

# Novel Inorganic Coordination Polymers Based on Cadmium Oxalates

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Three new cadmium oxalate coordination polymers, I–III, with extended layered structures have been synthesized in the presence of imidazole. While I was prepared by the reaction between imidazolium oxalate and Cd, II and III were synthesized from their constituents using hydrothermal methods.  $[\text{Cd}(\text{C}_2\text{O}_4)(\text{C}_3\text{N}_2\text{H}_4)]_\infty$  (I): monoclinic, space group  $P2_1/c$  (no. 14),  $a = 8.7093(1)$  Å,  $b = 9.9477(3)$  Å,  $c = 8.4352$  Å,  $\beta = 93.796(1)^\circ$ ,  $Z = 4$ ;  $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$  (II): monoclinic, space group  $P2_1/c$  (no. 14),  $a = 7.8614(2)$  Å,  $b = 14.9332(3)$  Å,  $c = 15.9153(4)$  Å,  $\beta = 94.587(1)^\circ$ ,  $Z = 4$ ;  $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$  (III): monoclinic, space group  $P2_1/c$  (no. 14),  $a = 11.844(2)$  Å,  $b = 9.066(1)$  Å,  $c = 18.583(2)$  Å,  $\beta = 103.84(2)^\circ$ ,  $Z = 4$ . While the structure of I is made from  $\text{CdO}_5\text{N}$  distorted octahedra linked with oxalate, II and III are built-up from  $\text{CdO}_6\text{N}$ ,  $\text{CdO}_5\text{N}_2$  distorted pentagonal bi-pyramids connected to oxalate units. The framework formulas of II and III are identical and their structures closely related. In all the cases, the networking between the Cd–O/N polyhedra and oxalates give rise to layered architectures with the amine molecules pointing in a direction perpendicular to the layers (in the inter-lamellar region). The difference in the linkages between the oxalates and the Cd atoms in I–III, produces unusual Cd–O–Cd one-dimensional chains, which have been observed for the first time. © 2002 Elsevier Science (USA)

## INTRODUCTION

Solids possessing extended architectures continue to witness an exponential growth as newer materials with novel structural features are being discovered. Recently, the metal-organic frameworks provided examples of the importance of the metal-ion coordination and the organic molecule symmetry in designing materials with unusual structures and properties (1). To a modest extent, it has been possible to rationally design and build structures with specific architectures in one-, two- and three dimensions (2). The strategy for designing such materials generally relies on the

use of multidentate N and/or O donor ligands, which can act as a bridge between metal centers and form polymeric structures. Large number of such polymeric structures have been isolated using 4,4-bipyridine acting as a linear bridge forming one-dimensional chain polymers (3), and two-dimensional sheets (4). Recently, it has been established that polycarboxylic acids also form rigid networks and have properties similar to the aluminosilicate zeolites (5, 6).

The oxalate ion, on the other hand, is quite unique due to its function as a bis-bidentate ligand, and a number of its coordination compounds form with rigid framework structures (7–12). The formation of these structures largely depends on the shape of the ligand, the coordination preferences of the metal ion, solvent and the molar ratio between the metal and the ligand. The control of dimensionality, however, is a major problem in these coordination compounds, due to ancillary ligation by water or other solvent molecules resulting in low-dimensional structures. It is also observed that synthesis at higher temperatures promotes the formation of extended polymeric frameworks of higher dimensionality with the loss of terminal ancillary ligands (13).

In recent years, hydrothermal methods have been employed with great success for the synthesis of novel oxalate coordination polymers in the presence of organic amines (14, 15). In the course of a program to prepare novel materials with extended architectures, we have been investigating the formation of cadmium oxalates in the presence of amines under hydrothermal conditions, resulting in novel architectures (16). In the light of this, it is worth noting that the formation of unusual oxalate frameworks has been accomplished by the reaction between an amine-oxalate and metal ions (17). Amine oxalates are the hydrogen-bonded adducts between the amine and the oxalic acid and many such structures have been prepared and characterized recently (17). In order to expand the family of cadmium oxalates, we used hydrothermal methods employing two different synthesis strategies. In the first method, the reaction between  $\text{Cd}^{2+}$  ions with imidazolium-oxalate,  $[\text{C}_3\text{N}_2\text{H}_5][\text{HC}_2\text{O}_4]$ , (IMOx) was used, while in the second, the respective individual components were reacted. Our synthesis efforts,

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**TABLE 1**  
**Crystal Data and Structure Refinement Parameters for Compounds I, [Cd(C<sub>2</sub>O<sub>4</sub>)(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)]<sub>∞</sub>, II, [Cd(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)]<sub>∞</sub> and III, [Cd(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)]<sub>∞</sub>**

Structural parameter	I	II	III
Empirical formula	[Cd(C <sub>2</sub> O <sub>4</sub> )(C <sub>3</sub> N <sub>2</sub> H <sub>4</sub> )] <sub>∞</sub>	[Cd(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>3</sub> N <sub>2</sub> H <sub>4</sub> ) <sub>3</sub> (H <sub>2</sub> O)] <sub>∞</sub>	[Cd(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>3</sub> N <sub>2</sub> H <sub>4</sub> ) <sub>3</sub> (H <sub>2</sub> O)] <sub>∞</sub>
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no.14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)
<i>T</i> (K)	293(2)	293(2)	293(2)
Crystal size (mm)	0.08 × 0.2 × 0.2	0.1 × 0.08 × 0.08	0.02 × 0.02 × 0.12
<i>a</i> (Å)	8.7108 (1)	7.8614 (2)	11.844(2)
<i>b</i> (Å)	9.9451(3)	14.9332 (3)	9.066(1)
<i>c</i> (Å)	8.4311(2)	15.9153 (4)	18.583(2)
<i>β</i> (deg)	93.751(1)	94.587 (1)	103.84(2)
Volume (Å <sup>3</sup> )	728.1(3)	1862.41(8)	1937.4(4)
<i>Z</i>	4	4	4
Formula mass	268.50	623.10	621.09
<i>ρ</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.446	2.222	2.129
<i>λ</i> (MoKα) (Å)	0.71073	0.71073	0.71073
<i>μ</i> (mm <sup>-1</sup> )	2.967	2.347	2.256
<i>R</i> <sub>int</sub>	0.0799	0.0719	0.1654
<i>R</i> ( <i>F</i> <sub>o</sub> ) <sup>2</sup> [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0450 <sup>a</sup> , <i>wR</i> <sub>2</sub> = 0.1061 <sup>b</sup>	<i>R</i> <sub>1</sub> = 0.0464 <sup>a</sup> , <i>wR</i> <sub>2</sub> = 0.0974 <sup>b</sup>	<i>R</i> <sub>1</sub> = 0.0686 <sup>a</sup> , <i>wR</i> <sub>2</sub> = 0.1065 <sup>b</sup>

$$^a R_1 = \frac{||\sum F_o| - |F_{cl}||}{\sum |F_o|}$$

$$^b wR_2 = \frac{\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}}{\sum [w(F_o^2)^2]^{1/2}}, w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP], P = [\max(F_o^2, 0) + 2(F_c)^2]/3, \text{ where } a = 0.0810 \text{ and } b = 0.0 \text{ for I, and } a = 0.0514, b = 0.0 \text{ for II and } a = 0.0374 \text{ and } b = 0.0 \text{ for III.}$$

using both the methods, have indeed been successful with the isolation of three new cadmium oxalates. The compounds **I**, [Cd(C<sub>2</sub>O<sub>4</sub>)(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)]<sub>∞</sub>, **II**, [Cd(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)]<sub>∞</sub> and **III**, [Cd(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(C<sub>3</sub>N<sub>2</sub>H<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)]<sub>∞</sub> all have layered architectures formed by the linkage between the Cd and the oxalate moieties. While the structure of **I** is made from CdO<sub>5</sub>N distorted octahedra linked with oxalate, **II** and **III**, have CdO<sub>6</sub>N, CdO<sub>5</sub>N<sub>2</sub> distorted pentagonal bi-pyramids connected to oxalate units. Compounds **II** and **III** also have the same framework formula and their structures are related. The amine molecules, in all the cases, are directly bonded to the metal center and point in a direction perpendicular to the plane of the layers. The coordination preferences and the linkages between the Cd atoms, the oxalate and amine molecules differ between the three compounds. In this paper, we present the synthesis, structure and characterization of the three cadmium oxalates, **I–III**.

## EXPERIMENTAL

### Materials

The amine oxalate, imidazolium oxalate (IMOX) was synthesized following standard synthetic procedures. Imidazolium oxalate was prepared by adding 0.5 g oxalic

<sup>2</sup>Imidazolium oxalate: C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O<sub>4</sub>, *mw* = 158.12, monoclinic, space group *P*2<sub>1</sub>/*n* (no. 14), *a* = 5.6972(7) Å, *b* = 17.539(2) Å, *c* = 6.81699 Å, *β* = 105.593(2)°, *V* = 656.1(2) Å<sup>3</sup>, *Z* = 4, *R*<sub>1</sub> = 0.0452. TGA studies indicate complete mass loss (99.5%) in the range 250–320°C, as expected.

acid to 10 mL water, followed by the addition of 0.27 g of imidazole. The mixture was stirred to attain homogeneity and heated in a polypropylene bottle at 100°C for 12 h. The product containing large quantity of single crystals was filtered and dried at room temperature. Characterization of the imidazolium oxalate was carried out using single-crystal X-ray diffraction and thermogravimetric analysis (TGA)<sup>2</sup>. The other chemicals that are needed for the synthesis of **II** and **III** were purchased from Aldrich and used without further purification.

### Synthesis of Cadmium Oxalate, I

The cadmium oxalate, **I** was synthesized starting from a mixture containing imidazolium oxalate (0.788 g, 5.63 mM), cadmium acetate (0.25 g, 0.94 mM), butan-2-ol (3.5 mL, 38.25 mM) and water (0.9 mL, 50 mM). The mixtures were stirred to attain homogeneity, transferred into a PTFE-lined stainless-steel autoclave and heated at 165°C for 60 h under autogeneous pressure. The resulting product containing large quantities of colorless plate-like single crystals were filtered, washed thoroughly with deionized water and dried at room temperature under atmospheric conditions. The yield was about 50%.

### Synthesis of Cadmium Oxalates, II and III

The synthesis of cadmium oxalates, **II** and **III**, were carried out using the regular hydrothermal methods starting

**TABLE 2**  
Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **I**,  $[\text{Cd}(\text{C}_2\text{O}_4)(\text{C}_3\text{N}_2\text{H}_4)]_\infty$

Atom	x	y	z	$U_{\text{eq}}^a$
Cd(1)	3756(1)	2421(1)	1380(1)	20(1)
O(1)	5964(5)	1441(4)	715(6)	28(1)
O(2)	5044(5)	4353(4)	1938(5)	30(1)
O(3)	3066(5)	488(5)	68(5)	29(1)
O(4)	4112(5)	3673(4)	-1091(5)	25(1)
N(1)	1300(6)	2985(7)	1459(7)	29(1)
C(3)	641(9)	4118(8)	2010(10)	50(2)
C(2)	-1187(8)	2788(11)	1179(12)	30(2)
N(2)	-907(9)	3984(10)	1854(11)	80(3)
C(1)	155(10)	2208(8)	975(12)	42(2)
C(10)	5839(7)	272(7)	187(8)	24(2)
C(11)	4735(7)	4805(6)	-881(7)	22(2)

<sup>a</sup> $U_{\text{eq}}$  is defined as one-third trace of the orthogonalized tensor  $U_{ij}$ .

from identical synthesis mixtures. Thus, for **II** and **III**, cadmium acetate (0.25 g, 0.938 mM), oxalic acid (1.419 g, 11.26 mM), imidazole (0.128 g, 1.88 mM), butan-2-ol (3.5 mL, 38.3 mM) and water (0.9 mL, 40 mM) were taken as the starting mixture. The starting mixtures were stirred to attain homogeneity, transferred into a 23 mL (fill-factor = 40%) PTFE bottle, and sealed in a stainless-steel autoclave (Parr, USA). The sealed pressure bombs were heated at 180°C for 36 h for **II** and 165°C for 105 h for **III** under autogeneous pressure. The resulting products, which contained large quantities of colorless single crystals, were

**TABLE 3**  
Selected Bond Distances for **I**,  $[\text{Cd}(\text{C}_2\text{O}_4)(\text{C}_3\text{N}_2\text{H}_4)]_\infty$

Moiety	Distance ( $\text{\AA}$ )
Cd(1)–O(1)	2.261(4)
Cd(1)–O(2)	2.264(4)
Cd(1)–O(3)	2.282(4)
Cd(1)–O(4) # 1	2.391(4)
Cd(1)–O(4)	2.463(4)
Cd(1)–N(1)	2.215(5)
O(1)–C(10)	1.251(8)
O(2)–C(11) # 2	1.242(7)
O(3)–C(10) # 3	1.243(8)
O(4)–C(11)	1.251(7)
N(1)–C(1)	1.301(11)
N(1)–C(3)	1.359(10)
N(2)–C(2)	1.336(13)
N(2)–C(3)	1.349(12)
C(2)–C(1)	1.322(12)
C(10)–C(10) # 3	1.573(12)
C(11)–C(11) # 2	1.571(12)

Note. Symmetry transformations used to generate equivalent atoms: # 1:  $x, -y + 1/2, z + 1/2$ ; # 2:  $-x + 1, -y + 1, -z$ ; # 3:  $-x + 1, -y, -z$ .

**TABLE 4**  
Selected Bond Angles for **I**,  $[\text{Cd}(\text{C}_2\text{O}_4)(\text{C}_3\text{N}_2\text{H}_4)]_\infty$

Moiety	Angle (degree)
O(1)–Cd(1)–O(2)	89.3(2)
O(1)–Cd(1)–O(3)	73.4(2)
O(2)–Cd(1)–O(3)	158.0(2)
O(1)–Cd(1)–O(4) # 1	87.3(2)
O(2)–Cd(1)–O(4) # 1	99.3(2)
O(1)–Cd(1)–O(4)	81.9(2)
O(2)–Cd(1)–O(4)	69.74(14)
O(3)–Cd(1)–O(4)	93.1(2)
O(4) # 1–Cd(1)–O(4)	164.1(2)
O(3)–Cd(1)–O(4) # 1	93.1(2)
N(1)–Cd(1)–O(4) # 1	99.1(2)
N(1)–Cd(1)–O(3)	90.8(2)
N(1)–Cd(1)–O(1)	162.8(2)
N(1)–Cd(1)–O(2)	104.7(2)
N(1)–Cd(1)–O(4)	94.7(2)
C(10)–O(1)–Cd(1)	115.6(4)
C(11) # 2–O(2)–Cd(1)	121.5(4)
C(10) # 3–O(3)–Cd(1)	114.1(4)
C(11)–O(4)–Cd(1) # 4	124.9(4)
C(11)–O(4)–Cd(1)	114.8(4)
C(1)–N(1)–Cd(1)	124.6(6)
C(3)–N(1)–Cd(1)	128.8(5)
O(2) # 2–C(11)–O(4)	125.1(5)
O(3) # 3–C(10)–O(1)	124.8(6)
O(3) # 3–C(10)–C(10) # 3	118.6(7)
O(1)–C(10)–C(10) # 3	117.9(7)
O(2) # 2–C(11)–C(11) # 2	117.1(7)
O(4)–C(11)–C(11) # 2	117.4(6)
N(2)–C(3)–N(1)	109.8(7)
C(1)–N(1)–C(3)	105.8(6)
C(1)–C(2)–N(2)	108.1(7)
C(2)–N(2)–C(3)	106.9(7)
N(1)–C(1)–C(2)	110.8(8)

Note. Symmetry transformations used to generate equivalent atoms: # 1:  $x, -y + 1/2, z + 1/2$ ; # 2:  $-x + 1, -y + 1, -z$ ; # 3:  $-x + 1, -y, -z$ ; # 4:  $x, -y + 1/2, z - 1/2$ .

filtered, washed with deionized water and dried at ambient conditions. The yield of the products was 60 and 80%, respectively.

Initial characterization was carried out using powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), EDAX and infra-red spectrometry (IR). The TGA studies were performed under a flow of oxygen (50 mL/min) in the range 30–700°C. For **I**, the weight loss occurs in two steps and for **II** and **III** the weight loss occurs in four distinct steps. The total mass loss of 49.8% corresponds well with the loss of the oxalate and amine molecule from the structure (calcd. ~ 52.2%). In the case of **II** and **III**, the total mass losses are more or less identical with losses totaling 53.3%, which accounts very well for the loss of the water, oxalate and the amine from the structure (calcd. 58.7%). The powder XRD patterns of the decomposed products

**TABLE 5**  
Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **II**,  $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$

Atom	x	y	z	$U_{\text{eq}}^a$
Cd(1)	4085(1)	2552(1)	8987(1)	25(1)
Cd(2)	359(1)	682(1)	7739(1)	33(1)
O(1)	4095(9)	3538(12)	10115(6)	32(3)
O(2)	3584(9)	373(11)	9485(6)	33(3)
O(3)	2078(9)	2331(12)	8411(6)	32(3)
O(4)	5589(8)	4343(13)	9285(6)	31(3)
O(5)	5804(9)	1048(12)	9517(6)	40(3)
O(6)	3169(10)	4985(11)	8658(7)	39(3)
N(2)	1178(13)	703(20)	6768(9)	68(5)
N(3)	-582(13)	968(19)	8647(8)	53(5)
O(7)	1723(9)	-983(12)	8447(6)	44(3)
O(8)	535(9)	3409(11)	7695(6)	33(3)
O(9)	-1480(9)	1110(12)	6895(6)	39(3)
N(4)	5649(29)	2592(43)	7041(18)	48(10)
N(5)	2425(16)	369(33)	6085(11)	141(11)
C(13)	5407(12)	5200(18)	9746(9)	23(5)
C(12)	5638(14)	223(18)	9997(11)	30(5)
C(11)	1542(14)	3460(18)	8109(9)	24(4)
C(10)	2157(16)	4995(18)	8343(9)	25(4)
C(9)	2072(33)	-353(44)	6705(22)	42(11)
C(9A)	2250(39)	556(54)	6766(25)	61(13)
C(8)	783(22)	1439(28)	6120(15)	97(9)
C(7)	5197(26)	1313(33)	7660(17)	24(8)
C(6)	4485(24)	2385(36)	6643(15)	16(7)
C(6A)	5020(35)	3171(40)	6875(20)	33(10)
C(5)	4560(27)	3658(35)	7445(17)	28(9)
C(5A)	3825(28)	2408(41)	7176(18)	43(10)
C(4)	-1646(18)	678(27)	8669(13)	78(7)
C(3)	-460(36)	2297(51)	9157(23)	69(13)
C(3A)	33(39)	828(54)	9457(27)	88(15)
C(2)	1621(23)	1192(29)	5669(14)	96(9)
N(4A)	5469(27)	1776(34)	7007(17)	36(9)
C(7A)	5662(30)	2571(42)	7821(19)	47(10)
C(1)	-1978(37)	1246(54)	9237(25)	24(13)
C(1A)	-2046(35)	688(47)	9253(23)	25(13)
N(6)	-1013(43)	812(58)	9757(26)	139(18)
N(6A)	-1398(52)	2279(69)	9446(31)	170(22)
N(1)	4571(10)	2435(15)	7882(6)	24(3)

<sup>a</sup> $U_{\text{eq}}$  is defined as one-third trace of the orthogonalized tensor  $U_{ij}$ .

indicated a poorly crystalline product with very weak reflections corresponding to CdO.

Fourier-transform IR spectra were recorded (KBr pellets) with a Bruker IFS-66V/S spectrometer. The compounds show oxalate stretching and bending vibrations as expected for this type of bonding in the mid-IR region. Thus, the IR spectra of compounds **I–III** show broad bands at 1666s and 1597s  $\text{cm}^{-1}$  [ $\nu_{\text{as}}(\text{O}-\text{C}-\text{O})$ ], 1315s and 1260s  $\text{cm}^{-1}$  [ $\nu_{\text{a}}(\text{O}-\text{C}-\text{O})$ ], 833s, 790s and 748  $\text{m cm}^{-1}$  [ $\delta(\text{O}-\text{C}-\text{O})$ ]. The far-IR region shows the M–O (Cd–O, in the present cases) and M–N vibrations, reflects clearly the differences between the coordination environments of Cd. From the single-crystal structural study it is clear that **I** possesses Cd in octahedral (six) coordination, whereas **II** and **III** have Cd in

pentagonal bi-pyramidal (seven) coordination. The observed far-IR bands in **I** are: 439.5, 401.3  $\text{cm}^{-1}$  (Cd–O) and 272.8, 243  $\text{cm}^{-1}$  (Cd–N), in **II** 412.7, 396.8  $\text{cm}^{-1}$  (Cd–O) and 258.0, 232.7  $\text{cm}^{-1}$  (Cd–N) and in **III** 412.1, 407.6  $\text{cm}^{-1}$  (Cd–O) and 259.8, 232.7  $\text{cm}^{-1}$  (Cd–N). The appearance of both M–O and M–N bands at higher wave numbers in **I** might be due to the lower coordination environment of Cd compared to **II** and **III**, confirming the single-crystal data.

#### Single-Crystal Structure Determination

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyano-acrylate (super glue) adhesive. Single-crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube x-ray source (MoK $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with  $\omega$  scans (width of  $0.30^\circ$  and exposure time of 20 s per frame) in the  $2\theta$  range  $3\text{--}46.5^\circ$ . For compound **I**, the data were collected with an

**TABLE 6**  
Selected Bond Distances in **II**,  $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$

Moiety	Distance ( $\text{\AA}$ )
Cd(1)–O(1)	2.276(10)
Cd(1)–O(2)	2.319(10)
Cd(1)–O(3)	2.371(10)
Cd(1)–O(4)	2.376(11)
Cd(1)–O(5)	2.453(11)
Cd(1)–O(6)	2.469(11)
Cd(2)–O(7)	2.265(11)
Cd(2)–O(8) # 1	2.24(2)
O(8)–Cd(2) # 4	2.369(10)
Cd(2)–O(9)	2.247(13)
Cd(2)–O(8)	2.367(10)
Cd(2)–O(3)	2.369(10)
Cd(1)–N(1)	2.392(10)
Cd(2)–N(2)	2.484(11)
Cd(2)–N(3)	2.592(10)
O(1)–C(13) # 2	1.29(2)
O(2)–C(12) # 3	1.28(2)
O(3)–C(11)	1.26(2)
O(4)–C(13)	1.21(2)
O(5)–C(12)	1.22(2)
O(6)–C(10)	1.20(2)
O(8)–C(11)	1.26(2)
O(1)–C(13) # 2	1.29(2)
O(9)–C(10) # 1	1.30(2)
O(2)–C(12) # 3	1.28(2)

Note. Symmetry transformations used to generate equivalent atoms: # 1:  $-x, y - 1/2, -z + 3/2$ ; # 2:  $-x + 1, -y + 1, -z + 2$ ; # 3:  $-x + 1, -y, -z + 2$ ; # 4:  $-x, y + 1/2, -z + 3/2$ .

**TABLE 7**  
Selected Bond Angles in **II**,  $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$

Moiety	Angle (deg)
O(1)–Cd(1)–O(4)	71.3(3)
O(2)–Cd(1)–O(4)	137.6(4)
O(3)–Cd(1)–O(4)	141.1(4)
O(1)–Cd(1)–O(2)	85.0(4)
O(1)–Cd(1)–O(3)	103.5(4)
O(2)–Cd(1)–O(3)	77.5(4)
O(1)–Cd(1)–O(5)	91.6(4)
O(2)–Cd(1)–O(5)	68.5(3)
O(3)–Cd(1)–O(5)	141.3(4)
O(4)–Cd(1)–O(5)	77.4(4)
O(1)–Cd(1)–O(6)	77.5(4)
O(2)–Cd(1)–O(6)	136.1(4)
O(3)–Cd(1)–O(6)	68.3(4)
O(4)–Cd(1)–O(6)	73.0(4)
O(5)–Cd(1)–O(6)	150.4(4)
N(1)–Cd(1)–O(1)	155.2(4)
N(1)–Cd(1)–O(2)	117.8(4)
N(1)–Cd(1)–O(3)	91.8(4)
N(1)–Cd(1)–O(4)	84.5(4)
N(1)–Cd(1)–O(5)	88.4(4)
N(1)–Cd(1)–O(6)	90.5(4)
C(13)#2–O(1)–Cd(1)	115.8(10)
C(12)#3–O(2)–Cd(1)	116.8(10)
C(11)–O(3)–Cd(1)	118.4(10)
C(11)–O(3)–Cd(2)	90.0(9)
C(13)–O(4)–Cd(1)	110.6(10)
C(12)–O(5)–Cd(1)	111.8(11)
C(10)–O(6)–Cd(1)	117.1(11)
C(11)–O(8)–Cd(2)#4	117.3(10)
C(11)–O(8)–Cd(2)	95.2(9)
C(10)#1–O(9)–Cd(2)	119.2(10)
O(4)–C(13)–O(1)#2	124(2)
O(7)–Cd(2)–O(9)	149.5(4)
O(8)#1–Cd(2)–O(9)	69.8(4)
O(7)–Cd(2)–O(8)#1	79.9(4)
O(7)–Cd(2)–O(8)	127.0(4)
O(8)#1–Cd(2)–O(8)	152.72(14)
O(9)–Cd(2)–O(8)	83.5(4)
O(7)–Cd(2)–O(3)	75.4(3)
O(8)#1–Cd(2)–O(3)	154.3(4)
O(9)–Cd(2)–O(3)	135.2(4)
O(8)–Cd(2)–O(3)	51.7(3)
N(2)–Cd(2)–N(3)	171.8(6)
N(2)–Cd(2)–O(7)	94.8(5)
N(3)–Cd(2)–O(7)	92.9(5)
N(2)–Cd(2)–O(8)#1	88.7(5)
N(3)–Cd(2)–O(8)#1	95.4(5)
N(2)–Cd(2)–O(9)	88.4(5)
N(3)–Cd(2)–O(9)	86.3(5)
N(2)–Cd(2)–O(8)	84.8(5)
N(3)–Cd(2)–O(8)	88.3(5)
N(2)–Cd(2)–O(3)	86.6(5)
N(3)–Cd(2)–O(3)	92.6(5)
O(5)–C(12)–O(2)#3	127(2)
O(8)–C(11)–O(3)	123(2)
O(6)–C(10)–O(9)#4	129(2)
O(4)–C(13)–C(13)#2	122(2)
O(1)#2–C(13)–C(13)#2	114(2)
O(5)–C(12)–C(12)#3	119(2)
O(2)#3–C(12)–C(12)#3	114(2)
O(8)–C(11)–C(10)	120(2)
O(3)–C(11)–C(10)	116(2)
O(6)–C(10)–C(11)	118(2)
O(9)#4–C(10)–C(11)	113(2)

Note. Symmetry transformations used to generate equivalent atoms: #1:  $-x, y - 1/2, -z + 3/2$ ; #2:  $-x + 1, -y + 1, -z + 2$ ; #3:  $-x + 1, -y, -z + 2$ ; #4:  $-x, y + 1/2, -z + 3/2$ .

exposure time of 30 s per frame. Pertinent experimental details for the structure determinations are presented in Table 1.

The structure was solved and refined by direct methods using SHELXTL-PLUS (18) and difference Fourier syntheses. The amine molecule was heavily disordered in the case of **III**. All the hydrogen positions for **I** and **II** were initially located in the difference Fourier maps, and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles 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 (**I** and **II**). Full-matrix-least-squares structure refinement against  $|F^2|$  was carried out using SHELXTL-PLUS (18) package of programs. Details of the final refinements are given in Table 1. The final atomic coordinates, selected bond distances and angles for **I** are presented in Tables 2–4, for **II** in Tables 5–7, and for **III** in Tables 8–10.

**TABLE 8**  
Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **III**,  $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Cd(1)	2456(1)	1465(1)	4562(1)	22(1)
Cd(2)	2504(1)	5527(1)	4938(1)	27(1)
O(1)	784(8)	2721(4)	4817(4)	32(2)
O(2)	4192(8)	2683(4)	4914(4)	31(2)
O(3)	1123(9)	158(4)	4097(4)	38(2)
O(4)	5220(8)	– 671(5)	5902(4)	38(2)
O(5)	3880(9)	636(5)	5698(4)	37(2)
O(6)	– 319(8)	– 1027(4)	4487(4)	34(2)
N(1)	2184(10)	2056(5)	3185(5)	30(2)
N(2)	2437(10)	5452(5)	3536(5)	32(2)
N(3)	2573(10)	5808(5)	6313(5)	28(2)
O(7)	823(8)	4188(4)	5092(4)	29(2)
O(8)	2406(12)	7109(6)	4656(5)	40(2)
O(9)	5732(8)	5831(4)	5018(4)	28(2)
N(4)	2888(16)	2439(8)	1916(6)	81(4)
C(1)	3348(14)	1893(7)	2596(6)	39(3)
C(2)	1491(12)	2906(6)	2072(6)	23(2)
C(3)	1123(14)	2656(7)	2836(6)	41(3)
N(5)	2849(12)	5090(6)	2240(5)	44(2)
C(4)	3028(13)	4840(7)	3044(7)	39(3)
C(5)	2066(14)	5880(8)	2192(6)	43(3)
C(6)	1784(15)	6121(7)	3007(6)	44(3)
N(6)	2191(11)	5622(6)	7657(5)	43(2)
C(7)	3274(12)	6523(7)	6772(6)	32(2)
C(8)	3022(14)	6397(7)	7591(6)	41(3)
C(9)	1927(13)	5271(7)	6878(6)	37(3)
C(11)	214(12)	– 257(6)	4611(6)	23(2)
C(12)	4753(12)	– 19(7)	5462(5)	25(2)
C(13)	1525(12)	3454(6)	4945(5)	22(2)
C(14)	6483(11)	6561(7)	5056(5)	20(2)

<sup>a</sup> $U_{\text{eq}}$  is defined as one-third trace of the orthogonalized tensor  $U_{ij}$ .

**TABLE 9**  
**Selected Bond Distances for III,  $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$**

Moiety	Distance (Å)
Cd(1)–O(3)	2.309(6)
Cd(1)–O(2)	2.316(6)
Cd(1)–O(1)	2.343(6)
Cd(1)–O(4) # 1	2.347(7)
Cd(1)–O(5)	2.394(6)
Cd(1)–O(6) # 2	2.439(6)
Cd(1)–N(1)	2.356(8)
Cd(2)–O(8)	2.406(9)
Cd(2)–O(7)	2.419(6)
Cd(2)–O(7) # 4	2.646(6)
Cd(2)–O(9) # 3	2.454(6)
Cd(2)–O(9)	2.571(6)
Cd(2)–N(3)	2.224(8)
Cd(2)–N(2)	2.230(8)
O(1)–C(13)	1.250(10)
O(2)–C(14) # 3	1.249(10)
O(3)–C(11)	1.287(11)
O(4)–C(12)	1.238(10)
O(5)–C(12)	1.269(11)
O(6)–C(11)	1.234(10)
O(7)–C(13)	1.257(10)
O(9)–C(14)	1.239(10)
N(1)–C(3)	1.316(11)
N(1)–C(1)	1.382(13)
N(2)–C(4)	1.313(12)
N(2)–C(6)	1.378(12)
N(3)–C(9)	1.335(12)
N(3)–C(7)	1.384(11)
N(4)–C(2)	1.340(14)
N(4)–C(1)	1.380(13)
N(5)–C(5)	1.330(12)
N(5)–C(4)	1.330(12)
N(6)–C(8)	1.337(12)
N(6)–C(9)	1.346(12)
C(2)–C(3)	1.327(13)
C(5)–C(6)	1.381(14)
C(7)–C(8)	1.347(13)
C(11)–C(11) # 2	1.52(2)
C(12)–C(12) # 1	1.55(2)
C(13)–C(14) # 3	1.567(13)

Note. Symmetry transformations used to generate equivalent atoms: # 1:  $-x + 1, -y, -z + 1$ ; # 2:  $-x, -y, -z + 1$ ; # 3:  $-x + 1, -y + 1, -z + 1$ ; # 4:  $-x, -y + 1, -z + 1$ .

## RESULTS

### $[\text{C}_3\text{N}_2\text{H}_5][\text{HC}_2\text{O}_4]$ , IMOx

The asymmetric unit of IMOx contains 11 non-hydrogen atoms (Fig. 1a). The structure consists of a hydrogen-bonded assembly between the oxalic acid and the amine. The oxalic acid donates one of the hydrogen atoms to the amine molecule, imidazole, and the remaining hydrogen forms nearly linear O–H...O hydrogen bond with O–O distance of 2.595(3) Å and O–H...O bond angle of 172(2)°.

The bond distance and angle is in the range classified as strong hydrogen bond (20). The oxalic acid also interacts with the amine through N–H...O bonds with N–O distance of 2.766(3) Å and N–H...O angle of 163.7(3)°, forming a sheet structure (Fig. 1b). C–H...O interactions also exist between the amine and oxalic acid, but are of intermediate strength in nature (Fig. 1b) (19). The C–O, C–C and C–N distances and angles are in good agreement with those reported for similar compounds in the literature (17). The structure of IMOx has been reported recently (20).

### $[\text{Cd}(\text{C}_2\text{O}_4)(\text{C}_3\text{N}_2\text{H}_4)]_\infty$ , I

The asymmetric unit contains 12 non-hydrogen atoms (Fig. 2a). The single crystallographically independent Cd atom is octahedrally coordinated to five oxygen atoms and one nitrogen atom. The Cd–O distances are in the range 2.261(4)–2.463(4) Å (av. 2.334 Å) and the O–Cd–O/N bond angles are in the range 69.74(1)–164.1(2)° (av. 109.6°). The bond distances and angles reveal that the local environment about the cadmium atom is a distorted octahedron (Fig. 2b). The C–O and O–C–O bond distances and angles are as expected. The selected bond distances and angles are presented in Tables 3 and 4.

The structure of I comprises a network of CdO<sub>5</sub>N octahedra and the oxalate units. The connectivity between the Cd and the oxalate units forms a layered architecture in the *bc* plane as shown in Fig. 3. The imidazole molecule is bound directly to the cadmium center and point in a direction perpendicular to the sheet (Fig. 4). Of the three-oxalate units that link with the Cd atom, two are shared between two neighboring Cd atoms via a  $\mu$ -3 oxygen (three-coordinated oxygen atom) and the remaining oxalate has the normal bis-bidentate connectivity. The unusual connectivity of the oxalate moieties with the Cd, gives rise to infinite Cd–O–Cd chains in the *bc* plane (Fig. 3). To our knowledge, This is the first time, such Cd–O–Cd linear chains have been observed in a cadmium oxalate coordination polymer.

### $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$ , II

The asymmetric unit of II contains 30 non-hydrogen atoms (Fig. 5). There are two crystallographically independent cadmium atoms, Cd(1) and Cd(2). While Cd(1) is surrounded by six oxygen atoms and one nitrogen atom, Cd(2) is coordinated by five oxygen atoms and two nitrogen atoms. Of the five oxygens that are bound to Cd(2), one oxygen [O(8)] is a terminal linkage, found to be a water molecule. The hydrogen position found in the difference Fourier maps agrees with this assignment. The Cd–O distances are in the range 2.309(6)–2.646(6) Å [(Cd(1)–O)<sub>av</sub> = 2.358, (Cd(2)–O)<sub>av</sub> = 2.499 Å] and the O–Cd–O/N bond angles are in the range 65.7(2)–170.1(2)° [(O–Cd(1)–O/N)<sub>av</sub> = 100.8, (O–Cd(2)–O/N)<sub>av</sub> = 102.5°]. The Cd–N bond

**TABLE 10**  
Selected Bond Angles for **III**,  $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$

Moiety	Angle (deg)
O(3)–Cd(1)–O(2)	170.1(2)
O(3)–Cd(1)–O(1)	119.0(2)
O(2)–Cd(1)–O(1)	70.0(2)
O(3)–Cd(1)–O(4) # 1	79.4(2)
O(2)–Cd(1)–O(4) # 1	90.8(2)
O(1)–Cd(1)–O(4) # 1	157.0(2)
O(3)–Cd(1)–O(5)	88.7(2)
O(2)–Cd(1)–O(5)	89.6(2)
O(1)–Cd(1)–O(5)	121.2(2)
O(4) # 1–Cd(1)–O(5)	69.3(2)
O(3)–Cd(1)–O(6) # 2	69.8(2)
O(2)–Cd(1)–O(6) # 2	118.8(2)
O(1)–Cd(1)–O(6) # 2	71.6(2)
O(4) # 1–Cd(1)–O(6) # 2	130.7(2)
O(5)–Cd(1)–O(6) # 2	72.3(2)
N(1)–Cd(1)–O(5)	153.9(3)
O(3)–Cd(1)–N(1)	90.8(2)
O(2)–Cd(1)–N(1)	86.5(2)
O(1)–Cd(1)–N(1)	81.5(3)
O(4) # 1–Cd(1)–N(1)	84.9(3)
O(8)–Cd(2)–O(7) # 4	79.7(3)
O(7)–Cd(2)–O(7) # 4	65.7(2)
O(9) # 3–Cd(2)–O(7) # 4	133.5(2)
O(9)–Cd(2)–O(7) # 4	160.5(2)
O(8)–Cd(2)–O(9) # 3	145.7(3)
O(7)–Cd(2)–O(9) # 3	68.1(2)
O(8)–Cd(2)–O(7)	145.2(3)
O(8)–Cd(2)–O(9)	81.5(3)
O(7)–Cd(2)–O(9)	133.3(2)
O(9) # 3–Cd(2)–O(9)	65.9(2)
N(1)–Cd(1)–O(6) # 2	131.5(3)
N(3)–Cd(2)–N(2)	172.0(3)
N(3)–Cd(2)–O(8)	89.8(3)
N(2)–Cd(2)–O(8)	82.2(3)
N(3)–Cd(2)–O(7)	91.5(3)
N(2)–Cd(2)–O(7)	95.2(3)
N(3)–Cd(2)–O(9) # 3	99.1(2)
N(2)–Cd(2)–O(9) # 3	87.4(2)
N(3)–Cd(2)–O(9)	88.4(2)
N(2)–Cd(2)–O(9)	90.1(3)
N(3)–Cd(2)–O(7) # 4	86.2(2)
N(2)–Cd(2)–O(7) # 4	92.6(2)
C(13)–O(1)–Cd(1)	118.0(6)
C(14) # 3–O(2)–Cd(1)	118.3(6)
C(11)–O(3)–Cd(1)	117.6(6)
C(12)–O(4)–Cd(1) # 1	115.0(6)
C(12)–O(5)–Cd(1)	114.0(5)
C(11)–O(6)–Cd(1) # 2	113.1(6)
C(3)–N(1)–Cd(1)	130.8(7)
C(1)–N(1)–Cd(1)	123.3(7)
C(4)–N(2)–Cd(2)	130.6(7)
C(6)–N(2)–Cd(2)	123.6(7)
C(9)–N(3)–Cd(2)	124.7(7)
C(7)–N(3)–Cd(2)	130.0(6)
C(13)–O(7)–Cd(2)	116.7(6)
C(13)–O(7)–Cd(2) # 4	125.8(6)
Cd(2)–O(7)–Cd(2) # 4	114.3(2)
C(14)–O(9)–Cd(2) # 3	117.4(6)
C(14)–O(9)–Cd(2)	128.5(6)

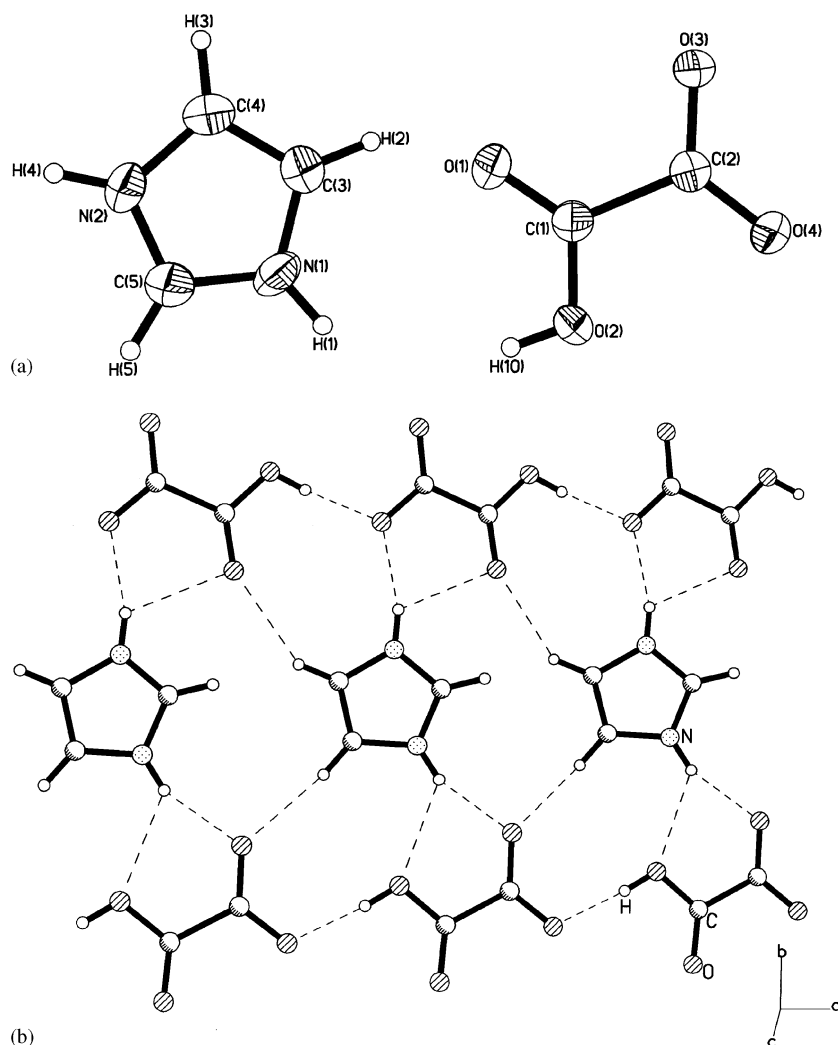
**TABLE 10—Continued**

Moiety	Angle (deg)
Cd(2) # 3–O(9)–Cd(2)	114.1(2)
C(5)–N(5)–C(4)	108.5(9)
C(2)–N(4)–C(1)	109.3(10)
C(8)–N(6)–C(9)	107.8(9)
C(3)–N(1)–C(1)	105.4(9)
C(4)–N(2)–C(6)	105.8(9)
C(9)–N(3)–C(7)	105.3(8)
C(3)–C(2)–N(4)	105.3(9)
C(8)–C(7)–N(3)	108.7(9)
N(1)–C(3)–C(2)	113.6(10)
N(4)–C(1)–N(1)	106.3(10)
N(3)–C(9)–N(6)	110.4(9)
N(2)–C(4)–N(5)	111.3(10)
N(5)–C(5)–C(6)	106.6(9)
N(2)–C(6)–C(5)	107.8(10)
N(6)–C(8)–C(7)	107.9(9)
O(6)–C(11)–O(3)	123.0(8)
O(6)–C(11)–C(11) # 2	120.5(11)
O(3)–C(11)–C(11) # 2	116.5(10)
O(4)–C(12)–O(5)	125.6(8)
O(4)–C(12)–C(12) # 1	118.7(11)
O(5)–C(12)–C(12) # 1	115.7(10)
O(1)–C(13)–O(7)	126.1(9)
O(1)–C(13)–C(14) # 3	116.1(8)
O(7)–C(13)–C(14) # 3	117.8(8)
O(9)–C(14)–O(2) # 3	126.5(8)
O(9)–C(14)–C(13) # 3	117.3(9)
O(2) # 3–C(14)–C(13) # 3	116.2(8)

*Note.* Symmetry transformations used to generate equivalent atoms: # 1:  $-x + 1, -y, -z + 1$ ; # 2:  $-x, -y, -z + 1$ ; # 3:  $-x + 1, -y + 1, -z + 1$ ; # 4:  $-x, -y + 1, -z + 1$ .

distances have values of 2.356(8), 2.230(8) and 2.224(8) Å, respectively, for Cd(1) and Cd(2). The C–O bond distances and O–C–O bond angles are as expected. The selected bond distances and angles are listed in Tables 6 and 7. The coordination environment around the central cadmium atoms in **II** is a distorted pentagonal bi-pyramid.

The framework structure of **II** comprises a network of Cd(1)O<sub>6</sub>N, Cd(2)O<sub>5</sub>N<sub>2</sub> and oxalate units forming an extended two-dimensional layered structure, with one and two imidazole molecules being directly bonded to Cd(1) and Cd(2), respectively. The connectivity between the Cd atoms and the oxalate units forms a layered architecture, in the *bc* plane, with eight-membered rectangular apertures (five Cd and three oxalate units) within the layers as shown in Fig. 6. The terminal water molecule attached to Cd(2), projects into this aperture (Fig. 6). The linkages between the oxalate units and the cadmium atoms are distinctly different in **II**. Whilst Cd(1) is connected to three oxalates in a typical tetradentate fashion (bis-bidentate, two  $\eta^4$ -chelation), Cd(2) is linked through one oxalate in the tetradentate mode and the remaining two-oxalate units are connected via a  $\mu(3)$  oxygen [O(7) and O(9)]. This type of connectivity gives rise to



**FIG. 1.** (a) ORTEP plot of IMOx,  $[\text{C}_3\text{N}_2\text{H}_5][\text{HC}_2\text{O}_4]$ . Thermal ellipsoids are given at 50% probability. (b) Packing diagram of IMOx showing the linear O-H...O arrangement of oxalates separated by the imidazole molecule. Dashed lines represent the hydrogen bond interactions.

a one-dimensional chain of Cd(2)-O-Cd(2) with the Cd(1) polyhedra hanging from the chain. The connectivity between the cadmium and the oxygen atoms appears to be unique. The stacking of layers is similar to that observed in **I**, with the cadmium oxalate layers separated by the imidazole molecule (Fig. 7). The layer arrangement, however, produces pseudo-one-dimensional channels in **II** via hydrogen bond interactions.

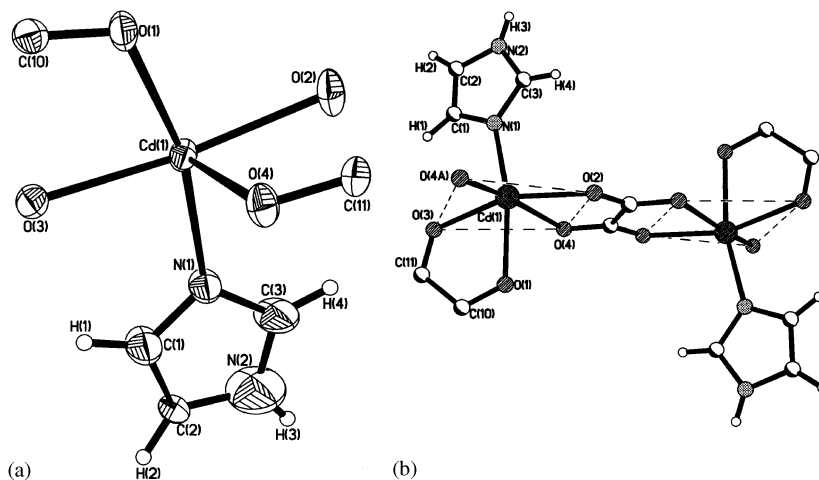
### $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$ , **III**

The asymmetric unit of **III** contains 30 non-hydrogen atoms. There are two crystallographically independent cadmium atoms in the asymmetric unit. Cd(1) is linked with three oxalates and one imidazole molecule and Cd(2) is connected with two oxalates, two imidazole and one water molecule completing the pentagonal bi-pyramidal arrange-

ment as shown in Figs. 8a and 8b. The Cd-O distances are in the range 2.276(10)–2.592(10) Å [ $(\text{Cd}(1)\text{-O})_{\text{av}} = 2.377$ ,  $(\text{Cd}(2)\text{-O})_{\text{av}} = 2.441$  Å] and the O-Cd-O/N bond angles are in the range 51.7(3)–155.2(4)° [ $(\text{O-Cd}(1)\text{-O/N})_{\text{av}} = 101.3$ ,  $(\text{O-Cd}(2)\text{-O/N})_{\text{av}} = 102.4$ °]. The Cd-N bond distances have values of 2.265(11), 2.24(2) and 2.247(13) Å, respectively, for Cd(1) and Cd(2). The C-O bond distance and O-C-O bond angle are as expected. The selected bond distances and angles are presented in Tables 9 and 10. Both Cd(1) and Cd(2) have distorted pentagonal bi-pyramidal coordination.

In the structure of **III**, the network of Cd(1)O<sub>6</sub>N, Cd(2)O<sub>5</sub>N<sub>2</sub> and oxalate units form an extended two-dimensional layered structure, with one and two imidazole molecules directly bonded to Cd(1) and Cd(2), respectively. The connectivity between the Cd atoms and the oxalate units forms a unique layered architecture, along the *ab* plane, with eight-membered rectangle-shaped apertures (five Cd and





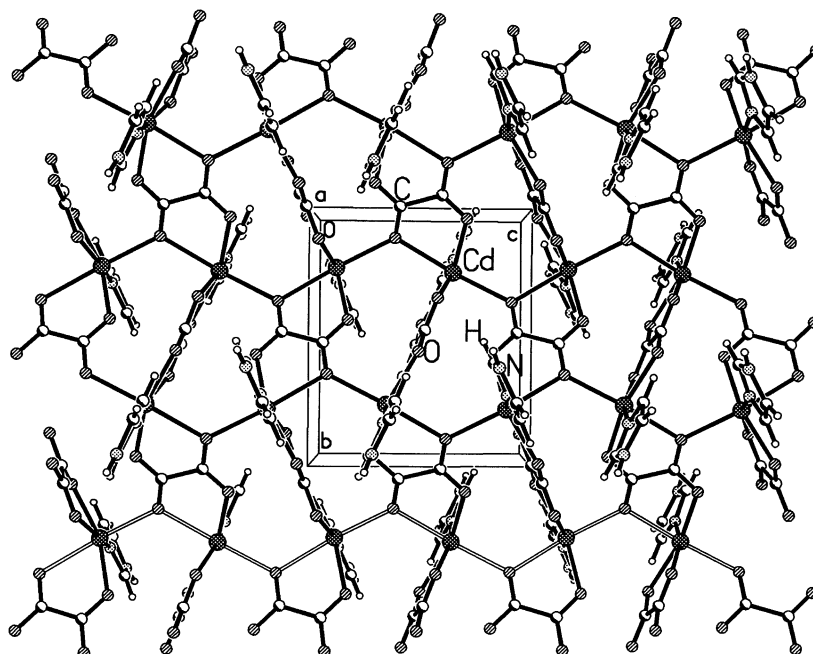
**FIG. 2.** (a) ORTEP plot of **I**,  $[\text{Cd}(\text{C}_2\text{O}_4)(\text{C}_3\text{N}_2\text{H}_4)]_\infty$ . Thermal ellipsoids are given at 50% probability. (b) Figure showing the coordination environment around Cd. Note that it is a distorted octahedron.

three oxalate units) within the layers as shown in Fig. 9. The terminal water molecule attached to Cd(2), projects into this aperture. The oxalate units link-up with the cadmium atom, Cd(2), forming a unique Cd–O chain structure through the  $\mu(3)$  connectivity of the oxygen atom. Cd(1) then connects these unusual Cd–O chains giving rise to the layered architecture (Fig. 9). Whilst Cd(1) is connected to three oxalates in a typical tetradentate fashion (bis-bidentate, two  $\eta^4$ -chelation), Cd(2) is linked through two-oxalate units connected via a  $\mu(3)$  oxygen, forming  $\text{Cd}_2\text{O}_2$  rings. This unusual

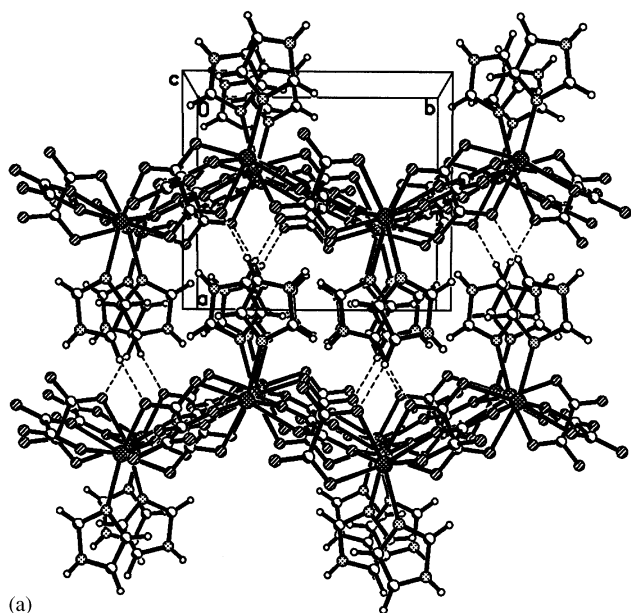
mode of oxalate bridging may be designated as ‘two- $(\eta^4$ -chelation) + monodentate’ in accordance with the haptic notation of Oldham (21). The layer arrangement, viewed along the  $bc$  plane, consists of cadmium oxalate layers separated by the imidazole molecule as shown in Fig. 10.

## DISCUSSION

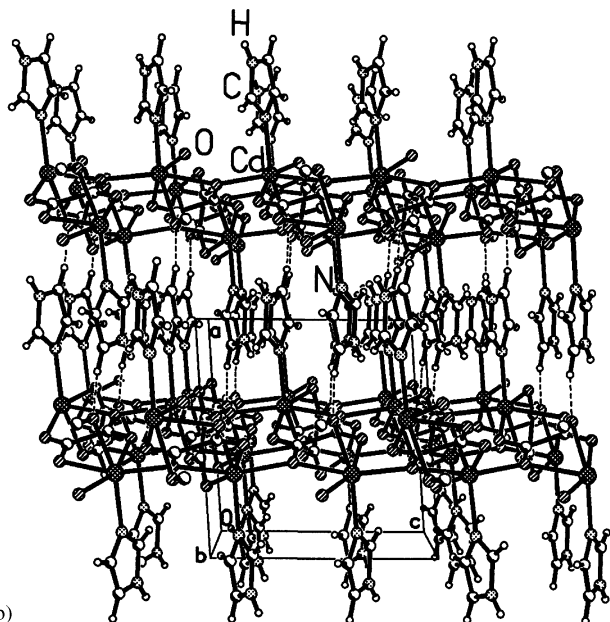
The three cadmium oxalates, **I**,  $[\text{Cd}(\text{C}_2\text{O}_4)(\text{C}_3\text{N}_2\text{H}_4)]_\infty$ , **II**,  $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$  and **III**,  $[\text{Cd}(\text{C}_2\text{O}_4)_2$



**FIG. 3.** Structure showing a single layer of **I**,  $[\text{Cd}(\text{C}_2\text{O}_4)(\text{C}_3\text{N}_2\text{H}_4)]_\infty$ . Note that the amine molecule is ligated to Cd centers and point above and below the plane of the layers. The arrow indicates the Cd–O–Cd chains (outlined).



(a)



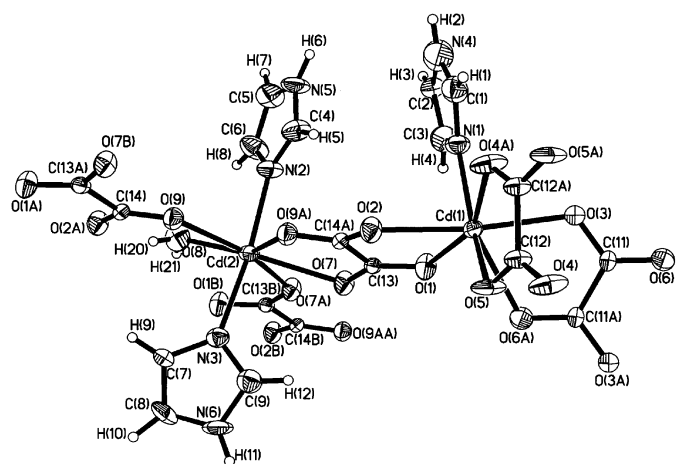
(b)

**FIG. 4.** (a) Structure of **I** in the *ab* plane, the layer arrangement. (b) Structure of **I** in the *ac* plane. Note that the amine molecules point into the inter-lamellar region (see text). The dotted lines represent the possible hydrogen bond interactions.

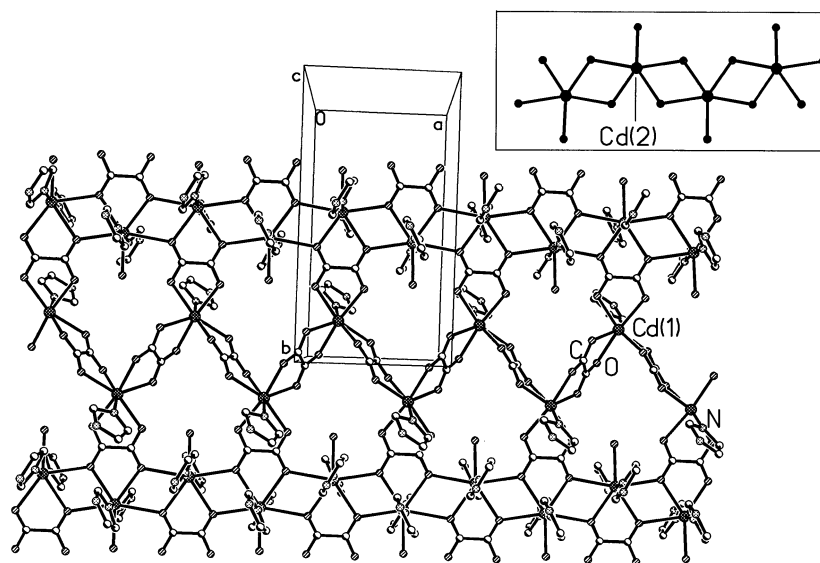
$(C_3N_2H_4)_3(H_2O)_\infty$  are a new family of coordination polymers synthesized for the first time. These oxalates are prepared by employing non-conventional hydrothermal methods and exhibit distinct structural differences amongst them. As with hydrothermal crystallizations, which is kinetically controlled, there is no correlation between the starting composition and final solid product stoichiometry. Whilst **I** is prepared by the reaction of the amine oxalate with Cd, **II**

and **III** are synthesized from the constituents and by varying the temperature of synthesis. Though **II** and **III** have the same framework formula, the connectivity between the oxalate, amine and the Cd atoms creates distinct differences between them. Ancillary ligation by the amine molecules has been observed in all the compounds, in addition to the water molecules bound to the metal center in **II** and **III**. Ligation by poly-functional amines such as 4,4-bipyridine forming rigid networks has been observed in oxalates and other related systems (3, 4, 7–12). The ligation of imidazole molecule in **I–III** is unusual as it binds with the metal that enters through only one of its nitrogen, forming a layered architecture with unusual Cd–O–Cd polymeric network (Figs. 11, 3, 6 and 9). The novel structural arrangements observed in **I–III** might probably be the result of the hydrothermal conditions employed in the present study. Recent studies indicate that unusual oxalate structures can be prepared by the reaction between amine oxalates and Zn under hydrothermal conditions (17). Unique structural features have also been observed in open-framework phosphates prepared by the reaction of amine phosphates with metal ions (22). It is interesting to note that the imidazole molecule, bonded with the cadmium, is neutral, unlike other framework oxalates of Sn and Zn, discovered recently (15). In Sn and Zn oxalates, the amine molecules are protonated neutralizing the anionic framework charge and are also not bonded directly to the metal (15). The amine molecules in **I–III** are positioned so as to point into the inter-lamellar region, unlike in the layered Sn and Zn oxalates (15), where the amine molecules are nestled in pseudo-channels.

The coordination environment of the cadmium atoms in **I–III** presents an interesting comparison. While Cd is octahedrally coordinated in **I**, it is in a distorted pentagonal bi-pyramidal environment in **II** and **III**. The lower coordination of Cd in **I** is due to the absence of secondary ligation



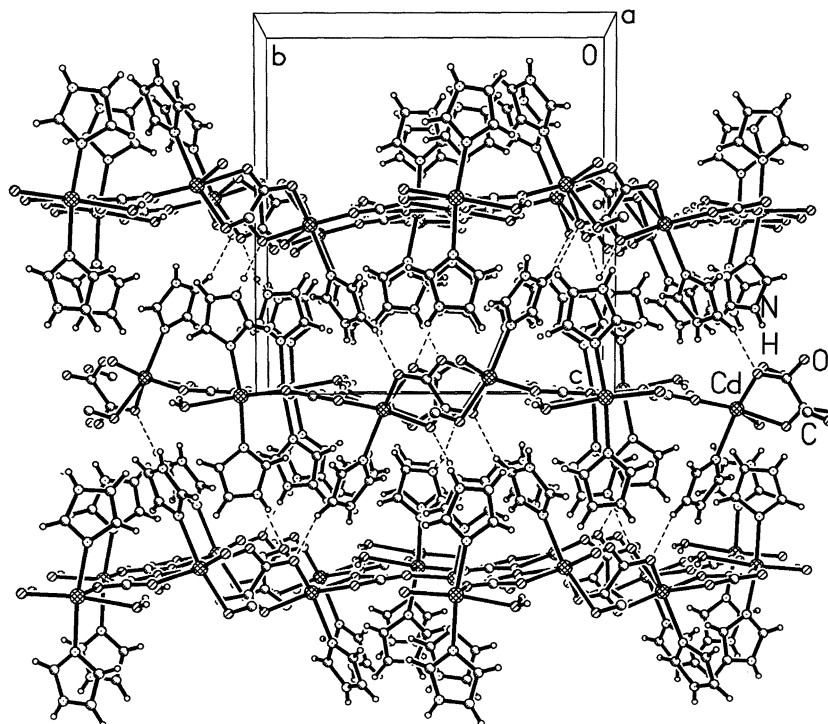
**FIG. 5.** ORTEP plot of **II**,  $[Cd(C_2O_4)_2(C_3N_2H_4)_3(H_2O)]_\infty$ . Thermal ellipsoids are given at 50% probability.



**FIG. 6.** Structure of a single layer in **II** showing the pear-shaped apertures. Note the water molecules pointing into the apertures. Inset shows the Cd–O–Cd polymeric chains.

by the water molecule and can be attributed to the modified synthetic approach. Seven coordinated Cd atoms with pentagonal bi-pyramidal arrangement have also been observed in a layered cadmium oxalate,  $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  (23). Three-dimensional cadmium oxalates, however, have eight-coor-

dinated Cd in dodecahedral arrangement (16a, 24). The coordination environment of Cd atoms in open-framework phosphates and oxalates are different and merits mention. The Cd atoms, in the cadmium phosphates with open architectures have an octahedral coordination (six-coordination)



**FIG. 7.** Structure of **II** along the *bc* plane showing the layer arrangement with the amine molecules pointing into the inter-lamellar region. The dotted lines represent the possible hydrogen bond interactions.

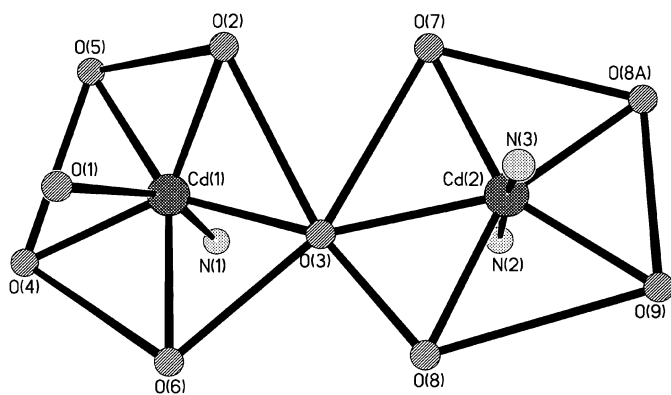


FIG. 8. The coordination environments around the Cd atoms in **III**,  $[\text{Cd}(\text{C}_2\text{O}_4)_2(\text{C}_3\text{N}_2\text{H}_4)_3(\text{H}_2\text{O})]_\infty$ , showing the distorted pentagonal bipyramidal arrangement.

(25). In the oxalates under discussion, we have six- and seven-coordination for the Cd atoms and eight-coordination for cadmium, in a cadmium oxalate with three-dimensional structure (16a, 24). This is probably because the average charge per oxygen on the oxalate (0.5) is less than that on the phosphate (0.75) and more oxalate oxygens are therefore needed to satisfy the valence of cadmium.

Although, all the compounds involve bonding between the oxalate units and the Cd atoms, there are no apertures within the layers in **I**, whereas **II** and **III** possess pear-shaped and rectangle-like apertures within the layers. The striking feature of these structures is the connectivity between the Cd atoms. Whilst in **I**, the linkages form an

infinite one-dimensional Cd–O–Cd wires (Fig. 3), in **II** it forms an infinite strip made from  $\text{Cd}_2\text{O}_2$  dimers (Fig. 6), and in **III** it forms an infinite tree-like arrangement with the central core being similar to that observed in **I** (Fig. 9). To our knowledge, this type of Cd–O–Cd linkages, has been observed for the first time. A careful investigation into the structures of the Cd–O–Cd infinite chains shows intricate relationship between the structures (Fig. 11). As can be seen from Fig. 11, it appears that the polymeric wire observed in **I** could be the precursor for all the other Cd–O structures observed in the present study. In **II**, the dimeric chain formed by the Cd(2) atoms with the Cd(1) atoms separating two such polymeric chains could be the intermediate for the tree-like Cd–O polymer observed in **III**, though it is difficult to identify which is the precursor phase. From the conditions employed for the preparation of these phases, it is likely that **III** could be the precursor for **II** as it is formed at a lower temperature. As the reactions involved in the preparation of these phases are kinetically controlled and their energies are likely to be similar (26), it is difficult to infer precursor phases from single-crystal study of the final product. A careful *in situ* investigation from the starting materials, using synchrotron X-ray radiation, may be used to identify the evolution of these phases. Such studies have been employed with great success in recent years for the understanding of the evolution as well as the formation of framework phosphates (27). Clearly, the Cd–O polymers are related. It is likely that the unique polymeric linkages between the Cd atoms might be the result of the novel synthetic approaches, such as the use of amine oxalate intermediates, employed in the present study.

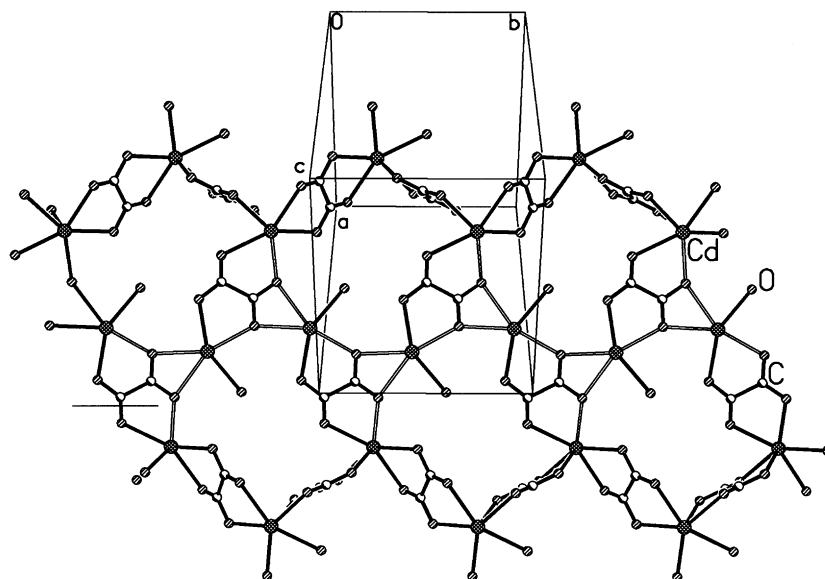


FIG. 9. Structure of a single layer of **III** showing the rectangular apertures. The water molecules project into these apertures. The amine molecules attached with the Cd center are not shown for clarity. The arrow indicates the Cd–O chains (outlined).

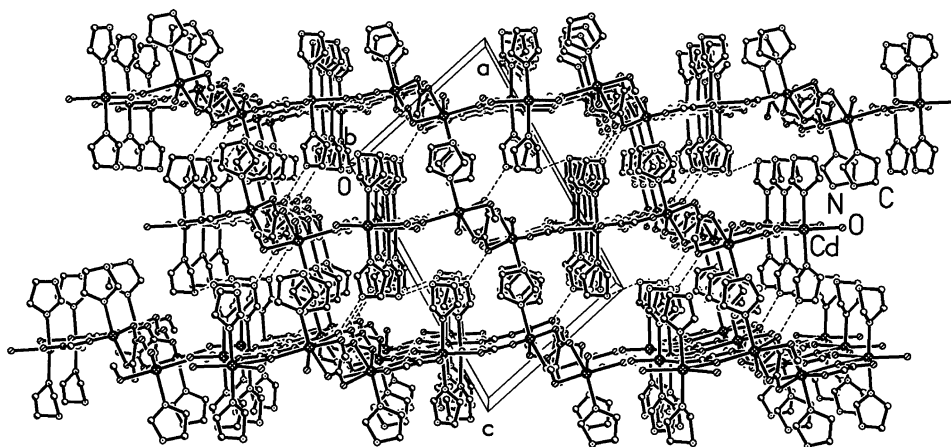


FIG. 10. Structure of III along the *ac* plane showing the layer arrangements. Note that the amine molecules point into the inter-lamellar region.

### CONCLUSIONS

The present study demonstrates the role of newer preparation techniques involving intermediates in the synthesis

of novel open-framework structures under hydrothermal conditions. The variations in the coordination environment of Cd in I–III and the presence of polymeric Cd–O–Cd networks are worthy of note. It is possible that the amine oxalate is not only the source for both the amine and oxalate, but also acts as a complex template species *in situ*. The amine oxalate may also be considered an ion pair, possibly occurring in an associated form in solutions. Such a situation would favor the formation of novel architectures. Further work is currently underway to evaluate the role of amine oxalates in the synthesis of other oxalates and related phases as well as phase relationships and other structural aspects within the family of oxalate structures.

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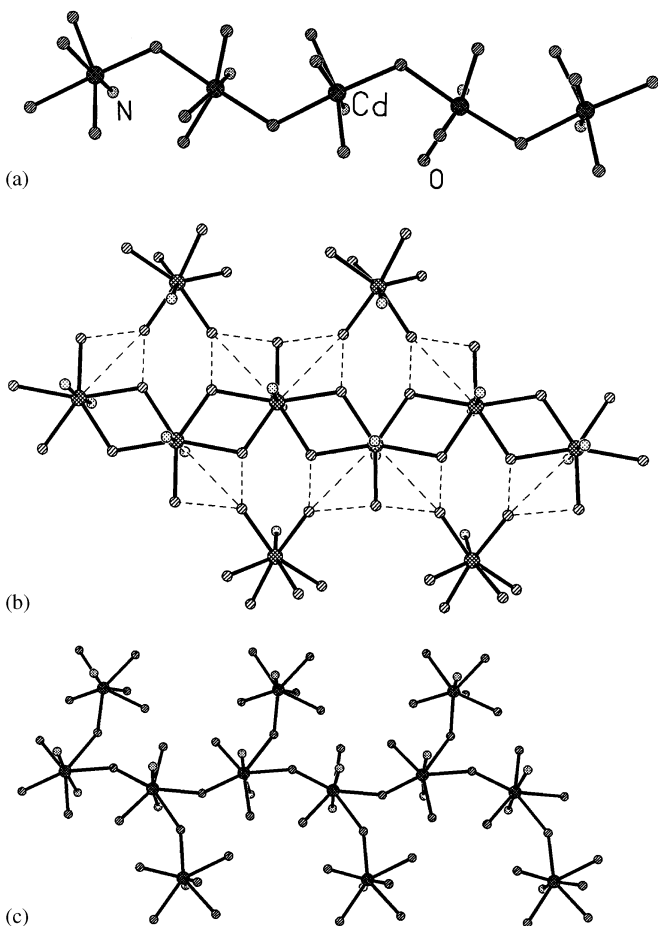


FIG. 11. (a)–(c) The various types of polymeric Cd–O chains observed in the cadmium oxalates I–III. Note the close similarity between them.

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