Inorganica Chimica Acta, 43 (1980) 237–241
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Coordination Chemistry in Anhydrous Monovalent Metallic Formates. I. The Crystal Structure of Anhydrous Potassium Formate KHCOO. C_{2h}-Octahedral Eight-coordination of the Potassium Atom

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Received June 9, 1980

KHCOO crystallizes in the orthorhombic space group Cmcm, with a = *5.890(1),* b = *6.793(1) and,* c = *7.014(1)* Å *with four formula-units in the centered cell. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares computations to $R = 0.0522$ (weighted $R_w = 0.0358$), for the 360 unique data collected. The coordination of the potassium atom is discussed on the basis of a purely C_{2h} symmetry model. The formate groups are of C_{2v} symmetry and lie on the mirror planes at $z = 1/4$ and $3/4$.*

Introduction

The structures of three complex uranyl formates, $NaUO_2(HCOO)_3 \cdot H_2O$, $SrUO_2(HCOO)_4 \cdot (1 + x)H_2O$ and $(NH_4)_2UO_2(HCOO)_4$ have recently been published [1–3]. The crystal structure of the hydrated uranyl diformate $UO_2(HCOO)_2 \cdot H_2O$ is orthorhombic [4] and we observed that the structures of the three above mentioned complex formates were respectively related to the corresponding structures of the anhydrous formates NaHCOO [5], α-$Sr(HCOO)_2$ [6] and NH_4HCOO [7]. These correlations are to be developed elsewhere [8]. Our investigations on complex uranyl formates did not yield a potassium salt on which we could verify our preceeding observations, but in another series of complex formates we could synthesize the anhydrous thorium(IV) derivative $KTh(HCOO)_5$, the structure of which revealed to be orthorhombic [9]. It may be surprising, but to the best of our knowledge, there are no structural data available on potassium formate in the literature. The only information existing on this compound are a powder diffraction pattern [10] and infrared spectra [11, 12]. In the scope of our investigations on the crystal chemistry of anhydrous monovalent metallic formates and in order to ascertain our structural correlation, we have undertaken the determination of the crystal structure of the anhydrous potassium formate KHCOO.

Experimental

The title compound has been directly synthesized from formic acid and potassium carbonate solutions; after evaporation, the bulky crystalline material has been recrystallized in methanol. The compound is very hygroscopic, and several crystals submitted for some hours to the action of the atmospheric moisture yielded nearly spherical specimens, one of which has been washed with ethanol and promptly introduced in a Lindemann glass capillary of 0.3 mm in diameter, together with a drop of Nujol, in order to prevent further action of atmospheric water vapor. The capillary has been mounted on the goniometer head of the Enraf-NONIUS, CAD-4 fully-automated four-circle diffractometer of the Centre de Diffractométrie, Lyon. Refinement of the orientation matrix based on the 25 reflections introduced in the reference list, and inspection of the Niggli values, showed that the crystal lattice symmetry is C-face-centered orthorhombic. The unit-cell parameters are listed in Table I, together with the principal data collection parameters. 566 intensities have been measured in the hkl octant, and after data reduction 360 unique reflections have been corrected for Lorentz and polarization factors. Owing to the low μR value of the nearly spherical specimen, absorption corrections were neglected.

Structure Determination and Refinement

Inspection of the hkl triplets showed that the conditions limiting possible reflections are hkl : $h + k = 2n$ and h0l : $l = 2n$; accordingly the possible space groups are $Cmc2_1$ or Cmcm. A Patterson map revealed that the space group is Cmcm, the four potassium atoms of the unit-cell being on inversion centers. Furthermore, the Patterson function yielded the locations of the oxygen, carbon and hydrogen atoms. After a few refinement cycles (Table 1) the anisotropic thermal

TABLE I. Crystal Data.

(A) Crystal parameters at 18 °C	
space group	Cmcm
a, Å	5.890(1)
b, Å	6.793(1)
c, Å	7.014(1)
gross formula	HCO_2K
mol wt	84.12
ρ calcd g cm^{-3}	1.991
ρ measd g cm^{-3} (flottation in ZnI_2)	1.95 (Z = 4 in the C-cell)
(B) Measurement of intensity data (Enraf-Nonius CAD-4)	
radiation, Å	MoK$\bar{\alpha}$ (0.71073)
monochromator	graphite
detector aperture	
horizontal: A + Btanθ	A = 2.1 mm; B = 0.6 mm
vertical	4 mm
rfltns measd	hkl octant
scan type (for 2n/6 ω–θ scan)	n = 2
ω-scan width, deg	0.80 + 0.35tanθ
bkgd	one-fourth additional scan at each end of scan
scan rate max, °/mn	10.06
min, °/mn	2.51
no. of rflctns measd	566
data used ($F^2 > 2\sigma(F^2)$)	360
max 2θ, deg	84
crystal dimensions	0.30 mm sphere in diameter
μ, cm^{-1}	16.03
μR	0.24
(C) Solution of the structure	
method used	heavy atom (Patterson function)
refinements	full-matrix least-squares
minimized function	$w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weighting functions: first cycles	$w = \left(2\lvert F_o\rvert_{min} + \lvert F_o\rvert + \frac{2F_o^2}{\lvert F_o\rvert_{max}}\right)^{-1}$
last cycles	$w = (a + b\lvert F_o\rvert)^2$
$R = (\Sigma \Vert F_o\rvert - \lvert F_c\Vert)/\Sigma\lvert F_o\rvert$	0.0522
weighted R(Rw) = $(\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(\Sigma wF_o^2))^{1/2}$	0.0358
refined scale factor	1.309(6)
F(000)	168

parameters were introduced for the four atoms of the asymmetric unit. The present formate is one of the rare cases where all the atoms are on special positions. The final positional and thermal parameters are listed in Table II, the conventional and weighted R, Rw values being 0.0522, 0.0358.

Description and Discussion of the Structure

The principal interatomic distances and bond angles are listed in Table III, and Fig. 1 and 2 respectively show the stereopairs for the unit-cell packing and for the coordination polyhedron of the potas-

TABLE II. Final Positional and Thermal Parameters and their Estimated Standard Deviations.

Atom	x/a	y/b	z/c	B_{eq}(Å^2)	$\beta_{(1,1)}$	$\beta_{(2,2)}$	$\beta_{(3,3)}$	$\beta_{(1,2)}$	$\beta_{(1,3)}$	$\beta_{(2,3)}$
K	0	0	0	2.1	0.0144(1)	0.0127(1)	0.00922(6)	0	0	–0.00002(7)
O	0.3114(2)	0.1810(2)	1/4	2.4	0.0129(2)	0.0130(2)	0.0185(2)	0.0017(2)	0	0
C	1/2	0.0994(3)	1/4	2.3	0.0140(8)	0.094(3)	0.0156(4)	0	0	0
H	1/2	–0.041(4)	1/4	3.8	0.03(1)	0.001(6)	0.034(6)	0	0	0

TABLE III. Principal Interatomic Distances (Å) and Bond Angles (°) with Esd s.[a]

$\mathrm{K^{i}{-}O^{v}}$	2.819(1)	$\mathrm{O^{i}{-}K^{i}{-}O^{x}}$	180
$\mathrm{K^{i}{-}O^{vi}}$	2.819(1)	$\mathrm{O^{ix}{-}K^{i}{-}O^{xi}}$	180
$\mathrm{K^{i}{-}O^{vii}}$	2.819(1)	$\mathrm{O^{v}{-}K^{i}{-}O^{vii}}$	180
$\mathrm{K^{i}{-}O^{viii}}$	2.819(1)	$\mathrm{O^{vi}{-}K^{i}{-}O^{viii}}$	180
$\mathrm{K^{i}{-}O^{i}}$	3.001(1)	$\mathrm{O^{i}{-}K^{i}{-}O^{xi}}$	43.46(2)
$\mathrm{K^{i}{-}O^{ix}}$	3.001(1)	$\mathrm{O^{i}{-}K^{i}{-}O^{viii}}$	73.18(2)
$\mathrm{K^{i}{-}O^{x}}$	3.001(1)	$\mathrm{O^{xi}{-}K^{i}{-}O^{v}}$	73.18(2)
$\mathrm{K^{i}{-}O^{xi}}$	3.001(1)	$\mathrm{O^{v}{-}K^{i}{-}O^{viii}}$	81.16(2)
$\mathrm{O^{i}{-}C^{i}}$	1.242(1)	$\mathrm{O^{i}{-}K^{i}{-}O^{vii}}$	78.91(2)
$\mathrm{C^{i}{-}H^{i}}$	0.954(3)	$\mathrm{O^{vi}{-}K^{i}{-}O^{xi}}$	78.91(2)
$\mathrm{O^{i} \ldots O^{xi}}$	2.222(2)	$\mathrm{O^{i}{-}C^{i}{-}O^{xi}}$	126.98(7)
		$\mathrm{O^{i}{-}C^{i}{-}H^{i}}$	116.51(9)

[a] Code for equipoints:

i	x	y	z
v	1/2 + x	1/2 + y	z
vi	1/2 + x	1/2 − y	−z
vii	1/2 − x	1/2 − y	−z
viii	1/2 − x	1/2 + y	z
ix	x	1 − y	−z
x	1 − x	1 − y	−z
xi	1−x	y	z

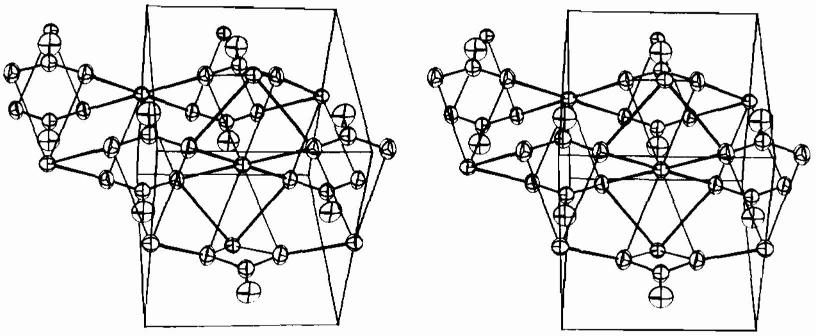

Fig. 1. Stereopair showing the unit-cell packing in the potassium formate structure. The origin is at the lower left; the x-axis runs to the right, the y-axis to the back and the z-axis upwards.

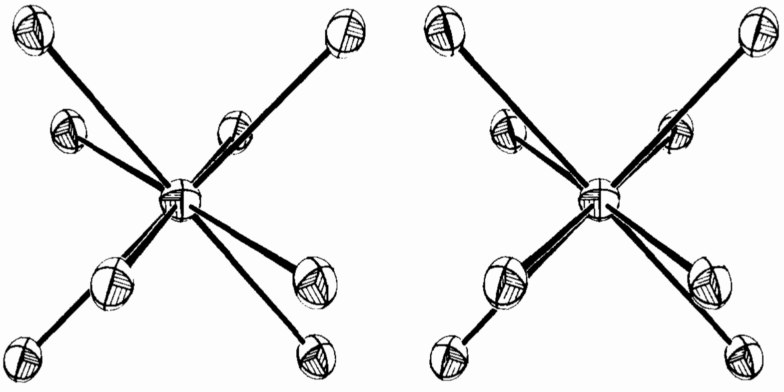

Fig. 2. Stereopair showing the C_{2h}-centered coordination polyhedron of the potassium atom in KHCOO. The labelling of the O atoms is roughly the same as on Fig. 3.

sium atom. On Fig. 1 the four shorter K–O bonds of 2.819(1) Å are represented by heavier sticks than the four longer K–O bonds of 3.001(1) Å. The octa-coordination polyhedron of the K atom has a pure C_{2h}-octahedron symmetry, and to the best of our knowledge, this type of 8-coordination has not yet been described in [13] or even considered in [14] where the eight atom family are of D_{2d}, C_{2v} or D_{4d}

symmetries. The fact that the K–8(O) polyhedron has an inversion center, shows that it can be considered as the distorsion of a hexahedral cubic O_h model with conservation of the symmetry center. The path from the cubic model to the C_{2h} polyhedron is depicted on Fig. 3 where the oxygen atoms are in roughly the same disposition as on Fig. 2. In a similar manner as in [13] we have calculated the dihedral angles (see Table IV) corresponding to the double lines shown on Fig. 3. The dihedral angles of the triangular faces (29.15°) are very close to those calculated for the ideal dodecahedron (29.5°). The dihedral angles between the remaining trapezoidal faces are of 75.02°, and correspond to the twisting along the *c*-type edges of the cubic model.

The formate groups are perfectly planar and of C_{2v} symmetry. This is the first example where the formate ion exhibits its highest possible molecular symmetry. In the structure of KHCOO the formate groups are confined in the mirror planes which are perpendicular to the [001] direction at z = 1/4 and 3/4. The two-fold rotation axis of the formate ions are running parallel to the [010] direction, and the OCO groups run parallel to the [100] direction. Concerning the ligation mode of the bidentate formato groups, the most commonly encountered are of the chelating or the bridging modes. In some structures, as in α-$Ca(HCOO)_2$, α-$Sr(HCOO)_2$ [6] or in $(NH_4)_2UO_2(HCOO)_4$ [3], both ligation modes are observed. In other cases, as in $Ba(HCOO)_2$ [6] or $UO_2(HCOO)_2 \cdot H_2O$ [4] only the bridging bidentate formate ligand is observed. In the present case, it might be considered that the longer and shorter K–O bonds at 2.819 and 3.001 Å are sufficiently close to have the same ionic character; accordingly it must be discussed whether the HCOO groups are bridging or chelating. It has been asserted in [6] that the chelate-like formate groups present a smaller OCO angle (122–124°) than the bridging ones (125–127°). In $(NH_4)_2UO_2(HCOO)_4$ the chelating HCOO group has an OCO angle of 122.3° [3]. Hence, it must be considered that in KHCOO, all the formate groups are of the bridging bidentate type, since their OCO angle is 126.98° [7]; in that case the K–O interactions at 3.001 Å are much weaker than the shorter ones at 2.819 Å. This latter distance is closer to the sums of the ionic radii of the potassium and the oxygen ions, *i.e.* 1.36 Å [6] + 1.52 Å [15], and the mean distance reported in [16] for octacoordinated potassium atoms (2.80–2.83 Å).

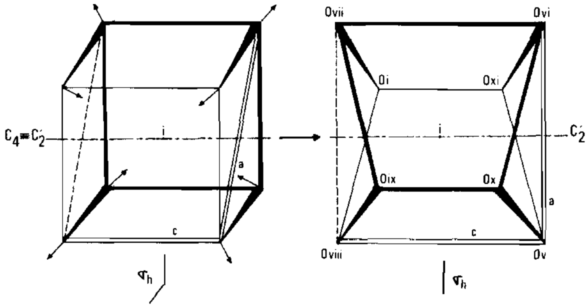

Fig. 3. Correlation between the O_h model and the C_{2h}-octahedron corresponding to the coordination polyhedron of the K atom in KHCOO. The K atom is located on the symmetry center and the σ_h mirror plane is normal to the right C_{2h} model.

TABLE IV. Ideal and Observed Angles (°) for Octacoordination.

Polyhedron	Angles	
ideal dodecahedron (D_{2d})	29.5, 29.5 29.5, 29.5	
ideal cube (O_h)	0.0, 0.0	a edges
	90.0, 90.0	c edges
K–8(O) in KHCOO	29.15, 29.15	a edges
(C_{2h})	75.02, 75.02	c edges

On the basis of the results reported in the present work, and in a similar way as that described in [17], the infrared spectrum of the formate ion in KHCOO may now be interpreted. The molecular and site groups are both of C_{2v} symmetry, and since the primitive cell of KHCOO contains only two formate groups, the factor group analysis (D_{2h} symmetry) predicts that each internal vibration must split into two components according to the correlations given in Table V, and in [18]. Accordingly, each vibration of the formate ion in the solid potassium formate has an infrared active and a Raman active mode. Hence, all the observed infrared absorption bands are explicitly attributed as shown in Table VI.

TABLE V. Correlation Table for KHCOO*.

Molecular and site group		Factor group
C_{2v}		D_{2h}
a_1	$\xrightarrow{2}$	$a_g(R)^{\S} + b_{1u}(ir)$
a_2	$\xrightarrow{2}$	$b_{1g}(R) + a_u(inactive)$
b_1	$\xrightarrow{2}$	$b_{2g}(R) + b_{3u}(ir)$
b_2	$\xrightarrow{2}$	$b_{3g}(R) + b_{2u}(ir)$

*The irreducible representation for the formate ion is $\Gamma = 3A_1 + 2B_1 + B_2$ (17).
§(R): Raman active, (ir): infrared active.

Conclusion

The crystallo-chemical investigations on anhydrous potassium formate show that this compound has a structure different from those in [5–7]. The coordination polyhedron is of a novel C_{2h}-octahedral

TABLE VI. Infrared Spectrum of KHCOO and Band Attribution.

Frequency	Species	Vibration	Observed Bands
ν_2	b_{1u}	ν(CH)	2808(2833)[a]
ν_4	b_{3u}	ν_{as}(CO)	1597(1590)
ν_5	b_{3u}	ρ_r(COO)	1389(1385)
ν_1	b_{1u}	ν_s(CO)	1357(1350)
ν_6	b_{2u}	π(CH)	1062(1064)
ν_3	b_{1u}	δ(OCO)	772(775)
Combinations and overtones			
$2\nu_5$			2730

[a] This work. Values in parenthesis correspond to those in [11].

type which can be derived from distorsion of the cubic O_h-hexahedron.

The formate ion in this compound exhibits its highest possible site-symmetry (C_{2v}), and the factor group analysis yields a correct band assignment for the infrared active vibrations in the solid state.

Acknowledgements

We thank the Centre National de la Recherche Scientifique and Professor B. Claudel for financial support and helpful discussions.

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