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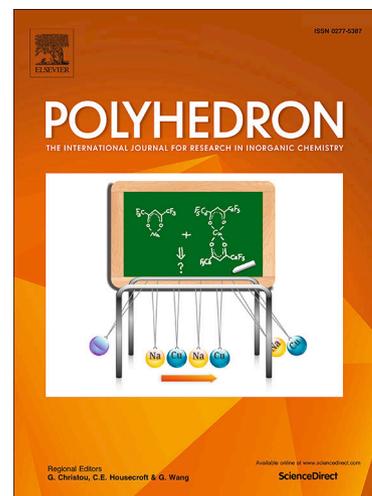
Tartrate bridging ligands in divalent Co(II)/Co(III) dinuclear anion

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Abstract

A cobalt(II/III) ionic compound with bridging tartaric acid (H₄L) anion (CH₆N₃)₃[Co₂^{II/III}(L)₂(H₂O)₂]·4H₂O **1** was synthesized. The crystallites were isolated from highly alkaline aqueous solution in the presence of guanidinium cations (CH₆N₃)⁺ being then incorporated as counter ions.

A determined structure reveals the dinuclear coordination anion with two cobalt centers, each within its distinctive coordination octahedron CoO₆ sphere showing different Co–O bond lengths. The metal center with shorter coordination bonds is assigned as Co(III), while the other with Co(II), all in agreement with overall net charge equilibrium. This involves three guanidinium cations, two tartrate(4-) anions, the latter within the coordination anion, as well as with bond valence sums for both cobalt centers. Both tartrates (L) are triply bonded on the Co(III) center, thus enabling Co^{III}O₆ coordination bonds. On the other hand, only two coordination bonds are enabled by each tartrate towards Co(II), while the remaining two in Co^{II}O₆ are completed by two terminal water molecules. The electronic spectrum shows clearly the *d-d* bands at 400 and 665 nm for Co(III), while at 520 nm for Co(II), for each CoO₆, respectively. The temperature dependent magnetic susceptibility shows the paramagnetic behavior of the compound, due to the d⁷ Co(II) ions being in a high spin state, while the d⁶ low spin Co(III) ions are diamagnetic.

Keywords: cobalt, tartrate, guanidine, structure, magnetism

Introduction

Tartrate salts may be applicable for many issues due to their exhibiting piezoelectricity [1], as laxatives, in Fehling's solutions and in many other examples [2-3]. Potassium hydrogen tartrate is a byproduct of winemaking. It can be used further for other household purposes. As transducers they may show exceptionally high output with typical pick-up cartridge outputs with 2 V [4]. A metal of this salt clearly changes some material characteristics. For instance, the cobalt ions expectedly have uncoupled electrons and are known for a variety of their magnetic properties [5]. Their tartrate species are thus interesting due to the potential electro-magnetic applications, as well as biological role as mimetics as are tartrates within biosystems. Cobalt coordination species being either Co(II) or Co(III) are common, due to the stability of their species with partially replaced ligands and are thus often described. The oxygen and nitrogen-based ligands most commonly form coordination octahedra as the principal metal center surrounding. Interestingly, only a few compounds with $\text{Co}^{\text{III}}\text{O}_6$ chromophores are reported, none of them being binuclear [6-9]. This can also be expected as the cobalt(III) species with O-donor ligands are generally less stable than those with N-donor ligands [10]. Tartrates are oxygen rich ligands, having four acidic protons. This polyanionic coordination moiety can generate some mono-, bi- and polynuclear Co(II) tartrates (tartaric acid H_4L), namely $[\text{Co}(\text{H}_3\text{L})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $\{[\text{Co}(\text{H}_2\text{L})(\text{H}_2\text{O})]_2\} \cdot 3\text{H}_2\text{O}$, and $\{[\text{Co}(\text{H}_2\text{L})]_2\}_n$ respectively, being reported [9,11-13]. To stabilize large, potentially polyanionic ligands, the guanidinium cations have been often reported to compensate the cationic net charge compensation. Along with its hydrogen bonding donation ability, guanidinium salts may play a crucial role for the isolation of the anionic coordination species, where large ligands, such as tartrate, e.g. citrates, are applied [14].

Herein we present a dinuclear Co(II)/Co(III) anionic tartrate coordination species, accompanied by a co-crystalline guanidinium cations and water molecules. Its synthesis, structure, spectral and magnetic characterizations are described.

Experimental Section**General Remarks**

All reagents and solvents were purchased from commercial sources and used as received. C,H,N analysis was performed with a Perkin-Elmer Elemental Analyzer Series II CHNS/O. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer, equipped with a Specac Golden Gate Diamond ATR as a sample support.

Electronic spectrum was recorded by powdered sample as major unit with a Perkin-Elmer UV/Vis/NIR spectrometer Lambda 750. The magnetic susceptibility data of powdered samples were measured with a Quantum Design MPMS-XL-5 SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants [15].

(CH₆N₃)₃[Co^{II/III}(L)₂(H₂O)₂]₂·4H₂O (1)

Tartaric acid (H₄L) 425 mg (2.83 mmol) was dissolved in 10.0 mL of water, into which 4 pellets (≈ 400 mg) of solid NaOH was added. It was dissolved by stirring after 5 min. Guanidinium carbonate (CH₆N₃)₂CO₃ 1.5 g (8.32 mmol) was then added that dissolved soon as well. Then Co(NO₃)₂·6H₂O 585 mg (2.01 mmol) was introduced and the solution colored blue-purple. The color darkened and changed to brown-green after two days. Dark green crystals of **1** were filtered off after two weeks and dried in a desiccator over solid KOH for one day. Yield: 94 mg (0.135 / Co). Elemental analysis %: C₁₁H₃₄Co₂N₉O₁₈ (698.3), calc. C 18.92, H 4.91, N 18.05; found C 18.04, H 4.73, N 17.10; IR(solid) cm⁻¹, 3329 ν(N-H), 3198 ν(N-H), 1660 ν(C=N), 1574 ν_{as}(COO⁻), 1410 δ(C-H), 1352 ν_s(COO⁻), 1301, 1177, 1055 ν(C-O); UV-Vis-NIR(solid) Kcm⁻¹, 37.7, 25.0 (shoulder), 19.2, 15.0.

Crystal structure determination

The single crystal of **1** was mounted on a tip of a glass fiber and transferred into the goniometer head and the liquid nitrogen cryostream. Diffraction data were collected on the SuperNova single crystal diffractometer equipped with Atlas detector using monochromated Mo Kα radiation 0.71073 Å at 150 K. Data reduction and integration were performed with the software package CrysAlis PRO [16]. The coordinates of all the non-hydrogen atoms were found *via* direct methods using the SIR2018 structure solution program [17]. A full-matrix least-squares refinement on *F*² magnitudes with anisotropic displacement parameters for all non-hydrogen atoms using SHELXL-2018/3 was employed with the exception of one guanidinium cation and one solvent water molecule, which were refined isotropically due to their disorder [18]. All hydrogen atoms were initially located in the difference Fourier maps and were subsequently treated as riding atoms in geometrically idealized positions. This holds also for the guanidinium cations hydrogen atoms (for their refinement, AFIX 93 command was further used, since the independent isotropic refinement was not stable). To enable stable refinement in the last refinement cycles, the DFIX restraint was also used to yield meaningful structure. The corresponding displacement parameters U_{iso}(H) were 1.5-times higher than those of the water oxygen atoms and 1.2-times higher

than all other hydrogen bearing atoms. One of the guanidinium cations and one water molecule are disordered, thus their ADPs are larger. Details on crystal data, data collection and structure refinement are given in Table 1.

Table 1. Crystal data, data collection and structure refinement of **1**.

Formula	C ₁₁ H ₃₄ Co ₂ N ₉ O ₁₈
<i>M_r</i>	698.33
Cell setting, space group	Tetragonal, <i>P4₃2₁2</i>
<i>a</i> (Å)	9.6186(3)
<i>c</i> (Å)	27.8506(10)
<i>V</i> (Å ³)	2 576.67(19)
<i>Z</i>	4
<i>D_x</i> (Mg m ⁻³)	1.800
<i>μ</i> (mm ⁻¹)	1.386
<i>F</i> (000)	1444
Crystal form, colour	Prism, dark green
Crystal size (mm ³)	0.35x0.30x0.30
No. of measured, independent and observed reflections	14582, 3591, 3210
<i>R_{int}</i>	0.0369
<i>R</i> (on <i>F_{obs}</i>), <i>wR</i> (on <i>F_{obs}</i>), <i>S</i>	0.0605, 0.1745, 1.086
No. of contributing reflections	3591
No. of parameters	167
No. of restraints	1
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (eÅ ⁻³)	2.055, -1.245

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ where *n* is the number of independent reflections and *p* is the total number of parameters refined.

Results and Discussion

Structure analysis

The title compound (CH₆N₃)₃[Co₂^{II/III}(L)₂(H₂O)₂] \cdot 4H₂O crystallizes in a highly symmetrical tetragonal unit cell in a space group *P4₃2₁2* (No. 96). A large dinuclear anion is surrounded by three guanidinium cations (CH₆N₃⁺) to obtain electroneutral compound, along with the additional four water molecules appearing in the formula unit of **1** [19]. The alkaline

mother liquid (NaOH and carbonates) removes the protons from the O-donor ligands easily, but the N-donor amino type guanidinium cations retain the H-bonding ability (amino acids phenomenon).

The dinuclear coordination anionic species $[\text{Co}_2^{\text{II/III}}(\text{L})_2(\text{H}_2\text{O})_2]^{3-}$ consists of two cobalt centers bridged by a pair of fully deprotonated tartrate anions (L^{4-}) as shown in Figure 1. Both cobalt centers lie on a twofold axis that runs along *ab* unit-cell plane diagonally, and each of them is surrounded by six oxygen atoms from the ligands attached. To the best of our knowledge, this is the first cobalt compound in which two cobalt centers are in such an oxygen-rich environment, resulting in a formation of two interconnected CoO_6 chromophores [9]. In the other compounds with two different cobalt centers, each in CoO_6 environment, either polynuclear (chain) structure is formed [20] or additional metal centers, such as nickel(II), are present. [21-22] These do not resemble the structure of the title compound, especially when considering two different oxidation states of the metal centers. The oxidation state of Co1 is +3, and this central ion is surrounded with three oxygen atoms from each of the two tartrate ligands. One of these oxygen atoms, namely O2, originates from the terminal carboxylate group and the remaining two, O4 and O3, from deprotonated hydroxylic groups. O4 represents a monoatomic bridge between both

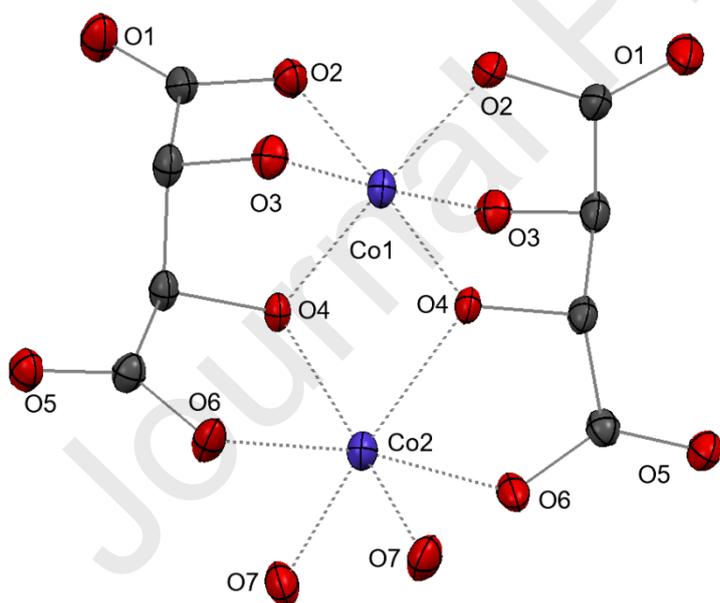


Figure 1. The representation of dinuclear coordination anion $[\text{Co}_2^{\text{II/III}}(\text{L})_2(\text{H}_2\text{O})_2]^{3-}$ of **1** revealing the octahedral environment around each cobalt(II/III) centers. The displacement ellipsoids are drawn at the 50% probability level and the hydrogen atoms are omitted for clarity [19].

metal centers. The geometry around Co1 is distorted octahedral with the Co–O range distances being 1.899(4)–1.937(4) Å (Table 2).

On the other hand, the oxidation state of Co2 is +2. Also, here the coordination sphere consists of three pairs of oxygen atoms leading to the distorted octahedron around Co2. Two pairs of oxygen atoms are from two different tartrate ligands (O4, O6) and the remaining two (O7) from a pair of coordinated water molecules that complement the coordination sphere of Co2. From the chemical point of view, these three oxygen atoms are chemically different – O4 is from hydroxylic, O6 from carboxylate group and O7 from water molecules. Either monodentate (O6, O7) or bidentate (O4), all Co2–O distances are significantly longer, namely in the range 2.073(4)–2.112(4) Å (Table 2), compared to Co1–O distances. These Co–O distances are however in agreement with the reported ones for Co(II) and Co(III) species, respectively [9]. The bond valence sums are 2.80 and 2.04 for Co1 and Co2, respectively [24]. Additionally, fully deprotonated oxygen rich polyanionic citrate anion appears as a ligand with similar coordination modes as in the title compound when the synthesis is performed in highly alkaline medium [14]. These features clearly support the determination of cobalt oxidation states. They are also in agreement with a presence of an additional proton on all three guanidinium cations and thus final net charge of the whole title compound.

Table 2. Selected bond lengths and angles (Å, °) of **1**.

Co1–O2	1.937(4)	Co2–O4	2.112(4)
Co1–O3	1.899(4)	Co2–O6	2.073(4)
Co1–O4	1.920(4)	Co2–O7	2.090(5)
O3–Co1–O3 ⁱ	177.1(3)	O6–Co2–O6 ⁱ	170.2(3)
O2–Co1–O4	176.45(19)	O7–Co2–O4 ⁱ	160.92(18)
O3–Co1–O4 ⁱ	85.55(18)	O6–Co2–O7	87.68(19)
O4–Co1–O4 ⁱ	86.2(2)	O6–Co2–O7 ⁱ	85.74(18)
O4–Co1–O2	90.52(18)	O7–Co2–O7 ⁱ	95.9(3)
O3–Co1–O2	84.4(2)	O6–Co2–O4	79.92(16)
O3–Co1–O2 ⁱ	93.60(19)	O7–Co2–O4	96.01(18)
O2–Co1–O2 ⁱ	92.8(3)	O4–Co2–O4 ⁱ	76.8(2)

Symmetry code *i* : $-y+1, -x+1, -z+1/2$

AS two tartrate anions almost completely surround two diverse cobalt ions by many oxygen coordination bonds, the dinuclear coordination species outer sphere in **1** is also filled with many oxygen atoms. Thus, the hydrogen bonding donation ability of the guanidinium cations clearly plays an important role together with the coordination anion and network water molecules to form extensive hydrogen bonding network that stabilizes the structure (Table 3).

Table 3. Hydrogen bonding geometry in the structure of **1** (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A	Symm. code of A
O7-H7A...O8	0.87	1.90	2.745(7)	163.0	$x, y-1, z$
O7-H7B...O1	0.87	1.88	2.715(6)	159.8	$-x+3/2, y-1/2, -z+3/4$
N1-H1A...O6	0.88	2.02	2.871(7)	160.9	$x-1, y, z$
N1-H1B...O2	0.88	2.22	3.053(8)	157.0	x, y, z
N2-H2A...O5	0.88	2.04	2.847(8)	151.8	$-x+3/2, y-1/2, -z+3/4$
N2-H2B...O4	0.88	2.01	2.815(7)	152.4	x, y, z
N3-H3A...O5	0.88	2.17	2.943(8)	146.6	$-x+3/2, y-1/2, -z+3/4$
N3-H3B...O1	0.88	1.99	2.848(8)	164.6	$-x+1/2, y-1/2, -z+3/4$
N4-H4A...O2	0.88	2.21	3.044(16)	157.2	x, y, z
N4-H4A...O8	0.88	2.52	2.991(15)	114.0	$-y+1, -x+1, -z+1/2$
N4-H4B...O9	0.88	1.95	2.819(18)	167.5	$x-1, y, z$
N5-H5A...O7	0.85	2.47	3.249(18)	153.1	$x-1, y+1, z$
N5-H5A...O9	0.85	2.57	3.07(10)	118.0	$x-1, y, z$

The donors of O-H...O hydrogen bonds are coordinated water molecules; the acceptors are either solvent water molecules or tartrate ligands (O5 and O1). Additionally, the guanidinium cations and the remaining solvent water molecules take part in N-H...O hydrogen bonding that leads to the formation of chains, which are further connected to 3D network (Figure 2). The strongest H-bonds are seen on the coordinated water molecules (Table 3), which is also the most exposed position to replace the ligands of the Co metal

centers. Therefore, asymmetric coordination on both metal centers can lead also to an interesting catalytic possibility at Co₂ metal site. Monodentate water molecules are namely expected to be removed easier than pentadentate tartrate ligands. This would enable a coordination pocket for a potential alternative ligand that could therein catalytically react with a metal center.

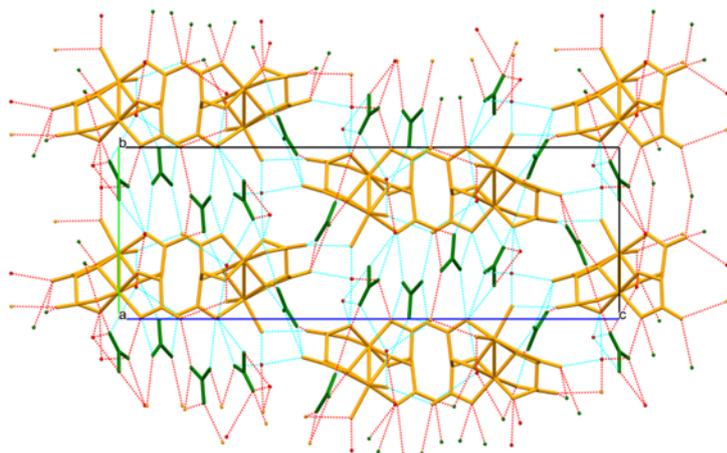


Figure 2. A hydrogen bonding scheme for **1** along *a* axis. Involved coordination anions (orange), guanidinium cations (green) and water molecules (red), respectively.

Spectroscopy and magnetism

The IR spectrum of **1** shows a broad absorption at 3500-2700 cm⁻¹ with two peaks at 3329 and 3198 cm⁻¹ due to the water molecules O-H bonds, as well as N-H guanidinium bonds. A broad area covering around 3000 cm⁻¹ is related to the weakly bound proton, herein at the counter-cation. A band at 1660 cm⁻¹ is also assigned to guanidinium cations, namely to the C=N bond. The asymmetric and symmetric COO⁻ carboxylate vibrations are assigned with 1574 and 1352 cm⁻¹ bands, respectively, while the hydroxyl C-O being at 1050 cm⁻¹ [25-27].

The solid title compound colour is dark green and resembles mostly the respective mother liquid colour. Its suspension electronic spectrum shows three distinctive bands in the 50.0-11.6 Kcm⁻¹ UV-Vis region; namely 37.7 (with a shoulder at 25.0), 19.2 and 15.0 Kcm⁻¹. The literature species spectrum analysis [10] reveals that for the low spin Co(III) [Co(H₂O)₆]³⁺ species, the bands are expected at 16.6 and 24.8 Kcm⁻¹ originating from ¹A_{1g} ground term to ¹T_{2g} and ¹T_{1g}. On the other hand, for the high spin Co(II) [Co(H₂O)₆]²⁺ species, a band at 19.4 Kcm⁻¹ from ⁴T_{1g}(*F*) ground term to ⁴T_{1g}(*P*) transition is proposed. These

experimental and theoretical data for the basic octahedral CoO_6 chromophores, thus seem to corroborate with two Co oxidation states present in **1**. Future cyclic voltammetry research seems to shed also some additional light to this data.

The temperature dependence of magnetic susceptibility $\chi(T)$ in Figure 3 reveals a paramagnetic, $1/T$ behavior. Indeed, the inverse susceptibility χ^{-1} versus temperature T (inset in Figure 3) is practically linear in all investigated temperature range. The fit with a Curie-Weiss law $\chi = C/(T-\vartheta)$ gave us a Curie constant $C = 1.58$ emu K/mol, Curie-Weiss temperature $\vartheta \approx 0$ K and is shown as a green line in Figure 3. The latter result corroborates with the paramagnetic behavior of **1** with no magnetic interaction between cobalt ions.

The obtained Curie constant C is discussed in the frame of the electronic spectroscopy and structure determination results: equimolar ratio of high spin d^7 Co(II) and low spin d^6 Co(III) ions. Low spin Co(III) ions are diamagnetic [28] and thus do not contribute to the paramagnetic response. In order to calculate an effective magnetic moment per Co(II) ion, the measured Curie constant $C = 1.58$ emu K/mol has to be normalized per mole of Co(II) ions - i.e., divided by the concentration of Co(II) ions, 0.5. Thus $C_{(\text{per mole of Co(II)})} = 3.16$ emu K/(mol Co(II)) and effective magnetic moment per Co(II) ion $\mu_{\text{eff(per Co(II))}} = 5.0 \mu_{\text{B}}$. This value is very close to the usually measured value $4.8 \mu_{\text{B}}$ for the high spin divalent cobalt complexes [29]. Therefore **1** can be described as a paramagnet composed of the 50 % high spin Co(II) ions with no magnetic interaction between them, and the 50 % diamagnetic Co(III) ions.

A short Co-Co intraduclear distance 3.058 \AA , not considered as a metal-metal bond and two short Co-O4-Co hydroxyl bridges therefore cannot enable any intermetal magnetic interaction.

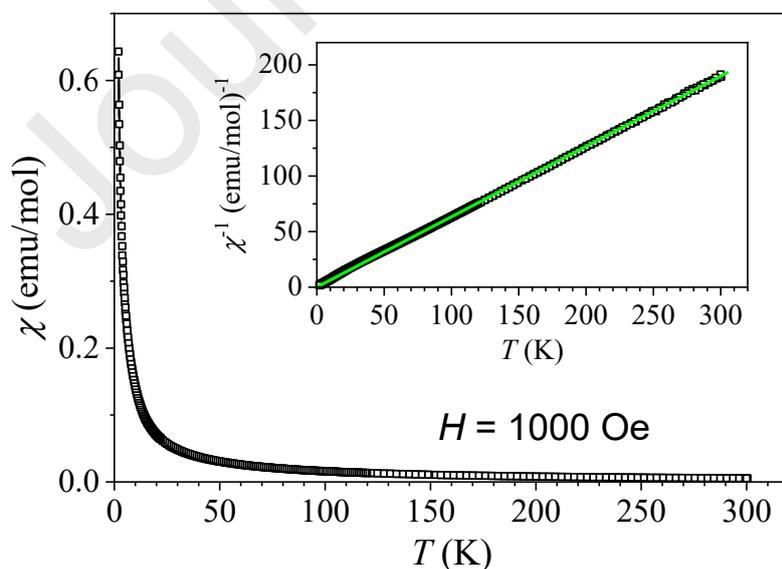


Figure 3. Temperature dependent susceptibility and inverse susceptibility (inset). Full green line is a fit with Curie-Weiss law.

Conclusions

A dinuclear CoII/III anionic coordination moiety in $(\text{CH}_6\text{N}_3)_3[\text{Co}_2^{\text{II/III}}(\text{L})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ **1** has been synthesized from alkaline mother liquid. Both metal centers are in a very similar CoO_6 coordination octahedron, enabling insight for their comparison. The electronic spectrum shows transitions for each of them, namely for Co(II) as well as for Co(III) oxidation state chromophores. Furthermore, the magnetic susceptibility shows paramagnetic behavior of **1**, due to the high spin divalent Co(II) only, as the Co(III) ions are diamagnetic.

A biologically and technically important tartrate species with cobalt metal ions in different oxidation states may play an important role in cobalt chemistry and tartrate application potential understanding. Future electrochemical study would also help in this issue. Since the coordination compound is asymmetric and monodentate loosely bound water molecules occupy only the terminal position of the paramagnetic center, the compound is potentially also catalytically interesting.

Research data policy and data availability statements

All data generated or analyzed during this study are included in this published article and its supplementary information files.

CRedit authorship contribution statement

B. K.: Supervision, Conceptualization, Investigation, Writing – original draft, review & editing, Funding acquisition; M. T.: Investigation; M. P.: Structural analysis, Writing – review & editing, Funding acquisition; Z. J.: Magnetic analysis, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be available on request.

Acknowledgments

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Supplementary Data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2208601 (1). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44 1223/336033; e-mail:deposit@ccdc.cam.ac.uk].

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