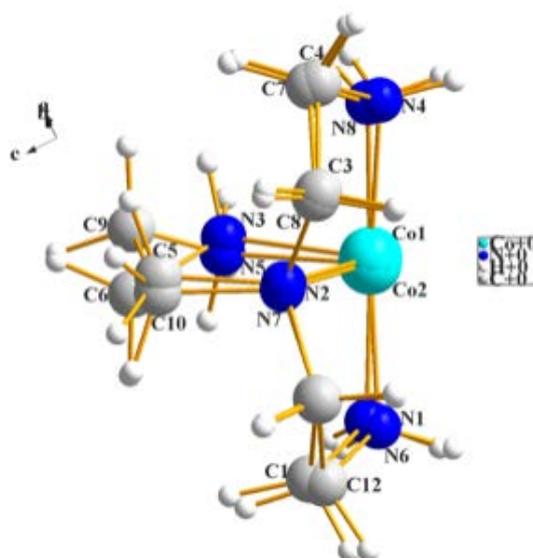


Figure 2 Overlay of Co1 and Co2 for structure **(1)**, after inverting Co2 portion. This overlay was obtained using the MERCURY routine of CSD [1] to create a CIF file, which was then used with the graphics computer program DIAMOND [14] to generate the overlapped figure. As you can readily see, the overlay is different, if for no other reason than the sequence of torsional signs differ significantly (see below). The torsional angles for the two independent molecules are: for Co1 moiety: 45.6(14), -48.4(14) & -38.5(16), and for the Co2 moiety: 39.8(17), 42.5(15) & -47.0(15)°.

Table 1 X-Ray structural parameters for **(1)**.

(1)	
Crystal data	
Chemical formula	C ₁₂ H ₃₇ Co ₂ N ₈ O ₃ ·3(I ₃)·2(H ₂ O)
<i>M_r</i>	1637.49
Crystal system, space group	Orthorhombic, <i>P2₁2₁2₁</i>
Temperature(K)	100
a, b, c (Å)	11.1416(2), 16.0553(3), 20.7699(3)
α, β, γ (°)	90., 90., 90.
<i>V</i> (Å ³)	3715.36 (11)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	66.008
Crystal size (mm)	0.10 × 0.24 × 0.26
Data collection	
Diffractometer	Bruker APEX2 diffractometer
Absorption correction	Numerical
<i>T_{min}</i> , <i>T_{max}</i>	0.002, 0.115
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	41325, 6536, 6285

R_{int}	0.08
$(\sin \theta/\lambda)_{\text{max}} (\text{\AA}^{-1})$	0.595
Refinement	
$R[F > 2\sigma(F)], wR(F), S$	0.038, 0.092, 1.08
No. of reflections	6536
No. of parameters	329
No. of restraints	4
H-atom treatment	Treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} (\text{e \AA}^{-3})$	2.62, -1.67
CCDC number	1977410

Computer programs: Bruker (2009) *SAINT*, *APEX*, *SADABS*, Sheldrick (2015) *SHELXL* [9-13], Putz & Brandenburg (2019) *DIAMOND* [14]

4. Conclusions

Above, we present the structure of a di- μ -bridged di-cobalt compound (**1**) which was heretofore unknown. Interestingly, while we initially obtained this di-cobalt complex (**1**) by an unexpected route, we describe a second, rational method of preparing it under a dry N_2 atmosphere, and then exposing it to air to produce the exact same material. In either case, the procedures described above are reproducible.

From the time the μ -peroxo compounds were initially discovered, it has been a challenge to determine how they are formed. Thus, mechanistically, and thermodynamically, our study provides some clues as to how this can be achieved by someone equipped to do fast kinetics as a function of temperature; i.e., (a) The μ -hydroxo- μ -peroxo product has been isolated in solid form. It can be spectroscopically characterized. The tri-iodide is well known that way already. Suitable, non-interfering wavelengths and extinction coefficients can be identified to follow the reactions. (b) The reaction products can then be followed at different temperatures, AND, (c) from the temperature dependence of those reactions, the rate laws and thermodynamic constants (ΔH , etc., values) can be determined.

We demonstrated that the reaction proceeds in a stepwise manner since oxygen can be introduced at the end, independently, and the product is the same. Therefore, the above spectroscopic methodology can be used to follow the kinetics, etc., of this last step and may be observed independently. Such studies would be of great value as biological models, since similar Co-O_2 interactions occur in living systems.

Finally, note that the kinetics of the disappearance of the precursor of the final product can also be followed and those data correlated with the formation of the μ -hydroxo- μ -peroxo complex obtained above.

Acknowledgments

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Additional Materials

The following additional materials are uploaded at the page of this paper.

1. Figure S1: ORTEP for $C_{12}H_{37}Co_2N_8O_3 \cdot 3(I_3) \cdot 2(H_2O)$, (1): Ellipsoids are drawn at 30% probability level.

Author Contributions

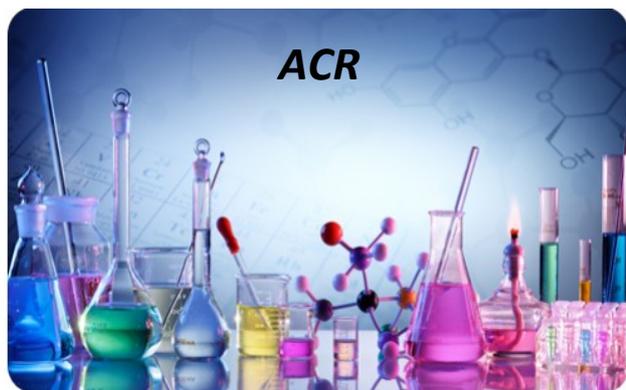
Yashiro Rojas, Evana Halaka, Mary Hanna, Alex Sidoti, Jehan Joma, Mina Mikhael are undergraduate students who prepared the complexes under direct supervision of RAL. IB and RAL wrote the manuscript.

Competing Interests

The authors have declared that no competing interests exist.

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