Fig. 2. Hydrogen-bond scheme in (I). Hydrogen bonds are indicated by broken lines.

$O(4) \cdots N(3)$ 2·90 (1) Å with the $O \cdots H$ distances 2·1, 2·2 Å. Indeed, the orientation of the NO_2 group around the $Ni-N(3)$ bond facilitates formation of these hydrogen bonds as N(3), N(9) are as close as possible to the plane of the $Ni-NO_2$ fragment with deviations of only 0·05, 0·58 Å. It is clear then that Karn & Busch (1969) were correct in their view that the nitrite ion would find it difficult to N-bond to this side of the macrocycle. It is only the formation of the hydrogen bonds that permits this.

The O-bonded nitrite occupies the opposite less crowded* side of the macrocycle. N(1) takes up the least crowded positions over the pyridine ring [the $N(6)-Ni-O(1)-N(1)$ torsion angle is $-2\cdot0°$]. Thus the planes of the two nitrites are almost perpendicular,

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* Models indicate that this side also is too crowded to permit nitrite to bond through N.

the angle of intersection being 85·5°. O(2) is hydrogen bonded to two water molecules [O(5) at 2·75 (2) Å, $O(5)(\frac{1}{2} - x, -y, \frac{1}{2} - z)$ at 2·63 (2) Å] related by a centre of symmetry. It is surprising that despite these short distances the occupancy factor of the water molecule is only 0·5. This pattern of hydrogen bonding in the unit cell is illustrated in Fig. 2. Apart from this, there is one other short intermolecular distance that could represent a hydrogen bond – albeit a very weak one: $N(13) \cdots O(3)(-x, -y, -z)$ 3·15 Å, with an $N-H \cdots O$ angle of 163°. There are no other intermolecular distances less than the sum of the van der Waals radii.

References

DEWAR, R. & FLEISCHER, E. (1969). Nature (London), 222, 372–373.
DREW, M. G. B. & HOLLIS, S. (1980). Acta Cryst. B36, 718–720.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
KARN, J. L. & BUSCH, D. H. (1969). Inorg. Chem. 8, 1149–1153.
SHELDRICK, G. M. (1976). SHELX 76. Program for crystal structure determination. Univ. of Cambridge, England.

The Structure of Anhydrous Cadmium Formate

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Abstract. $Cd(CHO_2)_2$, $2CHO_2^- \cdot Cd^{2+}$, $M_r = 202\cdot44$, $C2/c$, $a = 11\cdot614$ (4), $b = 6\cdot185$ (3), $c = 12\cdot409$ (5) Å, $\beta = 112\cdot51$ (5)°, $Z = 8$, $D_c = 3\cdot266$ Mg m^{-3}. $R = 0\cdot053$ for 1634 independent reflexions. Formate ion (1) is tridentate and bridges symmetry-related cations. Both O atoms of the quadridentate formate ion (2) chelate one Cd atom and are also in bridging positions to two symmetry-related cations. Four-membered rings are a significant feature of the polymeric lattice thus formed. Cd is seven-coordinate in pseudo-octahedral geometry with Cd–O distances in the range 2·259 (4)–2·599 (7) Å.

Introduction. The isomorphism of the formate dihydrates of Ni^{II}, Cd, Zn, Mg, Mn^{II}, Fe^{II} and Cu^{II} has

been proved by investigations of the pure formates (Krogmann & Mattes, 1963; Post & Trotter, 1974a; Burger & Fuess, 1977; de With, Harkema & van Hummel, 1976; Osaki, Nakai & Watanabe, 1963, 1964; Kay, Almodovar & Kaplan, 1968; Bukowska-Strzyżewska, 1965; Hoy, de S. Barros, de S. Barros & Friedberg, 1965; Malard & Pascal, 1966a) as well as mixed formates (Ogata, Taga & Osaki, 1977a,b; March, Weber & Nagorny, 1973). Heating leads to dehydration by a mechanism which is similar for all the formates mentioned above (Masuda & Shishido, 1979). This might indicate isomorphism of the anhydrous formates, some of which are reported to exist in an unstable α and a stable β form (Malard & Pascal, 1966b; Dollimore, Gupta & Nowell, 1979). The

Table 1. *Atom coordinates* (×10^4) *and isotropic temperature factors* (Å^2 ×10^3)

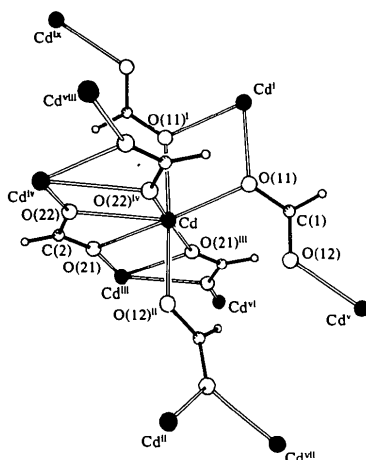|	x	y	z	U
Cd	3141 (1)	4872 (1)	4477 (1)	26 (1)*
O(11)	1913 (5)	1834 (7)	3875 (3)	37 (2)*
O(12)	1953 (4)	1778 (7)	2107 (3)	33 (2)*
C(1)	1672 (5)	986 (9)	2901 (4)	27 (2)*
H(1)	1245	−378	2753	50
C(2)	4752 (8)	8471 (12)	5935 (6)	45 (3)*
H(2)	5248	9668	6354	50
O(21)	5192 (7)	6981 (13)	5582 (6)	89 (4)*
O(22)	3656 (8)	8346 (13)	5733 (9)	115 (5)*

* Equivalent isotropic *U* calculated from anisotropic *U*.

Fig. 1. Perspective view of the interactions in Cd(CHO$_2$)$_2$. Atoms are given arbitrary radii. Superscripts refer to: (i) 0·5 − *x*, 0·5 − *y*, 1 − *z*; (ii) 0·5 − *x*, 0·5 + *y*, 0·5 − *z*; (iii) 1 − *x*, 1 − *y*, 1 − *z*; (iv) 0·5 − *x*, 1·5 − *y*, 1 − *z*; (v) 0·5 − *x*, −0·5 + *y*, 0·5 − *z*; (vi) 0·5 + *x*, −0·5 + *y*, *z*; (vii) *x*, 1 − *y*, −0·5 + *z*; (viii) −0·5 + *x*, 0·5 + *y*, *z*; (ix) *x*, 1 − *y*, 0·5 + *z*.

structure determination of the stable anhydrous Cd formate seemed, therefore, to be interesting.

Colourless prisms of anhydrous Cd formate were grown from a solution of Cd carbonate in aqueous formic acid (*ca* 50%) at about 350 K. Cell dimensions were obtained by least squares from the centring of 30 strong reflexions between 2θ = 20 and 30° on an automated Stoe four-circle diffractometer. A crystal *ca* 500 × 50 × 30 μm was used for the collection of 2028 diffractometer data up to 2θ = 70° with mono-chromated Mo *K*α radiation (λ = 0·7107 Å).

Although μ = 5·168 mm^{-1}, no empirical absorption correction could be found that improved the merging *R* for equivalent reflexions obtained by azimuthal scan. Probably anisotropic extinction effects have greater influence than absorption effects on the quality of the data.

After Lp corrections had been applied, equivalents averaged, and three low-angle reflexions omitted, 1634 independent *hkl* with *F* > 4σ(*F*) remained.

The structure was solved in *Cc* by Patterson methods and subsequent difference syntheses, and assigned as centrosymmetric only after several cycles of blocked-cascade least-squares refinement. H atoms could not be located but were positioned according to stereochemical criteria and refined as riding atoms with *U* = 0·05 Å^2.

After application of an empirical correction for isotropic extinction, the final difference map showed no further significant features; the final *R* was 0·053.

Atomic parameters are given in Table 1,* structural details in Fig. 1.

Discussion. As expected, and in contrast to Cd formate dihydrate (Post & Trotter, 1974*a*), there is only one crystallographic site for the cation in the present structure.

Each Cd is surrounded by 5 + 2 O atoms. Five O atoms, O(11), O(11)^i, O(12)^{ii}, O(21)^{iii} and O(22)^{iv}, from five different formates (three of which are symmetry related, Fig. 1), coordinate strongly to the Cd atom in a distorted square-pyramidal arrangement (for distances and angles see Table 2), the basal atoms and Cd being coplanar to within 0·07 Å. The variation in Cd—O distances [2·259 (4)−2·323 (5) Å] is within the range found for Cd formate dihydrate (Post & Trotter, 1974*a*).

Application of the empirical parameters of Brown & Wu (1976) for this fivefold coordination gives rise to a bond valence of 1·78 for Cd^{2+}. Only when the weaker interactions of both the O atoms of the chelating formate (2) with Cd are taken into account is the bond valence increased to 2·06, which seems more reason-

Table 2. *Distances* (Å) *and angles* (°) *within the coordination polyhedron with e.s.d.'s in parentheses*

For superscripts see Fig. 1.

Cd—O(11)	2·303 (4)	Cd—O(21)^{iii}	2·275 (9)
Cd—O(11)^i	2·323 (5)	Cd—O(22)	2·586 (9)
Cd—O(12)^{ii}	2·259 (4)	Cd—O(22)^{iv}	2·285 (10)
Cd—O(21)	2·599 (7)		
O(11)^i—Cd—O(11)	72·1 (2)	O(12)^{ii}—Cd—O(22)^{iv}	84·9 (3)
O(11)^i—Cd—O(21)	95·3 (2)	O(21)^{iii}—Cd—O(11)	90·4 (2)
O(11)^i—Cd—O(21)^{iii}	96·3 (2)	O(21)^{iii}—Cd—O(21)	69·5 (3)
O(11)^i—Cd—O(22)	85·7 (3)	O(21)^{iii}—Cd—O(22)	115·7 (3)
O(11)^i—Cd—O(22)^{iv}	89·3 (3)	O(22)^{iv}—Cd—O(11)	86·1 (2)
O(12)^{ii}—Cd—O(11)	109·0 (1)	O(22)^{iv}—Cd—O(21)	115·5 (3)
O(12)^{ii}—Cd—O(21)	85·8 (2)	O(22)^{iv}—Cd—O(22)	70·0 (3)
O(12)^{ii}—Cd—O(21)^{iii}	89·6 (3)	O(11)—Cd—O(21)	155·4 (2)
O(12)^{ii}—Cd—O(22)	90·8 (3)	O(11)—Cd—O(22)	147·6 (3)

able. The most regular polyhedron for sevenfold coordination, the pentagonal bipyramid, has been observed for Cd (Post & Trotter, 1974b; Drew, Hollis, McFall & Nelson, 1978), but seemed less likely a priori in the present structure considering the octahedral coordination of Cd in the formate dihydrate (Post & Trotter, 1974a). The polyhedron about the central metal might be characterized as distorted square-base trigonal-capped [basal atoms O(11), O(11)^i, O(22)^{iv} and O(22) are coplanar within 0·5 Å], as reported for Cd diacetate dihydrate (Harrison & Trotter, 1972), but is probably best described as a distorted pseudo-octahedron (because of the coplanarity, see above) in which one apical region is occupied by O(21) and O(22). The somewhat long Cd–O(21) and Cd–O(22) distances (ca 2·6 Å) are common for bridging O atoms of chelating carboxylate ligands (Harrison & Trotter, 1972; Post & Trotter, 1974b), though recently a similar distance has been reported for a non-chelating O in Cd maleate (Hempel, Hull, Ram & Gupta, 1979). Indeed, O(21) and O(22) also coordinate symmetry-related cations to make formate (2) quadridentate. Thus twisted strips of four-membered rings, each sharing two atoms, are formed along a (Fig. 1). Perpendicular to these strips, the polymeric structure is further extended by formate (1) bridging Cd cations approximately along c (Cd^{ix}···Cd···Cd^{vii} and Cd^i···Cd^v in Fig. 1). Moreover, O(11) coordinates a second Cd atom, thus giving rise to another four-membered ring [Cd, O(11)^i, Cd^i, O(11) in Fig. 1] and additionally linking the Cd–formate–Cd chains. The fact that the bridging and chelating atoms O(21) and O(22) are not equally shared between Cd atoms may explain the high thermal motion of these O atoms which may make the short bond distances and the small angle observed in formate (2) unreliable.

Distances and the angle in the non-chelating formate (1), however, are normal (Post & Trotter, 1974a; de With, Harkema & van Hummel, 1976; Burger & Fuess, 1977) and reflect the mesomeric state of this anion. Values are listed in Table 3. The structure of anhydrous Cd formate appears to be more closely related to those of Cd with higher carboxylates, especially to that of Cd malonate monohydrate (Post & Trotter, 1974b), than to that of Cd formate dihydrate. One fundamental difference is the impossibility of

strengthening the polymer by hydrogen bonds via water molecules, though some O atoms of symmetry-related formates are only 2·7 to 2·8 Å apart.

It is, therefore, difficult to speculate about the rearrangement of the lattice of Cd formate dihydrate upon dehydration.

References

BROWN, I. D. & WU, K. K. (1976). Acta Cryst. B32, 1957–1959.

BUKOWSKA-STRZYŻEWSKA, M. (1965). Acta Cryst. 19, 357–362.

BURGER, N. & FUESS, H. (1977). Z. Kristallogr. 145, 346–355.

DOLLIMORE, D., GUPTA, J. P. & NOWELL, D. V. (1979). Thermochim. Acta, 30, 339–350.

DREW, M. G. B., HOLLIS, S., MCFALL, S. G. & NELSON, S. M. (1978). J. Inorg. Nucl. Chem. 40, 1595–1596.

HARRISON, W. & TROTTER, J. (1972). J. Chem. Soc. Dalton Trans. pp. 956–960.

HEMPEL, A., HULL, S. E., RAM, R. & GUPTA, M. P. (1979). Acta Cryst. B35, 2215–2216.

HOY, G. R., DE S. BARROS, S., DE S. BARROS, F. & FRIEDBERG, S. A. (1965). J. Appl. Phys. 36, 936–937.

KAY, M. I., ALMODOVAR, I. & KAPLAN, S. F. (1968). Acta Cryst. B24, 1312–1316.

KROGMANN, K. & MATTES, R. (1963). Z. Kristallogr. 118, 291–302.

MALARD, C. & PASCAL, P. (1966a). C. R. Acad. Sci. Sér. C, 262, 736–738.

MALARD, C. & PASCAL, P. (1966b). C. R. Acad. Sci. Sér. C, 263, 480–483.

MARCH, J. F., WEBER, G. & NAGORNY, K. (1973). Z. Phys. Chem. (Frankfurt), 85, 97–105.

MASUDA, Y. & SHISHIDO, S. (1979). Thermochim. Acta, 28, 377–385.

OGATA, T., TAGA, T. & OSAKI, K. (1977a). Bull. Chem. Soc. Jpn, 50, 1674–1679.

OGATA, T., TAGA, T. & OSAKI, K. (1977b). Bull. Chem. Soc. Jpn, 50, 1680–1682.

OSAKI, K., NAKAI, Y. & WATANABÉ, (1963). J. Phys. Soc. Jpn, 18, 919.

OSAKI, K., NAKAI, Y. & WATANABÉ, T. (1964). J. Phys. Soc. Jpn, 19, 717–723.

POST, M. L. & TROTTER, J. (1974a). Acta Cryst. B30, 1880–1882.

POST, M. L. & TROTTER, J. (1974b). J. Chem. Soc. Dalton Trans. pp. 1922–1925.

WITH, G. DE, HARKEMA, S. & VAN HUMMEL, G. J. (1976). Acta Cryst. B32, 1980–1983.

Table 3. *Bond lengths (Å) and angles (°) of the formate anions with e.s.d.'s in parentheses*

C(1)–O(11)	1·247 (7)	O(11)–C(1)–O(12)	124·7 (5)
C(1)–O(12)	1·251 (8)	O(21)–C(2)–O(22)	115·8 (8)
C(2)–O(21)	1·214 (12)		
C(2)–O(22)	1·202 (13)		