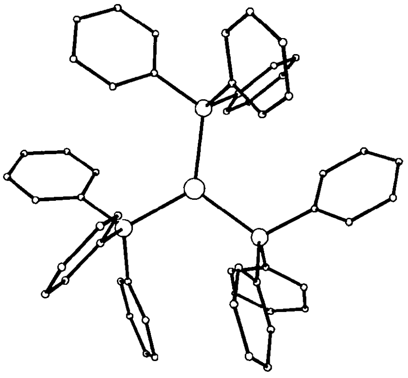

Fig. 1. The $[Au(Ph_3P)_3]^+$ cation.

in $[Au(SnCl_3)(Me_2PhP)_2]$ (Clegg, 1978) a long Au—Sn bond of 2·881 (1) Å is reflected in a wide P—Au—P angle of 153·8 (2)°. The compounds $L_2AuX$ [$X$ = Cl (Baenziger, Dittemore & Doyle, 1974), and $X$ = I (Beindorf & Strähle, 1980)] also exhibit P—Au—P angles wider than ideal [132·1 (1), 131·2 (3)° respectively], and the chloride shows a long Au—Cl bond of 2·500 (4) Å. The Au—I bond of the iodide is 2·776 (2) Å; no Au—I bonds are available for comparison. More regular geometry is only attained with three identical ligands, *e.g.* in the ternary compounds $Au_7P_{10}I$, possessing trigonal $AuP_3$ moieties with Au—P 2·339 (7) Å, P—Au—P 118·5 (2)°, site symmetry $3m$ (Jeitschko & Möller, 1979), and $Tl_6Au_2I_{10}$, possessing $AuI_3$ units with Au—I 2·74 (1), 2·81 (1) Å, all angles 120°, site symmetries 32 and $\bar{6}$ respectively (Stoeger & Rabenau, 1979). The only non-polymeric structure with three identical ligands is $L_3Au^+.B_9H_{19}S^-$ (Guggenberger, 1974). Despite the fact that this cation and that of the present compound are formally identical, they display significant structural differences. The thiadecaborate derivative displays less regular geometry, with Au—P 2·345, 2·384, 2·389 Å, P—Au—P 112·3, 121·5, 124·1°; the Au atom lies 0·2 Å out of the $P_3$ plane. (The first of these bond lengths was reported as 2·373 Å, but this is not consistent with the atomic coordinates and cell constants.) Differing phenyl-ring orientations in the two cations suggest that packing forces may be responsible for their structural differences. Neither compound displays unusually short non-bonded distances.

I thank Professor J. Strähle for making unpublished results available to me, and the Fonds der Chemischen Industrie for financial support. All calculations were carried out with programs written by Professor G. M. Sheldrick.

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*Acta Cryst.* (1980). B**36**, 3107–3109

# Iron(II) Formate Dihydrate

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(*Received* 13 *August* 1980; *accepted* 1 *September* 1980)

**Abstract.** $Fe(HCO_2)_2.2H_2O$, $2CHO_2^-.Fe^{2+}.2H_2O$, $M_r$ = 181·91, monoclinic, $P2_1/c$, $a$ = 8·740 (3), $b$ = 7·192 (3), $c$ = 9·428 (4) Å, $\beta$ = 97·47 (2)°, $Z$ = 4, $D_c$ = 2·056 Mg m$^{-3}$, $\mu_{\mathrm{Mo}\,K\alpha}$ = 2·483 mm$^{-1}$, $R$ = 0·032, $R_w$ = 0·028 for 1319 independent reflexions. The compound is isostructural with isomorphous formate dihydrates of other bivalent metals; coordination distances range from 2·084 (2) to 2·180 (2) Å.

**Introduction.** The isomorphous formate dihydrates of Mg (de With, Harkema & van Hummel, 1976), Zn (Burger & Fuess, 1977), Cd (Post & Trotter, 1974), $Co^{II}$ (Antsyshkina, Guseinova & Porai-Koshits, 1967), $Ni^{II}$ (Krogmann & Mattes, 1963), $Cu^{II}$ (Bukowska-Strzyżewska, 1965; Kay, Almodovar & Kaplan, 1968), $Mn^{II}$ (Osaki, Nakai & Watanabé, 1964; Kay, Almodovar & Kaplan, 1968) and $Fe^{II}$ (Hoy, de S.

0567-7408/80/123107-03$01.00

Barros, de S. Barros & Friedberg, 1965; Malard & Pascal, 1966) are known to form mixed crystals in which one cation species sometimes prefers one of the two metal sites present in the asymmetric unit (Ogata, Taga & Osaki, 1977*a*,*b*; Nagorny & March, 1972; March, Weber & Nagorny, 1973; Wagner, Schumacher & Friedberg, 1966). The extent of this preferential site occupation seems to be related to structural (for references see above) and magnetic properties (Wagner, Schumacher & Friedberg, 1966; Burlet, Burlet, Rossat-Mignod, de Combarieu & Bedin, 1975; Yamakawa & Matsuura, 1976; Burlet, Rossat-Mignod & Matsuura, 1979) of the pure salts. Since for $Fe^{II}$ formate dihydrate, only cell dimensions determined from powder data have been reported so far, the present investigation was undertaken to provide more accurate structural information.

Colourless platelets were grown by diffusion of ethanol into a saturated solution of $Fe^{II}$ formate prepared from metal powder and aqueous formic acid (*ca* 50%). Cell dimensions were obtained by least squares from 28 strong reflexions between $2\theta = 18$ and 27° on an automated four-circle diffractometer with monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). A crystal $0{\cdot}3 \times 0{\cdot}4 \times 0{\cdot}1$ mm, sealed in a glass capillary, was used for data collection in a profile-fitting procedure (Clegg, 1981). From 1935 measured reflexions with $6 < 2\theta < 60°$, 1319 unique data with $F > 4\sigma(F)$ were obtained after equivalent reflexions had been averaged. Lp corrections and an empirical absorption correction based on measurements of equivalent reflexions at different azimuthal angles were applied.

Starting from the parameters of Zn formate dihydrate (Burger & Fuess, 1977), anisotropic blocked-cascade least-squares refinement of non-hydrogen atoms and a subsequent difference synthesis yielded the positions of all H atoms. Those of the water molecules were assigned one common isotropic temperature factor which was allowed to vary, and O—H vectors were held constant. H atoms of the formate ions were refined isotropically without constraints.

Omission of five low-angle reflexions and inclusion of an isotropic extinction correction [$F^* = F(1 - xF^2/\sin\theta)$, $x = 1{\cdot}35\,(6) \times 10^{-6}$] resulted in a final $R = 0{\cdot}032$ and $R_w = 0{\cdot}028$ [$w = 1/\sigma^2(F)$]. Atom parameters are listed in Table 1,† bond distances and angles in Table 2.

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* ($Å^2 \times 10^4$)

| | $x$ | $y$ | $z$ | $U_{eq}$* |
|---|---|---|---|---|
| Fe(1) | 0 | 0 | 0 | 132 (1)* |
| Fe(2) | 5000 | 5000 | 0 | 175 (1)* |
| C(1) | 363 (3) | 2232 (3) | 2741 (2) | 238 (7)* |
| H(1) | −628 (32) | 2836 (39) | 2252 (24) | 581 (83) |
| C(2) | 3257 (3) | 6167 (4) | 4359 (2) | 233 (7)* |
| H(2) | 3301 (30) | 4904 (32) | 3991 (25) | 315 (69) |
| O(1) | 979 (2) | 1065 (2) | 2020 (1) | 219 (5)* |
| O(2) | 877 (2) | 2712 (2) | 3996 (2) | 220 (5)* |
| O(3) | 4363 (2) | 7222 (2) | 4207 (2) | 273 (5)* |
| O(4) | 2110 (2) | 6573 (2) | 4970 (2) | 232 (5)* |
| O(5) | 2757 (2) | 4769 (2) | 695 (2) | 235 (5)* |
| H(51) | 2095 | 3992 | 201 | 555 (48) |
| H(52) | 2343 | 6003 | 576 | 555 (48) |
| O(6) | 4118 (2) | 1055 (3) | 3002 (2) | 376 (6)* |
| H(61) | 3100 | 956 | 2652 | 555 (48) |
| H(62) | 4663 | 1179 | 2379 | 555 (48) |

* $U_{eq} = \frac{1}{3}$ of the trace of the orthogonalized $U_{ij}$ matrix.

Table 2. *Bond distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| C(1)—O(1) | 1·246 (3) | C(2)—O(3) | 1·252 (3) |
| C(1)—O(2) | 1·258 (3) | C(2)—O(4) | 1·254 (3) |
| C(1)—H(1) | 1·02 (3) | C(2)—H(2) | 0·98 (2) |
| O(1)—C(1)—O(2) | 124·8 (2) | O(3)—C(2)—O(4) | 125·9 (2) |
| O(1)—C(1)—H(1) | 116 (1) | O(3)—C(2)—H(2) | 117 (2) |
| O(2)—C(1)—H(1) | 119 (1) | O(4)—C(2)—H(2) | 117 (2) |
| O(5)—H(51) | 0·891 | O(6)—H(61) | 0·910 |
| O(5)—H(52) | 0·959 | O(6)—H(62) | 0·808 |
| H(51)—O(5)—H(52) | 108·0 | H(61)—O(6)—H(62) | 112·8 |

**Discussion.** Except for $c$, which differs by about 0·06 Å, cell dimensions obtained in the present study confirm those of Malard & Pascal (1966) ($a = 8{\cdot}74$, $b = 7{\cdot}18$, $c = 9{\cdot}37$ Å, $\beta = 97{\cdot}45°$). General features of the structure displayed in Fig. 1 can be summarized as follows: $Fe(1)^{2+}$ ions occupy $A$ sites, *i.e.* they are octahedrally coordinated to $HCOO^-$ groups only. They are linked in (100) by bridging formates (1) [O(1),C(1),O(2)] to form planes in which antiferromagnetic interactions of neighbouring cations (1), *via* the delocalized $\pi$-electron clouds of the anions, are observed (Burlet, Burlet, Rossat-Mignod, de Combarieu & Bedin, 1975; Hoy, de S. Barros, de S. Barros & Friedberg, 1965). On $B$ sites, however, four water molecules surround each $Fe(2)^{2+}$ ion and thus preclude a coupling of these cations in (200). Both (100) and (200) sheets are connected by bridging formates (2) [O(3),C(2),O(4)] which allows an additional $A$–$B$ coupling (Burlet, Burlet, Rossat-Mignod, de Combarieu & Bedin, 1975) and completes the coordination octahedra of $Fe(2)^{2+}$ ions.

Fe—O distances in both polyhedra (Table 3) are comparable to those found in $Fe^{II}$ oxalate dihydrate (Deyrieux & Peneloux, 1969) and about 0·02 Å longer than in Zn formate (Burger & Fuess, 1977), though the radii of both cations are considered to be of the same size (*Handbook of Chemistry and Physics*, 1970). The greatest difference is for Fe(2)—O(5) (0·05 Å). As in

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35630 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

other formates, the O atoms of sheet-linking formates (2) display the longest distances to the cation. The rather short contact between Fe(2) and O(6) may be due to the strong anisotropic motion of this atom (Fig. 1) which was also found in the respective Zn compound (Burger & Fuess, 1977).

The lattice is further strengthened by a system of hydrogen bridges, which is described in Table 4.

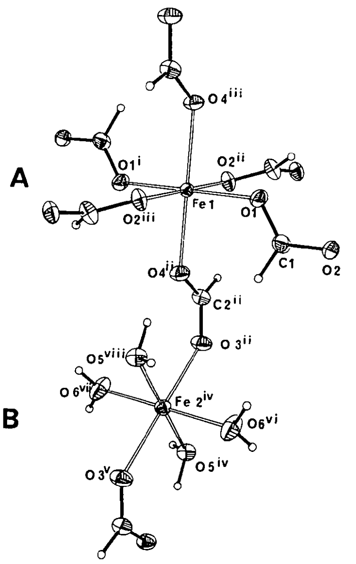

Fig. 1. A perspective plot of the two coordination octahedra. Thermal ellipsoids indicate 50% probability; radii of H atoms are arbitrary. Positions of atoms with superscripts are derived from coordinates given in Table 1 by: (i) $-x, -y, -z$; (ii) $-x, -0{\cdot}5 + y, 0{\cdot}5 - z$; (iii) $x, 0{\cdot}5 - y, -0{\cdot}5 + z$; (iv) $-1 + x, y, z$; (v) $-1 + x, 1{\cdot}5 - y, -0{\cdot}5 + z$; (vi) $-x, 0{\cdot}5 + y, 0{\cdot}5 - z$; (vii) $-1 + x, 0{\cdot}5 - y, -0{\cdot}5 + z$; (viii) $-x, 1 - y, -z$.

Table 3. *Coordination distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Fe(1)–O(1) | 2·127 (1) | Fe(2)–O(5) | 2·153 (2) |
| Fe(1)–O(2)$^{i}$ | 2·093 (2) | Fe(2)–O(3)$^{ii}$ | 2·180 (2) |
| Fe(1)–O(4)$^{i}$ | 2·167 (2) | Fe(2)–O(6)$^{iii}$ | 2·084 (2) |
| O(1)–Fe(1)–O(2)$^{i}$ | 90·4 (1) | O(3)$^{ii}$–Fe(2)–O(5) | 91·5 (1) |
| O(1)–Fe(1)–O(4)$^{i}$ | 92·6 (1) | O(3)$^{ii}$–Fe(2)–O(6)$^{iii}$ | 88·6 (1) |
| O(2)$^{i}$–Fe(1)–O(4)$^{i}$ | 92·4 (1) | O(5)–Fe(2)–O(6)$^{iii}$ | 89·8 (1) |

Superscripts refer to: (i) $-x, -0{\cdot}5 + y, 0{\cdot}5 - z$; (ii) $1 - x, -0{\cdot}5 + y, 0{\cdot}5 - z$; (iii) $1 - x, 0{\cdot}5 + y, 0{\cdot}5 - z$.

Table 4. *Distances* (Å) *and angles* (°) *within the system of hydrogen bridges*

| | | | |
|---|---|---|---|
| O(1)···O(6) | 2·779 (2) | O(1)···H(61) | 1·874 (2) |
| O(2)···O(5)$^{v}$ | 2·787 (2) | O(2)···H(51)$^{v}$ | 1·901 (2) |
| O(3)···O(6)$^{iv}$ | 2·743 (2) | O(3)···H(62)$^{iv}$ | 1·963 (2) |
| O(4)···O(5)$^{vi}$ | 2·758 (2) | O(4)···H(52)$^{vi}$ | 1·838 (2) |

| | |
|---|---|
| O(1)···H(61)–O(6) | 172·6 (1) |
| O(2)···H(51)$^{v}$–O(5)$^{v}$ | 172·9 (1) |
| O(3)···H(62)$^{iv}$–O(6)$^{iv}$ | 161·9 (1) |
| O(4)···H(52)$^{vi}$–O(5)$^{vi}$ | 159·9 (1) |

Superscripts refer to: (iv) $1 - x, 0{\cdot}5 + y, 0{\cdot}5 - z$; (v) $x, 0{\cdot}5 - y, 0{\cdot}5 + z$; (vi) $x, 1{\cdot}5 - y, 0{\cdot}5 + z$.

Calculations were performed with programs written by Professor G. M. Sheldrick, Göttingen.

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