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Note

Hydrothermal synthesis of polymeric metal carboxylates from benzene-1,2,4,5-tetracarboxylic acid and benzene-1,2,4-tricarboxylic acid

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Abstract

Crystallisation of benzene-1,2,4,5-tetracarboxylic acid or benzene-1,2,4-tricarboxylic acid with divalent metal-ions Co, Mn or Zn and 2,2-bipyridyl gives coordination solids of composition $[Co_2(C_{10}H_2O_8)(C_{10}H_8N_2)_2(H_2O)]$ (**1**), $[Co_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$ (**2**), $[Mn_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$ (**3**) or $[Zn_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$ (**4**). Each has a sheet structure with a distorted octahedral coordination environment. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrothermal; Coordination polymers; CRystal engineering

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1. Introduction

Coordination networks crystallised from polyaromatic acids and metal-ions are of interest for their polymeric network structure and their porous properties [1–6]. Our early studies and those of others showed the capability of metal-ion salts of 1,3,5-benzenetricarboxylic acid to maintain void volume after the removal of co-crystallised solvent. Our studies showed that networked solids can remain crystalline after the desorption of non-co-ordinating water molecules. Leaving the metal-ion coordination environment intact maintains structural rigidity or crystallinity of the lattice despite the creation of void volume in the lattice [4,5]. Dehydration of the metal-ion coordination environment inevitably leads to a partial loss of crystallinity that can be easily restored by rehydration. Hydrothermal methods of synthesis are used to obtain suitably sized crystals for characterisation purposes[1]. In this paper we report the structures of Co(II), Mn(II) and Zn(II) salts of benzene-1,2,4,5-tetracarboxylic acid and benzene-1,2,4-tricarboxylic acid.

2. Experimental

All organic chemicals were purchased from either Aldrich or Lancaster while metal salts were purchased from Aldrich. Hydrothermal reactions were performed using previously desribed equipment [4]. All infra-red spectra were recorded on KBr discs using a ATI Mattson Genesis series FTIR spectrometer. Thermal gravimetric analyses were performed in an atmosphere

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[1] Larger crystals have a lower surface area to weight ratio compared to smaller crystals so are expected to form on extended heating for thermodynamic reasons. Re-dissolution of a large crystal would be slower than for an equivalent weight of smaller crystals. By examination of hydrothermal reactions of polyaromatic acids performed in pyrex tubes it can be seen that the bulk of the material remains undissolved.

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of either flowing nitrogen gas or air using a Stanton Redcroft STA-780. Microanalyses was preformed by Butterworth Laboratories Ltd while cobalt analyses was carried out using a Varian Spectra AA-10 using an air/acetylene flame.

2.1. Synthesis of $[Co_2(C_{10}H_2O_8)(C_{10}H_8N_2)_2(H_2O)]$ *(**1**)*

Benzene-1,2,4,5-tetracarboxylic acid (100 mg, 0.39 mmol), cobalt acetate tetrahydrate (196 mg, 0.787 mmol), and 2,2′-bipyridyl (123 mg, 0.788 mmol) were placed together in a 45 ml bomb with water (20 ml). After sealing the bomb was heated at a rate of 100°C h^{-1} to 180°C. After maintaining at this temperature for 2 h the bomb was cooled at a rate of 2°C h^{-1} to 20°C. The dark red product (248 mg, 93%) was collected by filtration and air dried. (*Anal.* Found: C, 52.1; H, 2.9; N, 8.0; Co, 17.4. $[Co_2(C_{10}H_2O_8)$(2,2′-bipy)$_2(H_2O)]$ requires: C, 51.6; H, 2.9; N, 8.0; Co, 16.9%); IR (KBr) 1604m, 1578s, 1561s, 1489w, 1470m, 1439s, 1420m, 1386s, 1320w, 1311m, 1247w, 1166w, 1152w, 1135m, 1114w, 1110w, 1055w, 1025m, 945m, 896w, 882w, 858m, 823w, 802m, 767s, 735m, 722w, 662m, 653m, 634w, 590w, 542m, 454m and 416m (cm^{-1}); TGA (air) no change occurred until at 300°C a vigorous exothermic mass loss commenced.

2.2. Synthesis of $[Co_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$ *(**2**)*

Benzene-1,2,4-tricarboxylic acid (101 mg, 0.481 mmol), cobalt acetate tetrahydrate (119 mg, 0.480 mmol), 2,2-bipyridyl (76 mg, 0.487 mmol) and water (10 ml) were placed in a 23 ml bomb. After sealing the bomb was heated at 20°C h^{-1} to 230°C. After maintaining at this temperture for 2 h the bomb was cooled at a rate of 5°C h^{-1} to 180°C. After a further 6 h the bomb was cooled at 2°C h^{-1} to 90°C before cooling to 50°C at 4°C h^{-1} and then cooling at 5°C h^{-1} to room

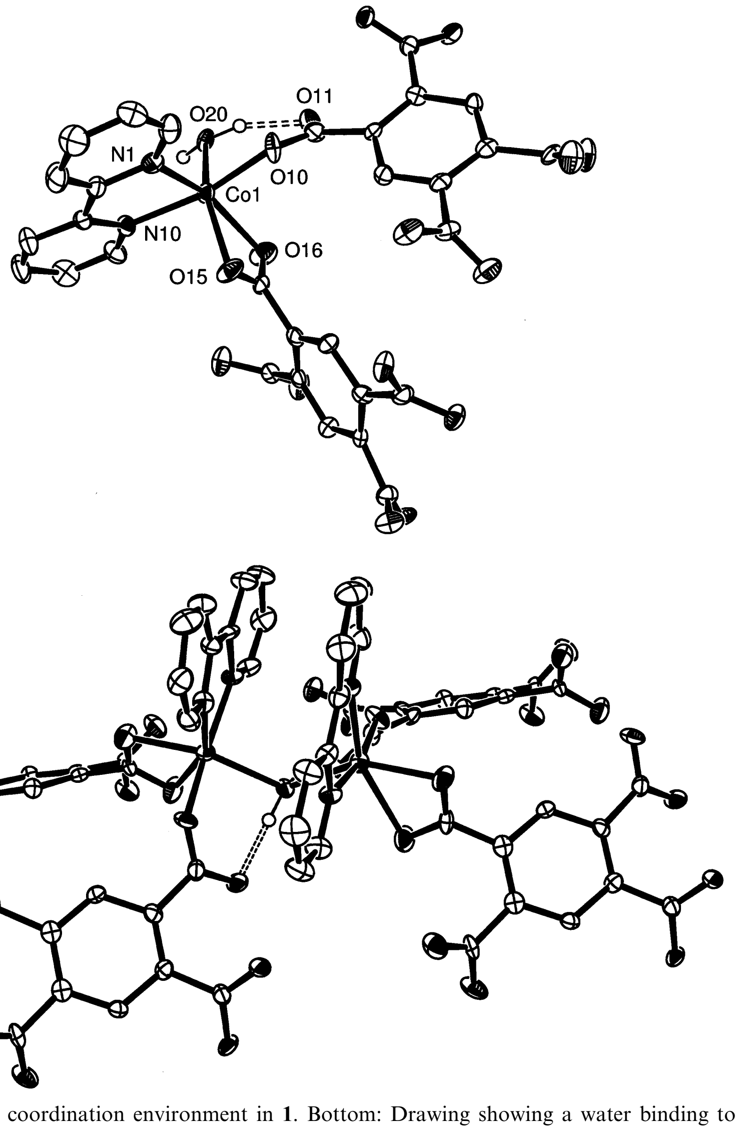

Fig. 1. Top: Drawing of the Co coordination environment in **1**. Bottom: Drawing showing a water binding to two Co cations.

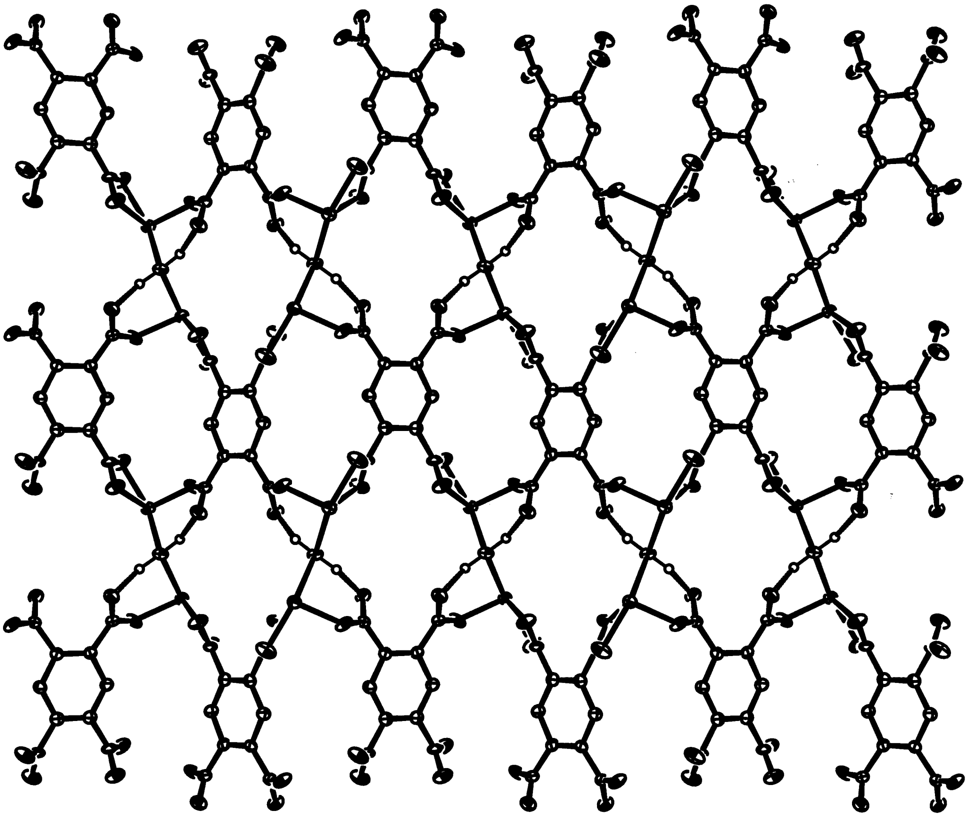

Fig. 2. Drawing showing the 2-D sheets in **1**. 2,2-Bipyridyl ligands are omitted for clarity.

temperture (r.t.). Red crystals were harvested (209 mg, 81%). (*Anal.* Found: C, 48.3; H, 2.6; N, 5.7. $[Co_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$ requires: C, 48.6; H, 2.8; N, 6.0%); IR (KBr) 3467br, 1620s, 1599m, 1577m, 1561m, 1534w, 1508w, 1491m, 1474m, 1438m, 1401s, 1384sh, 1314w, 1286w, 1249w, 822w, 806m, 770m, 736m (cm^{-1}); TGA above 200°C decomposition occurs.

2.3. Synthesis of $[Mn_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$ (3)

Benzene-1,2,4-tricarboxylic acid (151 mg, 0.722 mmol), manganese acetate tetrahydrate (178 mg, 0.726 mmol), 2,2-bipyridyl (114 mg, 0.730 mol) and water (20 ml) were placed in a 45 ml bomb. After sealing the bomb was heated at 20°C h^{-1} to 230°C. After maintaining at this temperature for 2 h the bomb was cooled at a rate of 5°C h^{-1} to 180°C. After a further 6 h the bomb was cooled at 2°C h^{-1} to 90°C before cooling to 50°C at 4°C h^{-1} and then cooling at 5°C h^{-1} to r.t. Crystals were harvested (178 mg, 80%). (*Anal.* Found: C, 48.8; H, 2.4; N, 6.1. $[Mn_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$ requires: C, 49.2; H, 2.8; N, 6.0%); IR (KBr) 3415br, 1678w, 1635sh, 1621s, 1597s, 1577s, 1561s, 1527m, 1490m, 1475w, 1436m, 1399s, 1355w, 1318w, 1293w, 1246w, 1218w, 1176w 1154w, 1134w, 1076w, 1056w, 1018m, 949w, 931w, 898w, 871w, 823w, 802m, 783w, 769m, 730m, 666w, 650w, 627w, 607w, 505m and 411m (cm^{-1}); TGA above 170°C decomposition occurs.

2.4. Synthesis of $[Zn_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$ (4)

Benzene-1,2,4-tricarboxylic acid (99.9 mg, 0.476 mmol), zinc acetate dihydrate (158 mg, 0.720 mmol), 2,2-bipyridyl (113 mg, 0.723 mmol) and water (10 ml) were placed in a 23 ml bomb and heated as for structure **2**. The product was harvested as a white solid (170 mg, 74%). (*Anal.* Found: C, 47.6; H, 2.3; N, 5.4. $[Zn_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$ requires: C, 47.6; H, 2.7; N, 5.8%); IR (KBr) 3419br, 1621s, 1599s, 1585s, 1567s, 1544m, 1491m, 1476w, 1438m, 1396s, 1384s, 1317w, 1288w, 1251w, 1223w, 1173w, 1156w, 1131w, 1101w, 1076w, 1057w, 1025w, 1012w, 972w, 944w, 933w, 906w, 872w, 824m, 725w, 669w, 652w, 630w, 609w, 540w and 415m (cm^{-1}); TGA above 170°C decomposition occurs.

2.5. X-ray crystallographic studies

Details of the structure determinations are given in Table 5. X-ray diffraction measurements were made with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using a Bruker SMART diffractometer [7].

Table 1
Selected bond distances (Å) and angles (°) for structures **1**, **2** and **3** [a]

Compound ***1***					
Co1–O10	2.013(4)	O10–Co1–O15 # 1	95.6(2)	O10–Co1–N1	90.0(2)
Co1–N1	2.102(5)	O15 # 1–Co1–N1	97.2(2)	O10–Co1–N10	167.1(2)
Co1–O20	2.155(3)	O15 # 1–Co1–N10	91.2(2)	N1–Co1–N10	78.2(2)
Co1 # 1–O16	2.326(5)	O10–Co1–O20	88.7(2)	O15 # 1–Co1–O20	148.7(2)
Co1–O15 # 1	2.083(5)	N1–Co1–O20	113.9(2)	N10–Co1–O20	91.2(2)
Co1–N10	2.103(5)	O10–Co1–O16 # 1	92.9(2)	O15 # 1–Co1–O16 # 1	59.4(2)
		N1–Co1–O16 # 1	156.5(2)	N10–Co1–O16 # 1	100.0(2)
		O20–Co1–O16 # 1	89.5(2)		
Compound ***2***					
Co1–O4 # 1	2.035(2)	O4 # 1–Co1–O5 # 1	87.0(1)	O1–Co1–O2	58.6(1)
Co1–O5 # 1	2.065(2)	O4 # 1–Co1–O1	96.4(1)	N1–Co1–O2	99.3(1)
Co1–O1	2.095(2)	O5 # 1–Co1–O1	103.5(1)	N2–Co1–O2	101.0(1)
Co1–N1	2.098(2)	O4 # 1–Co1–N1	109.8(1)	O6 # 2–Co2–O3 # 4	86.8(1)
Co1–N2	2.143(2)	O5 # 1–Co1–N1	88.1(1)	O6 # 3–Co2–O3 # 4	93.3(1)
Co1–O2	2.360(2)	O1–Co1–N1	151.9(1)	O6 # 3–Co2–O3	86.7(1)
Co2–O6 # 2	2.080(2)	O4 # 1–Co1–N2	97.7(1)	O6 # 2–Co2–O7	86.6(1)
Co2–O3	2.118(2)	O5 # 1–Co1–N2	164.7(1)	O6 # 3–Co2–O7	93.4(1)
Co2–O7	2.133(2)	O1–Co1–N2	90.5(1)	O3 # 4–Co2–O7	89.9(1)
		N1–Co1–N2	76.6(1)	O3–Co2–O7	90.1(1)
		O4 # 1–Co1–O2	147.9(1)	O6 # 2–Co2–O7 # 4	93.4(1)
		O5 # 1–Co1–O2	80.6(1)		
Compound ***3***					
Mn1–O5 # 1	2.258(4)	O5 # 1–Mn1–O3 # 1	82.1(2)	O5 # 1–Mn1–N2	160.2(1)
Mn1–O3 # 1	2.267(4)	O5 # 1 –Mn1–O2	84.4(2)	O3 # 1–Mn1–N2	103.4(2)
Mn1–O2	2.299(4)	O3 # 1–Mn1–O2	141.4(1)	O2–Mn1–N2	101.5(2)
Mn1–O1	2.342(3)	O5 # 1–Mn1–O1	110.0(1)	O1–Mn1–N2	89.1(2)
Mn1–N1	2.359(4)	O3 # 1–Mn1–O1	91.4(1)	N1–Mn1–N2	72.3(2)
Mn1–N2	2.374(4)	O2–Mn1–O1	60.0(1)	O4 # 2–Mn2–O6 # 3	84.5(1)
Mn2–O4	2.250(3)	O5 # 1–Mn1–N1	88.1(1)	O4–Mn2–O6 # 3	95.5(1)
Mn2–O6 # 3	2.305(4)	O3 # 1–Mn1–N1	114.3(1)	O4–Mn2–O6 # 4	84.5(1)
Mn2–O7	2.391(4)	O2–Mn1–N1	101.1(2)	O4 # 2–Mn2–O7	91.8(1)
		O1–Mn1–N1	150.8(2)	O4–Mn2–O7	88.2(1)
		O5 # 1–Mn1–N2	160.2(1)	O6 # 3–Mn2–O7	86.3(1)
		O3 # 1–Mn1–N2	103.4(2)	O6 # 4–Mn2–O7	93.7(1)
		O2–Mn1–N1	101.1(2)	O4 # 2–Mn2–O7 # 2	88.2(1)
		O1–Mn1–N1	150.8(2)	O4–Mn2–O7 # 2	91.8(1)
				O6 # 3–Mn2–O7 # 2	93.7(1)
				O6 # 4–Mn2–O7 # 2	86.3(1)

[a] Symmetry transformations used to generate equivalent atoms: for **1**: # 1 $-x+1, y, -z+3/2$; # 2 $x, -y+1, -z+2$; # 3 $-x+2, y, -z+3/2$; for **2**: # 1 $-x, -y, -z+1$; # 2 $-x, -y-1, -z+1$; # 3 $x-1, y, z$; # 4 $-x-1, -y-1, -z+1$; # 5 $x+1, y, z$.

Table 2
Hydrogen bonds (Å and °) for structure **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O20–H20–O11		1.71(1)		151.5(7)

Table 3
Hydrogen bonds (Å and °) for structure **2** [a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(7)–H(7WA)···O(4)	0.74(4)	1.99(4)	2.684(3)	155(4)
O(7)–H(7WB)···O(2) # 6	0.79(5)	2.25(5)	2.910(3)	142(4)
O(7)–H(7WB)···O(5) # 3	0.79(5)	2.32(5)	2.959(3)	138(4)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x, -y, -z+1$; # 2 $-x, -y-1, -z+1$; # 3 $x-1, y, z$; # 4 $-x-1, -y-1, -z+1$; # 5 $x+1, y, z$; # 6 $-x-1, -y, -z+1$.

Table 4
Hydrogen bonds (Å and °) for structure **3** [a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(7)–H(7WA)···O(3)	0.64(8)	2.04(8)	2.677(6)	179(10)
O(7)–H(7WB)···O(2) # 6	1.20(9)	1.89(9)	3.005(6)	153(6)
O(7)–H(7WB)···O(5) # 4	1.20(9)	2.44(8)	3.187(6)	118(5)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x, -y, -z+1$; # 2 $-x-1, -y-1, -z+1$; # 3 $-x, -y-1, -z+1$; # 4 $x-1, y, z$; # 5 $x+1, y, z$; # 6 $-x-1, -y, -z+1$.

Intensity data were collected using 0.3° width steps accumulating area detector frames spanning at least a hemisphere of reciprocal space for all structures (data were integrated using the SAINT program [7]). All data were corrected for Lorentz, polarisation and long-term

Table 5
Summary of key crystallographic data for compounds **1**–**3**

Compound	**1**	**2**	**3**
Formula	$C_{30}H_{20}Co_2N_4O_9$	$C_{19}H_{13}Co_{1.5}N_2O_7$	$C_{19}H_{13}Mn_{1.5}N_2O_7$
M	698.4	469.7	463.72
T (K)	293(2)	300(2)	293(2)
Crystal system	orthorhombic	triclinic	triclinic
Space group	$C222_1$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2
Unit cell dimensions			
a (Å)	10.9864(10)	7.6299(3)	7.8295(6)
b (Å)	19.128(2)	10.7948(4)	11.3147(9)
c (Å)	12.4073(11)	11.6418(5)	12.6076(11)
α (°)		81.657(2)	82.024(2)
β (°)		76.043(1)	75.835(2)
γ (°)		71.052(2)	73.651(2)
V (Å^3)	2607.4(4)	877.79(6)	1036.21(15)
Density calc. (Mg m^{-3})	1.779	1.777	1.486
μ (mm^{-1})	1.342	1.483	0.970
Crystal size (mm^3)	$0.12 \times 0.12 \times 0.14$	$0.03 \times 0.02 \times 0.01$	$0.2 \times 0.1 \times 0.02$
Reflections collected	8135	10765	9435
Independent reflections/R_{int}	3099/0.1075	4647/0.0109	6245/0.0868
Data/restraints/parameters	3047/1/209	4647/0/276	6245/0/276
GoF on F^2	0.923	0.995	0.843
R_1/wR_2 ($F^2 > 2\sigma(F^2)$]	0.0615/0.1237	0.0380/0.0873	0.0635/0.1409
(all data)	0.1216/0.1568	0.0607/0.0954	0.1613/0.2225
Largest difference peak and hole (e Å^{-3})	0.722/−1.051	0.487/−0.317	0.780/−0.615

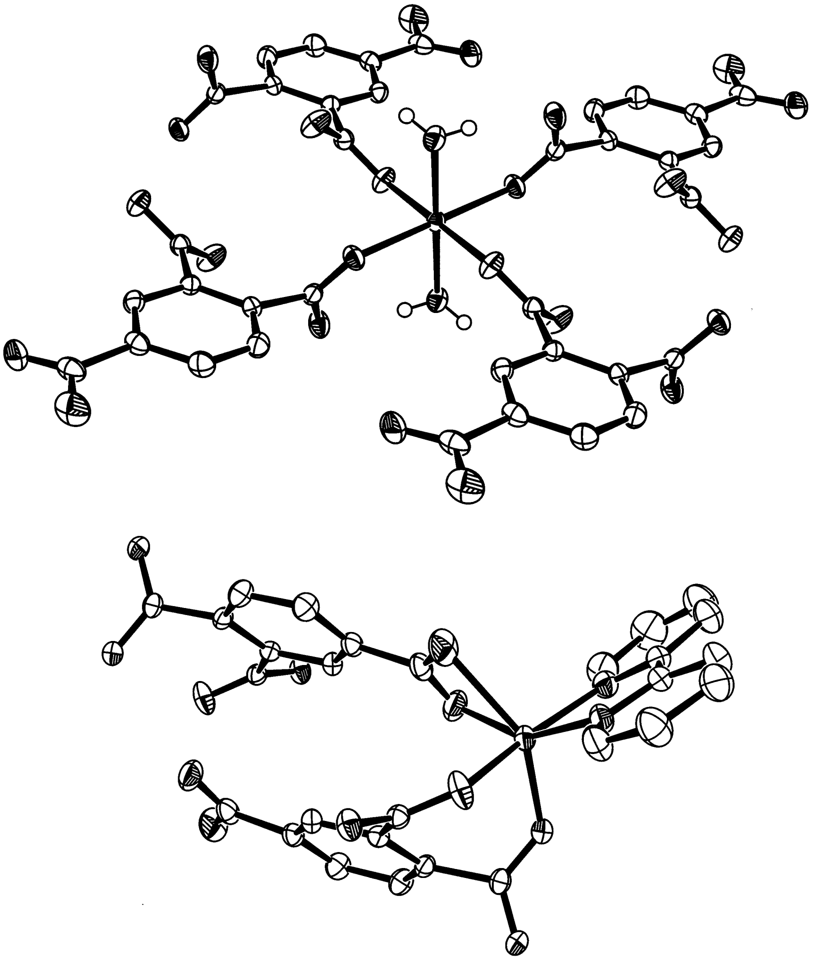

Fig. 3. Top: Drawing of the coordination environment of Co1 in structure **2**. Bottom: Drawing of the coordination environment of Co2.

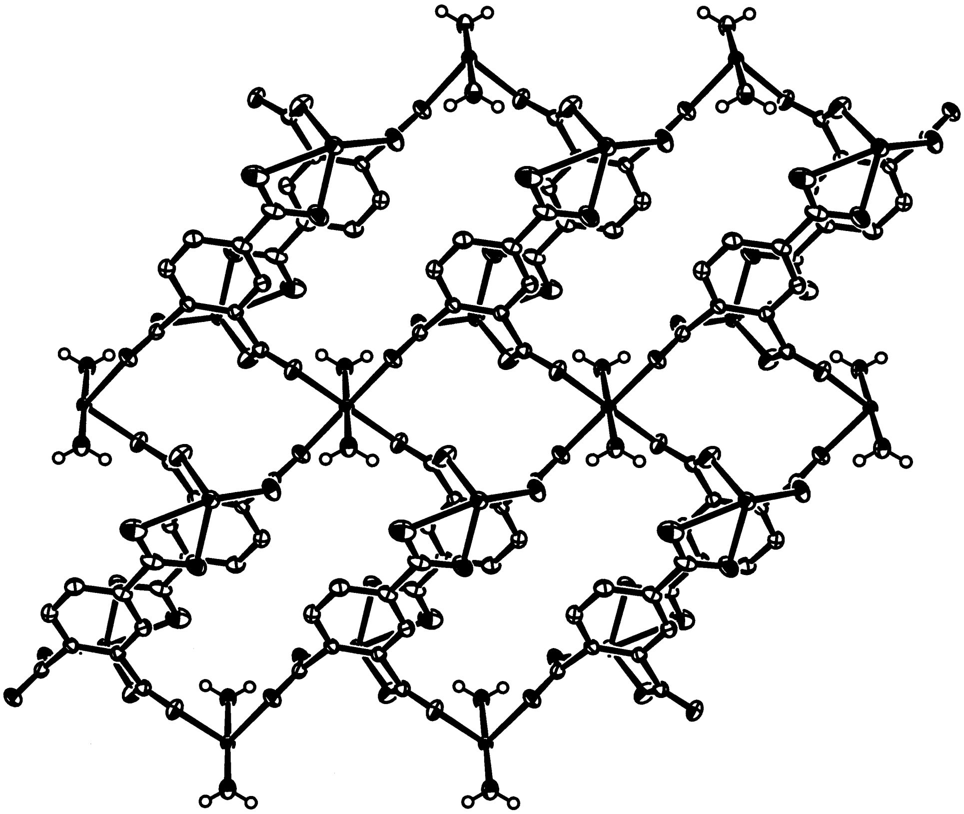

Fig. 4. Drawing of the double layer sheets in structure **2**.

intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods using SADABS [7]. Structure **1** was solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXTL). The water hydrogen atom was refined isotropically subject to a distance constraint. All other hydrogen atoms were assigned riding isotropic displacement parameters and were constrained to idealised geometries. Refinements converged to residuals given in Table 5. All calculations were made with SHELXTL [7]. For structures **2** and **3**, structures were solved by Patterson methods in SHELXS-86 [8] and refined using SHELXL-97 [8]. These structures were found to be isostructural, and for these structures the water hydrogen atoms were located from the difference Fourier map and refined freely. All other hydrogen atoms were constrained as for structure **1**. Structure **4** was confirmed to be isostructural with **2** and **3** by powder diffraction.

3. Results and discussion

3.1. Structural description of $[Co_2(C_{10}H_2O_8)(C_{10}H_8N_2)_2(H_2O)]$ (1)

The structure is shown in Figs. 1 and 2. The cobalt has a distorted octahedral geometry. Two bipyridine nitrogens bind to the cobalt, one carboxylate chelates to the cobalt while a second carboxylate binds through only one oxygen. To complete the coordination sphere a water is binding to the metal. The water ligand bridges between two cobalts and the water hydrogen bonds to a carboxylate oxygen O11. The Co–O–Co angle is 120.8° (Tables 1–4). The crystal structre consists of infinite layers consisting of cobalt atoms cross linked by both waters and the carboxylates. Between these hydrated cobalt carboxylate layers are layers of 2,2′-bipyridine ligands.

3.2. Structural description of $[Co_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$ (2)

Compound **2** contains cobalt atoms in two different coordination environments (Figs. 3 and 4). The two different cobalts are separated by a distance of 5.105 Å. Co1 has a distorted octahedral coordination geometry and consists of a chelating bipyridine ligand, a chelating carboxylate group and two more carboxylate oxygens. The two carboxylates which are binding through one oxygen to Co1 have an *ortho* relationship on the benzene ring. The coordination geometry of Co2 is also distorted octahedral, and consists of two waters arranged *trans* and four carboxylate groups.

Each of the carboxylates bridges to a cobalt Co1 but no bridges through a single oxygen are present in contrast with the solid formed from the isomer 1,3,5-benzenetricarboxylic acid, cobalt acetate and 2,2-bipyridyl.

*3.3. Structural description of [$Mn_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2$] (**3**) and [$Zn_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2(H_2O)_2$] (**4**)*

Structures **3** and **4** are isostructural to **2**.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 157777, 157778 and 157843. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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