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Hydrogen Atom Positions in Manganous Formate Dihydrate and a Rerefinement of Copper Formate Dihydrate

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(Received 31 May 1967 and in revised form 26 October 1967)

Three zones of neutron diffraction data were obtained for $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$ and the positions of the hydrogen atoms determined. The hydrogen bonding scheme proposed by Osaki, Nakai and Watanabe was found to be correct. The crystal structure of copper formate dihydrate was rerefined by means of the method of least squares. Some changes in bond distances were noted.

Introduction

Manganous formate dihydrate, $\text{Mn}(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$, is representative of a large number of more or less isostructural formate dihydrates having bivalent cations of similar ionic radius. The space group of these compounds is $P2_1/c$. There are four formula weights per unit cell with two independent metal ions in two kinds of twofold special positions and two independent formate ions and water molecules in the fourfold general positions. The structures of the Mg, Zn, and Mn salts have been determined by Osaki, Nakai & Watanabe (1963, 1964; hereafter referred to as ONW), the Ni salt by Krogman & Mattes (1963), and the Cu salt by Bukowska-Strzyzewska (1965; BS). The Cd and Fe salts (Hoy, Barros, Barros & Friedberg, 1965) are also known to be of similar structure. Since these compounds have important magnetic properties (Abe & Matsura, 1964; Abe, Morigaki, Matsura, Torii & Yamagata, 1964; Abe & Torii, 1965; Hoy *et al.*, 1965), and Cohen, Friedberg & Wagner (1964), it was decided to determine the hydrogen positions in at least one of them to permit a better correlation of structure with other properties, particularly proton magnetic resonance spectra. The chemical binding, and its relationship to different degrees of hydration of the copper salt, is also of interest in its own right.

The structure of copper formate tetrahydrate was determined by Kiriya, Ibamoto & Matsuo (1954) and refined with neutron data by Okada, Kay, Cromer & Almodovar (1966), who found layers of copper formate alternating with layers of water containing disordered hydrogen atoms. The dihydrate structures are characterized by (100) layers of metal formate similar to the (001) layers of the $P2_1/a$ tetrahydrate, with the metal atoms at 0, 0, 0 and $0, \frac{1}{2}, \frac{1}{2}$. In the second layer near $x = \frac{1}{2}$, however, there is a second set of metal ions at $\frac{1}{2}, \frac{1}{2}, 0$ and $\frac{1}{2}, 0, \frac{1}{2}$, connected to the first set by a formate group and also connected to four water oxygen atoms which complete a coordination octahedron. That is, the metal ions of the first set at $x = 0$ are each surrounded by an octahedron of six formate oxygens while those of the second set at $x = \frac{1}{2}$ are each surrounded by an octahedron of two formate oxygen atoms and four water oxygen atoms. The metal atoms and formate groups thus form a three-dimensional network, in contrast to the two-dimensional system found in the tetrahydrate. All metal atoms are on symmetry centers. A stereoscopic view of the structure is given in Fig. 1.

The present work is concerned with the determination of the hydrogen positions in manganous formate dihydrate and a rerefinement of the structure of copper formate dihydrate. BS found large differences in the C–O distances in the latter compound which she ascribed to differences in Cu–O distances which in turn cause one C–O bond to have considerably more double-bond character than the other. This effect was not ob-

* Work carried out under the auspices of the U.S. Atomic Energy Commission.

served in manganous formate dihydrate. Since the refinement of BS was based on a Fourier synthesis with the Cu atoms removed, it was decided to carry out a least-squares refinement on the three zones of her published data to check this anomaly. Further evidence for the conjecture that Cu–O distances strongly affect C–O distances is given by the structure of $\text{CuBa}_2(\text{HCOO})_6 \cdot 4\text{H}_2\text{O}$ determined by Sundara Rau, Sundaramma & Sirasankara Rau (1958). These authors found C–O distances varying from 1.24 to 1.43 Å. The structure is based on a difference Fourier refinement of two zones of data taken on the triclinic ($P\bar{1}$) crystal. It is probably less precise than BS's structure which has standard deviations for the light atoms of about 0.1 Å ($\sigma_x = \sigma_y = \sigma_z$ was given as 0.01 for oxygen and 0.014 for carbon).

Manganous formate dihydrate

The cell data of ONW ($a=8.86$, $b=7.18$, $c=9.39$ Å; $\beta=97.6^\circ$), were used in this determination. Three zones of neutron diffraction data were taken by means of θ - 2θ step scans on two manganous formate dihydrate crystals grown from water solution. The $h0l$ data were collected on the first crystal and the $0kl$ and $hk0$ on the second. The crystals were plate-like, the large face being perpendicular to c^* with $\{100\}$, $\{110\}$, and $\{1\bar{1}0\}$ pairs of faces developed as described by Mascarenhas (1964). The crystals were of the order of 2 mm thick with 3 to 4 mm between members of the above mentioned pairs of faces. The $0kl$ and $h0l$ reflections were taken on a two (ω , 2θ) axis diffractometer. The $hk0$ reflections were collected with a Picker goniostat varying χ and 2θ appropriately. The wave length was 1.06 Å. A total of 282 reflections were collected, 213 of them of measurable intensity. A measurement was considered to give zero intensity when, from counting sta-

tistics, the intensity was less than twice its standard deviation. The effective linear absorption coefficient from the incoherent scattering cross section is 2.1 cm^{-1} . Neglect of this probably caused a 6 or 7% error in intensity in the worst cases. However, since the average error in intensity was of the order of 10% owing to high background and low reactor intensity and insufficient data were collected for the determination of anisotropic thermal parameters, no correction was made.

These coordinates were then refined with isotropic temperature factors by means of the method of least squares (based on F) and a set of distances calculated with programs by Cromer, Roof & Larson (1964, 1965). A least-squares weighting function $W=1/(\sigma^2(F)+0.05F^2)$ was used, where $\sigma(F)$ is the standard deviation of the structure factor calculated from counting statistics. An extinction correction of the form $|F_{\text{obs}}| = K|F_{\text{calc}}|/(1+gF_{\text{calc}}^2/\sin 2\theta)$ was included in the least-squares programs. The parameters g for the three projections are $(1.22, 23.4, 72.1) \times 10^{-5}$. The final R value ($\sum |F_o - F_c| / \sum |F_o|$) is 0.11. The neutron scattering lengths used were -0.360 for Mn, 0.661 for C, 0.577 for O, and -0.378 for H, all $\times 10^{-12}$ cm. A table of F_{obs} and F_{calc} is given as Table 1. Further difference maps showed no significant density. The final coordinates are given in Table 2 together with the coordinates of ONW. The distances and angles are given in Table 3 together with the results of ONW. The O–H and C–H distances are listed together with the results of a correction for thermal motion, as given by Busing & Levy (1964), in square brackets.

Although the O–H distances in water 1 are slightly high, a shift of σ puts them into the range of usual hydrogen bond distances given by Hamilton (1962). The results are in agreement with the hydrogen bonding scheme proposed by ONW.

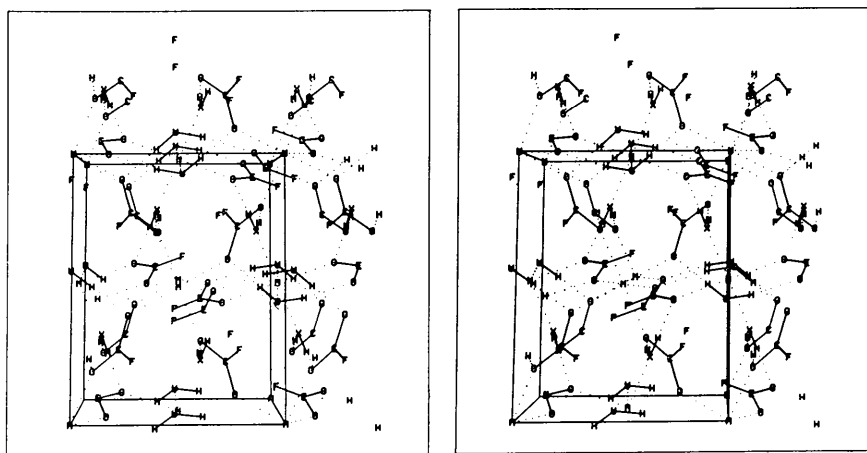


Fig. 1. Stereoscopic view of manganous formate dihydrate looking along the $[100]$ direction. The b axis is horizontal and the c axis is vertical. The symbols are: $M = \text{Mn}(1)$, $N = \text{Mn}(2)$, $C = \text{C}(1)$, $E = \text{C}(2)$, $O =$ all formate oxygen atoms, *i.e.* $\text{O}(1) + \text{O}(2) + \text{O}(3) + \text{O}(4)$, $F =$ formate hydrogen atoms, $H_F(1) + H_F(2)$, $W = \text{O}_w(1)$, $X = \text{O}_w(2)$, $H =$ water hydrogen atoms, $H_w(1) + H_w(2) + H_w(3) + H_w(4)$. The figure was produced by the Sc-4020 microfilm plotter using a code developed by Larson (1966).

It may be noted from Table 2 that the two formate hydrogen atoms have very large amplitudes of thermal motion. Fig. 1 shows that there is a good deal of room about these atoms. Closest interionic approaches are greater than 2.5 Å.

Copper formate dihydrate

The published data of BS were refined by means of the method of least squares (Cromer *et al.*, 1964, 1965)

with a weight $W=1/(F_o+0.02F^2)^{1/2}$. The final $R=0.095$ is about the same as that found by BS. Coordinates are given in Table 4, distances and angles in Table 3. BS's results are noted in parentheses. For the sake of easy comparison with the isostructural Mn compound the Cu salt coordinates were transformed from the origin used by BS to that used in the present study of Mn formate and by ONW. The reported lattice parameters are: $a=8.54$, $b=7.15$, $c=9.59$ Å; $\beta=96^\circ 48'$.

Table 1. Observed and calculated structure factors ($\times 100$) for manganous formate dihydrate

H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c	H	K	L	F _o	F _c
0	0	0	533	-571	0	0	0	533	-571	0	0	0	533	-571	0	0	0	533	-571	0	0	0	533	-571
0	2	0	287	-251	0	2	0	287	-251	0	2	0	287	-251	0	2	0	287	-251	0	2	0	287	-251
0	4	0	163	-153	0	4	0	163	-153	0	4	0	163	-153	0	4	0	163	-153	0	4	0	163	-153
0	6	0	107	-107	0	6	0	107	-107	0	6	0	107	-107	0	6	0	107	-107	0	6	0	107	-107
0	8	0	67	-67	0	8	0	67	-67	0	8	0	67	-67	0	8	0	67	-67	0	8	0	67	-67
0	10	0	44	-44	0	10	0	44	-44	0	10	0	44	-44	0	10	0	44	-44	0	10	0	44	-44
0	12	0	29	-29	0	12	0	29	-29	0	12	0	29	-29	0	12	0	29	-29	0	12	0	29	-29
0	14	0	19	-19	0	14	0	19	-19	0	14	0	19	-19	0	14	0	19	-19	0	14	0	19	-19
0	16	0	13	-13	0	16	0	13	-13	0	16	0	13	-13	0	16	0	13	-13	0	16	0	13	-13
0	18	0	9	-9	0	18	0	9	-9	0	18	0	9	-9	0	18	0	9	-9	0	18	0	9	-9
0	20	0	6	-6	0	20	0	6	-6	0	20	0	6	-6	0	20	0	6	-6	0	20	0	6	-6
0	22	0	4	-4	0	22	0	4	-4	0	22	0	4	-4	0	22	0	4	-4	0	22	0	4	-4
0	24	0	3	-3	0	24	0	3	-3	0	24	0	3	-3	0	24	0	3	-3	0	24	0	3	-3
0	26	0	2	-2	0	26	0	2	-2	0	26	0	2	-2	0	26	0	2	-2	0	26	0	2	-2
0	28	0	1	-1	0	28	0	1	-1	0	28	0	1	-1	0	28	0	1	-1	0	28	0	1	-1
0	30	0	1	1	0	30	0	1	1	0	30	0	1	1	0	30	0	1	1	0	30	0	1	1
0	32	0	1	1	0	32	0	1	1	0	32	0	1	1	0	32	0	1	1	0	32	0	1	1
0	34	0	1	1	0	34	0	1	1	0	34	0	1	1	0	34	0	1	1	0	34	0	1	1
0	36	0	1	1	0	36	0	1	1	0	36	0	1	1	0	36	0	1	1	0	36	0	1	1
0	38	0	1	1	0	38	0	1	1	0	38	0	1	1	0	38	0	1	1	0	38	0	1	1
0	40	0	1	1	0	40	0	1	1	0	40	0	1	1	0	40	0	1	1	0	40	0	1	1
0	42	0	1	1	0	42	0	1	1	0	42	0	1	1	0	42	0	1	1	0	42	0	1	1
0	44	0	1	1	0	44	0	1	1	0	44	0	1	1	0	44	0	1	1	0	44	0	1	1
0	46	0	1	1	0	46	0	1	1	0	46	0	1	1	0	46	0	1	1	0	46	0	1	1
0	48	0	1	1	0	48	0	1	1	0	48	0	1	1	0	48	0	1	1	0	48	0	1	1
0	50	0	1	1	0	50	0	1	1	0	50	0	1	1	0	50	0	1	1	0	50	0	1	1
0	52	0	1	1	0	52	0	1	1	0	52	0	1	1	0	52	0	1	1	0	52	0	1	1
0	54	0	1	1	0	54	0	1	1	0	54	0	1	1	0	54	0	1	1	0	54	0	1	1
0	56	0	1	1	0	56	0	1	1	0	56	0	1	1	0	56	0	1	1	0	56	0	1	1
0	58	0	1	1	0	58	0	1	1	0	58	0	1	1	0	58	0	1	1	0	58	0	1	1
0	60	0	1	1	0	60	0	1	1	0	60	0	1	1	0	60	0	1	1	0	60	0	1	1
0	62	0	1	1	0	62	0	1	1	0	62	0	1	1	0	62	0	1	1	0	62	0	1	1
0	64	0	1	1	0	64	0	1	1	0	64	0	1	1	0	64	0	1	1	0	64	0	1	1
0	66	0	1	1	0	66	0	1	1	0	66	0	1	1	0	66	0	1	1	0	66	0	1	1
0	68	0	1	1	0	68	0	1	1	0	68	0	1	1	0	68	0	1	1	0	68	0	1	1
0	70	0	1	1	0	70	0	1	1	0	70	0	1	1	0	70	0	1	1	0	70	0	1	1
0	72	0	1	1	0	72	0	1	1	0	72	0	1	1	0	72	0	1	1	0	72	0	1	1
0	74	0	1	1	0	74	0	1	1	0	74	0	1	1	0	74	0	1	1	0	74	0	1	1
0	76	0	1	1	0	76	0	1	1	0	76	0	1	1	0	76	0	1	1	0	76	0	1	1
0	78	0	1	1	0	78	0	1	1	0	78	0	1	1	0	78	0	1	1	0	78	0	1	1
0	80	0	1	1	0	80	0	1	1	0	80	0	1	1	0	80	0	1	1	0	80	0	1	1
0	82	0	1	1	0	82	0	1	1	0	82	0	1	1	0	82	0	1	1	0	82	0	1	1
0	84	0	1	1	0	84	0	1	1	0	84	0	1	1	0	84	0	1	1	0	84	0	1	1
0	86	0	1	1	0	86	0	1	1	0	86	0	1	1	0	86	0	1	1	0	86	0	1	1
0	88	0	1	1	0	88	0	1	1	0	88	0	1	1	0	88	0	1	1	0	88	0	1	1
0	90	0	1	1	0	90	0	1	1	0	90	0	1	1	0	90	0	1	1	0	90	0	1	1
0	92	0	1	1	0	92	0	1	1	0	92	0	1	1	0	92	0	1	1	0	92	0	1	1
0	94	0	1	1	0	94	0	1	1	0	94	0	1	1	0	94	0	1	1	0	94	0	1	1
0	96	0	1	1	0	96	0	1	1	0	96	0	1	1	0	96	0	1	1	0	96	0	1	1
0	98	0	1	1	0	98	0	1	1	0	98	0	1	1	0	98	0	1	1	0	98	0	1	1
0	100	0	1	1	0	100	0	1	1	0	100	0	1	1	0	100	0	1	1	0	100	0	1	1
0	102	0	1	1	0	102	0	1	1	0	102	0	1	1	0	102	0	1	1	0	102	0	1	1
0	104	0	1	1	0	104	0	1	1	0	104	0	1	1	0	104	0	1	1	0	104	0	1	1
0	106	0	1	1	0	106	0	1	1	0	106	0	1	1	0	106	0	1	1	0	106	0	1	1
0	108	0	1	1	0	108	0	1	1	0	108	0	1	1	0	108	0	1	1	0	108	0	1	1
0	110	0	1	1	0	110	0	1	1	0	110	0	1	1	0	110	0	1	1	0	110	0	1	1
0	112	0	1	1	0	112	0	1	1	0	112	0	1	1	0	112	0	1	1	0	112	0	1	1
0	114	0	1	1	0	114	0	1	1	0	114	0	1	1	0	114	0	1	1	0	114	0	1	1
0	116	0	1	1	0	116	0	1	1	0	116	0	1	1	0	116	0	1	1	0	116	0	1	1
0	118	0	1	1	0	118	0	1	1	0	118	0	1	1	0	118	0	1	1	0	118	0	1	1
0	120	0	1	1	0	120	0	1	1	0	120	0	1	1	0	120	0	1	1	0	120	0	1	1
0	122	0	1	1	0	122	0	1	1	0	122	0	1	1	0	122	0	1	1	0	122	0	1	1
0	124	0	1	1	0	124	0	1	1	0	124	0	1	1	0	124	0	1	1	0	124	0	1	1
0	126	0	1	1	0	126	0	1	1	0	126	0	1	1	0	126	0	1	1	0	126	0	1	1
0	128	0	1	1	0	128	0	1	1	0	128	0	1	1	0	128	0	1	1	0	128	0	1	1
0	130	0	1	1	0	130	0	1	1	0	130	0	1	1	0	130	0	1	1	0	130	0	1	1
0	132	0	1	1	0	132	0	1	1	0	132	0	1	1	0	132	0	1	1	0	132	0	1	1
0	134	0	1	1	0	134	0	1	1	0	134	0	1	1	0	134	0	1	1	0	134	0	1	1
0	136	0	1	1	0	136	0	1	1	0	136	0	1	1	0	136	0	1	1	0	136	0	1	1
0	138	0	1	1	0	138	0	1	1	0	138	0	1	1	0	138	0	1	1	0	138	0	1	1
0	140	0	1	1	0	140	0	1	1	0	140	0	1	1	0	140	0	1	1	0	140	0	1	1
0	142	0	1	1	0	142																		

The present refinement does not seem to indicate much significant difference in C–O bond length. BS's O(5)–O(4) [our O_w(2)–O(3)] distance of 2.99 Å, which was identified as a hydrogen bond, is not analogous to the hydrogen bond found in the manganese compound. Rather if the O(4) related by a screw axis is taken, a distance of 2.76 Å, or 2.67 Å in the present refinement results. This latter approach is equivalent to the hydrogen bond determined in manganous formate dihydrate.

Conclusions

It has been shown, at least in the case of manganese formate dihydrate, that an ordered hydrogen bonding scheme exists in the dihydrates. The same is probably true of the isostructural copper formate dihydrate and the other similar transition metal compounds. The high thermal parameters of the formate hydrogen are probably simply due to the lack of close intermolecular approaches in the vicinity of the atom.

Table 3. Bond distances and angles in manganese and copper formate dihydrates with standard deviations

X-ray results for the Mn (ONW) and the previous X-ray refinement of the copper compound (BS) are given in parentheses. The corrected values of bond distances involving hydrogens due to the hydrogen 'riding' on the oxygen are given in square brackets. Standard deviations refer to rightmost digit.

	Manganese		Copper	
I. Metal–oxygen octahedra				
M(1)–O(1)	2.172 ± 12	(2.15)	2.304 ± 18	(2.28)
M(1)–O(2)	2.135 ± 17	(2.15)	1.988 ± 16	(2.02)
M(1)–O(4)	2.218 ± 14	(2.21)	2.019 ± 17	(2.03)
O(1)–M(1)–O(2)	89.7 ± 5	(88.7)	89.2 ± 7	(90)
O(1)–M(1)–O(4)	88.4 ± 5	(88.2)	88.5 ± 6	(87)
O(2)–M(1)–O(4)	88.1 ± 5	(87.3)	86.8 ± 7	(89)
M(2)–O(3)	2.219 ± 15	(2.21)	2.368 ± 19	(2.35)
M(2)–O _w (1)	2.216 ± 13	(2.24)	2.044 ± 17	(2.02)
M(2)–O _w (2)	2.168 ± 15	(2.16)	1.974 ± 15	(1.97)
O(3)–M(2)–O _w (1)	86.6 ± 5	(87.0)	87.6 ± 6	(88)
O(3)–M(2)–O _w (2)	89.1 ± 6	(88.4)	86.9 ± 6	(87)
O _w (1)–M(2)–O _w (2)	89.8 ± 5	(89.8)	87.5 ± 7	(89)
II. Formate groups				
C(1)–O(1)	1.26 ± 2	(1.25)	1.26 ± 3	(1.29)
C(1)–O(2)	1.27 ± 2	(1.26)	1.30 ± 3	(1.19)
O(1)–C(1)–O(2)	124.5 ± 12	(1.26)	121 ± 2	(124)
C(1)–H _F (1)	1.05 ± 5	[1.11]		
O(1)–C(1)–H _F (1)	117 ± 4			
O(2)–C(1)–H _F (1)	119 ± 4			
C(2)–O(3)	1.25 ± 2	(1.25)	1.26 ± 3	(1.27)
C(2)–O(4)	1.26 ± 2	(1.27)	1.24 ± 3	(1.21)
C(2)–H _F (2)	1.03 ± 5	[1.08]		
O(3)–C(2)–O(4)	123 ± 1	(128)	130 ± 2	(124)
O(3)–C(2)–H _F (2)	118 ± 2			
O(4)–C(2)–H _F (2)	119 ± 2			
III. Hydrogen bonds and water molecules				
O _w (1)–H _w (1)	1.00 ± 4	[1.02]		
O _w (1)–H _w (2)	0.99 ± 4	[1.01]		
H(1)–O _w (1)–H(2)	109 ± 2			
O _w (1)–O(4)	2.75 ± 2	(2.73)	2.78 ± 2	(2.85)
H _w (1)–O(4)	1.79 ± 4			
O _w (1)–H _w (1)–O(4)	158 ± 3			
O _w (1)–O(2)	2.79 ± 2	(2.81)	2.82 ± 2	(2.82)
H _w (2)–O(2)	1.80 ± 3			
O _w (1)–H _w (2)–O(2)	177 ± 3			
O _w (2)–H _w (3)	0.95 ± 3	[0.96]		
O _w (2)–H _w (4)	0.89 ± 3	[0.89]		
H _w (3)–O _w (2)–H _w (4)	107 ± 2			
O _w (2)–O(1)	2.80 ± 2	(2.81)	2.77 ± 3	(2.79)
O(1)–H _w (3)	1.86 ± 3			
O _w (2)–H _w (3)–O(1)	172 ± 3			
O _w (2)–O(3)	2.75 ± 2	(2.75)	2.67 ± 2	(2.76)
O(3)–H _w (4)	1.86 ± 3			
O _w (2)–H _w (4)–O(3)	178 ± 2			

Table 4. *Copper formate dihydrate. Rerefined parameters and standard deviations from X-ray data of M. Bukowska-Strzyewska. Original parameters in parentheses*

	Standard deviations refer to right-most digit.			
	X	Y	Z	B
Cu(1)	0	0	0	1.4 ± 1
Cu(2)	$\frac{1}{2}$	$\frac{1}{2}$	0	1.7 ± 1
C(1)	0.022 ± 3 (0.033)	0.214 ± 4 (0.217)	0.296 ± 3 (0.302)	2.6 ± 5
C(2)	0.312 ± 3 (0.308)	0.606 ± 4 (0.600)	0.423 ± 2 (0.422)	2.1 ± 4
O(1)	0.094 ± 2 (0.094)	0.101 ± 2 (0.096)	0.224 ± 2 (0.223)	2.0 ± 3
O(2)	0.085 ± 2 (0.087)	0.268 ± 3 (0.267)	0.421 ± 2 (0.417)	1.9 ± 3
O(3)	0.430 ± 2 (0.425)	0.703 ± 3 (0.705)	0.401 ± 2 (0.406)	2.6 ± 3
O(4)	0.204 ± 2 (0.204)	0.642 ± 3 (0.644)	0.494 ± 1 (0.493)	1.8 ± 3
O _w (1)	0.285 ± 2 (0.289)	0.494 ± 2 (0.484)	0.073 ± 2 (0.075)	2.3 ± 3
O _w (2)	0.415 ± 2 (0.411)	0.107 ± 2 (0.103)	0.315 ± 2 (0.316)	2.2 ± 3

Except possibly in the nickel compound, differences in C–O bond lengths are obscured by the statistical uncertainty in the determinations. The average of the C–O distances in the manganese, copper and magnesium formate dihydrates, and the anhydrous copper formate (Barclay & Kennard, 1961) is 1.26 Å and in the nickel dihydrate and copper tetrahydrate compound 1.25 Å. The only distances more than 2σ from the average are the 1.22 Å and 1.28 Å approaches in the nickel formate dihydrate in two different formate groups. In other words, except for nickel formate dihydrate and anhydrous copper formate the quality of the data is insufficient to determine small differences (0.02 or 0.03 Å) in bond lengths with any degree of certainty. The structures in which larger differences occur [Cu(HCO₂)₂·2H₂O and CuBa₂(HCO₂)₆·4H₂O] are less accurate. This is not to say that differences do not exist but rather the collected data are insufficient to prove their existence.

Magnetic measurements of several transition metal formates dihydrate by Friedberg and coworkers show that at low temperatures one type of manganese and nickel atom is antiferromagnetically ordered whereas both symmetry-unrelated iron atoms are ordered in the respective formate compounds. It would be of interest to determine the ferrous formate structure to determine if a correlation exists between the surroundings of the metal atoms and the different magnetic ordering schemes.

The authors would like to thank Dr D.T. Cromer of Los Alamos Scientific Laboratory for running his least-squares and distance and angle programs for the problem and for providing the stereoscopic figure.

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