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Synthesis, structure and magnetic properties of a cobalt(II) mesoxalate 1D coordination polymer

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Dedicated to Prof. Christoph Janiak on the Occasion of his 60th Birthday

Mesoxalate ligand $(H_2mesox)^{2-}$, the conjugate base of the mesoxalic acid (2,2'-dihydroxyl-malonic acid) reacts with cobalt(II) ions to form the 1-D coordination polymer $\{[Co(H_2mesox)(H_2O)_2]\cdot H_2O\}_n$. This compound displays a structure based on homochiral polymeric chains which stack together in an *AABB* fashion through hydrogen bonding by both coordination and crystallisation water molecules. Although the magnetic properties for such a Co(II) compound are difficult to interpret in the whole temperature range, at low temperatures the Co(II) behaves as an $S=1/2$ effective spin and equation derived by Fisher from the Ising model was applied to analyse the data in the 4–40 K range. The magnetic interactions in this compound are compared with the magnetic interactions displayed by similar compounds reported in the literature.

Introduction

In the last decade, we have studied the formation of coordination polymers with the mesoxalate ligand, the conjugated base of the mesoxalic acid (mesoxalic acid = 2,2-dihydroxyl-propanedioic acid or 2,2-dihydroxyl-malonic acid, H_4mesox) (Scheme 1). This ligand has six-donor oxygens, four from the two carboxylate groups and two from the two hydroxyl groups, and it's complex formation has resulted in great structural diversity.[1–10]

In some of the complexes we have prepared such as $(Ph_4P)[MnCu_3(Hmesox)_3Cl]$ or $[LaCu_3(Hmesox)_3(DMSO)]$, the mesoxalate ligand acted as $Hmesox^{3-}$ giving the $[Cu_3(Hmesox)_3X]^{4-}$ ($X=Cl^-$ and Br^-) and $[Cu_3(Hmesox)_3Y]^{3-}$ ($Y=H_2O$ or DMSO) trinuclear copper(II) metalloligands.[5–7,9,10]

Furthermore, it acted as H_2mesox^{2-} when linked to Ln(III) in $[Ln_2(H_2mesox)_6]\cdot 6H_2O$ compounds.[3,4] We have found that the compounds formed exhibited from molecular to three-dimensional structures. The study of the magnetic properties of those complexes revealed that the intensity of the coupling is related to the bridging mode of the mesoxalate ligand. Strong magnetic coupling is found for the $Hmesox^{3-}$ compounds where the carboxylate and alkoxido bridges mediate the magnetic coupling.[5–7,9,10] On the other hand, weak magnetic coupling is found in the H_2mesox^{2-} compounds where the magnetic coupling is mediated by a diol bridge.[3,4]

Some other authors have studied the formation of coordination polymers with the same ligand and prepared the compounds $\{Na[Mn(Hmesox)(H_2O)_2]\}_n$ and
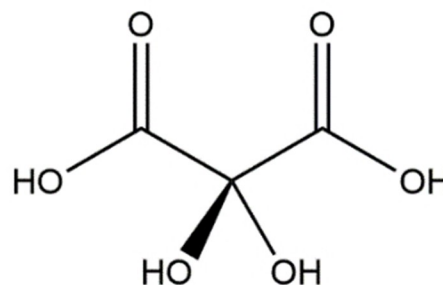
Scheme 1. Mesoxalic acid, H_4mesox.

$\{Na[Zn(Hmesox)(H_2O)_2]\}_n$ which display 1D polymeric structures with the ligand acting as $Hmesox^{3-}$ and a weak magnetic coupling was found in the Mn(II) compound.[1,2] Also, those prepared by Fedosseev et al. display identical structure to those prepared by us with the ligand acting as H_2mesox^{2-}.[11]

In this work, we study the structure and the magnetic properties of the compound $\{[Co(H_2mesox)(H_2O)_2]\cdot H_2O\}_n$ to compare the bridging mode of the ligand together with the intensity of the magnetic coupling with other mesoxalate-bridged compounds and other carboxylate-bridged cobalt(II) compounds such as $\{[Co(\mu\text{-ox})(H_2O)_2]\cdot 2H_2O\}_n$.[12]

Results and Discussion

The reaction of a water solution of sodium mesoxalate monohydrate with $CoCl_2\cdot 6H_2O$ gave after a few days rise to prismatic dark pink crystals of $\{[Co(H_2mesox)(H_2O)_2]\cdot H_2O\}_n$ (compound **1**). The phase purity of the whole batch of crystals was confirmed by positive matching of the experimental powder X-Ray diffractogram with the simulated one obtained from the single-crystal X-Ray diffraction data (Figure S1 Supporting Information).

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Compound 1 crystallises in the centrosymmetric space group $P2_1/n$. The asymmetric unit contains one cobalt atom, one mesoxalate ligand $(H_2mesox)^{2-}$, two coordination water molecules (O1W, O2W) and one crystallisation water molecule

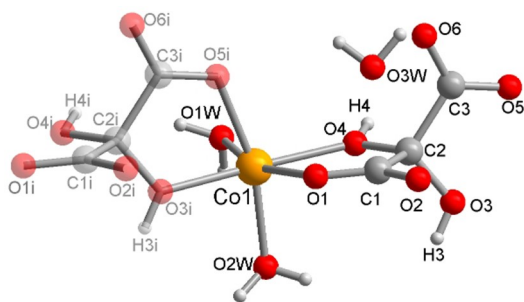**Figure 1.** Extended asymmetric unit of $\{[Co(H_2mesox)(H_2O)_2]\cdot H_2O\}_n$. Symmetry transformation: i = 1 + x, y, z. Atoms without transparency represent the asymmetric unit. Selected bond lengths and angles can be found in Table 1.
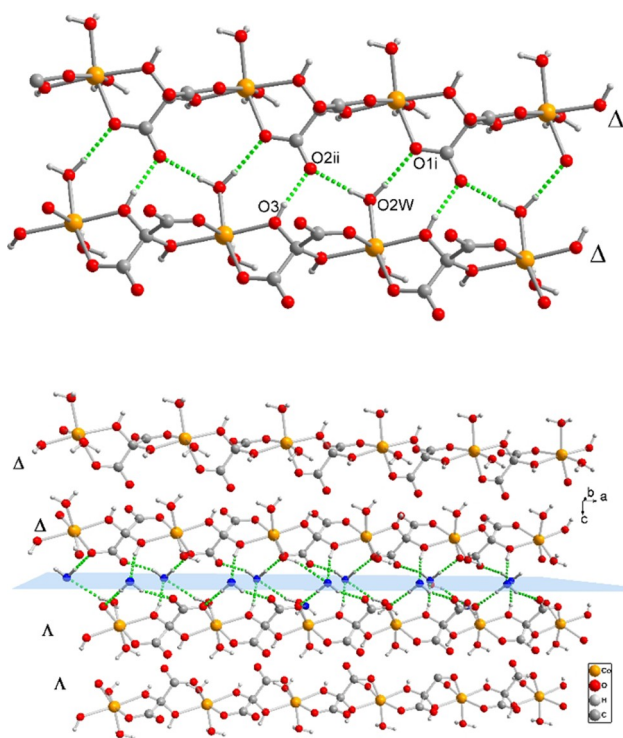

Figure 2. a) Hydrogen bonds between chains with homochiral Co(II) ions forming double strands which run parallel along the a direction. The chain with Δ-absolute configuration for Co(II) has been taken as an example. Symmetry codes: i = 1.5-x, −0.5 + y, 0.5-z; ii = 0.5-x, −0.5 + y, 0.5-z. b) 2-D hydrogen-bonded supramolecular structure for $\{[Co(H_2mesox)(H_2O)_2]\cdot H_2O\}_n$. The hydrogen-bonded double strands are further assembled with opposite chirality chains by a crystallisation water molecule to yield a two-dimensional layer in the ac plane. O3W crystallisation water molecules (depicted in blue) locate in the plane between two opposite chirality chains. Hydrogen bonding interactions of O3W with neighbour mesoxalate oxygen atoms are represented with green dashed lines (see hydrogen bonding interactions in Table 2).

(O3W) (Figure 1). Crystal data and details on the structure refinement can be found in Table 3.

The structure of **1** consists of one-dimesional bis-bidentate mesoxalate-bridged neutral polymeric chains of $[Co(H_2mesox)(H_2O)_2]_n$ running along the a-axis which contain homochiral (Δ or Λ) octahedral cobalt(II) ions and crystallisation water molecules (Figure 2).

The Co(II) ions display an octahedral coordination environment built up from the four oxygen atoms of two bidentate mesoxalate ligands and two oxygen atoms of two water molecules (Table 1, Figure 1). The equatorial positions are occupied by the oxygen atom of a water molecule (O1W), one carboxylate oxygen and one hydroxyl oxygen of the same mesoxalate forming a five-membered chelate ring (O1,O4) and one hydroxyl oxygen of another mesoxalate ligand (O3i). The two apical positions are occupied by an oxygen atom of a water molecule (O2W) and the carboxylate oxygen atom of the same mesoxalate ligand than O3i (O5i, i = 1 + x, y, z).

The Co—O distances are quite regular and span in the range 2.0372 (19) Å to 2.1573 (18) Å (see Table 1). The two chelating bidentate mesoxalate ligands and the two water molecules in cis-configuration make the Co(II) ion a chiral centre which displays Δ and Λ isomerism. The mesoxalate ligands have lost the two carboxylic hydrogens $(H_2mesox)^{2-}$ and act as a bridge between two cis-$[Co(H_2O)_2]^{2+}$ ions in a bis-bidentate fashion μ_2-H_2mesox (μ_2-$\kappa O,O'':O''',O''''$) through two carboxylate oxygen atoms and two hydroxyl oxygen atoms (Figures 2a, 2b). This bridging mode results in linear 1D polymeric chains of

Table 1. Selected bond lengths (Å) and angles (°) for compound **1**.

Co1—O1W	2.0372 (19)	Co1—O3^i	2.0867 (19)
Co1—O2W	2.075 (2)	Co1—O5^i	2.0988 (19)
Co1—O1	2.084 (2)	Co1—O4	2.1573 (18)
O1—Co1—O3^i	101.54 (8)	O1W—Co1—O3^i	96.90 (8)
O1—Co1—O4	73.60 (7)	O1W—Co1—O4	87.96 (8)
O1—Co1—O5^i	88.82 (8)	O1W—Co1—O5^i	89.18 (8)
O3^i—Co1—O4	175.12 (8)	O2W—Co1—O1	93.87 (9)
O3^i—Co1—O5^i	74.84 (7)	O2W—Co1—O3^i	88.69 (8)
O5^i—Co1—O4	105.04 (8)	O2W—Co1—O4	91.31 (8)
O1W—Co1—O2W	93.61 (9)	O2W—Co1—O5^i	163.51 (8)
O1W—Co1—O1	160.23 (8)		

Symmetry codes: (i) x + 1, y, z; (ii) x-1, y, z.

Table 2. Hydrogen bonding interactions in compound 1. Distances (Å) and angles (°).

D–H···A	d (D–H)	d (H···A)	d (D···A)	< (D–H···A)
O1W–H1W2···O3W^{ii}	0.86	1.96	2.758 (3)	155
O2W–H2W2···O1^{iii}	0.83	1.95	2.770 (3)	171
O2W–H2W1···O2^{iv}	0.85	1.90	2.745 (3)	176
O3W–H3W1···O5^v	0.85	1.83	2.676 (3)	174
O3W–H3W2···O6^{vi}	0.83	1.97	2.738 (3)	155
O3–H3···O2^{iv}	0.79 (4)	1.76 (4)	2.543 (3)	171 (4)
O4–H4···O3W	0.86 (1)	1.79 (1)	2.623 (3)	163 (3)

(i) x + 1, y, z; (ii) -x + 1, -y, -z + 1; (iii) -x + 3/2, y-1/2, -z + 1/2; (iv) -x + 1/2, y-1/2, -z + 1/2; (v) -x, -y + 1, -z + 1; (vi) -x + 1, -y + 1, -z + 1.

$[Co(H_2mesox)(H_2O)_2]_n$ in which all the Co(II) ions have the same Δ or Λ configuration. The dihedral angle formed by both mesoxalate chelate-ring planes is of 69° and the Co—Co distance through the mesoxalate bridge is 5.899 Å (Figure 2a). The chains are equivalent to those found in $\{Na[Mn(Hmesox)(H_2O)_2]\}$ and $\{Na[Zn(Hmesox)(H_2O)_2]\}$[1,2] with the exception that in these latter compounds the mesoxalate ligands act as trivalent anions $(Hmesox)^{3-}$ with one of the hydroxyl groups deprotonated. The chelating and bridging mode of $(H_2mesox)^{2-}$ is also found in $\{[Ln_2(H_2mesox)_3(H_2O)_6]\}_n$ [Ln = lanthanoid(III)].[3,4,11,13]

A coordination water molecule (O2W) and a hydroxyl oxygen atom (O3) of a mesoxalate ligand are hydrogen-bonded to the mesoxalate carboxylate oxygen atoms (O1i and O2ii) of a contiguous chain thus assembling neighbouring homochiral
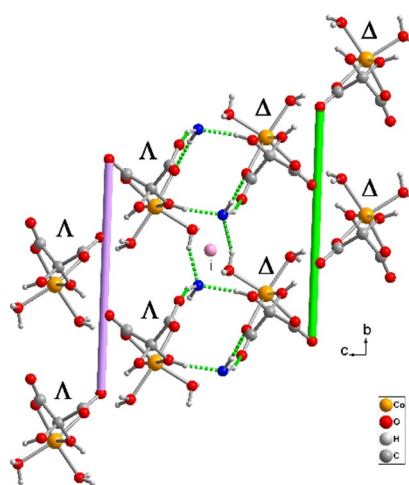

Figure 3. Neighbouring chains of the same chirality for Co atoms related by 2_1 screw axes (violet and green). The inversion centre (depicted as a violet ball) between opposite chirality chains is also shown.
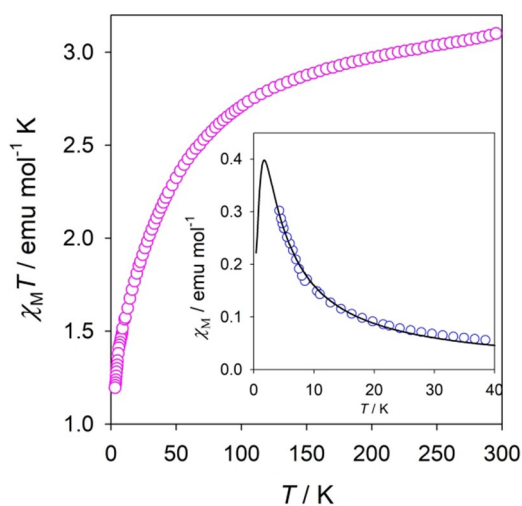

Figure 4. Temperature dependence of the $\chi_M T$ product and the χ_M (inset) for $\{[Co(H_2mesox)(H_2O)_2]\cdot H_2O\}_n$.

chains (Figure 2a). Homochiral chains are related through a 2_1 screw axis which runs along the b-axis (Figure 3).

Besides, this group of two homochiral chains connect through crystallisation water molecules (O3W) to another group of two chains which display opposite chirality than the former, giving rise to a two-dimensional supramolecular layer in the ac plane (Figure 2b) which stacks in an AABB fashion along the b axis. A and B being chains which exhibit opposite chirality for the six-coordinated cobalt atoms.

An inversion centre relates by symmetry both groups of chains of opposite chirality, leading the compound to crystallise in a centrosymmetric $P2_1/n$ space group (Figure 3).

The minimum distance between cobalt atoms of different chains of the same chirality is 5.8554(2) Å, whereas between chains of different chirality is 6.8499(2) Å.

The temperature dependence of the $\chi_M T$ product for **1** is shown in Figure 4. χ_M is the magnetic susceptibility per one Co(II) ion. At room temperature $\chi_M T$ has a value of 3.09 emu mol^{-1} K which is higher than the spin-only value expected for a $S = 3/2$ with $g = 2.0$ (expected 1.874 emu mol^{-1} K).[14] This value is indicative of the occurrence of a significant orbital contribution to the magnetic moment. On lowering T, the $\chi_M T$ continuously decreases to reach a minimum value of 1.25 emu mol^{-1} K at 2.0 K. The value at low temperatures is lower than the expected for a mononuclear Co(II) complex. Therefore, antiferromagnetic interactions mediated by the diol bridge cannot be discarded in addition to the decay of the high magnetic moment states of the cobalt(II).[15]

A full analysis of the magnetic properties of antiferromagnetically coupled six-coordinated cobalt(II) ions in the whole temperature range is rather complicated, and several approaches can be found. The $3d^7$ electronic configuration of the cobalt (II) ion gives a ^4F term, which is split into two ^4T and one ^4A levels in a perfect O_h geometry. Besides, the lower energy ^4T state is further split by first-order spin-orbit coupling into a sextet ($J = 5/2$), a quadruplet ($J = 3/2$) and a doublet ($J = 1/2$), this one is the lowest in energy.

The analysis of the temperature dependence of magnetic susceptibility requires the consideration of the energy of those states together with parameters such as the orbital reduction factor and the distortion from the ideal O_h geometry, in addition to the magnetic coupling interactions among the cobalt (II) ions. This analysis is highly complex and requires specific software (VPMAG package[16]) which is not freely available.

Nevertheless, in the low-temperature region, the Co(II) ion behaves as an effective spin $S = 1/2$ with a very anisotropic g tensor and the magnetic susceptibility data can be analysed with the equation derived by Fisher from the Ising model for a chain of $S = 1/2$ effective spins.[12,17–20] That expression can be used for either ferromagnetic or antiferromagnetically coupled compounds with chain structure, but only at temperatures below 40 K when only the lower energy doublet is populated. The best-fit parameters to the Ising model are $g_x = 1.77$, $g_z = 3.77$ and $J = -0.95$ cm^{-1}. A good match is observed in the 4–40 K range (inset Figure 4), and the values found for g_x and g_z fit the conditions of the Ising model $g_z > g_x$. The value obtained

for J indicates the occurrence of a weak antiferromagnetic interaction among the Co(II) ions through the diol bridge. This weak interaction is in agreement with the previous studies in $[Gd_2(H_2mesox)_3(H_2O)_6]$[3] and in $Na[Mn(Hmesox)(H_2O)_2]$[1] for which a value of $J = -0.0039$ cm^{-1} and $J = -0.0544$ cm^{-1} was found, respectively. The magnetic coupling is much weaker to that found in the analogous oxalate derivative, ${[Co(\mu-ox)(H_2O)_2] \cdot 2H_2O}_n$ where the *anti-anti* carboxylate-bridged Co(II) ions display antiferromagnetic coupling of $J = -13.4$ cm^{-1}.[12]

Conclusions

One new coordination polymer ${[Co(H_2mesox)(H_2O)_2] \cdot H_2O}_n$ was synthesised by the reaction of sodium mesoxalate and cobalt (II) chloride. The compound displays a structure based on homochiral neutral polymeric chains which stack together through hydrogen bonding in an *AABB* fashion.

This compound is isostructural with the previously reported ${Na[Mn(Hmesox)(H_2O)_2]}_n$ and ${Na[Zn(Hmesox)(H_2O)_2]}_n$ but the two alcohol groups retain their hydrogens in ${[Co(H_2mesox)(H_2O)_2] \cdot H_2O}_n$, which results in a water molecule occupying the position of the Na(I) in the Mn(II) and Zn(II) compounds.

As for the magnetic properties, the $\chi_M T$ product at room temperature indicates that it exists an orbital contribution to the magnetic moment that cannot be underestimated. The coordination mode of the mesoxalate ligand (H$_2$mesox^{2-}) connects the Co(II) ions through a diol bridge giving rise to antiferromagnetic interactions at low temperatures which occur together with the decay of the high magnetic moment states of the cobalt (II) ion. The magnetic interaction through the diol bridge is much weaker than that found in ${[Co(\mu-ox)(H_2O)_2] \cdot 2H_2O}_n$ through the *anti-anti* carboxylate bridge. Moreover, the coupling between cobalt(II) ions in **1** is as weak as that found in the isostructural compound ${Na[Mn(Hmesox)(H_2O)_2]}_n$ in which the mesoxalate ligand only retains one of the hydrogens of the two alcohol groups. The intensity of the magnetic coupling in **1** is comparable to that of $[Ln_2(H_2mesox)_6] \cdot 6H_2O$ with the same bridging mode of the ligand. Finally, the obtained compound extends the family of functional Co(II) and Co(III) carboxylate-driven coordination polymers.[21–23]

Experimental Section

General: Reagents were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Thermo Fisher CNHS FLASH EA 1112 Analyzer.

IR spectra (400–4000 cm^{-1}) were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrometer with the sample prepared as KBr disks.

Magnetic susceptibility measurements on polycrystalline samples were carried out employing a Quantum Design SQUID MPMS XL magnetometer. The dc measurements were performed in the

temperature range 1.9–300 K at applied magnetic fields of 0.100 T. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[18] and experimental susceptibilities were also corrected for the the magnetisation of the sample holder. X-ray powder diffraction pattern on the polycrystalline sample was collected with a PANanalytical X'pert X-ray diffractometer (Cu K$_\alpha$ radiation = 1.54184 Å) at room temperature.

Single Crystal X-Ray Structures: Suitable crystals were carefully selected under a polarising microscope, covered in protective oil and mounted on a 0.05 mm cryo-loop.

Data collection: Single-crystal XRD data were collected with an Agilent SuperNova diffractometer with a micro-focus X-ray under Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å). CrysalisPro software was used to collect, index, scale and apply analytical absorption correction based on the multiscan method.[24]

Structure analysis and refinement: All the structures were solved by direct methods using SHELXL2016;[25] refinement was done by full-matrix least-squares on F2 using the SHELXL-2016 program suite and the graphical user interface (GUI) ShelXle[26] was used. Crystal data and details on the structure refinement are given in Table 3.

All non-hydrogen positions were refined with anisotropic temperature factors. Hydrogen atoms on the mesoxalate-OH (H3 and H4) and hydrogen atoms of the water molecules were found and allowed to ride on the oxygen atom with Uiso(H) = 1.5 Ueq(O). For H4 DFIX and DANG commands were also necessary.

Graphics and simulated PXRD diffractograms were drawn with Diamond.[27]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited in the Cambridge Crystallographic Database with depository number CCDC-2038688.

Synthesis of ${[Co(H_2mesox)(H_2O)_2] \cdot H_2O}_n$ (1)

Sodium mesoxalate monohydrate (180,0 mg, 1 mmol) was dissolved in 5 mL of water at 50 °C. An excess of Cobalt (II) chloride

Table 3. Crystal data and structure refinement details of **1**.

Empirical formula	C$_3$H$_8$CoO$_9$
M/g mol^{-1}	247.02
Temperature (K)	293
λ/Å	1.54184
Crystal system, space group	Monoclinic, $P2_1/n$
a, b, c (Å)	5.8992 (2), 7.1846 (3), 19.4522 (8)
b (°)	94.058 (4)
V (Å^3)	822.38 (6)
Z	4
D_{calc}/g cm^{-3}	1.995
μ/(mm^{-1})	16.74
Theta range/°	4.558-71.922
No. of measured, independent and observed [$I > 2$ s(I)] reflections	3040, 1582, 1454
R_{int}	0.031
$R_1[I > 2\sigma(I)]$[a]	0.0336
$wR_2[I > 2\sigma(I)]$[b]	0.0888
GOF on F^2 [b]	1.082

[a] $R_1 = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. Goodness-of-fit $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$.

hexahydrate (356.9 mg, 1.5 mmol) was dissolved in 5 mL of water and it was added to the former solution while stirring. The dark pink solution was allowed to crystallise at 23 °C in an oven. After four days prismatic dark pink crystals were separated by filtration from the mother liquor and washed three times with 5 mL water each. Yield: 145 mg, 59%. The IR spectrum is given in Figure S2 in Supporting Information. The most intense bands correspond to asymmetric and symmetric carboxylate absorptions υ_{as} and υ_s: 1670–1590 (s,b) and 1460–1370 (s) cm^{-1}, respectively. The C–O stretching bands are observed around 1100 (υ_s) cm^{-1} and broad O–H and H_2O associated bands at 3500–3300 cm^{-1}. $CoC_3H_8O_9$ calcd C 14.60%, H 3.24%; found: C 14.58%, H 3.01.

Supporting Information

Experimental and simulated PXRD Patterns, IR Spectrum.

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