Inorganica Chimica Acta, 48 (1981) 129–132
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Coordination Chemistry in Anhydrous Monovalent Metallic Formates. II. The Crystal Structure of Anhydrous Thallium(I) formate TlHCOO

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Received June 18, 1980

TlHCOO crystallizes in the orthorhombic space group Pna2_1 with a = *6.728(2),* b = *5.937(2) and* c = *7.808(2)* Å, *with four formula-units per primitive unit-cell. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares computations to R = 0.023 for the 226 unique data collected. The results are compared to those reported for other monovalent metallic formates (including ammonium formate).*

Introduction

In a preceeding paper one of us has described the preparation of anhydrous Tl(I) formate [1]. The scope of our laboratory is devoted to the coordination chemistry of the Tl^+ ion in the solid state. Several structures on this topic have already been published [2–4], and it seemed worthwhile completing this series by the determination of the structure of TlHCOO, and compare the environment of the metallic center and the ligation mode of the formate ion with known structures of other monovalent metallic formates.

Experimental

In a previous article it has been reported that TlHCOO crystallizes in an orthorhombic system with a = 6.73, b = 5.94, c = 7.82 Å and Z = 4 [5]. A single crystal shaped into a sphere of 0.12 mm diameter has been mounted on the Enraf-Nonius CAD-4 four-circle automatic diffractometer of the Université Claude-Bernard, Lyon I, using graphite monochromatized MoKα radiation. The final cell-parameters are obtained by least-squares calculations on 25 reflections of the reference list. Table I lists the unit-cell and data collection parameters together with the relations used for the structure solution. The unit-cell parameters of the title compound have been compared to those of KHCOO [2], NaHCOO [3, 6] and (NH_4)HCOO [4]. Out of the 1517 intensities measured, 226 unique data obeying I > 3σ(I) have been retained. These intensities have been corrected for Lorentz and polarization and for absorption (μR = 3.2 for the nearly spherical specimen).

TABLE I. Crystal and Data Collection Parameters.

(A) Crystal parameters at 18 °C	
Space group	Pna2_1
a, A	6.728(2)
b, A	5.937(2)
c, A	7.808(2)
Gross formula	HCO_2Tl
mol wt	249.39
ρ_{calcd} g cm^{-3}	5.310 (Z = 4 in the P-cell)
ρ_{measd} g cm^{-3}	5.20
(B) Solution of the structure	
Method used	Heavy-atom (Patterson function)
Minimized function	$W(\lvert F_o\rvert-\lvert F_c\rvert)^2$
$R_1 = (\Sigma\lVert F_o\rvert-\lvert F_c\rVert)/\Sigma\lvert F_o\rvert$	0.023
$R_2 = [\Sigma(\lvert F_o\rvert-\lvert F_c\rvert)^2/\Sigma F_o^2]^{1/2}$	0.033
Refined scale factor	1.177(1)
F(000)	416

Determination of the Structure

All the observed intensities obeyed 0kl: h + k = 2n and h0l: h = 2n. Accordingly, the possible space groups are Pna2_1 or Pnam. The heavy atom has been localized by the conventional Patterson function, and a subsequent difference-Fourier synthesis revealed that the space group was Pna2_1 and gave the posi-

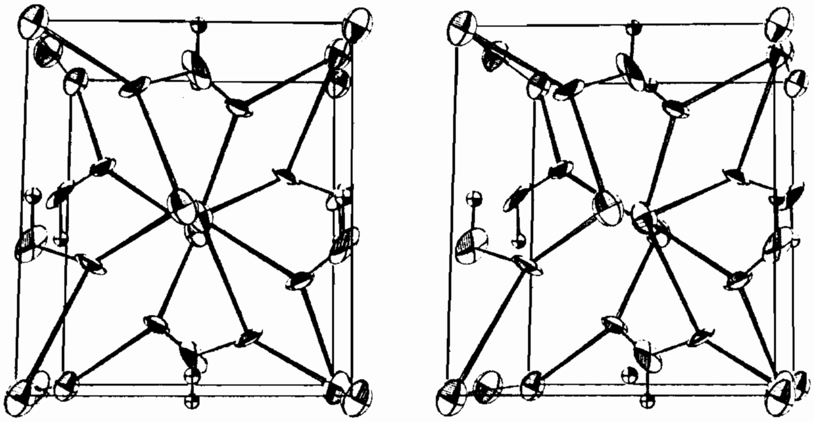

Fig. 1. Stereopair showing the unit-cell packing in the thallium formate structure. The origin is at the upper left, the x-axis runs to the right, the y-axis downwards and the z-axis to the back.

TABLE II. Atomic and Thermal Parameters for TlHCOO.

Atom	x/a	y/b	z/c	B_{eq}[c]
Tl	0.00557(8)	−0.01458(1)	0.00000[a]	2.99
C	0.4075(4)	−0.0077(8)	0.7423(7)	4.51
O(1)	0.3502(4)	0.1872(5)	0.7027(4)	2.57
O(2)	0.1887(4)	0.3542(6)	0.3325(4)	2.51
H[b]	0.545	−0.011	0.768	

[a] In space group $Pna2_1$ the third coordinate of the Tl atom has arbitrarily been fixed at z = 0.00000. [b] Calculated position of the H atom (see text). [c] The equivalent isotropic factor has been calculated according to $B_{eq} = 4/3(\beta(1,1)a^2 + \beta(2,2)b^2 + \beta(3,3)c^2)$.

TABLE III. Some Interatomic Distances (A) in TlHCOO– Tl–O ⩽ 3.1 A.

Tl^{iii}–$O(1)^{i}$	2.565(2)	$Tl^{iii}\cdots Tl^{ii}$	3.909(1)
Tl^{iii}–$O(1)^{ii}$	3.047(2)	$Tl^{iii}\cdots C^{iii}$	3.371(3)
Tl^{iii}–$O(2)^{i}$	2.559(2)	$Tl^{iii}\cdots C^{ii}$	3.364(3)
Tl^{iii}–$O(2)^{ii}$	2.736(2)	$C^{i}\cdots C^{iv}$	4.099(7)

Code for equivalent positions:

i	x	y	z
ii	½ + x	½ − y	z
iii	½ − x	½ + y	½ + z
iv	−x	−y	½ + z

tions of the C and O atoms. The refinements were performed using full-matrix least-squares routines SFLS-5 [7]. The atomic scattering factors used are those corresponding to the first order functions of Vand *et al.* [8], the coefficients being those given by Moore [9]. Anomalous scattering has been introduced for the Tl atom [10], and all the atoms were refined with anisotropic thermal parameters. The final R_1 and R_2 (Table I) residues converged respectively to 0.023 and 0.033. The corresponding atomic and thermal parameters are listed in Table II, together with their esds.

Discussion

A comparative structural study of the title compound with the formates of potassium, sodium and ammonium, shows that the chemical bonds in these compounds are very similar.

Environment of the Thallium Atom

The principal interatomic distances concerning the environment of the Tl atom, with Tl–O 3.1 Å, together with the shortest Tl···Tl, Tl···C, O···O and C···C contacts are given in Table III. Two short Tl–O distances at 2.565(2) and 2.559(2) Å are comparable to those observed for Tl_3PO_4 [11] and Tl_2HPO_4 [12]. The two longer distances are similar to those in $TlH_5(PO_4)_2$ [13] and TlH_2PO_4 [14], where they range between 2.8 and 3.1 Å. The ionic radii of Tl^+ and K^+ are respectively 1.40 and 1.33 Å [15] and the substitution of a K^+ by a Tl^+ in the structure of KHCOO [2] does not result in a great modification in the formate groups, which are bridging bidentate ligands. The mean Tl–O distance (2.727 Å) in TlHCOO is comparable to the short K–O distances (2.819 Å) in KHCOO [2]. The shift of the Tl atom compared to the K atom yields a tetracoordinated metallic center, which is significantly different from the eight-coordinated K atom in KHCOO and the hexacoordinated Na atom in NaHCOO [3].

TABLE IV. Comparison of the Geometry of the Formate ion in TlHCOO, KHCOO, NaHCOO and $(NH_4)HCOO$. Distances are in Å and angles in degrees.

Distance or angle	TlHCOO	KHCOO [2]	NaHCOO		$(NH_4)HCOO$ [4]
			[3]	[6]	
C–O(1)	1.258(5)	1.242(1)	1.246(1)	1.237(2)	1.232(7)
C–O(2)	1.260(5)				1.239(7)
O(1)–C–O(2)	125.4(2)	126.98(7)	126.3(2)	126.9(3)	126.3(6)
O(1)···O(2)	2.237(3)	2.222(2)		2.213(4)	

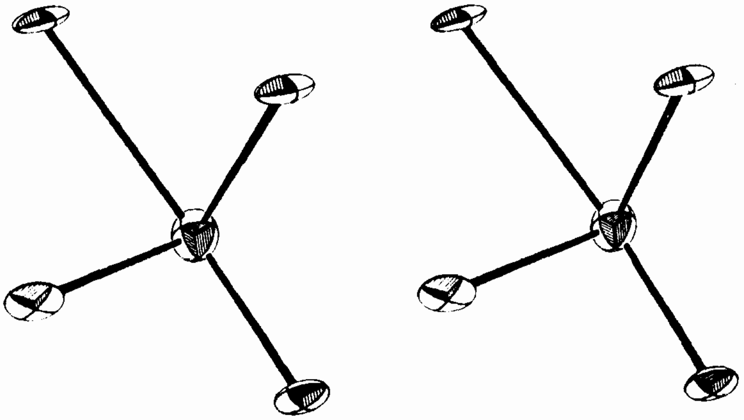

Fig. 2. Stereopair showing the coordination polyhedron of the Tl atom in TlHCOO. The labelling of the oxygen atoms is the same as in Fig. 3.

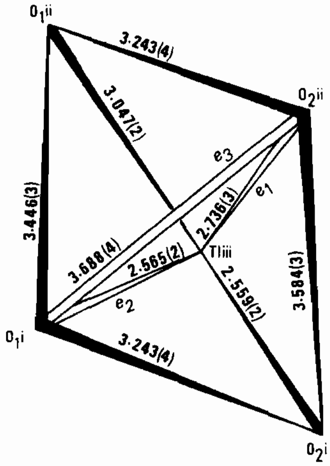

Fig. 3. Coordination polyhedron of the Tl atom in TlHCOO. The double lines correspond to the e_3, e_2 and e_1 dihedral angles as they are described in [17].

Figures 1 and 2 respectively show ORTEP stereoviews [16] of the unit-cell packing and of the Tl–4(O) polyhedron. The labelling of the Tl and O atoms for Fig. 2 are given in Fig. 3. In order to decide between a distorted tetragonal pyramid and a trigonal bipyramid for this Tl–4(O) moiety, the e_3 = 41.0, e_1 = 26.56 and e_2 = 26.86° dihedral angles have been calculated as shown in Fig. 3, according to the method described by Muetterties and Guggenberger [17]. The values of these angles show that we are far from a tetragonal pyramid. Hence, the coordination polyhedron of the thallium atom can best be described as a rather elongated trigonal bipyramid.

The Formate Ion

The geometrical parameters of the formate ion in TlHCOO is compared in Table IV to those of the same ion in KHCOO, NaHCOO and $(NH_4)HCOO$. It appears thus that the C–O(1) and C–O(2) bonds which are respectively 1.258(5) and 1.260(5) Å are significantly longer in TlHCOO than the C–O bonds in the other formates, where they range between 1.232(7) and 1.242(1) Å. As is the case for KHCOO, NaHCOO and $(NH_4)HCOO$, it might reasonably be admitted that within the estimated standard deviations the formate ion in TlHCOO is in complete resonance, the two C–O bonds being chemically equivalent. The O(1)–C–O(2) angle which is 125.4(2)° in TlHCOO is slightly smaller than in the

TABLE V. Infrared Spectrum of TlHCOO and Band Attribution.

Frequency	Species	Vibration	Observed bands	
ν_2	$a_1 + b_1 + b_2$	ν(CH)	2775^a	(2786)
ν_4	id	ν_{as}(CO)	1606 1572	(1590)
ν_5	id	ρ_r(COO)	1357	(1406) (1387)
ν_1	id	ν_s(CO)	1342	(1355) (1333)
ν_6	id	π(CH)	–	–
ν_3	id	δ(OCO)	759	(758)

[a]This work (values in parenthesis are those reported in [18]).

other formates where it ranges from 126.3 to 127°, and this is a normal trend which maintains a comparable value for the O(1)···O(2) contact in the formate ion of most formates. For the above mentioned formates this value ranges from 2.213 to 2.237 Å. As reported in [2], the formate ion in TlHCOO is of the bridging bidentate type.

Assuming that the geometry of the formate ion in TlHCOO is planar, one may calculate the theoretical position of the hydrogen atom as being (0.545, −0.011, 0.768). This hydrogen atom is pictured on the stereoview of Fig. 1.

In Table V the infrared absorption bands of the formate ion in TlHCOO observed in the present work are compared to those reported earlier by Donaldson *et al.* [18]. In a similar way as described in [2], a factor group analysis (C_{2v}) shows that each internal vibration of the formate ion in general site symmetry (C_1) must split into four components $a_1 + a_2 + b_1 + b_2$, three of which are i.r. active (Table VI). In our case, only the ν_{as}(CO) vibration seems to be split on the i.r. spectrum, and all the other vibrations are attributed as being unresolved $a_1 + b_1 + b_2$ triplets.

Conclusion

The determination of the crystal structure of anhydrous thalleous formate adds one more example in the series of monovalent metallic formates. As in most formates, the HCOO group is a bidentate ligand bridging two metallic centers, forming thus infinite ...HCOO–Tl–HCOO–Tl... zig-zagging chains in the tridimentional solid state. The coordination polyhedron of the Tl atom has been established as being an elongated trigonal bipyramid with the heavy atom on one apex of the equatorial plane. A comparison of this structure with that of KHCOO shows that they are of the same type, the Tl atom being shifted from the (O,O,O) position of the K atom in KHCOO, yielding thus a tetracoordinated Tl, if one accepts to consider only the four shortest Tl–O distances which are less than 3.1 Å.

At this stage of our investigations, it seems worthwhile establishing, in the near future, the structures of the remaining anhydrous monovalent metallic formates, for which no geometrical informations are available at this date, *i.e.* AgHCOO, CsHCOO and RbHCOO.

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