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Synthesis, Structure, and Magnetism of a Highly Thermally Stable Microporous Metal Organodiphosphonate with Reversible Dehydration/Rehydration Behavior

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The synthesis and crystal structure of a novel organic–inorganic hybrid material $Co_2(H_2O)_2[O_3PCH_2(C_6H_4)CH_2PO_3]$ is described. It crystallizes in the orthorhombic space group *Pca*2(1) [a = 9.6214(19), b = 5.6855(11), c = 21.725(4) Å, V = 1188.4(4) $Å^3$], which consists of two-dimensional cobalt–oxygen inorganic layers pillared by *p*-xylylenediphosphonate to form a three-dimensional framework, which has 10.850 × 5.687 Å channels running along the *b*-axis. The material is exceptionally stable, even when heated up to 500 °C in air. More interestingly, the framework components display a reversible dehydration/rehydration behavior. There is an antiferromagnetic interaction between the cobalt ions.

Introduction

Organic–inorganic hybrid materials have received considerable interest because of their potential ability to incorporate an organic functionality within a robust framework and promising applications in adsorbents, optical materials, magnets, catalysts, and so forth.[1–4] One such group of hybrid materials that has attracted much attention is the metal phosphonate/diphosphonate family, which exhibits great possibilities for application in the areas of sensors, charge and energy storage, biotechnology, and so forth.[5–8] As one hydroxy group (OH) of the phosphonic acid can be replaced by other organic groups, the organic diphosphonic acid has a greater advantage in the synthesis of open-framework compounds than phosphonic acid. The structure and functionality of these materials can be rationally designed by controlling the organic portion of organodiphosphonate ligands ($[O_3P{-}R{-}PO_3]^{4-}$, R = organic unit). The combination of organodiphosphonate ligands with metal ions is expected to lead to new three-dimensional structures with open frameworks and unique properties.[9–11] Not only do these ligands form materials with progressively longer organic chains to expand the pore size or contain organic functional groups to present both metal and organic species to guest molecules within the pores,[12,13] but they are also desirable in their pillared framework with clearly different organic and inorganic parts. Investigations of di-, tri-, and tetravalent metal phosphonates in recent years have yielded exciting structural diversity with interesting properties.[14–16]

Because the metal polyhedra are bridged by phosphonic tetrahedra to form two-dimensional layers, many $M^{II}(RPO_3)\cdot H_2O$ compounds are two-dimensional structures, with the metal/PO_3 layer arrangement and the adsorption behavior of some dehydrated layered phosphates reported in the literature.[17–21] The hydrothermal method has proved to be a promising technique in the preparation of highly stable and infinite metal–ligand frameworks.[22,23] The organophosphorus compound *p*-xylylenediphosphonate, which possesses much longer chains and a more rigid framework, has been used successfully in the hydrothermal synthesis of diphosphonates. Ferey et al. solved the structure of the copper diphosphonate $Cu_2(H_2O)_2[O_3PCH_2(C_6H_4)CH_2PO_3]$ by powder X-ray diffraction to reveal that it was built up from inorganic layers covalently linked by the organic chains.[24] The inorganic layers are constructed by the dimers of edge-sharing $CuO_4(H_2O)$ square pyramids and the PO_3C tetrahedron. Harvey et al. have reported $Ga_2[O_3PCH_2(C_6H_4)CH_2PO_3](H_2O)_2F_2$, containing linear chains of corner-sharing GaO_4F_2 octahedra connected by diphosphonate groups to form two-dimensional framework structures.[12] *meta*-Xylylenediphosphonic acid has been used instead of the *para* isomer, leading to a layered compound.[25]

However, frameworks of organic–inorganic hybrid materials showing simultaneously permanent porosity and high

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thermal stability are extremely rare.[26,27] The inability of these materials to support a stable framework at higher temperatures or after removing guest molecules has hindered further application in many fields.[28] So the application of diphosphonates is still quite limited relative to that of zeolites or aluminophosphates, despite the extensive studies. Generally, they are thermally unstable when compared with inorganic phosphates and most of them are destroyed at high temperature (>300 °C).

Some diphosphonates containing coordinated water and showing dehydration behavior have been reported, but their dehydration behaviors are diverse. The copper ethylenediphosphonate loses water irreversibly from the metal center, resulting in the collapse of the structure.[29] The aluminum and gallium diphosphonates lose water in two stages: first the water residing within channels and subsequently the water from positions coordinated to metal cations, and the latter stage leads to loss of crystallinity.[30,31] The aluminum and vanadium ethylenediphosphonates show reversible dehydration/rehydration behavior without losing their crystallinity and may therefore have potential applications as adsorbents, sensors, and catalysts, but such diphosphonates are still not very common.[32,33]

We have successfully synthesized a novel three-dimensional cobalt diphosphonate $Co_2(H_2O)_2[O_3PCH_2(C_6H_4)CH_2PO_3]$ with two-dimensional infinite cobalt–oxygen inorganic layers pillared by an organophosphorus *p*-xylylenediphosphonate. The compound is exceptionally stable even when heated up to 500 °C in air. More interestingly, the framework components display a reversible dehydration/rehydration behavior.

Results and Discussion

Description of Crystal Structure

Single-crystal X-ray analysis shows that the compound is a 3D structure that possesses 2D infinite cobalt–oxygen inorganic layers pillared by the $P–CH_2–C_6H_4–CH_2–P$ group. As shown in Figure 1, the asymmetric unit contains two crystallographically independent cobalt atoms, one *p*-xylylenediphosphonate ligand, and two water molecules. Each of the cobalt atoms is located in an octahedral coordination environment with five oxygen atoms (O1, O2, O3, O4, O5 for Co1; O1, O2A, O3A, O4A, O8 for Co2) from the *p*-xylylenediphosphonate ligand, and one oxygen atom (O6 for Co1; O7 for Co2) from the water molecule.

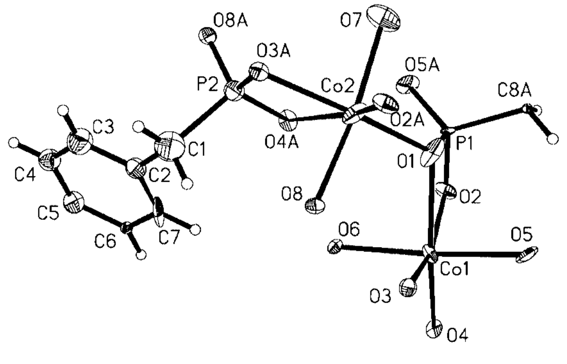

Figure 1. Thermal ellipsoid plot showing an asymmetric unit of $Co_2(H_2O)_2[O_3PCH_2(C_6H_4)CH_2PO_3]$.

The compound crystallizes in the orthorhombic space group *Pca*2(1). Interestingly, the structure consists of infinite inorganic layers of corner-sharing CoO_6 octahedra, which is totally different from other reported metal phosphonates using *p*-xylylenediphosphonate as the ligand.[24] The coordination between the cobalt atoms and the PO_3 groups in the compound is similar to that found in $Mn(C_6H_5PO_3)·H_2O$[17] or $Zn(C_6H_5PO_3)·H_2O$,[20] but these are 2D layered structures and the former is a 3D pillared

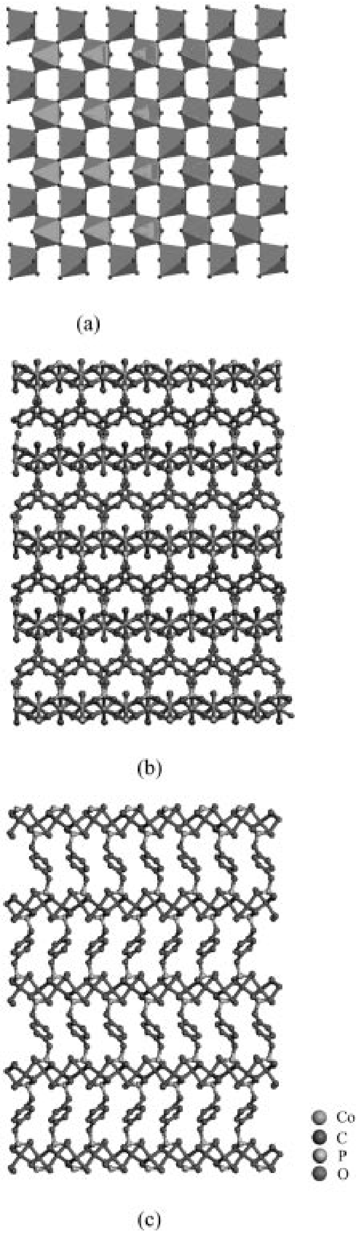

Figure 2. (a) The view of the Co–O layers of $Co_2(H_2O)_2[O_3PCH_2(C_6H_4)CH_2PO_3]$ in the [001] plane. (b) A ball-and-stick representation of the structure viewed along the [100] and (c) [010] directions. Hydrogen atoms are omitted for clarity.

layered structure. As shown in Figure 2a, such a compound is a rare example of a hybrid metal oxide containing an infinite 2D –M–O–M–O– net framework.[34] The adjacent cobalt–oxygen layers are interconnected to each other through the organic part of *p*-xylylenediphosphonate, P–CH_2–C_6H_4–CH_2–P, to produce a 3D structure (Figure 2b). The pillars can connect the inner layers of the Co–O network and, thus, further stabilize the structure. As presented in Figure 2b, The *p*-xylylenediphosphonate groups link the inorganic octahedral layers in the fashion of an alternately left and right arrangement along the [100] direction. As indicated in Figure 2c, the framework along the [010] direction contains a 10.850 Å [Co1–Co1] × 5.687 Å [C3–C3] one-dimensional channel system. The overall structure may be described in terms of alternating inorganic infinite metal oxygen layers and organic pillars (P–CH_2–C_6H_4–CH_2–P). To the best of our knowledge, inorganic metal oxygen layers pillared by organophosphorus groups with the in situ hydrothermal method have not been reported so far.

Thermal Stability

The thermal stability of the sample has been studied by using TGA and XRD at different temperatures. Thermogravimetric analysis (TGA) of the compound (Figure 3) showed that the first weight loss of 8.61 % from 200 to 500 °C corresponds to the loss of two coordinated water molecules (calculated: 8.66 %). The decomposition of the compound starts above 500 °C, which is in good agreement with the TGA of the calcined sample, except for the absence of the first weight loss, indicating that the coordinated water had already been removed during calcination (Figure S1). Considering the thermal stability of the compound, X-ray powder diffraction (PXRD) studies are performed for the as-synthesized sample and the samples heated at 350 °C, 400 °C, and 500 °C. Figure 4 presents X-ray diffraction (XRD) patterns simulated from single-crystal X-ray diffraction data as well as those of the as-synthesized sample, the calcined samples, and the rehydrated sample. The XRD pattern of the as-synthesized sample fits well with the simulated one, indicating that the sample is a pure phase. The XRD patterns for the calcined samples (Figure 4c, d, e) are similar to that of the as-synthesized sample (Figure 4b). The very intense peaks, (002) and (004), located at two Bragg angles 2θ of 8.06° and 16.3°, are always maintained after calcination and rehydration, indicating that the structure of 2D cobalt–oxygen pillared by organophosphate does not collapse after the removal of the coordinated water molecules and that the calcined sample retains high crystallinity and pure phase. It is quite surprising that the compound could maintain its structure even when heated up to 500 °C, which is extremely rare in organophosphates and suggests that the compound can preserve its rigid and stable framework at high temperature. It is also clear that the dehydration of the water lattice is reversible (Figure 4f).

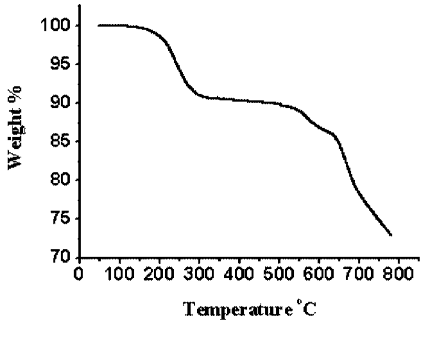

Figure 3. TGA curves of the sample.

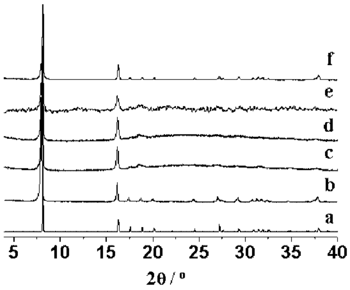

Figure 4. Simulated powder X-ray diffraction patterns of the single-crystal crystallography data (a), as-synthesized sample (b), dehydrated sample after calcination at 350 °C (c), 400 °C (d), 500 °C (e), and rehydrated sample after calcination at 350 °C (f).

Dehydration/Rehydration Properties

Interestingly, it was found that the color of the crystals changed from pink to blue when they were heated at 350 °C for 2 h, while optical microscopy showed that they maintained their transparency and morphology (Figure 5a). Because of the difference in the crystal field splitting energy between the octahedral field and the square-pyramidal field,[35] the observed color of the compound containing octahedrally coordinated cobalt ions is pink, while that of the compound containing square-pyramidally coordinated cobalt is blue. Therefore, accompanying the change of color from pink to blue, the coordination environment of the cobalt ion is changed from octahedral to square-pyramidal.

For a deep understanding of how the structure of the compound changes with temperature and how it undergoes a reversible dehydration/rehydration process, it is instructive to simulate the distorted square-pyramidal coordination geometry of the cobalt atom in the dehydrated compound (Figure 5b). Notably, all the coordinated water can be removed from the structure at 350 °C within 2 h without loss of framework periodicity. The coordinated water is removed and diffuses out along the [100] direction, which is confirmed by the observation that some partly dehydrated crystals presented different colors after being calcined at 300 °C for 2 h: pink at the central part and blue at the two ends of the crystal (Figure 5c). Therefore, without sufficient time or higher temperature, the central part could not be fully dehydrated. More significantly, the crystals can be fully rehydrated when they are immersed in water for several hours. Thus, the rehydration process is accompanied by a return

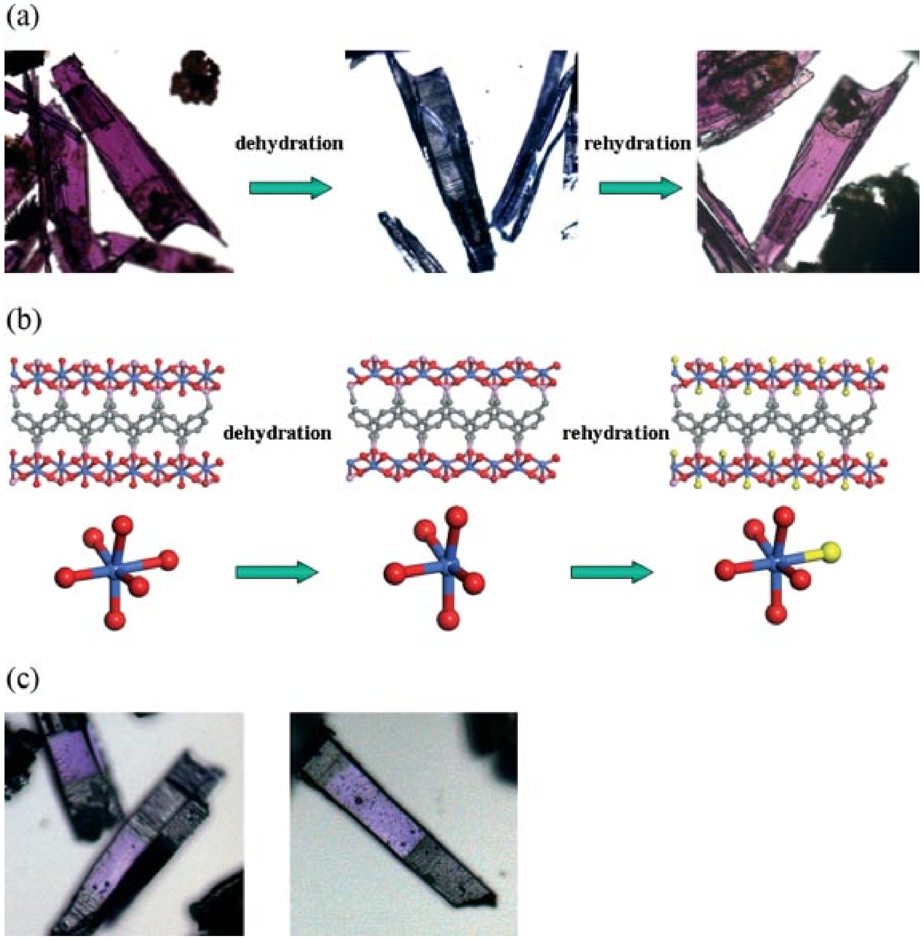

Figure 5. Pictorial representation of the dehydration/rehydration process and the partly dehydrated crystals. The pink crystals turned blue after dehydration, then changed back to pink after rehydration (a). Correspondingly, the cobalt coordination environment changed from octahedral to square pyramidal, and finally returned to octahedral (b). The partly dehydrated crystals are pink at the center and blue at the two ends (c).

of the original pink color (Figure 5a). The XRD pattern of the rehydrated sample (Figure 4f) indicates that a high degree of crystallinity is retained after water is resorbed.

Water Sorption Properties

The phenomenon of dehydration/rehydration in the microporous frameworks and the thermal stability encouraged us to try to create the micropores after removing the coordinated and guest water molecules. The calcined compound was evacuated under reduced pressure (1×10^{-5} Torr) until no more weight loss occurred at 150 °C, and then it was exposed to water vapor. As shown in Figure S2, type I behavior is observed in the water adsorption isotherm of the sample in the range P/P_0 = 0–0.7. At saturation, the amount of water sorbed is 87.6 mg g^{-1}, which is equivalent to the adsorption of about eight water molecules per formula unit. Therefore, the pore volume is estimated to be approximately 0.09 mL g^{-1} by the water adsorption isotherm.

IR Spectrum

This dehydration process can be further confirmed by IR spectroscopy (Figure 6). The IR spectrum of the as-synthesized sample (Figure 6a) presents broad peaks at 3494 cm^{-1}

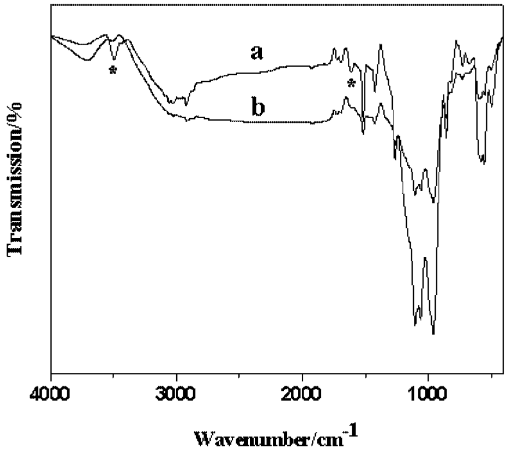

Figure 6. IR spectrum of the sample (a) and of the sample after calcination at 350 °C (b).

corresponding to the stretching of water molecules and a sharp peak at 1618 cm^{-1} corresponding to the bending vibration of coordinated water. After calcination at 350 °C for 2 h, the two types of peaks mentioned above decreased in size significantly (Figure 6b). The main structure peaks could correspondingly be observed in the spectrum of the calcined sample as compared to the as-synthesized sample, indicating that the main framework of the compound is retained after calcination.

Magnetic Properties

The temperature-dependent (4–300 K) magnetic susceptibility of the compound is shown in Figure 7. Between 4 and 300 K, χ_m continuously increases with decreasing temperature and achieves a maximum of 0.115 cm^3 mol^{-1} at 8.99 K. In the $1/\chi_m$ versus T plot, the susceptibility can be fitted to the Curie–Weiss law with $C = 6.87$ cm^3 K mol^{-1}. The Weiss temperature, $\theta = -50.97$ K, indicates that antiferromagnetic interactions exist between the metallic Co centers.

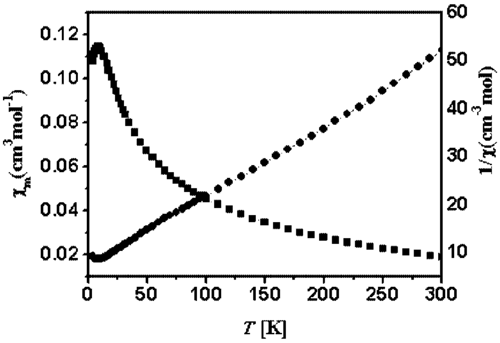

Figure 7. χ_m vs. T and $1/\chi_m$ vs. T plots of $Co_2(H_2O)_2[O_3PCH_2(C_6H_4)CH_2PO_3]$.

Conclusions

A cobalt diphosphonate with micropores has been synthesized by a hydrothermal method. The structure was solved by single-crystal X-ray diffraction and found to be constructed of infinite cobalt oxygen layers pillared by *p*-xylylenediphosphonate groups. The compound is stable up to 500 °C, illustrating the exceptional stability of the framework. The more important feature is that it undergoes a reversible dehydration/rehydration process driven by temperature, which can be detected by changes in crystal color. This is a rare example of a metal diphosphonate framework that has a "defect" site with incomplete coordination, which can be created without loss of framework architecture. Such defect sites in compounds can result in changes in physical properties, such as color, and are expected to show shape-selective adsorption behavior for small molecules and could be potentially used as sensors, adsorbents, catalysts and so forth.

Currently, we are carrying out investigations into the ability of dehydrated compounds to absorb molecules other than water. Efforts toward the preparation of new hybrid materials containing other transition metals based on this type of ligand are underway.

Experimental Section

General Remarks: All chemicals purchased were of reagent grade or better and were used without further purification. The elemental analyses were carried out with a Perkin–Elmer 240C elemental analyzer. TGA (thermal gravimetric analyses) were performed under nitrogen with a heating rate of 10 °C min^{-1} by using a Perkin–Elmer TGA 7 thermogravimetric analyzer. XRD was performed with a Siemens D5005 diffractometer with Cu-K_α radiation, 40 kV, 35 mA at a scanning rate of 0.3°min^{-1} (2θ). The IR spectra were recorded (400–4000 cm^{-1} region) with a Nicolet Impact 410 FTIR spectrometer by using KBr pellets.

Synthesis of $Co_2(H_2O)_2[O_3PCH_2(C_6H_4)CH_2PO_3]$: As a typical preparation procedure, a mixture of tetraethyl *p*-xylylenediphosphonate (0.03 mmol) and $Co(NO_3)_2\cdot 4H_2O$ (0.03 mmol) was suspended in deionized water (8 mL) and cyclohexanol (2 mL), and then triethylamine (0.1 mL) was added while stirring to adjust the pH value of the mixture. The mixture (pH $\approx$ 6) was sealed in a 15-mL Teflon-lined autoclave after being stirred for 60 min. Upon being heated at 160 °C for 2 d, the autoclaved mixture was naturally cooled to room temperature. The pink crystals were collected, washed with deionized water, and dried at room temperature. The compound was stable in air and insoluble in water and common organic solvents. $C_8H_{12}Co_2O_8P_2$: calcd. C 23.10, H 2.90, Co 28.33, P 14.89; found C 23.40, H 3.34, Co 28.03, P 14.20.

X-ray Crystallographic Study: The intensity data were collected with a Smart CCD diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation at 293 K in the ω-scan mode. An empirical absorption correction was applied to the data by using the SADABS program.[36] The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined by using a riding mode. All calculations were performed with the SHELXTL program.[37] The crystallographic data are summarized in Table 1, and the selected bond lengths and bond angles of the compound are listed in Table 2. CCDC-608190 for $Co_2(H_2O)_2[O_3PCH_2(C_6H_4)CH_2PO_3]$ contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for the compound.

Empirical formula	$C_8H_{12}Co_2O_8P_2$
Formula mass	415.98
Crystal system	orthorhombic
Space group	*Pca*2(1)
a [Å]	9.6214(19)
b [Å]	5.6855(11)
c [Å]	21.725(4)
V [Å^3]	1188.4(4)
Z	4
$\rho_{calcd.}$ [g cm^{-3}]	0.2325
μ [mm^{-1}]	3.096
$R^{[a]}$ [$I > 2\sigma(I)$]	0.0582
$R_w^{[b]}$	0.1316

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

Table 2. Selected bond lengths [Å] and angles [°] for the compound.[a]

Co1–O1	2.275(5)	Co1–O2	2.088(4)
Co1–O3	2.012(5)	Co1–O4	2.046(5)
Co1–O5	2.102(5)	Co1–O6	2.156(5)
Co2–O1	2.095(5)	Co2–O2A	2.068(5)
Co2–O3B	2.192(5)	Co2–O4C	2.342(5)
Co2–O7	2.150(6)	Co2–O8	2.082(5)
O2–Co1–O1	66.62(17)	O3–Co1–O1	90.39(19)
O4–Co1–O1	164.72(17)	O5–Co1–O1	85.12(18)
O6–Co1–O1	91.72(18)	O3–Co1–O2	156.82(18)
O4–Co1–O2	98.12(19)	O5–Co1–O2	87.81(18)
O3–Co1–O4	104.9(2)	O3–Co1–O5	93.41(19)
O4–Co1–O5	93.80(19)	O2–Co1–O6	88.51(18)
O3–Co1–O6	89.24(18)	O4–Co1–O6	88.55(18)
O5–Co1–O6	175.88(19)	O2A–Co2–O1	104.95(19)
O2A–Co2–O3B	93.05(19)	O1–Co2–O3B	162.00(18)
O7–Co2–O3B	85.9(2)	O8–Co2–O3B	88.13(19)
O1–Co2–O4C	95.89(19)	O3B–Co2–O4C	66.36(17)
O7–Co2–O4C	90.5(2)	O8–Co2–O4C	83.67(18)
O2A–Co2–O4C	157.89(16)	O1–Co2–O7	91.6(2)
O2A–Co2–O7	96.12(19)	O8–Co2–O7	173.0(2)
O1–Co2–O8	92.99(19)	O2A–Co2–O8	87.87(17)

[a] Symmetry transformations used to generate equivalent atoms: A: $x, y-1, z$; B: $x-1/2, -y, z$; C: $x-1/2, -y+1, z$.

Water Sorption Isotherm: Water sorption isotherm studies were performed by measuring the increase in weight at equilibrium as a function of relative pressure. The weight of the sample was measured by a CAHN 2000 electrobalance and the adsorbate (H_2O) was added incrementally and manually.

Supporting Information (see footnote on the first page of this article): Figure S1, TGA curves of the compound after being calcined at 350 °C, and Figure S2, water sorption isotherm for the dehydrated compound, are available.

Acknowledgments

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