

# Poly[dimethylammonium [tris( $\mu_2$ -formate- $\kappa^2$ O:O')cadmate(II)]]

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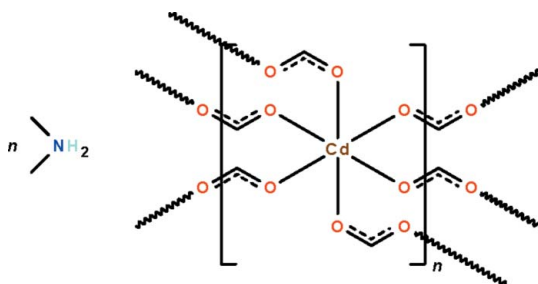
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{O}-\text{C}) = 0.001$  Å; disorder in main residue;  $R$  factor = 0.022;  $wR$  factor = 0.055; data-to-parameter ratio = 11.2.

In the coordination polymer,  $\{(\text{C}_2\text{H}_8\text{N})[\text{Cd}(\text{CHO}_2)_3]\}_n$ , the  $\text{Cd}^{\text{II}}$  atom lies on a special position of  $\bar{3}$  site symmetry in an octahedron of O atoms. The formate unit bridges the metal atoms, generating a three-dimensional polyanionic framework. The disordered cations occupy the cavities within the framework, and are  $\text{N}-\text{H}\cdots\text{O}$  hydrogen-bonded to the framework.

## Related literature

For the tris(formate)zincate cation, see; Fortier & Creber (1985); Marsh (1986). Tris(formate)cadmate is not isotypic to the aforementioned Zn structures.



## Experimental

### Crystal data

$(\text{C}_2\text{H}_8\text{N})[\text{Cd}(\text{CHO}_2)_3]$   
 $M_r = 293.55$   
 Trigonal,  $R\bar{3}c$   
 $a = 8.5121$  (4) Å  
 $c = 23.0022$  (9) Å  
 $V = 1443.36$  (9) Å<sup>3</sup>

$Z = 6$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.27$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.22 \times 0.19 \times 0.15$  mm

### Data collection

Rigaku R-Axis RAPID diffractometer  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
 $T_{\text{min}} = 0.635$ ,  $T_{\text{max}} = 0.727$

4250 measured reflections  
 370 independent reflections  
 352 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$   
 $wR(F^2) = 0.055$   
 $S = 1.09$   
 370 reflections  
 33 parameters

9 restraints  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.73$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.36$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}$	0.88	1.99	2.84 (7)	163

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2747).

## References

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**supplementary materials**

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## Poly[dimethylammonium [tris( $\mu_2$ -formato- $\kappa^2O:O'$ )cadmate(II)]]

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### Comment

For some hydrothermal syntheses involving carboxylic acids, the *N,N*-dimethylformamide that is used as solvent is partially converted to the dimethylammonium cation, whose charge is balanced by the carboxylate ion. In the present study, the attempt to synthesize a coordination compound of a cadmium carboxylate yielded the tris(formato)cadmate anion (Scheme I). In the salt (Fig. 1), the cadmium atom lies on a special position of  $\bar{3}$  site symmetry in an octahedron of O atoms. The formate unit bridges the metal atoms to generate a three-dimensional polyanionic framework, whose cavities are occupied by disordered cations.

A similar tris(formato)zincate(II) has been reported; the compound was synthesized directly from a zinc salt and formic acid in DMF medium (Fortier & Creber, 1985; Marsh, 1986). The later study has assumed the cation to be the formamidinium cation,  $(\text{NH}_2)\text{CH}(\text{NH}_2)^+$ . Possibly, the cation is the dimethylammonium cation.

### Experimental

*N,N*-Dimethylformamide (10 ml), water (1 ml), ethanol (1 ml), formic acid (0.1 ml), cadmium nitrate (5 mmol), 1,10-phenanthroline (5 mmol) and benzoic acid (5 mmol) were heated in a 23-ml Teflon-lined autoclave at 383 K for 3 days. After slow cooling the autoclave to room temperature, colorless crystals were obtained.

### Refinement

Hydrogen atoms were placed in calculated positions (C–H 0.93, N–H 0.88 Å) and were included in the refinement in the riding model approximation, with  $U(\text{H})$  set to  $1.2\text{--}1.5U_{\text{eq}}(\text{C},\text{N})$ .

The dimethylammonium cation was allowed to refine off the special position; the two N–C distances were restrained to  $1.50\pm 0.01$  Å and the C···C distance to  $2.35\pm 0.01$  Å. The anisotropic temperature factors of the carbon atoms were restrained to be nearly isotropic.

### Figures

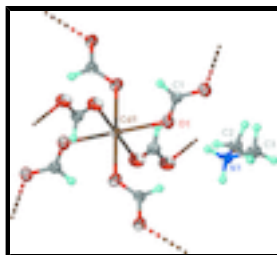


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of a portion of poly[dimethylammonium tris(formato)cadmate] at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

## Poly[dimethylammonium [tris( $\mu_2$ -formato- $\kappa^2$ O:O')cadmate(II)]]

### Crystal data

(C <sub>2</sub> H <sub>8</sub> N)[Cd(CHO <sub>2</sub> ) <sub>3</sub> ]	$D_x = 2.026 \text{ Mg m}^{-3}$
$M_r = 293.55$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Trigonal, $R\bar{3}c$	Cell parameters from 3921 reflections
Hall symbol: -R 3 2" c	$\theta = 3.3\text{--}37.5^\circ$
$a = 8.5121 (4) \text{ \AA}$	$\mu = 2.27 \text{ mm}^{-1}$
$c = 23.0022 (9) \text{ \AA}$	$T = 293 \text{ K}$
$V = 1443.36 (9) \text{ \AA}^3$	Prism, colorless
$Z = 6$	$0.22 \times 0.19 \times 0.15 \text{ mm}$
$F(000) = 864$	

### Data collection

Rigaku R-Axis RAPID diffractometer	370 independent reflections
Radiation source: fine-focus sealed tube graphite	352 reflections with $I > 2\sigma(I)$
Detector resolution: 10.000 pixels $\text{mm}^{-1}$	$R_{\text{int}} = 0.024$
$\omega$ scans	$\theta_{\text{max}} = 27.5^\circ$ , $\theta_{\text{min}} = 3.3^\circ$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.635$ , $T_{\text{max}} = 0.727$	$k = -11 \rightarrow 9$
4250 measured reflections	$l = -29 \rightarrow 29$

### Refinement

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.022$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.055$	H-atom parameters constrained
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.5666P]$
370 reflections	where $P = (F_o^2 + 2F_c^2)/3$
33 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
9 restraints	$\Delta\rho_{\text{max}} = 0.73 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cd1	0.0000	0.0000	0.0000	0.02669 (17)	
O1	0.23112 (15)	0.21016 (15)	0.05612 (5)	0.0452 (3)	

C1	0.2265 (2)	0.3333	0.0833	0.0328 (4)	
H1A	0.1173	0.3333	0.0833	0.039*	
N1	0.578 (6)	0.252 (5)	0.0797 (17)	0.040 (4)	0.167
H1B	0.5788	0.1489	0.0798	0.048*	0.167
H1	0.4646	0.2277	0.0792	0.048*	0.167
C2	0.680 (5)	0.365 (4)	0.0282 (14)	0.041 (4)*	0.167
H2A	0.6061	0.3181	-0.0061	0.062*	0.167
H2B	0.7899	0.3619	0.0232	0.062*	0.167
H2C	0.7079	0.4881	0.0344	0.062*	0.167
C3	0.676 (7)	0.364 (4)	0.1320 (15)	0.041 (4)*	0.167
H3A	0.6210	0.2961	0.1667	0.062*	0.167
H3B	0.6687	0.4732	0.1322	0.062*	0.167
H3C	0.8010	0.3952	0.1306	0.062*	0.167

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cd1	0.02630 (19)	0.02630 (19)	0.0275 (2)	0.01315 (10)	0.000	0.000
O1	0.0397 (6)	0.0420 (6)	0.0554 (7)	0.0215 (5)	-0.0121 (5)	-0.0206 (5)
C1	0.0301 (8)	0.0326 (11)	0.0367 (10)	0.0163 (5)	-0.0006 (4)	-0.0011 (8)
N1	0.040 (8)	0.028 (6)	0.055 (8)	0.019 (4)	-0.006 (7)	0.002 (7)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cd1—O1 <sup>i</sup>	2.2841 (10)	N1—C3	1.505 (10)
Cd1—O1	2.2841 (10)	N1—H1B	0.8800
Cd1—O1 <sup>ii</sup>	2.2841 (10)	N1—H1	0.8800
Cd1—O1 <sup>iii</sup>	2.2841 (10)	C2—H2A	0.9600
Cd1—O1 <sup>iv</sup>	2.2841 (10)	C2—H2B	0.9600
Cd1—O1 <sup>v</sup>	2.2841 (10)	C2—H2C	0.9600
O1—C1	1.2384 (14)	C3—H3A	0.9600
C1—O1 <sup>vi</sup>	1.2383 (14)	C3—H3B	0.9600
C1—H1A	0.9300	C3—H3C	0.9600
N1—C2	1.499 (10)		
O1 <sup>i</sup> —Cd1—O1	180.00 (5)	C2—N1—C3	105.3 (8)
O1 <sup>i</sup> —Cd1—O1 <sup>ii</sup>	91.20 (4)	C2—N1—H1B	110.7
O1—Cd1—O1 <sup>ii</sup>	88.80 (4)	C3—N1—H1B	110.7
O1 <sup>i</sup> —Cd1—O1 <sup>iii</sup>	91.20 (4)	C2—N1—H1	110.7
O1—Cd1—O1 <sup>iii</sup>	88.80 (4)	C3—N1—H1	110.7
O1 <sup>ii</sup> —Cd1—O1 <sup>iii</sup>	91.20 (4)	H1B—N1—H1	108.8
O1 <sup>i</sup> —Cd1—O1 <sup>iv</sup>	88.80 (4)	N1—C2—H2A	109.5
O1—Cd1—O1 <sup>iv</sup>	91.20 (4)	N1—C2—H2B	109.5
O1 <sup>ii</sup> —Cd1—O1 <sup>iv</sup>	88.80 (4)	H2A—C2—H2B	109.5
O1 <sup>iii</sup> —Cd1—O1 <sup>iv</sup>	180.00 (7)	N1—C2—H2C	109.5
O1 <sup>i</sup> —Cd1—O1 <sup>v</sup>	88.80 (4)	H2A—C2—H2C	109.5

## supplementary materials

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O1—Cd1—O1 <sup>v</sup>	91.20 (4)	H2B—C2—H2C	109.5
O1 <sup>ii</sup> —Cd1—O1 <sup>v</sup>	180.00 (5)	N1—C3—H3A	109.5
O1 <sup>iii</sup> —Cd1—O1 <sup>v</sup>	88.80 (4)	N1—C3—H3B	109.5
O1 <sup>iv</sup> —Cd1—O1 <sup>v</sup>	91.20 (4)	H3A—C3—H3B	109.5
C1—O1—Cd1	124.71 (11)	N1—C3—H3C	109.5
O1 <sup>vi</sup> —C1—O1	125.90 (19)	H3A—C3—H3C	109.5
O1 <sup>vi</sup> —C1—H1A	117.1	H3B—C3—H3C	109.5
O1—C1—H1A	117.1		
O1 <sup>ii</sup> —Cd1—O1—C1	151.34 (11)	O1 <sup>v</sup> —Cd1—O1—C1	-28.66 (11)
O1 <sup>iii</sup> —Cd1—O1—C1	60.11 (7)	Cd1—O1—C1—O1 <sup>vi</sup>	-174.40 (11)
O1 <sup>iv</sup> —Cd1—O1—C1	-119.89 (7)		

Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $y, -x+y, -z$ ; (iii)  $x-y, x, -z$ ; (iv)  $-x+y, -x, z$ ; (v)  $-y, x-y, z$ ; (vi)  $x-y+1/3, -y+2/3, -z+1/6$ .

### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O1	0.88	1.99	2.84 (7)	163

Fig. 1

