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Amine-templated metal squarates

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Abstract

Two layered amine-templated cobalt squarates, $[C_6N_2H_{14}]_2[Co_2(C_4O_4)_3(H_2O)_4]$, **I**, and $[C_3N_2H_5]_2[Co_2(C_4O_4)_3(H_2O)_4]$, **II**, have been prepared under hydrothermal conditions. Both **I** and **II** contain chains formed by dimers comprising two cobalt atoms bound to the squarate units, the chains being connected through hydrogen bond interactions. An amine-templated cobalt squarate of the formula $[C_4N_2H_{12}][Co(C_4O_4)_2(H_2O)_4][H_2O]_2$, **III**, as well as its Ni, Zn and Cd analogues have been prepared by room temperature reactions. **III** has a layered architecture wherein the cobalt-squarate monomers are linked by the amine molecules. Co and Zn analogues of $[Ni(C_4O_4)(H_2O)_2(C_3N_2H_4)]$ with ligating imidazole units have also been prepared and characterized.
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1. Introduction

Among the various families of inorganic open-framework materials, besides those of silicates and phosphates [1], the family of metal-carboxylates is an important one [2–4]. Metal-carboxylates are of special interest as they not only show interesting three-dimensional channel structures but also a hydrophobic environment in the channels [3]. There has been considerable work recently on open-framework metal oxalates prepared hydrothermally in the presence of organic amines [4]. We were interested in investigating metal squarates prepared under similar conditions. Although several metal squarates have been reported in the literature, including zeolite related ones, most of them are coordination compounds [5]. To our knowledge there are only two reports of amine-containing metal squarates, $[Ni(C_4O_4)(H_2O)_2(C_3N_2H_4)]$ [6] and $[[Ni_2(C_4O_4)(H_2O)_2(tren)_2][ClO_4]_2$ [7] but the amine is ligated to the metal in these compounds. Metal squarates containing ligated dimethylsulfoxide (DMSO), dimethylformamide (DMF) with the formula $[M(C_4O_4)(H_2O)_2(DMSO/DMF)]$ with $M =$ Mn, Co, Ni, Cu and Zn are also known [8,9].

In this paper, we report the synthesis and characterization of cobalt squarates templated by organic amines.

The compounds are $[C_6N_2H_{14}]_2[Co_2(C_4O_4)_3(H_2O)_4]$, **I**, $[C_3N_2H_5]_2[Co_2(C_4O_4)_3(H_2O)_4]$, **II**, and $[C_4N_2H_{12}][Co(C_4O_4)_2(H_2O)_4][H_2O]_2$, **III**, all of which possess layered structures. In the case of **III**, we have also obtained isomorphous compounds of Ni, Zn and Cd. In all the squarates reported in the present study, the amine does not act as a ligand to the metal, but is present in the interlamellar space thus providing unique examples of two-dimensional open-framework metal squarates.

2. Experimental

2.1. Synthesis and initial characterization

Compounds **I–III** were synthesized by employing mild hydro/solvothermal methods. In a typical synthesis of **I** and **II**, to a solution of $CoCl_2 \cdot 6H_2O$ in a suitable solvent, the amine (1,4-diazabicyclo[2.2.2] octane, [DABCO], and imidazole, respectively) was added under constant stirring followed by squaric acid and the final mixture stirred for 30 min to obtain a homogenous gel. The reaction mixture was then transferred into a 23 mL PTFE-lined acid digestion bomb and heated at 150°C for 5–7 days. **I** could also be synthesized by taking DABCO-squarate, as the source of DABCO and squaric acid, and reacting it with

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$CoCl_2 \cdot 6H_2O$ in water at 150°C for 5 days. Compounds **I** and **II** are identical, but for the amine present in them.

In the synthesis of **III**, squaric acid was added under stirring to a solution of $CoCl_2 \cdot 6H_2O$ in water and the mixture stirred for 45 min to obtain a clear solution, KOH beads were added to this solution and the reaction mixture stirred for 1 h, to obtain a precipitate which was filtered. To the filtrate, piperazine was added under constant stirring and the stirring continued for 30 min to obtain a clear solution and the solution kept at room temperature for 6 days. Compound **III** could also be obtained by taking a mixture of $CoCl_2 \cdot 6H_2O$, squaric acid and piperazine in water and keeping the mixture at room temperature for 2 days. This method yielded cubic $CoC_4O_4 \cdot 2H_2O$ [10] along with **III**. Compounds of Zn, Cd and Ni isomorphous with **III** could also be prepared by the second procedure.

The synthetic conditions for **I–III** are summarized in Table 1. The yields are generally good exceeding 70%. The resulting products were vacuum filtered and

Table 1
Synthetic Conditions for Compounds **I** to **III**

	Starting composition	T (K)	Time (days)	Formula
I	$CoCl_2 \cdot 6H_2O + 10$ DABCO[a] $+ 2.5$ SA[b] $+ 3$ mL THF[c]	423	7	$[C_6N_2H_{14}]_2[Co_2(C_4O_4)_3(H_2O)_4]$
I	$CoCl_2 \cdot 6H_2O + (C_6N_2H_{14})(C_4O_4) + 3$ mL H_2O	423	5	$[C_6N_2H_{14}]_2[Co_2(C_4O_4)_3(H_2O)_4]$
II	$CoCl_2 \cdot 6H_2O + 6.5$ Imd[d] $+ 2.5$ SA $+ 3$ mL THF	423	5	$[C_3N_2H_5]_2[Co_2(C_4O_4)_3(H_2O)_4]$
III	$CoCl_2 \cdot 6H_2O + 2$ SA $+ 5$ mL H_2O + KOH + PIP[e]	300	6	$[C_4N_2H_{12}][Co(C_4O_4)_2(H_2O)_4][H_2O]_2$

[a] DABCO = 1,4-Diazabicyclo[2.2.2]octane.
[b] SA = Squaric acid.
[c] THF = Tetrahydrofuran.
[d] Imd = Imidazole.
[e] PIP = Piperazine.

Table 2
Crystal data and structure refinement parameters for compounds **I–III**

Parameters	I	II	III
Empirical formula	$C_6H_4CoO_8C_6H_{14}N_2$	$C_9H_9CoO_8N_2$	$C_8H_8CoO_{12}C_4H_{12}N_2 \cdot 2(H_2O)$
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P21/n$	P-1	P-1
Crystal size (mm)	$0.25 \times 0.26 \times 0.25$	$0.21 \times 0.15 \times 0.12$	$0.3 \times 0.23 \times 0.23$
a (Å)	8.032(2)	7.778(4)	7.0479(3)
b (Å)	9.359(2)	8.289(3)	8.2054(4)
c (Å)	19.336(4)	9.451(4)	8.9840(3)
α (deg)	90.0	91.41(4)	72.533(2)
β (deg)	96.70(3)	104.34(5)	88.584(2)
γ (deg)	90.0	97.86(4)	66.035(2)
Volume (Å^3)	1443.6(6)	583.7(5)	450.05(3)
Z	4	2	2
Formula mass	377.22	332.11	479.26
ρ_{calc} (g/cm^3)	1.736	1.890	1.768
λ (Mo$K\alpha$) (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	1.235	1.514	1.035
Θ range (deg)	2.12–23.27	2.23–23.29	2.39–23.26
Total data collected	5874	2469	1933
Limiting indices	$-8 \leqslant h \leqslant 8, -10 \leqslant k \leqslant 5,$ $-21 \leqslant l \leqslant 21$	$-8 \leqslant h \leqslant 8, -9 \leqslant k \leqslant 9,$ $-6 \leqslant l \leqslant 10$	$-7 \leqslant h \leqslant 7, -8 \leqslant k \leqslant 9,$ $-9 \leqslant l \leqslant 9$
Unique data	2072	1664	1288
Observed data ($I > 2\sigma(I)$)	1665	1341	1201
Refinement method	Full-matrix least-squares on $\lvert F^2 \rvert$	Full-matrix least-squares on $\lvert F^2 \rvert$	Full-matrix least-squares on $\lvert F^2 \rvert$
R_{int}	0.0778	0.0387	0.0139
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0561$, w$R_2 = 0.1039$	$R_1 = 0.0659$, w$R_2 = 0.1254$	$R_1 = 0.0350$, w$R_2 = 0.0961$
R (all data)	$R_1 = 0.0862$, w$R_2 = 0.1123$	$R_1 = 0.0860$, w$R_2 = 0.1334$	$R_1 = 0.0362$, w$R_2 = 0.0968$
Goodness of fit	1.301	1.134	1.059
No. of variables	224	197	157
Largest difference map peak and hole e/Å^3	0.414 and -0.438	0.413 and -0.487	0.480 and -0.478

$R_1 = \sum \lVert F_o \rvert - \lvert F_c \rVert / \sum \lvert F_o \rvert$; w$R_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$, w $= 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$, $a = 0.001$ and $b = 5.007$ for **I**, where $a = 0.0388$ and $b = 1.2566$ for **II**, $a = 0.0806$ and $b = 0.0$ for **III**.

thoroughly washed with water. The compounds were characterized by powder X-ray diffraction (XRD) which indicated the products to be new materials, the corresponding patterns being consistent with the structures determined by single-crystal XRD. Elemental

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[C_6N_2H_{14}]_2[Co_2(C_4O_4)_3(H_2O)_4]$, **I**

Atom	x	y	z	U_{eq}[a]
Co(1)	−0423(1)	1028(1)	−0683(1)	18(1)
O(1)	−2651(5)	1559(4)	−0333(2)	26(1)
O(2)	1700(4)	0328(4)	−1103(2)	25(1)
O(3)	−1789(6)	0778(6)	−1649(3)	31(1)
O(4)	0161(5)	3189(4)	−0793(2)	25(1)
O(5)	−0871(6)	−1127(4)	−0363(2)	21(1)
O(6)	−6174(5)	2342(4)	0147(2)	26(1)
O(7)	−0212(5)	3393(4)	0882(2)	30(1)
O(8)	−5173(5)	0709(4)	1634(2)	30(1)
C(1)	−4905(7)	1670(6)	0437(3)	18(1)
C(2)	−2892(7)	470(6)	0857(3)	20(1)
C(3)	−3309(7)	1284(6)	0212(3)	19(1)
C(4)	−4488(6)	0915(6)	1099(3)	20(1)
C(5)	0074(6)	4163(6)	−0353(3)	22(1)
C(6)	−0099(6)	4270(6)	0395(3)	19(1)
N(1)	0293(6)	0175(6)	2775(3)	33(1)
N(2)	−0788(7)	1192(6)	3828(3)	45(2)
C(7)	0059(10)	1708(8)	2690(4)	49(2)
C(8)	−1296(8)	−0492(8)	2864(4)	49(2)
C(9)	1489(10)	−0101(10)	3390(4)	64(3)
C(10)	−2005(11)	0132(10)	3498(5)	83(3)
C(11)	−0551(9)	2367(7)	3340(4)	42(2)
C(12)	0872(12)	0486(9)	4034(4)	67(3)

[a] U_{eq} is defined as one-third trace of the orthogonalized tensor U_{ij}.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[C_3N_2H_5]_2[Co_2(C_4O_4)_3(H_2O)_4]$, **II**

Atom	x	y	z	U_{eq}[a]
Co(1)	3328(1)	5059(1)	−1432(1)	18(1)
O(1)	2106(6)	2775(5)	−1159(5)	24(1)
O(2)	0953(9)	5947(9)	−1807(8)	44(2)
O(3)	2905(6)	4486(6)	−3661(5)	28(1)
O(4)	4515(6)	7391(6)	−1766(5)	24(1)
O(5)	5934(6)	4247(7)	−0873(5)	21(1)
O(6)	5784(6)	11223(6)	−1798(5)	29(1)
O(7)	9141(6)	11003(6)	1052(5)	32(1)
O(8)	7302(6)	5444(6)	−2928(5)	32(1)
C(1)	5836(8)	8365(8)	−0989(7)	17(2)
C(2)	2688(8)	1718(8)	−0271(7)	18(2)
C(3)	6408(9)	10119(8)	−1036(7)	20(2)
C(4)	7911(8)	10029(8)	0254(7)	21(2)
C(5)	4065(9)	4767(8)	−4362(7)	23(2)
C(6)	6033(9)	5205(8)	−4055(7)	23(2)
N(1)	2479(9)	8554(8)	5700(7)	41(2)
N(2)	0715(9)	8604(9)	3610(7)	42(2)
C(7)	1210(11)	7674(11)	4694(9)	44(2)
C(8)	2809(10)	10088(10)	5260(9)	39(2)
C(9)	1669(11)	10110(11)	3904(9)	45(2)

[a] U_{eq} is defined as one-third trace of the orthogonalized tensor U_{ij}.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[C_4N_2H_{12}][Co(C_4O_4)_2(H_2O)_4][H_2O]_2$, **III**

Atom	x	y	z	U_{eq}[a]
Co(1)	0	0	0	18(1)
O(1)	−2573(3)	1105(3)	−1652(2)	25(1)
O(2)	−1522(4)	−1251(3)	1656(2)	29(1)
O(3)	−1171(3)	2240(2)	0942(2)	24(1)
O(4)	−4028(3)	5790(3)	1963(2)	30(1)
O(5)	−4311(3)	8592(3)	−1602(2)	32(1)
O(6)	−1143(3)	4953(3)	−2534(2)	29(1)
C(1)	−3285(4)	5612(3)	0703(3)	21(1)
C(2)	−1963(4)	3997(4)	0238(3)	19(1)
C(3)	−1986(4)	5216(3)	−1325(3)	20(1)
C(4)	−3393(4)	6866(4)	−0888(3)	22(1)
N(1)	−1968(4)	11414(3)	4139(3)	29(1)
C(5)	−1732(5)	9481(4)	5045(3)	30(1)
C(6)	−0490(5)	11945(4)	4834(3)	30(1)
O(100)	−4168(4)	6702(4)	4909(3)	48(1)

[a] U_{eq} is defined as one-third trace of the orthogonalized tensor U_{ij}.

Table 6
Selected bond distances for $[C_6N_2H_{14}]_2[Co_2(C_4O_4)_3(H_2O)_4]$, **I**

Moiety	Distance (Å)	Moiety	Distance (Å)
Co(1)–O(1)	2.047(4)	C(2)–O(2)[#1]	1.263(6)
Co(1)–O(3)	2.066(5)	C(2)–C(3)	1.466(8)
Co(1)–O(2)	2.079(4)	C(2)–C(4)	1.475(7)
Co(1)–O(4)	2.093(4)	C(5)–C(6)[#2]	1.469(8)
Co(1)–O(5)	2.152(4)	C(5)–C(6)	1.473(8)
Co(1)–O(5)[#1]	2.165(4)	C(6)–C(5)[#2]	1.469(8)
O(1)–C(3)	1.259(6)	N(1)–C(8)	1.449(8)
O(2)–C(2)[#1]	1.263(6)	N(1)–C(7)	1.453(8)
O(4)–C(5)	1.254(7)	N(1)–C(9)	1.462(9)
O(5)–Co(1)[#1]	2.165(4)	N(2)–C(11)	1.476(9)
O(6)–C(1)	1.271(6)	N(2)–C(10)	1.483(9)
O(7)–C(6)	1.260(7)	N(2)–C(12)	1.500(9)
O(8)–C(4)	1.242(6)	C(7)–C(11)	1.530(9)
C(1)–C(3)	1.447(7)	C(8)–C(10)	1.526(10)
C(1)–C(4)	1.466(8)	C(9)–C(12)	1.498(10)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x, -y + 1, -z$.

Table 7
Selected bond distances for $[C_4N_2H_{12}][Co(C_4O_4)_2(H_2O)_4][H_2O]_2$, **III**

Moiety	Distance (Å)	Moiety	Distance (Å)
Co(1)–O(1)	2.074(2)	O(6)–C(3)	1.259(3)
Co(1)–O(1)[#1]	2.074(2)	C(1)–C(2)	1.453(4)
Co(1)–O(2)	2.078(2)	C(1)–C(4)	1.472(4)
Co(1)–O(2)[#1]	2.078(2)	C(2)–C(3)	1.455(4)
Co(1)–O(3)[#1]	2.108(2)	C(3)–C(4)	1.477(4)
Co(1)–O(3)	2.108(2)	N(1)–C(5)	1.492(4)
O(3)–C(2)	1.267(3)	N(1)–C(6)	1.493(4)
O(4)–C(1)	1.259(3)	C(5)–C(6)[#2]	1.509(4)
O(5)–C(4)	1.252(3)	C(6)–C(5)[#2]	1.509(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x, -y + 2, -z + 1$.

Table 8
Hydrogen bonding interaction in compounds **I** and **III**

	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
	Intra O(5)–H(1)···O(7)	1.00(11)	1.56(11)	2.543(6)	167(9)
	O(3)–H(2)···O(8)	0.90(9)	1.91(9)	2.812(6)	177(9)
	O(3)–H(3)···N(1)	0.64(6)	2.12(6)	2.755(8)	172(7)
	O(5)–H(4)···O(6)	0.79(6)	1.94(5)	2.708(6)	164(4)
	N(2)–H(17)···O(6)	0.91(1)	2.08(1)	2.944(7)	158.8(6)
I	N(1)–H(18)···O(3)	0.91(1)	1.85(1)	2.755(8)	171.5(6)
	C(12)–H(5)···O(6)	0.97(1)	2.43(1)	3.337(9)	155.7(9)
	C(12)–H(6)···O(1)	0.97(1)	2.31(1)	3.196(9)	151.6(9)
	C(11)–H(8)···O(1)	0.97(1)	2.59(1)	3.410(8)	141.9(7)
	C(11)–H(8)···O(8)	0.97(1)	2.52(1)	3.181(8)	125.2(7)
	C(10)–H(9)···O(7)	0.97(1)	2.42(1)	3.116(10)	128.8(9)
	C(10)–H(10)···O(4)	0.97(1)	2.56(1)	3.203(10)	123.6(9)
	N(1)–H(1)···O(100)	0.90(1)	1.96(1)	2.792(4)	153.8(3)
	N(1)–H(2)···O(3)	0.90(1)	1.97(1)	2.843(3)	164.3(3)
	O(2)–H(7)···O(5)	0.71(4)	2.17(4)	2.851(4)	159(4)
	O(1)–H(8)···O(5)	0.79(4)	2.00(4)	2.784(3)	175(3)
	O(1)–H(9)···O(4)	0.87(5)	1.77(5)	2.637(3)	177(5)
III	O(100)–H(10)···O(6)	0.86(5)	1.93(5)	2.768(3)	164(4)
	Intra O(2)–H(11)···O(6)	0.78(5)	2.00(5)	2.716(3)	154(5)
	O(100)–H(12)···O(4)	0.77(6)	2.24(6)	2.948(3)	154(6)
	C(5)–H(3)···O(100)	0.97(1)	2.57(1)	3.394(5)	142.6(3)
	C(6)–H(5)···O(1)	0.97(1)	2.57(1)	3.447(3)	150.2(4)
	C(6)–H(5)···O(2)	0.97(1)	2.57(1)	3.281(3)	130.3(4)
	C(6)–H(6)···O(6)	0.97(1)	2.49(1)	3.343(4)	146.8(4)

analysis calculated for **I**: C, 38.21%; H, 4.81%; N, 7.43%; Analysis observed: C, 37.98%; H, 4.47%; N, 7.55%. For **III**: calculated: C, 30.07%; H, 5.05%; N, 5.85%; Analysis observed: C, 30.56%; H, 4.99%; N, 6.11%.

IR spectra of compounds **I**–**III** were recorded with a Brucker 66v/s spectrometer taking the samples as a KBr pellet. All the samples showed the characteristic features of the squarate dianion, $C_4O_4^{2-}$ with a broad and strong band centered at around $1530\,cm^{-1}$ and a band at around $1100\,cm^{-1}$ due to ν_s(C–O) and ν_s(C–C), respectively [11].

2.2. Single-crystal structure determination

A suitable single crystal of each of the compounds **I**–**III** was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyano-acrylate (super glue) adhesive. Single-crystal structure determination by XRD was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073\,Å$) operating at 40 kV and 40 mA. A hemisphere of intensity data was collected at room temperature with ω space scans (width of 0.30° and exposure time of 20 s/frame). Pertinent experimental details for the structure determinations are presented in Table 2.

Each structure was solved by direct methods using SHELXS-86 [12], which readily established the heavy
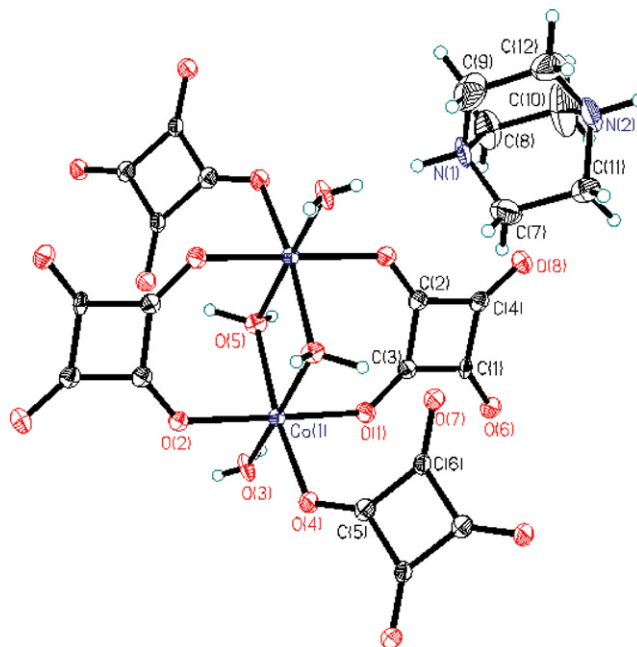

Fig. 1. ORTEP plot of [$C_6N_2H_{14}$]$_2$[$Co_2(C_4O_4)_3(H_2O)_4$], **I**. The asymmetric unit is labeled. Thermal ellipsoids are given at 50% probability. Note that the dimer formed by the bridging squarate unit and water molecules is the basic building block in **I** and [$C_3N_2H_5$]$_2$[$Co_2(C_4O_4)_3$ $(H_2O)_4$], **II**.

atom position (Co) and facilitated the identification of the light atoms (O, N, C, H) from difference Fourier maps. An empirical absorption correction based on

symmetry equivalent reflections was applied using SADABS programme [13]. All the hydrogen positions were initially located in the difference Fourier maps and the hydrogen atoms were placed geometrically and held in the riding mode for the final refinement. The last cycle of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS [14] package of programs. Details of the crystal data and final refinements are given in Table 2. The atomic coordinates of I–III are given in Tables 3–5, respectively, and the bond lengths in I and III are listed in Tables 6 and 7, respectively. Hydrogen bond details in I and III are listed in Table 8.

3. Results and discussion

3.1. $[C_6N_2H_{14}]_2[Co_2(C_4O_4)_3(H_2O)_4]$, I and $[C_3N_2H_5]_2[Co_2(C_4O_4)_3(H_2O)_4]$, II

Compounds I and II have similar structures and are therefore discussed together. The asymmetric unit of I contains 23 non-hydrogen atoms of which 15 are involved in the formation of the framework and 8 belong to the protonated DABCO molecule. The asymmetric unit of II contains 20 non-hydrogen atoms of which 15 are involved in the formation of the framework and 5 belong to the monoprotonated imidazole moiety. The cobalt atom in both these squarates is octahedrally coordinated. There are two types of squarate, C_4O_4, units with different modes of connectivity, one of them connecting two cobalt atoms through the adjacent carbonyl groups resulting in the formation of a dimer (Fig. 1). The dimers, in turn, are connected through another squarate ligand via *trans*-carbonyl groups, forming chains parallel to the *b*-axis in I (Fig. 2) and the *c*-axis in II (Fig. 3a). The cobalt atoms in the dimer are further connected by bridging water molecules. Thus, each cobalt atom is surrounded by two bridging squarate oxygen atoms, one squarate oxygen linking the dimers, two bridging water molecules and one terminal water molecule to complete the octahedral environment. In I, two adjacent chains are separated by a unit cell length along the *a*-axis (Fig. 2) while in II they are separated by a unit cell length along the *a*-axis. I and II, however, differ in the way the chains are oriented with respect to each other, the kind of hydrogen bonding in the layers also being different.
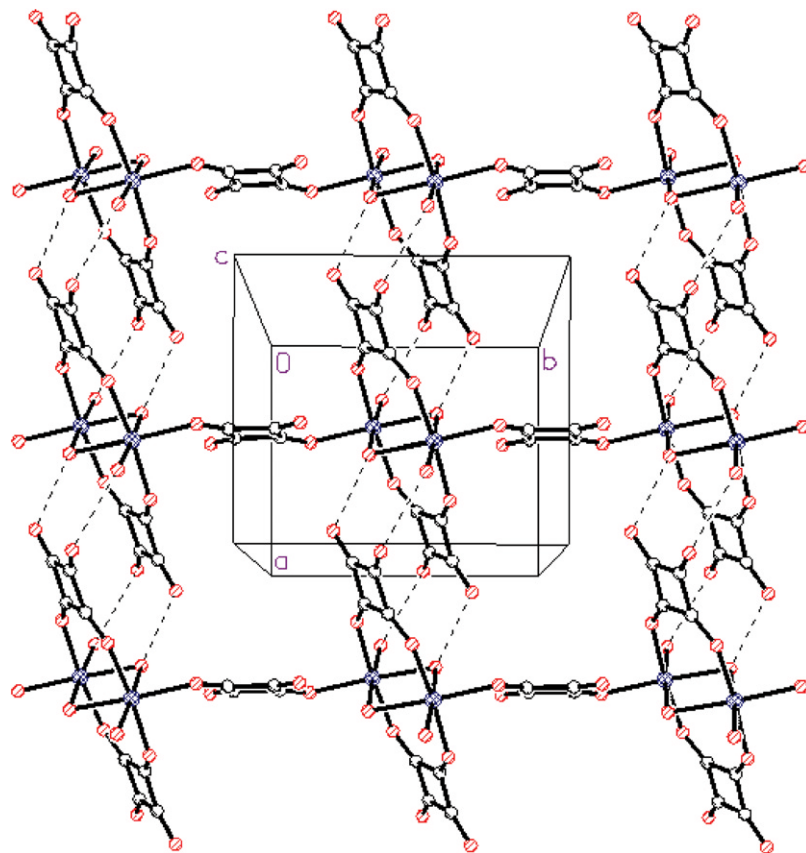

Fig. 2. Top view of the hydrogen-bonded layer parallel to the *ab*-plane in I. Dotted lines represent hydrogen-bond interactions.
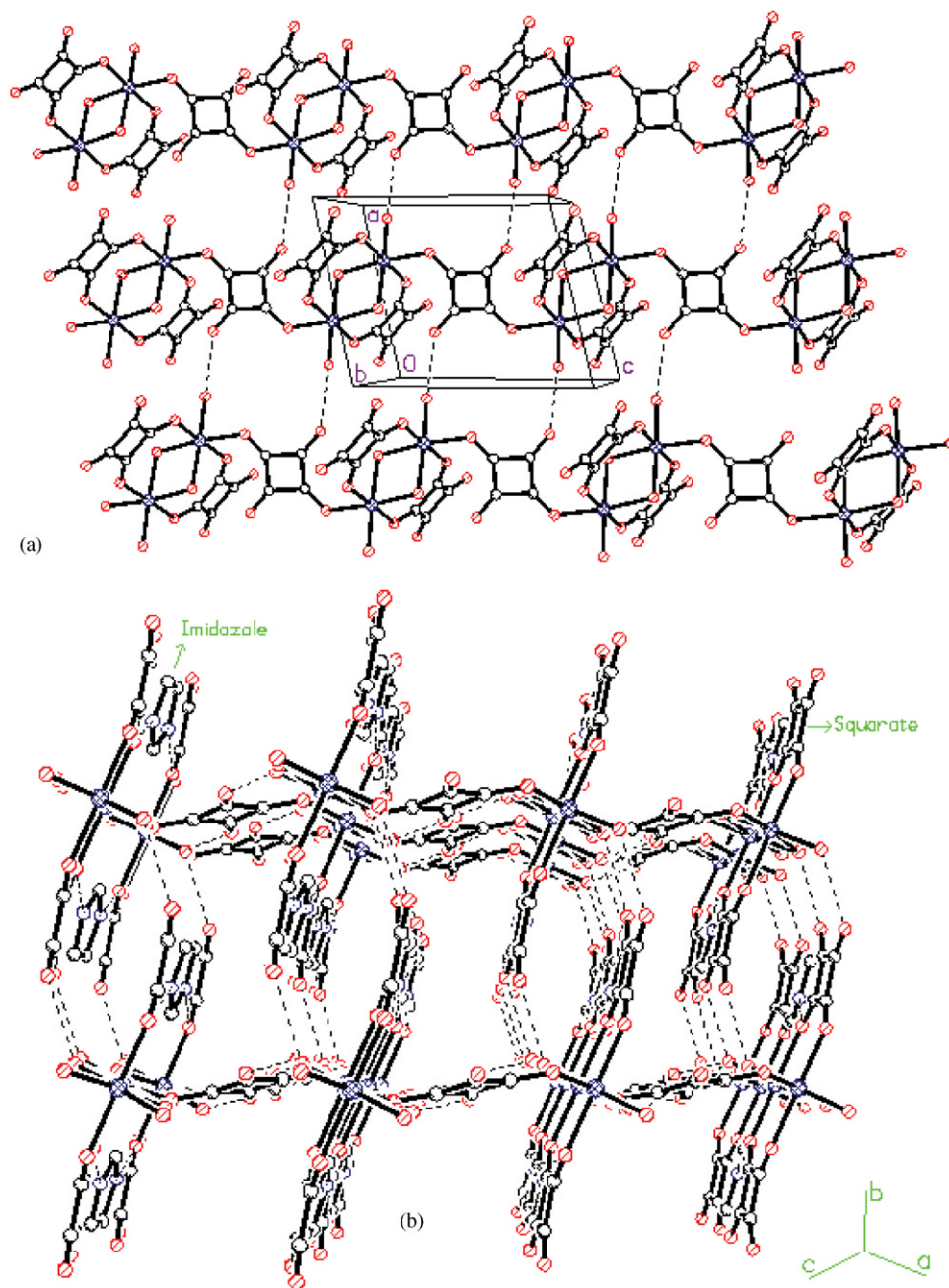
Fig. 3. (a) Top view of the hydrogen-bonded layer parallel to the *ac*-plane in $[C_3N_2H_5]_2[Co_2(C_4O_4)_3(H_2O)_4]$, **II**. Dotted lines represent hydrogen-bond interactions. (b) Stacking of layers in **II**, along the b-axis of the unit cell. Note the alignment of the imidazole molecules in the same line and same plane as bridging squarate molecules.

The adjacent chains in **I** are held together by O–H···O type hydrogen bonds between the carbonyl groups of the squarate of one chain with the terminal and bridging water molecules of the adjacent chain, thereby forming layers parallel to the *ab*-plane (Fig. 2). Two adjacent layers are separated by 1/2 the unit cell length along the *c*-axis and they get shifted by 1/2 the unit cell length along both the *a*- and *b*-axis, resulting in ABAB…. stacking along the *c*-axis. Protonated DABCO molecules reside in the interlamellar space, forming hydrogen

bonds with the nonbonding carbonyl groups of the bridging squarates as well as with the water molecules of one layer, besides the terminal water molecules of another layer (Table 8).

The non-bonding *trans*-carbonyl groups of the squarate ligand in **II** form hydrogen bonds with the terminal water molecules of the adjacent chains, forming layers parallel to the *ac*-plane-decorated by the bridging squarate ligands (Figs. 3a and b). Two adjacent layers are separated by an unit cell length along the *b*-axis, the
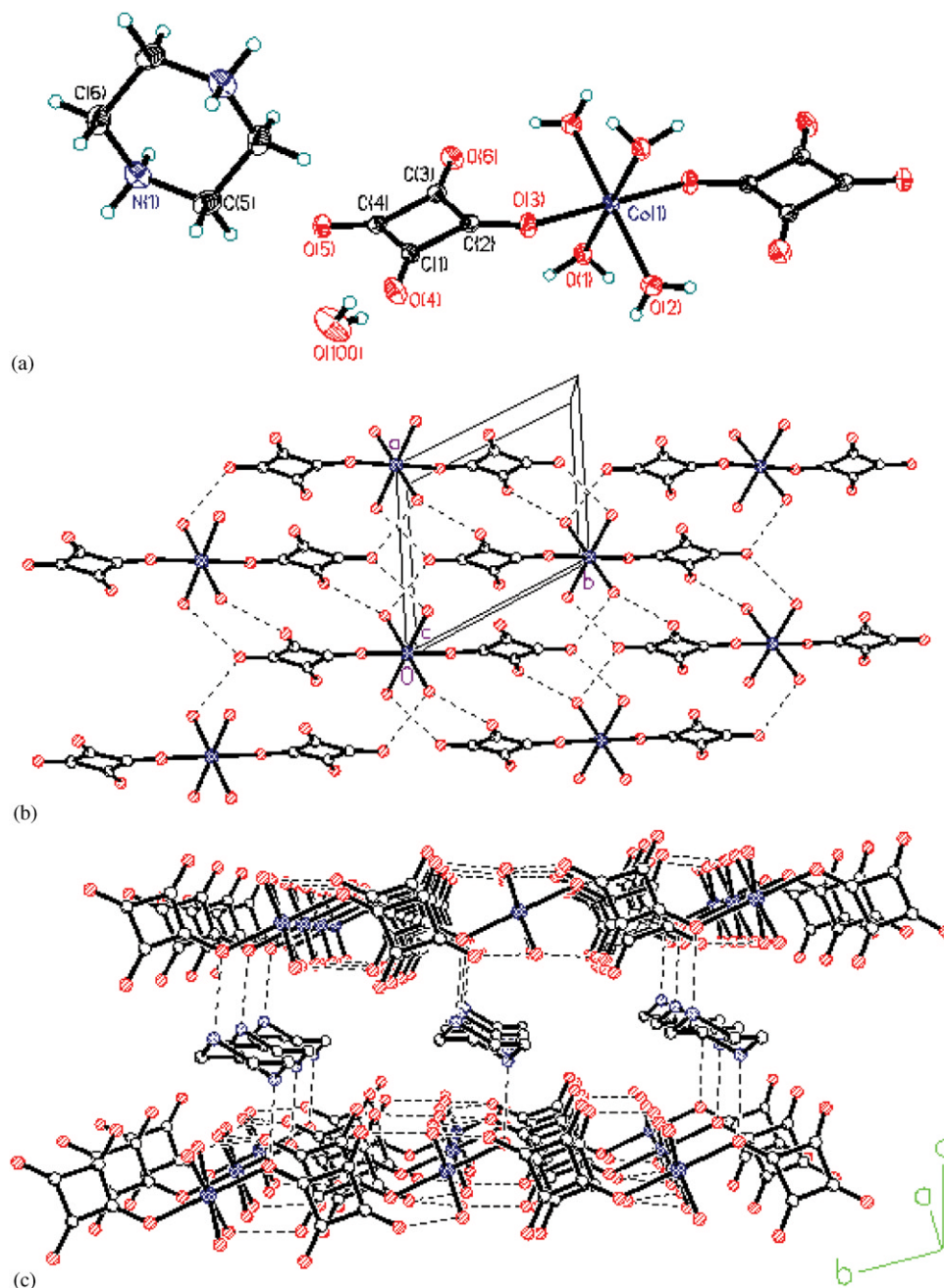
Fig. 4. (a) ORTEP plot of $[C_4N_2H_{12}][Co(C_4O_4)_2(H_2O)_4][H_2O]_2$, **III**. The asymmetric unit is labeled. Thermal ellipsoids are given at 50% probability. (b) Top view of the hydrogen-bonded layer parallel to the *ab*-plane in **III**. Dotted lines represent hydrogen-bond interactions. (c) Stacking of layers in **III**, along the *c*-axis of the unit cell. The cobalt-squarate layers and the layer formed by the protonated piperazine molecules are alternately stacked. Dotted lines represent hydrogen-bond interactions.

layers being stacked over one another in AAA... fashion. The protonated imidazole molecule forms extensive hydrogen bonds with carbonyl groups of bridging squarate ligands of adjacent dimers and lies in the same plane (Fig. 3b). The non-bonding adjacent carbonyl groups of the bridging molecules form hydrogen bonds with the terminal and the bridging water molecules of the adjacent layers, rendering additional stability to the structure (Fig. 3b).

The cobalt atom in **I** and **II** are connected to six oxygen atoms with Co–O distances in the range 2.035(6)–2.168(5) Å (av. = 2.100 Å for **I** and 2.097 Å for **II**) and O–Co–O angles in the range 81.4(2)–178.4(2)° (av. = 106.55° for **I** and 107.16° for **II**). The C–O distances of the squarate are in the range 1.240(8)–1.277(7) Å (av. = 1.259 Å in **I** and 1.257 Å in **II**), O–C–C angles in the range 131.2(6)–138.2(6)° (av. = 135.0° in **I** and 134.96° in **II**) and C–C–C angles in the range

88.7(4)–91.3(4)° (av. = 89.98° in **I** and 90° in **II**). The average C–N and C–C distances of the protonated DABCO molecule in **I** are 1.342 and 1.478 Å, respectively. The average C–N and C–C distances of the protonated imidazole molecule in **II** are 1.331 and 1.368 Å, respectively. The distances in the squarate unit found here are well in agreement with literature [5].

Thermogravimetric analysis of these amine-templated squarates, shows that the amine is removed partly along with the water in the 180–280°C range. Most of the amine and the squarate decompose continuously in the 320–600°C range. The final product of decomposition in N_2 atmosphere was CoO.

3.2. $[C_4N_2H_{12}][Co(C_4O_4)_2(H_2O)_4][H_2O]_2$, III

The asymmetric unit of **III** contains 15 non-hydrogen atoms of which 11 are invovled in the formation of the framework, 3 belong to the piperazinium cation and one to the interstitial water molecule (Fig. 4a). The cobalt atom is at a special position (center of inversion) and is octahedrally coordinated to two squarate oxygen atoms and four water molecules (Fig. 4a). The squarate acts as a monodentate ligand, connecting to one metal center. These monomers are arranged at the eight corners of the unit cell and are arranged parallel to each other. Two adjacent chains are shifted in the ABAB... fashion along the *a*-axis, separated by half a unit cell length along the *a*-axis. While there is no hydrogen bonding between the monomers in one chain, there is extensive hydrogen bonding between the monomers of adjacent chains resulting in the formation of hydrogen-bonded layers parallel to the *ab*-plane of the unit cell (Fig. 4b). The nonbonding *trans*-carbonyl groups of the squarate ligand of one monomer forms hydrogen bonds with the water molecules of the monomer of the adjacent chains. Two such layers are separated by a unit cell length along the *c*-axis. The layers are stacked over one another in an AAA.... fashion along the *c*-axis. Protonated piperazine molecules lie in the space between the layers, and in the

same line of the cobalt atoms of two adjacent layers along the *c*-axis. Each piperazine forms N–H⋯O type hydrogen bonds with the bonding carbonyl groups of the squarate (Fig. 4c). The interstitial water molecules (not shown in Fig. 4) are present in the interlamellar space, forming hydrogen bonds with the non-bonding carbonyl groups of the squarate unit. The water molecules form N–H⋯O and C–H⋯O type hydrogen bonds with the amine molecules. Hydrogen bonding between the monomeric units, the protonated amine and the water molecules makes the structure stable (Table 8).

The cobalt atom is connected to six oxygen atom with Co–O distances in the range 2.074(2)–2.108(2) Å (av. = 2.087 Å) and O–Co–O angles in the range 85.45(8)–180.0° (av. = 108°). The C–O distances of the squarate molecule are in the range 1.252(3)–1.267(3) Å (av. = 1.259 Å), O–C–C angles in the range 133.1(2)–136.7(2)° (av. = 134.99°) and C–C–C angles in the range 89.3(2)–90.9(2)° (av. = 89.98°). The average C–N and C–C distances of the protonated piperazine molecule are 1.493 and 1.509 Å, respectively.

Thermogravimetric analysis of **III** showed that lattice water is eliminated around 100°C and the bonded water in the 120–200°C range. The amine and the squarate decompose continuously in the 200–600°C range. The final product of decomposition in a N_2 atmosphere is CoO.

We have prepared Zn, Ni and Cd analogoues of **III** by a reaction of the metal salt, squaric acid and piperazine in water at room temperature. They are all isomorphous with the cobalt squarate described above. In Table 9 the crystal structure data of these three compounds are given.

The basic building block in **III** is comparable to that in $[Ni(C_4O_4)(H_2O)_2(C_3N_2H_4)]$ [6]. In the latter, amine is bonded to the metal center. We have also prepared Co and Zn analogues of the Ni compound containing ligated imidazole. The Co and Zn analogues crystallize in a higher symmetry space group (*Pbca*) than the

Table 9
Crystal structure data of other amine-templated metal squarates analogous to **III**

Parameters	Cd (**III**)	Zn (**III**)	Ni (**III**)
Empirical formula	$C_8H_8CdO_{12}C_4H_{12}N_2 \cdot 2(H_2O)$	$C_8H_8ZnO_{12}C_4H_{12}N_2 \cdot 2(H_2O)$	$C_8H_8NiO_{12}C_4H_{12}N_2 \cdot 2(H_2O)$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
Crystal size (mm)	$0.21 \times 0.21 \times 0.21$	$0.32 \times 0.23 \times 0.25$	$0.13 \times 0.13 \times 0.20$
a (Å)	7.1303	7.0572	7.0368
b (Å)	8.2722	8.1874	8.1657
c (Å)	9.2062	8.9845	8.9485
α (deg)	70.4263	72.6795	73.2269
β (deg)	88.5920	88.6848	88.6820
γ (deg)	67.5326	66.0136	65.7907
Volume (Å³)	469.447	449.916	446.327
Z	2	2	2

Ni analogue. The cell parameters of the Co and Zn are: Co, $a = 14.325$ Å, $b = 11.4247$ Å, $c = 7.9775$ Å, $\alpha = \beta = \gamma = 90°$, Vol. $= 1305.6$ Å^3 and Zn, $a = 14.2475$ Å, $b = 11.5258$ Å, $c = 8.0010$ Å, $\alpha = \beta = \gamma = 90°$, Vol. $= 1313.88$ Å^3.

4. Conclusions

Amine templated metal squarates have been synthesized and characterized for the first time. Unlike in metal coordination compounds involving the squarate unit, the amine-templated metal squarates possess open-framework like architectures with chain and layered structures.

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