

Synthesis and Crystal Structure of the First Example of a Tris-Chelated Co(II) Complex Based on Oxamide Dioxime Ligand

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Abstract

A new cobalt(II) complex, $[\text{Co}(\text{H}_2\text{oxado})_3]\text{C}_2\text{O}_4 \cdot \text{H}_2\text{oxado} \cdot 2\text{H}_2\text{O}$ (H_2oxado = oxamide dioxime), has been synthesized in aqueous solution and characterized by elemental analysis and single crystal X-ray structure determination. The complex crystallizes in the triclinic space group $P-1$, with the parameters $a = 9.46(4)$, $b = 11.84(5)$, $c = 12.81(5)$ Å, $\alpha = 104.94(6)$, $\beta = 99.29(5)$, $\gamma = 106.73(5)$, $V = 1284(9)$ Å³, $Z = 2$. The central cobalt(II) cation is pseudo-octahedrally coordinated by six imino N atoms of the neutral oxamide dioxime ligand. In the solid state, each of the following bricks, namely the cationic complexes, the oxalate dianions as well as the oxamide dioxime crystallization molecules, pile up parallel to the a axis. The bulk structure is consolidated by an extended three-dimensional network of hydrogen bridgings—that link the ionic partners, oxamide dioxime and water molecules to one another—and by coulombic interactions.

Keywords

Crystal Structure, Cobalt(II) Complex, Oxamide Dioxime, Oxalate, Hydrogen Bridging

1. Introduction

Transition metal complex cations of the form $[\text{M}(\text{H}_2\text{oxado})_3]^{n+}$ (M = metal(II) or metal(III), $n = 2$ or 3 , H_2oxado =

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oxamide dioxime), constitute an interesting family of chiral and—eventually—paramagnetic cations, due to their molecular structure (geometry and volume) that predestines them to undergo straightforward chemical combinations with suitable anionic counterparts such as the oxalatometalate series, $[M'(C_2O_4)_3]^{3-}$ ($M' = \text{metal(III)}$), thus generating a wide range of multifunctional crystalline materials [1] required in the development of emerging technologies [2]-[5]. It has been observed previously that in aqueous solution, the Co^{II} ion generally reacts with the oxamide dioxime ligand, yielding the familiar trischelated Co^{III} complex cation, $[\text{Co}(\text{H}_2\text{oxado})_3]^{3+}$ [6]-[8]. In our current research program which is focused on fabricating multifunctional materials involving N,N'- or O,O'-chelating ligands, the $[\text{Co}(\text{H}_2\text{oxado})_3]^{3+}$ building block and its homologous nickel(II) complex, $[\text{Ni}(\text{H}_2\text{oxado})_3]^{2+}$, have proven to be good partners in the formation of hydrogen-bonded functional solid-state assemblies [9] [10].

Along the line of this research program, an attempt to prepare the elusive tris(oxamide dioxime)cobalt(III) tris(oxalato)cobaltate(III), $[\text{Co}(\text{H}_2\text{oxado})_3][\text{Co}(\text{C}_2\text{O}_4)_3] \cdot n\text{H}_2\text{O}$, similar to $[\text{Co}(\text{H}_2\text{oxado})_3][\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 5\text{H}_2\text{O}$ [9] led to the serendipitous isolation of the cobalt(II) title compound, $[\text{Co}(\text{H}_2\text{oxado})_3]\text{C}_2\text{O}_4 \cdot \text{H}_2\text{oxado} \cdot 2\text{H}_2\text{O}$, the structure of which is reported herein. The present finding turns out to be quite interesting, in as much as it provides, to the best of our knowledge, the first example of a complex salt containing the dipositive $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$ cation, as highlighted in **Scheme 1**.

2. Experimental

2.1. Materials and Measurements

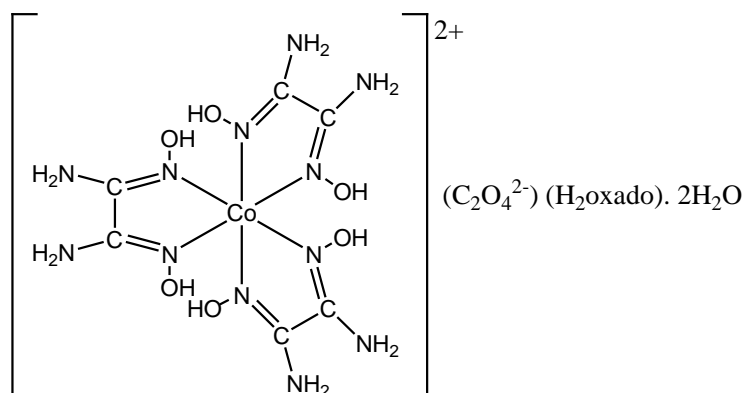
The organic ligand H_2oxado (analytical grade) was freshly prepared by the condensation of dithiooxamide (98.5%, Fluka) and hydroxylammonium chloride (99%, Merck) in presence of sodium carbonate (99.5%, Prolabo) as previously reported [9] [11]. The tripotassium tris(oxalato)cobaltate(III) trihydrate salt, $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, was synthesized as described by Bailar & Jones [12]. All other chemicals were purchased and used as received. Elemental analysis was performed on a VARIO EL (Heraeus) CHNS analyzer.

2.2. Synthesis of $[\text{Co}(\text{H}_2\text{oxado})_3]\text{C}_2\text{O}_4 \cdot \text{H}_2\text{oxado} \cdot 2\text{H}_2\text{O}$

The title compound was obtained as follows: dark green crystals of $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ (0.5 g, 1 mmol) were dissolved in H_2O (50 mL) acidified with a drop of HNO_3 . To the filtered solution were added with stirring at 30°C successive small portions of oxamide dioxime (0.36 g, 3 mmol), followed by portions of finely powdered $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3 g, 1 mmol). The reaction mixture was stirred magnetically for 1 h and allowed to decant over 2 h. The reddish-pink precipitate of CoC_2O_4 was carefully filtered off, and the solution left to evaporate slowly in a hood at room temperature. After two weeks, prismatic reddish crystals suitable for single crystal X-ray studies were harvested. Anal. Calcd. for $\text{C}_{10}\text{H}_{28}\text{CoN}_{16}\text{O}_{14}$: C, 18.33; H, 4.30; N, 34.20%. Found: C, 18.32; H, 4.30; N, 34.18%.

2.3. Crystal Structure Determination and Refinement

A suitable single crystal of the title compound with dimensions $0.5 \times 0.12 \times 0.10$ mm was mounted on a glass



Scheme 1. Chemical diagram of the title compound.

fiber and fixed to the goniometer head. Data collection [13] was carried out on a Bruker-Nonius X8 kappa APEX II CCD area-detector diffractometer using graphite-monochromatic radiation $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ at 296(2) K. Data reduction was performed using SAINT [13], and absorption corrections were carried out by multi-scan method by SADABS [14]. The structure was solved by direct methods and refined against F^2 by full-matrix least-squares techniques with SHELXTL [15]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective parent atoms with isotropic displacement parameters. Crystal data and structure refinement details for the title compound are summarized in **Table 1**, and selected bond lengths and angles in **Table 2**.

3. Results and Discussion

Single-crystal X-ray structural analysis reveals that the title compound crystallizes in the triclinic space group $P-1$. It is formulated $[\text{Co}(\text{H}_2\text{oxado})_3]\text{C}_2\text{O}_4 \cdot \text{H}_2\text{oxado} \cdot 2\text{H}_2\text{O}$. As shown in **Figure 1**, the molecular structure is composed of one $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$ complex cation, one oxalate (2-) anion, one oxamide dioxime molecule and two solvent water molecules. The point of prime interest in this report is the assessment of the existence of the pseudo-octahedral complex cation, tris(oxamide dioxime)cobalt(II), $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$, and this, as far as we know, is raised here for the first time. The oxamide dioxime acting as a crystallization molecule has been described previously [16]. Selected bond lengths and angles of the title compound are listed in **Table 2**, and compared with the corresponding values (in brackets) for the reported $[\text{Co}(\text{H}_2\text{oxado})_3]^{3+}$ cation [6]-[8]. Data derived from this tripostive cation reflect nicely the C_3 symmetry of the complex entity, whereas those derived from the dipositive complex cation, $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$, deviate noticeably from this symmetry. However, the pseudo-octahedral coordination of the central cobalt and the chiral nature of the complex cation are maintained. Whereas the O–N bond lengths within the $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$ entities of the present structure range from 1.290(3) to 1.490(2) \AA , its average value (1.383 \AA) is slightly shorter than O–N bonds in the familiar $[\text{Co}(\text{H}_2\text{oxado})_3]^{3+}$ cation whose common value is 1.391(6) \AA (**Table 2**). The projection of the structure along [100] highlights the $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$ ions disposed in centrosymmetric dimers leading to a zig-zag chain running along c axis (**Figure 2**). The three-dimensional crystal packing of the title compound is reinforced by extended O–H \cdots O, O–H \cdots N and N–H \cdots O bridges which interlink the complex cations, $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$, oxalate anions, oxamide dioxime molecules and water molecules.

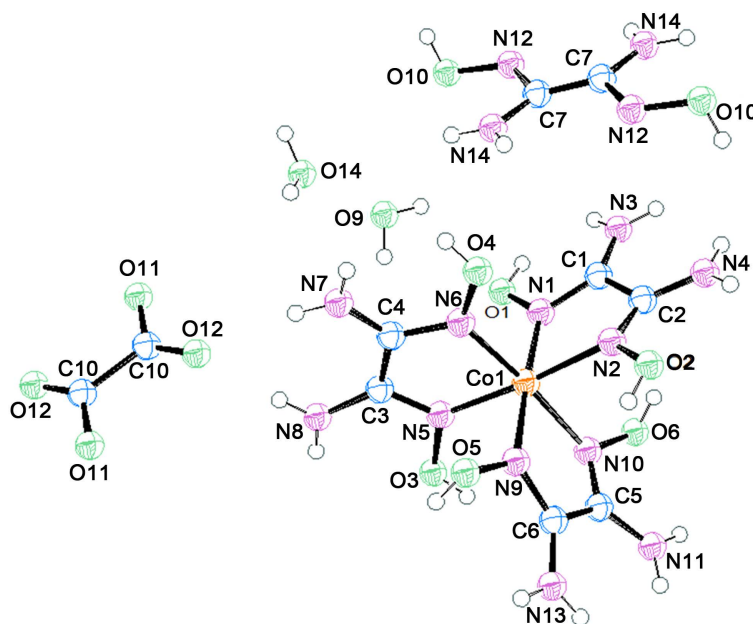


Figure 1. An ORTEP drawing of $[\text{Co}(\text{H}_2\text{oxado})_3]\text{C}_2\text{O}_4 \cdot \text{H}_2\text{oxado} \cdot 2\text{H}_2\text{O}$ showing atom-labelling scheme with displacement ellipsoids drawn at 50% probability level.

Table 1. Crystal data and structure refinement details for the title compound.

CCDC N°	CCDC-839359
Empirical formula	C ₁₀ H ₂₈ CoN ₁₆ O ₁₄
Formula weight	655.42
Temperature (K)	296 (2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	<i>P</i> -1
Unit cell dimensions	
<i>a</i> (Å)	9.46 (4)
<i>b</i> (Å)	11.84 (5)
<i>c</i> (Å)	12.81 (5)
α (°)	104.94 (6)
β (°)	99.29 (5)
γ (°)	106.73 (5)
Volume (Å ³)	1284 (9)
<i>Z</i>	2
Density (calculated, g·cm ⁻³)	1.696
Absorption coefficient (mm ⁻¹)	0.765
<i>F</i> (000)	678
Crystal size (mm)	0.50 × 0.12 × 0.10
Theta range for data collection (°)	1.70 - 25.00
Limiting indices	-11 ≤ <i>h</i> ≤ 11 -14 ≤ <i>k</i> ≤ 8 -15 ≤ <i>l</i> ≤ 15
Reflections collected	6152
Independent reflections	4429 [<i>R</i> (int) = 0.1281]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4429/0/379
Goodness-of-fit on <i>F</i> ²	1.008
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0324, <i>wR</i> ₂ = 0.0657
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0379, <i>wR</i> ₂ = 0.0685
Largest difference peak and hole (eÅ ⁻³)	4.812 and -3.307
Extinction coefficient	0.000 (9)
Completeness to $\theta = 25.00$, %	97.9

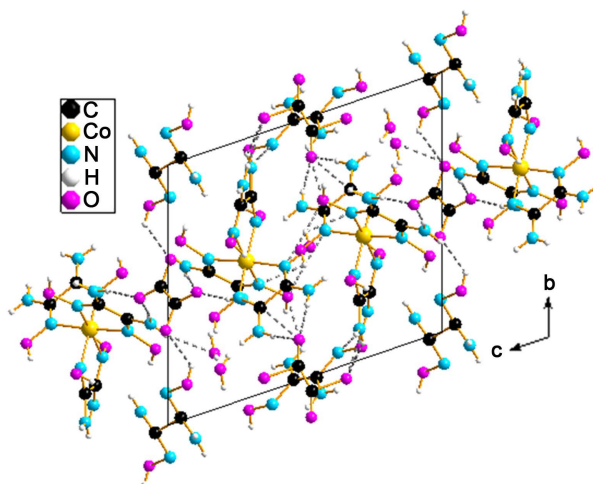


Figure 2. Projection of the achiral unit cell of the title compound along [100], showing centro-symmetric dimerization of Co^{II} complex cations and inter-connection of these dimers, $\text{C}_2\text{O}_4^{2-}$ dianions, H_2oxado and H_2O molecules via hydrogen bridges (dotted lines).

Table 2. Selected bond lengths (Å) and angles (°) for the title compound*.

Co(1)–N(1)	1.850 (3)	[1.910 (4)]
Co(1)–N(5)	1.939 (2)	[1.910 (5)]
Co(1)–N(6)	1.953 (2)	[1.910 (4)]
Co(1)–N(2)	1.952 (2)	[1.910 (4)]
Co(1)–N(9)	1.962 (2)	[1.910 (4)]
Co(1)–N(10)	2.020 (2)	[1.910 (5)]
O(1)–N(1)	1.370 (3)	[1.391 (6)]
O(2)–N(2)	1.390 (3)	[1.391 (6)]
O(3)–N(5)	1.490 (2)	[1.391 (6)]
O(4)–N(6)	1.380 (2)	[1.391 (6)]
O(5)–N(9)	1.290 (3)	[1.391 (6)]
O(6)–N(10)	1.380 (2)	[1.391 (6)]
N(1)–Co(1)–N(6)	89.8 (9)	[92.7 (2)]
N(6)–Co(1)–N(2)	95.5 (7)	[92.7 (2)]
N(5)–Co(1)–N(2)	175.6 (7)	[169.5 (2)]
N(5)–Co(1)–N(9)	85.2 (1)	[92.7 (2)]
N(1)–Co(1)–N(5)	97.5 (9)	[95.3 (2)]
N(5)–Co(1)–N(6)	80.9 (7)	[80.2 (2)]
N(1)–Co(1)–N(9)	176.9 (9)	[169.5 (2)]
N(1)–Co(1)–N(2)	80.0 (9)	[80.2 (2)]
N(2)–Co(1)–N(9)	97.5 (9)	[95.3 (2)]
N(6)–Co(1)–N(9)	92.2 (8)	[92.7 (2)]
N(9)–Co(1)–N(10)	81.6 (8)	[80.2 (2)]
N(1)–Co(1)–N(10)	96.5 (8)	[92.7 (2)]
N(2)–Co(1)–N(10)	86.6 (8)	[92.7 (2)]
N(6)–Co(1)–N(10)	173.7 (8)	[169.5 (2)]
N(5)–Co(1)–N(10)	97.4 (7)	[95.3 (2)]

*Comparative values in square brackets are from ref. [7].

Finally, it should be noted that the title compound, in spite of the fact that it contains an unfamiliar $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$ ion, happens to be a serendipitous isolation. Therefore, a systematic procedure designed to fabricate this compound is to be applied in our forthcoming works.

4. Conclusion

We have isolated from aqueous solution the salt $[\text{Co}(\text{H}_2\text{oxado})_3]\text{C}_2\text{O}_4 \cdot \text{H}_2\text{oxado} \cdot 2\text{H}_2\text{O}$ containing the unprecedented tris-chelated Co^{II} complex cation, $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$. In this cation, as well as in the familiar $[\text{Co}(\text{H}_2\text{oxado})_3]^{3+}$ ion, the central cobalt atom is in the same pseudo-octahedral coordination geometry of the six imino N atoms of H_2oxado . In the crystal, the $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$ ions are hydrogen-bonded into centrosymmetric dimers, thus generating zig-zag chains running parallel to [001]. It is interesting to note that the dipositive complex cation $[\text{Co}(\text{H}_2\text{oxado})_3]^{2+}$ appears as resulting from the reduction of the tripesitive complex cation $[\text{Co}(\text{H}_2\text{oxado})_3]^{3+}$, a process reminiscent of catalytic or biological reactions involving transfer of electrons.

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Appendix A. Supplementary Material

Detailed crystallographic data in CIF format for this paper were deposited with the Cambridge Crystallographic Data Centre (CCDC-839359). The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk].