

collection, structure solution and refinement are listed in Table 1. The final atomic coordinates are given in Table 2, selected bond distances and angles in Table 3.\* Figs. 1 and 2 show the numbering scheme and a stereoview, respectively.

**Related literature.** This structure is one of a series of Pd compounds with Schiff-base ligands. A previous struc-

ture is described in Hiller, Castineiras, Vila, Suarez, Pereira & Gayoso (1986).

We thank the DAAD for financial support.

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\* Lists of structure factors, anisotropic thermal parameters, further distances and angles, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44684 (14 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## The Structure of Two Gel-Grown Oxamate Complexes: Bis(oxamato-*O,O'*)calcium(II) Tetrahydrate and Bis(oxamato-*O,O'*)cadmium(II) Tetrahydrate

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**Abstract.** The two compounds of general formula  $M(\text{C}_2\text{O}_3\text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$ , where  $M = \text{Ca}^{\text{II}}$  (*A*),  $\text{Cd}^{\text{II}}$  (*B*), are isostructural, space group  $C2/c$ ,  $Z = 4$ ,  $Ag\ K\alpha$ ,  $\lambda = 0.56087 \text{ \AA}$ , 295 K. Compound (*A*):  $[\text{Ca}(\text{C}_2\text{H}_2\text{NO}_3)_2] \cdot 4\text{H}_2\text{O}$ ,  $M_r = 288.2$ ,  $a = 14.466$  (3),  $b = 5.993$  (1),  $c = 12.256$  (2)  $\text{\AA}$ ,  $\beta = 99.74$  (1) $^\circ$ ,  $V = 1047.3 \text{ \AA}^3$ ,  $D_x = 1.828 \text{ g cm}^{-3}$ ,  $\mu = 3.5 \text{ cm}^{-1}$ ,  $F(000) = 595$ ,  $R = 0.021$  and  $wR = 0.027$  for 895 reflections with  $I > 3\sigma(I)$ . Compound (*B*):  $[\text{Cd}(\text{C}_2\text{H}_2\text{NO}_3)_2] \cdot 4\text{H}_2\text{O}$ ,  $M_r = 360.5$ ,  $a = 14.347$  (6),  $b = 5.975$  (1),  $c = 12.184$  (2)  $\text{\AA}$ ,  $\beta = 100.09$  (2) $^\circ$ ,  $V = 1028.4 \text{ \AA}^3$ ,  $D_x = 2.328 \text{ g cm}^{-3}$ ,  $\mu = 10.3 \text{ cm}^{-1}$ ,  $F(000) = 704$ ,  $R = 0.020$  and  $wR = 0.022$  for 919 reflections with  $I > 1.5\sigma(I)$ . *M*, on a crystallographic twofold axis, is coordinated by two chelating ligands and four water molecules. The coordination number of the metal is eight and the resulting coordination polyhedron is a distorted square antiprism. The observed coordination number which is frequently encountered in the case of Ca compounds is, in contrast, very rarely adopted by  $\text{Cd}^{\text{II}}$  ions. The distances  $\text{Cd}-\text{O}$  are generally slightly shorter than  $\text{Ca}-\text{O}$  in accordance with small differences in the ionic radii of the metal ions. The crystal structure is stabilized by a three-dimensional network of hydrogen bonds of the types  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{O}$ .

Four of these bonds hold the molecules together in chains parallel to (010). The chains are joined to one another by the four remaining hydrogen bonds.

**Experimental.** Crystals prepared by slow diffusion of the corresponding hydrated metal(II) salt (chloride or nitrate) into a silica-gel mixture containing oxamic acid at neutral pH (Michaelides & Skoulika, 1988). The Cd compound was stored in the presence of its aqueous solution to prevent partial dehydration. Crystals  $0.25 \times 0.30 \times 0.20 \text{ mm}$  for (*A*) and  $0.25 \times 0.20 \times 0.20 \text{ mm}$  for (*B*) were used. Automated CAD-4 Enraf-Nonius diffractometer with incident-beam ( $\text{Ag K}\alpha$ ) graphite monochromator. 25 centered reflections within  $8.4 < \theta < 11.7^\circ$  for (*A*) and  $5.4 < \theta < 11.4^\circ$  for (*B*) used for determining lattice parameters.  $\omega$ ,  $2\theta$  scan mode, max.  $2\theta 20^\circ$ . Two standard reflections, no intensity variation. 895 reflections used [ $I > 3\sigma(I)$ ] from 953 unique reflections measured for (*A*) and 919 reflections used [ $I > 1.5\sigma(I)$ ] from 952 unique reflections for (*B*).  $-17 < h < 17$ ,  $0 < k < 7$ ,  $0 < l < 14$  for (*A*) and (*B*). Data corrected for Lorentz and polarization effects, empirical isotropic correction for (*B*),  $x = 2.1$  (1)  $\times 10^{-3}$ ,  $[F_c' = F_c(1 - 0.0001x F_c^2/\sin\theta)]$ . No absorption correction made. Data reduction with *SDP* package (Enraf-Nonius, 1979). Structure solved by Patterson and Fourier methods. Least-squares program *SHELX76* (Sheldrick, 1976). Refine-

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ment on *F*. Anisotropic thermal parameters for all non-H atoms. H atoms in refined positions. Compound (A):  $(\Delta/\sigma)_{\max} = 0.018$ ,  $(\Delta\rho)_{\max} = 0.26 \text{ e } \text{Å}^{-3}$ ,  $R = 0.021$ ,  $wR = 0.027$  and  $S = 1.01$ .  $w = 1/[\sigma^2(F) + 0.0015F^2]$ . Compound (B):  $(\Delta/\sigma)_{\max} = 0.007$ ,  $(\Delta\rho) = 0.44 \text{ e } \text{Å}^{-3}$ ,  $R = 0.020$ ,  $wR = 0.022$  and  $S = 0.82$ .  $w = 1/[\sigma^2(F) + 0.0011F^2]$ . Scattering factors from *International Tables for X-ray Crystallography* (1974). Table 1 contains the atomic coordinates of the two compounds and Table 2 lists some geometric data. The coordination polyhedron of the Cd<sup>II</sup> ion is shown in Fig. 1.\*

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44679 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates of non-H atoms and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
(a) Cd(C <sub>2</sub> O <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> .4H <sub>2</sub> O				
Cd	0.0000	0.1199 (<1)	0.2500	1.28 (1)
O(1)	0.3026 (1)	0.1571 (3)	0.3899 (2)	1.70 (4)
O(2)	0.1565 (1)	0.0229 (3)	0.3339 (2)	1.83 (4)
O(3)	0.0859 (1)	0.4365 (3)	0.3224 (2)	1.90 (4)
N(1)	0.2300 (2)	0.5823 (4)	0.3821 (2)	1.71 (5)
C(1)	0.2152 (2)	0.1767 (5)	0.3597 (2)	1.26 (5)
C(2)	0.1721 (2)	0.4151 (4)	0.3537 (2)	1.22 (5)
OW(1)	-0.0187 (1)	-0.1951 (3)	0.3691 (2)	1.76 (4)
OW(2)	-0.0801 (1)	0.2448 (3)	0.4081 (2)	2.14 (5)
(b) Ca(C <sub>2</sub> O <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> .4H <sub>2</sub> O				
Ca	0.0000	0.1185 (1)	0.2500	1.25 (1)
O(1)	0.3050 (1)	0.1571 (2)	0.3921 (1)	1.84 (3)
O(2)	0.1598 (1)	0.0255 (2)	0.3374 (1)	1.89 (3)
O(3)	0.0905 (1)	0.4363 (2)	0.3225 (1)	1.94 (3)
N(1)	0.2329 (1)	0.5829 (2)	0.3822 (1)	1.75 (3)
C(1)	0.2188 (1)	0.1775 (2)	0.3626 (1)	1.30 (3)
C(2)	0.1761 (1)	0.4154 (2)	0.3548 (1)	1.32 (3)
OW(1)	-0.0167 (1)	-0.2029 (2)	0.3704 (1)	1.75 (3)
OW(2)	-0.0771 (1)	0.2488 (2)	0.4071 (1)	2.12 (3)

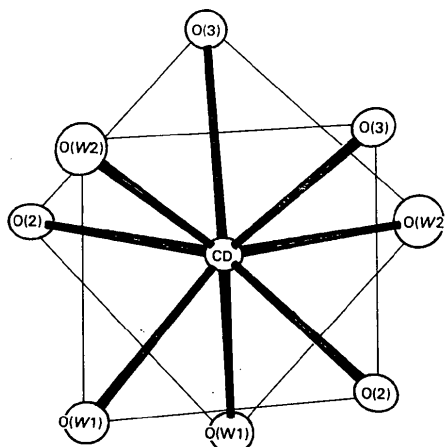


Fig. 1. View of the coordination polyhedron of the Cd<sup>II</sup> ion.

Table 2. Selected interatomic distances (Å) and angles (°)

	<i>M</i> = Cd	<i>M</i> = Ca
(a) Oxamate ions		
O(1)-C(1)	1.248 (3)	1.245 (1)
O(2)-C(1)	1.248 (3)	1.250 (1)
O(3)-C(2)	1.235 (3)	1.240 (1)
N(1)-C(2)	1.306 (3)	1.304 (1)
C(1)-C(2)	1.549 (3)	1.550 (1)
O(1)-C(1)-C(2)	118.1 (2)	118.5 (1)
O(1)-C(1)-O(2)	127.0 (2)	127.5 (1)
O(2)-C(1)-C(2)	114.7 (2)	113.9 (1)
O(3)-C(2)-C(1)	118.6 (2)	118.5 (1)
O(3)-C(2)-N(1)	123.9 (2)	123.7 (1)
N(1)-C(2)-C(1)	117.4 (2)	117.7 (1)
(b) Coordination polyhedron		
M-O(2)	2.370 (1)	2.442 (1)
M-O(3)	2.344 (1)	2.395 (1)
M-OW(1)	2.419 (1)	2.463 (5)
M-OW(2)	2.522 (2)	2.507 (1)
O(3)-M-O(2)	139.0 (1)	139.60 (5)
O(2)-M-O(2)	151.7 (1)	153.60 (5)
O(2)-M-O(3)	68.8 (1)	66.51 (3)
O(3)-M-O(3)	72.3 (1)	74.66 (4)
O(2)-M-OW(1)	75.3 (1)	74.93 (3)
O(2)-M-OW(1)	82.6 (1)	84.42 (3)
OW(1)-M-OW(1)	77.8 (1)	77.11 (5)
O(2)-M-OW(2)	105.4 (1)	104.18 (3)
O(2)-M-OW(2)	82.9 (1)	84.09 (3)
OW(2)-M-OW(2)	145.5 (1)	143.71 (5)
O(3)-M-OW(1)	138.3 (1)	137.86 (3)
O(3)-M-OW(1)	120.5 (1)	120.13 (3)
O(3)-M-OW(2)	76.6 (1)	75.61 (3)
O(3)-M-OW(2)	75.7 (1)	75.70 (3)
OW(1)-M-OW(2)	70.0 (1)	71.45 (3)
OW(1)-M-OW(2)	143.2 (1)	143.61 (4)
(c) Hydrogen bonds		
	<i>D</i> ... <i>A</i>	$\angle D-H\cdots A$
	<i>M</i> = Cd <i>M</i> = Ca	<i>M</i> = Cd <i>M</i> = Ca
N-H...O(2 <sup>b</sup> )	2.858 (2)    2.873 (1)	174.9 (1)    177 (2)
OW(2)-H...OW(1 <sup>iii</sup> )	2.849 (2)    2.845 (1)	176.0 (1)    170 (2)
OW(1)-H...O(3 <sup>v</sup> )	2.779 (2)    2.780 (1)	172.7 (1)    168 (1)
OW(2)-H...O(1 <sup>v</sup> )	2.970 (2)    2.970 (1)	162.4 (1)    168 (2)

Symmetry code: (i)  $-x, y, \frac{1}{2}-z$ ; (ii)  $x, 1+y, z$ ; (iii)  $-x, -y, 1-z$ ; (iv)  $x, y-1, z$ ; (v)  $x-\frac{1}{2}, \frac{1}{2}+y, z$ .

**Related literature.** Calcium coordination with carboxylic acids has been reviewed (Einspahr & Bugg, 1981).

The crystal and molecular structures of bis-(oxamato)*M*<sup>II</sup>.*n*H<sub>2</sub>O, where *M* = Co, Zn, Pb, have been reported (Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1972; Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971; Skoulika, Michaelides & Aubry, 1988).

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## A *cis*-Dichloro(1,10-phenanthroline)palladium(II) Complex

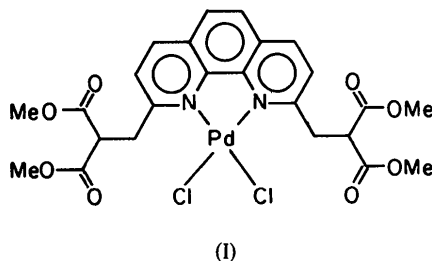
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**Abstract.** *cis*-{2,9-Bis[2,2-bis(methoxycarbonyl)ethyl]-1,10-phenanthroline}dichloropalladium(II), [PdCl<sub>2</sub>(C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>O<sub>8</sub>)], *M<sub>r</sub>* = 645.77, triclinic, *P* $\bar{1}$ , *a* = 8.408 (1), *b* = 10.222 (1), *c* = 15.402 (2) Å,  $\alpha$  = 96.45 (1),  $\beta$  = 96.26 (1),  $\gamma$  = 100.56 (1)°, *V* = 1281.6 (6) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.673 g cm<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71073 Å,  $\mu$  = 9.7 cm<sup>-1</sup>, *F*(000) = 652, *T* = 295 (1) K, *R* = 0.032 for 5327 reflections with *I* > 3.0σ(*I*). The 'square-planar' coordination about Pd is pyramidal, with Pd 0.196 (1) Å above the basal plane of two Cl and two N atoms. The five-membered metalocycle is in the envelope conformation, with Pd in the flap [dihedral angle 32.3 (2)°]. The phenanthroline is distorted into a crescent with limbs deviating from the mean plane by as much as 0.262 (3) Å.

**Experimental.** The compound (I) was synthesized as reported (Newkome, Puckett, Kiefer, Gupta, Fronczek, Pantaleo, McClure, Simpson & Deutsch, 1985) and recrystallized from dichloromethane/cyclohexane. An orange, prismatic crystal was mounted with epoxy on a glass fiber in random orientation. Details of data collection and structural refinement are given in Table 1.



The structure was solved using the Patterson heavy-atom method which revealed the position of Pd. The remaining atoms were located in successive difference Fourier syntheses. H-atom coordinates were

Table 1. *Experimental details*

Crystal	Orange, prismatic, 0.24 × 0.36 × 0.44 mm
Instrument	Enraf–Nonius CAD-4 diffractometer
Monochromator	Incident beam, graphite
Unit cell	25 reflections, 26.0 < 2θ < 27.9°
Mode	$\omega$ -2θ
Standards	400, 030, 003
Corrections	Background, Lorentz, polarization, empirical absorption (0.897–1.000 on <i>I</i> )
2θ range	2.0–56.0°
<i>hkl</i> ranges	<i>h</i> = 0 to 11 <i>k</i> = –13 to 13 <i>l</i> = –20 to 19
Reflections	6320 total 6157 unique 5327 with <i>I</i> > 3.0σ( <i>I</i> )
Solution	Patterson method
Function minimized	$\sum w( F_o  -  F_c )^2$
Weights	$4F_o^2 Lp^2 / [S^2(C + R^2B) + (0.020F_o^2)^2]$ , <i>S</i> = scan rate, <i>C</i> = integrated count, <i>R</i> = scan time/background time, <i>B</i> = background count
Parameters refined	334
<i>R</i> , <i>wR</i> , <i>R</i> (all)	0.032, 0.046, 0.043
Goodness of fit	2.14
Maximum shift/e.s.d.	0.01
$\Delta\rho$	0.85 (7), –0.39 (7) e Å <sup>-3</sup>

calculated assuming ideal geometry and were included in the refinement, constrained to ride the C atoms to which they are bonded; in addition, all H-atom isotropic temperature factors were set to 1.3 times *B<sub>eq</sub>* of each attached C.

The structure was refined in full-matrix least squares with Enraf–Nonius *SDP* (Frenz, 1978), where the function minimized was  $\sum w(|F_o| - |F_c|)^2$  and the weight *w* is defined as  $4F_o^2\sigma^2(F_o^2)$ . The final cycle of refinement included 334 variable parameters and converged to *R* = 0.032. Atomic scattering factors, including those for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974).

Final positional and equivalent isotropic thermal parameters are given in Table 2, and selected bond