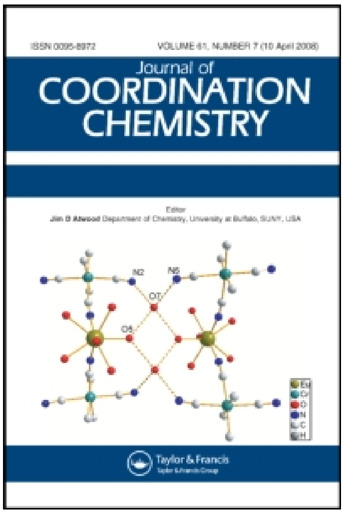

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Two malonato coordination polymers: syntheses and crystal structures of $M(H_2O)_2(C_3H_2O_4)$ with M=CO and Ni, $C_3H_4O_4$ = malonic acid

Yue-Qing Zheng[a]; Hong-Zhen Xie[a]
[a] Municipal Key Laboratory of Solid State Chemistry, Institute of Inorganic Chemistry, Ningbo University, Ningbo 315211, P. R. China

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TWO MALONATO COORDINATION POLYMERS: SYNTHESES AND CRYSTAL STRUCTURES OF $M(H_2O)_2(C_3H_2O_4)$ WITH M=Co AND Ni, $C_3H_4O_4$ = MALONIC ACID

YUE-QING ZHENG* and HONG-ZHEN XIE

Municipal Key Laboratory of Solid State Chemistry, Institute of Inorganic Chemistry,
Ningbo University, Ningbo 315211, P. R. China

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Two malonato-bridged coordination polymers, $M(H_2O)_2(C_3H_2O_4)$, with M=Co (**1**) and Ni (**2**), were prepared. X-ray analyses show that both title compounds are isostructural. Octahedral divalent metal atoms are interconnected by dicarboxylate anions to form 2D layers formulated as ${}^{2}_{\infty}\{[M(H_2O)_2][M(H_2O)_2(C_3H_2O_4)_2]_{4/4}\}$, where each malonato group chelates one metal atom through two distal oxygen atoms with the nonchelating carboxylate oxygen atoms each bonding to one metal atom. The 2D layers are connected by interlayer hydrogen bonds.

Keywords: Cobalt; Nickel; Coordination polymers; Malonato complexes; X-ray structures

INTRODUCTION

In recent years, the rational design and synthesis of coordination polymers has been one of the most active research fields in coordination chemistry and materials science [1–4]. The main interest in this area is focussed on the development of strategies for more directed construction of novel coordination architectures with interesting physical properties [5–7]. One special class of such compounds concerns coordination polymers based on assemblies of transition metal ions and aromatic dicarboxylic acids [6–9]. In contrast to rigid aromatic dicarboxylate anions, α,ω-dicarboxylates exhibit much more flexibility due to conformational and coordination variation [10–15]. As one of the lower members in the α,ω-dicarboxylate family, malonate anions are of particular interest in construction of coordination polymers with specific architectures [16]. The basic coordination mode of the malonate anions is as a chelate via two distal carboxylate oxygen atoms to form a six-membered ring and the coordinating ability of the nonchelating oxygen atoms makes the formation of polymeric networks possible. In the present work, we report the syntheses and crystal structures of two

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*Corresponding author. E-mail: zhengcm@nbu.edu.cn

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malonato-bridged layer compounds, $M(H_2O)_2(C_3H_2O_4)$, with M=Co (**1**) and Ni (**2**), along with the magnetic properties of **1**.

EXPERIMENTAL

All chemicals of p.a. grade were commercially available and used without further purification. C and H microanalyses were performed with a Perkin Elmer 2400II CHNO/S instrument. FT-IR spectra were recorded in the range 4000–400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer using the KBr pellet technique. Magnetic susceptibilities of **1** were measured on a powdered sample using a SQUID magnetometer (Quantum Design Model MPMS-7) in temperature range $5 \leq T(\mathrm{K}) \leq 300$ with an applied field of 10 000 G. Diamagnetic corrections were estimated from Pascal's constants [17].

Preparation of $Co(H_2O)_2(C_3H_2O_4)$ (1) and $Ni(H_2O)_2(C_3H_2O_4)$ (2)

$Co(H_2O)_2(C_3H_2O_4)$ **1** Dropwise addition of 6.0 cm^3 of 1 M aqueous Na_2CO_3 to a stirred aqueous solution of $CoCl_2 \cdot 6H_2O$ (0.59 g, 2.50 mmol) in 4 cm^3 of H_2O produced a violet $Co(OH)_{2-2x}(CO_3)_x \cdot yH_2O$ precipitate, which was then centrifuged and washed with doubly-distilled water until no Cl^- ions were detected in the washings. The fresh precipitate was subsequently added to a stirred solution of 0.26 g (2.50 mmol) of malonic acid in 50 cm^3 CH_3OH/H_2O (1:1 v/v) and the resulting mixture stirred for 30 min. After filtration, the rose-colored filtrate (pH = 7.29) was maintained at 50°C and rose-colored crystals formed in 2 days. Yield: 35% based on initial $CoCl_2 \cdot 6H_2O$. Anal. Calcd. for $C_3H_6CoO_6$ (%): C, 18.29; H, 3.07. Found: C, 18.33; H, 3.16. IR (cm^{-1}): 3461 m, 3190 m, 1569 s, 1450 w, 1375 m, 1278 w, 1174 w, 945 w, 881 w, 721 m, 582 m.

$Ni(H_2O)_2(C_3H_2O_4)$ **2** Some 3.0 ml of 1 M aqueous Na_2CO_3 was added dropwise to a methanolic/aqueous solution of $NiCl_2 \cdot 6H_2O$ (0.59 g, 2.50 mmol) and malonic acid (0.26 g, 2.50 mmol) in 50 cm^3 of CH_3OH/H_2O (1:1 v/v) to give a pale green solution (pH = 7.53). This was allowed to stand at room temperature. Pale green crystals were formed by slow evaporation during 1 month. Yield: 45% based on initial $NiCl_2 \cdot 6H_2O$. Anal. Calcd. for $C_3H_6O_6Ni$ (%): C, 18.27; H, 3.06. Found: C, 18.37; H, 3.09. IR (cm^{-1}): 3467 m, 3211 m, 1569 s, 1460 w, 1375 m, 1286 w, 1178 w, 945 w, 885 w, 732 m, 574 m.

Crystal Structure Determination

Reflection intensities for complexes **1** and **2** were collected at 293 K on a Bruker P4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the ϑ–2ϑ scan technique. SHELXS-97 [18] and SHELXL-97 [19] programs were used for the structure determination and refinement. The structures were solved with direct methods and refined with full-matrix least-squares techniques. Nonhydrogen atoms were refined anisotropically. The aqua hydrogen atoms were located from difference Fourier syntheses and those associated with carbon atoms were generated geometrically. Details of crystal data, and data collection and refinement details both for compounds are summarized in Table I, and selected interatomic distances and bond angles are listed in Tables II and III.

TABLE I Summary of crystal data, data collection, structure solution and refinement details for **1** and **2**

	1	**2**
Empirical formula	$C_3H_6CoO_6$	$C_3H_6NiO_6$
Formula weight	197.01	196.79
Description	Rose-colored block	Pale green block
Crystal size (mm)	0.222 × 0.111 × 0.111	0.178 × 0.156 × 0.156
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$
Unit cell dimensions		
a (Å)	12.641(3)	12.576(1)
b (Å)	7.415(2)	7.370(1)
c (Å)	7.302(2)	7.218(1)
β (°)	120.18(3)	120.31(1)
Volume (Å^3)	591.7(2)	577.6(1)
Z	4	4
D_{calc} (g cm^{-3})	2.212	2.263
F(000)	396	400
μ (mm^{-1})	2.869	3.327
Absorption correction	Empirical	Empirical
Min. and max. transmission	0.589, 0.867	0.483, 0.521
θ range (°)	3.23–27.50	3.27–27.49
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Reflections collected	952	933
Independent reflections (R_{int})	735 (0.0220)	718 (0.0208)
Data/restraints/parameters	701/0/69	656/0/69
Goodness-of-fit on F^2	1.107	1.066
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0218, 0.0600	0.0214, 0.0532
R_1, wR_2 (all data)^a	0.0227, 0.0605	0.0244, 0.0549
Extinction coefficients	0.060(3)	0.0028(9)
A, B values in weighting scheme^b	0.0243, 0.9300	0.0205, 0.7358
$\delta\rho_{\max}$, $\delta\rho_{\min}$ (e Å^{-3})	0.381, −0.291	0.320, −0.276

$^a wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$. $^b w = [\sigma^2(F_o^2) + (\mathrm{AP})^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

TABLE II Selected interatomic distances (Å) and bond angles (°) for **1**

Co(1)–O(1)	2.081(2)	Co(2)–O(2)	2.116(2)	C(1)–O(3)	1.265(2)
Co(1)–O(1)$^{\#1}$	2.081(2)	Co(2)–O(2)$^{\#2}$	2.116(2)	C(1)–O(4)	1.252(2)
Co(1)–O(4)	2.119(1)	Co(2)–O(3)	2.052(1)	C(1)–C(2)	1.520(2)
Co(1)–O(4)$^{\#1}$	2.119(1)	Co(2)–O(3)$^{\#2}$	2.052(1)	C(2)–C(1)$^{\#4}$	1.520(2)
Co(1)–O(4)$^{\#5}$	2.119(1)	Co(2)–O(3)$^{\#3}$	2.052(1)		
Co(1)–O(4)$^{\#6}$	2.119(1)	Co(2)–O(3)$^{\#4}$	2.052(1)		
O(1)–Co(1)–O(4)	86.32(5)	O(4)$^{\#1}$–Co(1)–O(4)	180	O(3)$^{\#2}$–Co(2)–O(2)	87.93(6)
O(1)–Co(1)–O(4)$^{\#1}$	93.68(5)	O(4)$^{\#5}$–Co(1)–O(4)	86.36(8)	O(3)$^{\#2}$–Co(2)–O(2)$^{\#2}$	92.07(6)
O(1)–Co(1)–O(4)$^{\#5}$	93.68(5)	O(4)$^{\#5}$–Co(1)–O(4)$^{\#1}$	93.64(8)	O(3)$^{\#2}$–Co(2)–O(3)	180
O(1)–Co(1)–O(4)$^{\#6}$	86.32(5)	O(4)$^{\#6}$–Co(1)–O(4)	93.64(8)	O(3)$^{\#2}$– Co(2)–O(3)$^{\#4}$	90.40(7)
O(1)$^{\#1}$–Co(1)–O(1)	180	O(4)$^{\#6}$–Co(1)–O(4)$^{\#1}$	86.36(8)	O(3)$^{\#3}$–Co(2)–O(2)	87.93(6)
O(1)$^{\#1}$–Co(1)–O(4)	93.68(5)	O(4)$^{\#6}$–Co(1)–O(4)$^{\#5}$	180	O(3)$^{\#3}$–Co(2)–O(2)$^{\#2}$	92.07(6)
O(1)$^{\#1}$–Co(1)–O(4)$^{\#1}$	86.32(5)	O(2)$^{\#2}$–Co(2)–O(2)	180	O(3)$^{\#3}$–Co(2)–O(3)	90.40(7)
O(1)$^{\#1}$–Co(1)–O(4)$^{\#5}$	86.32(5)	O(3)–Co(2)–O(2)	92.07(6)	O(3)$^{\#3}$–Co(2)–O(3)$^{\#2}$	89.60(7)
O(1)$^{\#1}$–Co(1)–O(4)$^{\#6}$	93.68(5)	O(3)–Co(2)–O(2)$^{\#2}$	87.93(6)	O(3)$^{\#3}$–Co(2)–O(3)$^{\#4}$	180
O(3)–C(1)–O(4)	123.0(2)				
Hydrogen bonding contacts					
D–H	*d(D–H)*	*d(H···A)*	*∠(D–H···A)*	*d(D–H···A)*	*A*
O(1)–H(1)	0.82	1.92	157	2.689	O(3)$^{\#5}$
O(2)–H(2)	0.82	2.16	145	2.871	O(4)$^{\#10}$

Symmetry codes: #1 = $-x+1$, $-y$, $-z+2$; #2 = $-x+1$, $-y+1$, $-z+1$; #3 = $-x+1$, y, $-z+1$; #4 = x, $-y+1$, z; #5 = $-x+1$, y, $-z+2$; #6 = x, $-y$, z; #7 = x, $y+1$, z; #8 = x, y, $z-1$; #9 = x, $y+1$, $z-1$; #10 = $-x+1/2$, $-y+1/2$, $-z+1$.

TABLE III Selected interatomic distances (Å) and bond angles (°) for **2**

Ni(1)–O(1)	2.054(2)	Ni(2)–O(2)	2.081(2)	C(1)–O(3)	1.268(2)
Ni(1)–O(1)$^{\#1}$	2.054(2)	Ni(2)–O(2)$^{\#2}$	2.081(2)	C(1)–O(4)	1.254(2)
Ni(1)–O(4)	2.086(1)	Ni(2)–O(3)	2.016(1)	C(1)–C(2)	1.514(2)
Ni(1)–O(4)$^{\#1}$	2.086(1)	Ni(2)–O(3)$^{\#2}$	2.016(1)	C(2)–C(1)$^{\#4}$	1.514(2)
Ni(1)–O(4)$^{\#5}$	2.086(1)	Ni(2)–O(3)$^{\#3}$	2.016(1)		
Ni(1)–O(4)$^{\#6}$	2.086(1)	Ni(2)–O(3)$^{\#4}$	2.016(1)		
O(1)–Ni(1)–O(4)	85.66(5)	O(4)$^{\#1}$–Ni(1)–O(4)	180	O(3)$^{\#2}$–Ni(2)–O(2)	87.55(6)
O(1)–Ni(1)–O(4)$^{\#1}$	94.34(5)	O(4)$^{\#5}$–Ni(1)–O(4)	86.96(8)	O(3)$^{\#2}$–Ni(2)–O(2)$^{\#2}$	92.45(6)
O(1)–Ni(1)–O(4)$^{\#5}$	94.34(5)	O(4)$^{\#5}$–Ni(1)–O(4)$^{\#1}$	93.04(8)	O(3)$^{\#2}$–Ni(2)–O(3)	180
O(1)–Ni(1)–O(4)$^{\#6}$	85.66(5)	O(4)$^{\#6}$–Ni(1)–O(4)	93.04(8)	O(3)$^{\#2}$–Ni(2)–O(3)$^{\#4}$	89.24(8)
O(1)$^{\#1}$–Ni(1)–O(1)	180	O(4)$^{\#6}$–Ni(1)–O(4)$^{\#1}$	86.96(8)	O(3)$^{\#3}$–Ni(2)–O(2)	87.55(6)
O(1)$^{\#1}$–Ni(1)–O(4)	94.34(5)	O(4)$^{\#6}$–Ni(1)–O(4)$^{\#5}$	180	O(3)$^{\#3}$–Ni(2)–O(2)$^{\#2}$	92.45(6)
O(1)$^{\#1}$–Ni(1)–O(4)$^{\#1}$	85.66(5)	O(2)$^{\#2}$–Ni(2)–O(2)	180	O(3)$^{\#3}$–Ni(2)–O(3)	89.24(8)
O(1)$^{\#1}$–Ni(1)–O(4)$^{\#5}$	85.66(5)	O(3)–Ni(2)–O(2)	92.45(6)	O(3)$^{\#3}$–Ni(2)–O(3)$^{\#2}$	90.76(8)
O(1)$^{\#1}$–Ni(1)–O(4)$^{\#6}$	94.34(5)	O(3)–Ni(2)–O(2)$^{\#2}$	87.55(6)	O(3)$^{\#3}$–Ni(2)–O(3)$^{\#4}$	180
O(3)–C(1)–O(4)	122.8(2)				
Hydrogen bonding contacts					
D–H	*d(D–H)*	*d(H···A)*	*∠(D–H···A)*	*d(D–H···A)*	*A*
O(1)–H(1)	0.79	1.92	160	2.680	O(3)$^{\#5}$
O(2)–H(2)	0.78	2.20	144	2.868	O(4)$^{\#8}$

Symmetry codes: $\#1=-x+1, -y, -z+2$; $\#2=-x+1, -y+1, -z+1$; $\#3=-x+1, y, -z+1$; $\#4=x, -y+1, z$; $\#5=-x+1, y, -z+2$; $\#6=x, -y, z$; $\#7=x, y+1, z$; $\#8=-x+1/2, -y+1/2, -z+1$.

RESULTS AND DISCUSSION

Structure of $Co(H_2O)_2(C_3H_2O_4)$ (1) and $Ni(H_2O)_2(C_3H_2O_4)$ (2)

IR spectra and X-ray analyses confirm that Compounds **1** and **2** are isostructural. The following discussion will be confined to the cobalt malonate, **1**.

As shown in Fig. 1, the cobalt compound **1** contains two crystallographically distinct cobalt atoms, Co(1) and Co(2), at crystallographic 2*b* and 2*c* sites, respectively. Both cobalt atoms have in octahedral coordination environments and possess 2/*m* symmetry. Co(1) atoms are coordinated by six oxygen atoms of four malonate anions and two aqua ligands in *trans* positions. Co–O bond distances to the malonate oxygen O(4) atoms are 2.119(1) Å, slightly larger than those to the aqua oxygen O(1) atoms at 2.081(2) Å. The *transoid* O–Co–O bond angles are exactly equal to 180° due to the local symmetry imposition, while the *cisoid* O–Co–O bond angles lie in the range 86.3–93.7°. Co(2) coordination is defined by six oxygen atoms of two chelating malonate anions and two *trans* aqua ligands with Co–O bond distances of 2.052(1) Å to the chelating malonate oxygen O(3) and 2.116(2) Å to the aqua oxygen O(2) atoms. In contrast to the compressed octahedral geometry around Co(1), the octahedra around Co(2) are elongated with *cisoid* O–Co–O bond angles in the range 87.9–92.1° and *transoid* O–Co–O bond angles of 180° due to the local symmetry imposition.

Malonate anions possess by an *m* symmetry through C(2). The dicarboxylate groups functions as a tetradentate ligand to chelate one Co(2) atom through two distal carboxylate oxygen atoms to form a six-membered ring with each nonchelating carboxyl oxygen atoms bonding to a Co(1) atom. As a result, 2D layers are generated parallel to (100) and the aqua ligand bonded to Co(1) atom donates hydrogen atoms to the chelating carboxylate O(3) atoms to form relatively strong intralayer hydrogen bonds, with

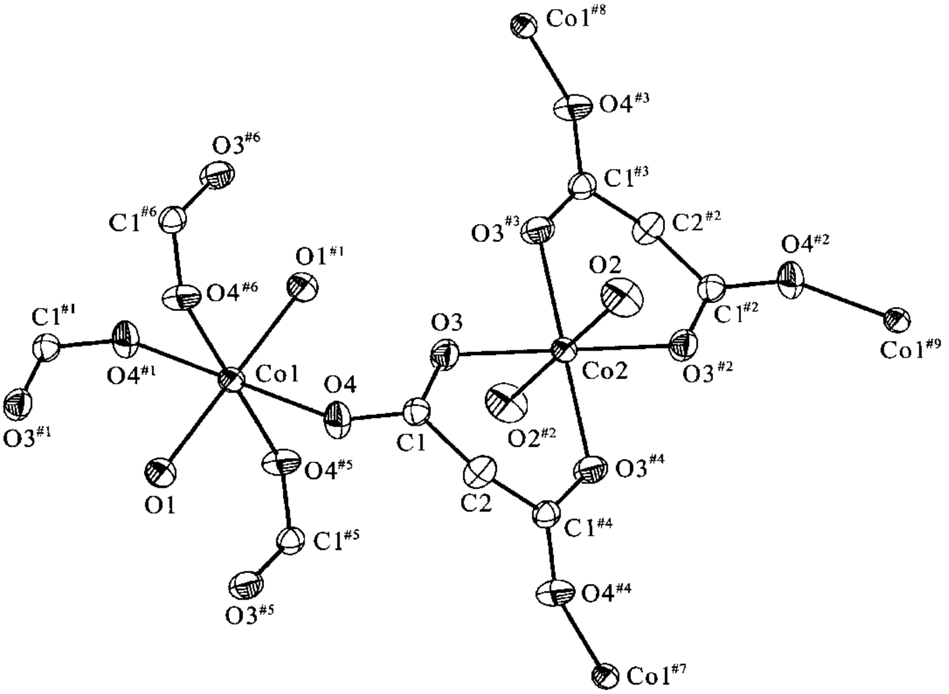

FIGURE 1 Coordination environments around the cobalt atoms with the atom labeling for **1** (displacement ellipsoids drawn at 45% probability and H atoms omitted for clarity).

$d(\mathrm{O}(1)\cdots\mathrm{O}(3)^{\#5}) = 2.689$ Å ($\#5 = -x+1$, y, $-z+2$; Table II). As demonstrated in Fig. 2, the 2D layers can be viewed as resulting from the *trans*-$[\mathrm{Co(H_2O)_2}]^{2+}$ cationic entities linked to *trans*-$[\mathrm{Co(H_2O)_2(C_3H_2O_4)_2}]^{2-}$ through nonchelating carboxylate oxygen atoms and in this way the formed 2D layers can be formulated as $^{2}_{\infty}\{[\mathrm{Co(H_2O)_2}][\mathrm{Co(H_2O)_2(C_3H_2O_4)_2}]_{4/4}\}$.

The polymeric 2D layers exhibit interesting patterns containing 6-, 12- and 16-membered rings. The 16-membered rings are adjacent to four 6-membered rings and four 12-membered rings. Each 12-membered ring is surrounded by two 6-membered rings and four 16-membered rings. The 6-membered rings are flanked by two 16-membered rings, one 12-membered ring and a further 6-membered ring. Along the [100] direction, 2D layers are assembled by interlayer hydrogen bonding interactions between aqua ligands and nonchelating oxygen atom, with $d(\mathrm{O}(2)\cdots\mathrm{O}(4)^{\#10}) = 2.871$ Å ($\#10 = -x+1/2$, $-y+1/2$, $-z+1$; Table II). Each layer is shifted by $0.5b$ with respect to the next layer, so that the *trans*-$[\mathrm{Co(H_2O)_2(C_3H_2O_4)_2}]^{2-}$ anions of one layer project on the centres of the 16-membered rings of neighboring layers.

Magnetic properties of $\mathrm{Co(H_2O)_2(C_3H_2O_4)}$ (1)

Magnetic measurements over 5–300 K show that the magnetic behavior of **1** obeys the Curie–Weiss laws $\chi_m(T-\Theta) = 3.35(2)\,\mathrm{cm^3\,mol^{-1}\,K}$ with the Weiss constant

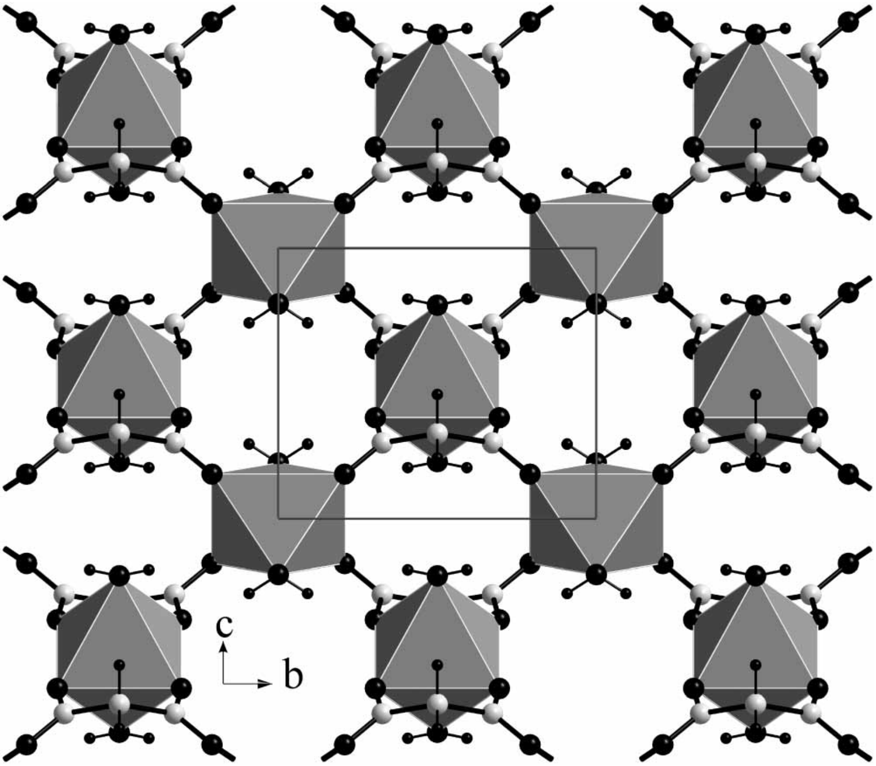

FIGURE 2 The 2D $^{2}_{\infty}\{[Co(H_2O)_2][Co(H_2O)_2(C_3H_2O_4)_2]_{4/4}\}$ layer in **1**.

$\Theta = -16.5(6)$ K, suggesting weak antiferromagnetic coupling at low temperature. The effective magnetic moment at room temperature is 5.00 BM, slightly less than the spin-only value expected for high-spin Co(II) in an octahedral crystal field [17].

Acknowledgments

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Supplementary Data

Crystallographic data (excluding structure factors) have been deposited with Cambridge Crystallographic Data Centre as supplementary publications CCDC 243838 ($C_3H_6O_6Co$) and CCDC 243839 ($C_3H_6O_6Ni$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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