

AgN₃ group but the three S atoms S(15), S(18), S(21) deviate from this plane by distances of 0.52 (1), 2.32 (1), -1.05 (1) Å respectively. Although S(18) is displaced 2.32 (1) Å from the AgN₃ plane, it is not in the axial position as the three S(18)-Ag-N angles range from 87.1 (2) to 122.0 (2)°.

In the aforementioned structures of L² and L³ macrocycles with Pb, Ca and Sr, the macrocycles are closer to planarity. A rough measure of this non-planarity is the deviations of the three donor atoms X, Y, X (X, Y = O or S) from the MN₃ plane, as in these structures the maximum deviations are ca 1.5 Å compared to 2.32 (1) Å for S(18) in the present structure.

The different macrocycle conformation in the present cation is caused by a mismatch between the small size of the silver ion and the larger macrocycle cavity, though it is possible that the non-coordinating nature of the anion may be a contributory factor. With thiocyanate (say) a more planar geometry of the macrocycle may have been observed. However, attempts to prepare compounds with coordinating unidentate anions were not successful. Because of the strong affinity of the silver(I) ions towards these anions, the simple silver(I) salts were precipitated.

Another feature of the structure which supports the suggestion of a mismatch between metal and 'hole' size is the variation in bond lengths between the metal and the donor atoms. In particular we note that Ag(1)-

N(1) is 0.20 Å longer than the equivalent Ag(1)-N(12) bond and that Ag-S(15) is ca 0.30 Å longer than the other two Ag-S bonds. N(1) and S(15) are on opposite sides of the molecule and clearly these increases are caused by the need to alleviate strain. However, there were no unexpected torsion angles in the macrocycle, the most strained being S(18)-C(19)-C(20)-S(21) at 46.0°.

There are no contacts between cation and anion of less than 3.7 Å. The geometry of the tetraphenylborate anion is as expected.

We thank SERC for a grant for the diffractometer and A. W. Johans for his help with the crystallographic investigations. SS thanks the Agricultural University of Malaysia for study leave.

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Acta Cryst. (1984). C40, 2016-2019

The Structures of α -Ketoglutaric Acid (I),* C₅H₆O₅, Sodium Hydrogen α -Ketoglutarate (II), Na⁺.C₅H₅O₅⁻, and Potassium Hydrogen α -Ketoglutarate (III), K⁺.C₅H₅O₅⁻

BY T. LIS

Institute of Chemistry, The University, 50-383 Wrocław, Poland

AND J. MATUSZEWSKI

Department of Inorganic Chemistry, Faculty of Engineering, School of Economics, 53-345 Wrocław, Komandorska 118/120, Poland

(Received 23 February 1984; accepted 2 July 1984)

Abstract. (I) $M_r = 146.1$, monoclinic, $P2_1/c$, $a = 16.71$ (2), $b = 6.375$ (4), $c = 5.525$ (6) Å, $\beta = 94.73$ (7)°, $V = 586.6$ Å³, $T = 302$ (2) K, $Z = 4$, $D_m = 1.64$, $D_x = 1.65$ Mg m⁻³, $F(000) = 304$, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ \AA}) = 0.16$ mm⁻¹, final $R = 0.051$ and $R_w = 0.052$ for 1338 non-zero reflexions. (II) $M_r = 168.1$, orthorhombic, $Pbca$, $a = 6.113$ (5),

$b = 5.859$ (7), $c = 34.76$ (4) Å, $V = 1245$ Å³, $T = 304$ (2) K, $Z = 8$, $D_m = 1.79$, $D_x = 1.79$ Mg m⁻³, $F(000) = 688$, $\mu(\text{Mo } K\alpha) = 0.23$ mm⁻¹, final $R = 0.040$ and $R_w = 0.047$ for 1594 non-zero reflexions. (III) $M_r = 184.2$, monoclinic, $P2_1/c$, $a = 6.517$ (4), $b = 17.816$ (9), $c = 8.050$ (4) Å, $\beta = 131.79$ (4)°, $V = 696.9$ Å³, $T = 298$ (2) K, $Z = 4$, $D_m = 1.74$, $D_x = 1.76$ Mg m⁻³, $F(000) = 376$, $\mu(\text{Mo } K\alpha) = 0.73$ mm⁻¹, final $R = 0.033$ and $R_w = 0.036$ for 1869

* 2-Oxoglutaric acid.

non-zero reflexions. In (II) and (III) the carboxyl group bonded to the keto group is deprotonated. In all crystals the α -ketoglutarate residue has a nearly planar zigzag carbon-chain conformation. All O atoms approximate to the plane through the C-atom chain except the carboxyl group in (III) which is perpendicular.

Introduction. α -Ketoglutaric acid is one of the simple compounds playing an important rôle in living organisms. Its activity in several biochemical reactions seems to be dependent on its structural properties. Unfortunately neither the structure of α -ketoglutaric acid itself nor the structural details of its salts have been available to date (Cooper, Ginos & Meister, 1983).

Experimental. α -Ketoglutaric acid crystals were obtained by slow evaporation of an aqueous solution of the compound supplied by Reanal. Sodium (potassium) hydrogen α -ketoglutarate was prepared by combining an equimolar ratio of α -ketoglutaric acid and sodium (potassium) hydroxide in water. After slow evaporation of water platy crystals of (II) [(III)] appeared. D_m measured (for all crystals) pycnometrically in 1,2-dibromoethane/ CCl_4 . Systematic absences on Weissenberg photographs uniquely indicated the space groups. A specimen $0.3 \times 0.3 \times 0.4$ mm for (I), $0.6 \times 0.6 \times 0.15$ mm for (II) and $0.5 \times 0.1 \times 0.5$ mm for (III) was cut from large crystals. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters [15 reflexions; $18 < 2\theta < 28^\circ$ for (I), $20 < 2\theta < 30^\circ$ for (II) and $18 < 2\theta < 24^\circ$ for (III)] and intensity measurements; 2θ - ω scan technique for (I) and (III) and ω scan for (II). 1982 intensities measured below $\theta = 32.5^\circ$ for (I) (h 0 to 25, k 0 to 9, l -8 to 8); 3106 reflexions below $\theta = 37.5^\circ$ for (II) (h 0 to 10, k 0 to 10, l 0 to 49); 2986 reflexions below $\theta = 32.5^\circ$ for (III) (h 0 to 9, k 0 to 26, l -12 to 9). After each group of 50 reflexions two standards were measured, variation $\pm 5\%$; no absorption correction. All calculations performed on a NOVA 1200 computer with programs supplied by Syntex (1976). Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); real and imaginary components of anomalous dispersion included for K atoms. Structures of (I) and (II) solved by direct methods. For (III) the K atoms were found from a Patterson synthesis; all other non-H atoms from a Fourier map. In each structure, refinement based on F [C, O, Na, K anisotropic, H (from difference maps) isotropic] for reflexions with $I > 3\sigma(I)$; $w = 1/\sigma^2(F_o)$; maximum least-squares shift to error 0.01. No correction for secondary extinction. For all crystals the highest residual peaks in the final difference Fourier maps were confined to the molecular bonds; it should be stressed that the highest peak in the three compounds could be ascribed to the same bond, namely C(2)-C(3) [0.37, 0.27 and 0.46 e \AA^{-3} for (I), (II) and (III) respectively]. The final atomic parameters for (I),

(II) and (III) are given in Tables 1, 2 and 3 respectively.*

Discussion. The bond lengths and the bond angles as well as the selected torsion angles for the three compounds are listed in Table 4. *ORTEP* drawings (Johnson, 1976) of the three ketoglutarate skeletons are presented in Figs. 1, 2 and 3 and the packing of the crystals is depicted in Figs. 4, 5 and 6.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39611 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *The final atom coordinates and isotropic thermal parameters of α -ketoglutaric acid*

For non-H atoms $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (\AA^2)
O(1)	0.4554 (1)	-0.1010 (4)	0.2133 (4)	3.42 (14)
O(2)	0.4063 (1)	0.0922 (3)	0.5049 (3)	3.18 (12)
O(3)	0.3106 (1)	-0.0975 (3)	-0.0291 (3)	3.35 (13)
O(4)	0.0981 (1)	0.0809 (3)	0.5193 (3)	2.90 (12)
O(5)	0.0330 (1)	-0.1180 (3)	0.2358 (4)	3.27 (13)
C(1)	0.3986 (2)	-0.0061 (4)	0.3165 (4)	2.37 (14)
C(2)	0.3157 (2)	-0.0271 (4)	0.1734 (4)	2.22 (14)
C(3)	0.2452 (2)	0.0426 (4)	0.3036 (5)	2.33 (14)
C(4)	0.1680 (2)	-0.0495 (4)	0.1874 (5)	2.36 (14)
C(5)	0.0967 (2)	-0.0195 (4)	0.3320 (4)	2.26 (14)

Table 2. *The final atom coordinates and isotropic thermal parameters of sodium hydrogen α -ketoglutarate*

For non-H atoms $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (\AA^2)
Na	0.0137 (2)	0.2716 (2)	0.21723 (2)	1.90 (4)
O(1)	-0.0969 (2)	0.1723 (3)	0.27992 (3)	1.88 (7)
O(2)	0.1355 (3)	0.4248 (3)	0.30570 (4)	2.13 (8)
O(3)	-0.0889 (3)	-0.0528 (3)	0.34826 (4)	2.27 (8)
O(4)	0.0791 (3)	0.5022 (3)	0.45302 (4)	2.66 (10)
O(5)	-0.1155 (3)	0.2365 (3)	0.48376 (4)	3.08 (11)
C(1)	0.0101 (3)	0.2590 (3)	0.30720 (4)	1.47 (9)
C(2)	-0.0179 (3)	0.1408 (4)	0.34709 (4)	1.51 (9)
C(3)	0.0466 (3)	0.2722 (4)	0.38215 (5)	1.83 (10)
C(4)	-0.0547 (4)	0.1773 (4)	0.41826 (5)	2.01 (11)
C(5)	-0.0207 (3)	0.3228 (4)	0.45312 (5)	1.95 (10)

Table 3. *The final atom coordinates and isotropic thermal parameters of potassium hydrogen α -ketoglutarate*

For non-H atoms $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (\AA^2)
K	0.4156 (1)	0.01782 (2)	0.2054 (1)	1.98 (2)
O(1)	0.8662 (3)	0.01580 (6)	0.2424 (3)	1.99 (7)
O(2)	1.2490 (3)	0.08504 (7)	0.4306 (3)	2.08 (7)
O(3)	0.5625 (3)	0.13937 (7)	0.0710 (3)	2.51 (9)
O(4)	0.9342 (3)	0.39290 (7)	0.4095 (3)	2.60 (8)
O(5)	0.8804 (3)	0.39312 (7)	0.1062 (3)	2.50 (8)
C(1)	0.9975 (4)	0.07712 (8)	0.3042 (3)	1.55 (8)
C(2)	0.8093 (4)	0.14742 (8)	0.2026 (3)	1.59 (8)
C(3)	0.9422 (4)	0.22330 (9)	0.2749 (3)	1.71 (9)
C(4)	0.7281 (4)	0.28548 (9)	0.1691 (4)	1.97 (10)
C(5)	0.8574 (4)	0.36230 (8)	0.2407 (3)	1.62 (8)

Crystals of α -ketoglutaric acid (I) consist of discrete molecules which are interlinked by hydrogen bonds. (Hydrogen-bond data for the three crystals are given in

Table 4. Bond lengths (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$) for (I), (II) and (III)

The torsion angles of (II) apply to the mirror-related (or inverted) molecule listed in Table 2.

	(I)	(II)	(III)
C(1)—O(1)	1.297 (3)	1.259 (2)	1.267 (2)
C(1)—O(2)	1.213 (3)	1.239 (2)	1.232 (3)
C(2)—O(3)	1.202 (3)	1.215 (2)	1.208 (3)
C(5)—O(4)	1.215 (3)	1.216 (2)	1.220 (2)
C(5)—O(5)	1.311 (3)	1.314 (2)	1.308 (3)
C(1)—C(2)	1.543 (3)	1.559 (2)	1.551 (2)
C(2)—C(3)	1.498 (3)	1.494 (2)	1.498 (2)
C(3)—C(4)	1.512 (3)	1.506 (2)	1.522 (3)
C(4)—C(5)	1.500 (3)	1.496 (3)	1.506 (2)
O(1)—C(1)—O(2)	126.1 (3)	127.3 (2)	127.0 (2)
O(1)—C(1)—C(2)	113.1 (2)	115.7 (2)	113.6 (2)
O(2)—C(1)—C(2)	120.8 (2)	117.0 (2)	119.5 (2)
C(1)—C(2)—O(3)	120.1 (2)	118.9 (2)	119.3 (2)
C(1)—C(2)—C(3)	115.9 (2)	117.9 (2)	118.3 (2)
O(3)—C(2)—C(3)	124.0 (2)	123.2 (2)	122.4 (2)
C(2)—C(3)—C(4)	111.0 (2)	112.4 (2)	111.3 (2)
C(3)—C(4)—C(5)	114.3 (2)	114.1 (2)	112.2 (2)
C(4)—C(5)—O(4)	124.1 (2)	124.1 (2)	122.8 (2)
C(4)—C(5)—O(5)	112.2 (2)	112.1 (2)	114.1 (2)
O(4)—C(5)—O(5)	123.7 (2)	123.8 (2)	123.1 (2)
O(1)—C(1)—C(2)—O(3)	-10.6 (9)	-18.8 (8)	-2.8 (5)
O(2)—C(1)—C(2)—O(3)	169.0 (9)	160.5 (9)	176.7 (5)
O(1)—C(1)—C(2)—C(3)	168.8 (7)	161.7 (6)	176.2 (5)
O(2)—C(1)—C(2)—C(3)	-11.6 (7)	-19.0 (6)	-4.2 (6)
C(1)—C(2)—C(3)—C(4)	-160.9 (5)	-160.8 (6)	-176.8 (4)
C(2)—C(3)—C(4)—C(5)	169.6 (4)	171.7 (6)	179.6 (4)
O(3)—C(2)—C(3)—C(4)	18.5 (6)	19.7 (7)	2.2 (5)
C(3)—C(4)—C(5)—O(4)	4.4 (5)	0.0 (9)	-86.7 (5)
C(3)—C(4)—C(5)—O(5)	-174.2 (4)	-178.6 (7)	93.2 (5)
C(4)—C(5)—O(5)—H(5)	171 (3)	177 (3)	-178 (3)
H(1)—O(1)—C(1)—C(2)	-175 (3)		

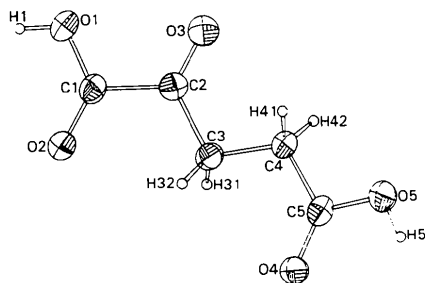


Fig. 1. ORTEP plot (Johnson, 1976) of α -ketoglutaric acid. The thermal ellipsoids are at 50% probability.

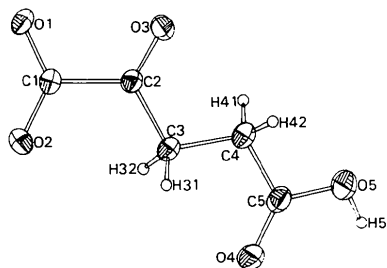


Fig. 2. ORTEP plot of α -ketoglutarate ion in sodium hydrogen α -ketoglutarate.

Table 5.) These molecules form infinite zigzag chains along c in which each carboxyl group participates in a hydrogen-bonded cyclic dimer about the centre of inversion thus forming the motif (23) in the classification of Leiserowitz (1976).

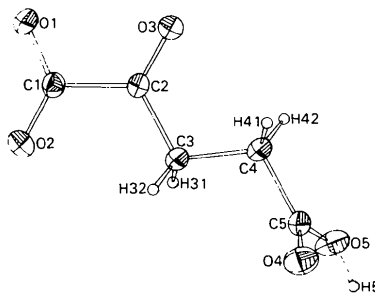


Fig. 3. ORTEP plot of α -ketoglutarate ion in potassium hydrogen α -ketoglutarate.

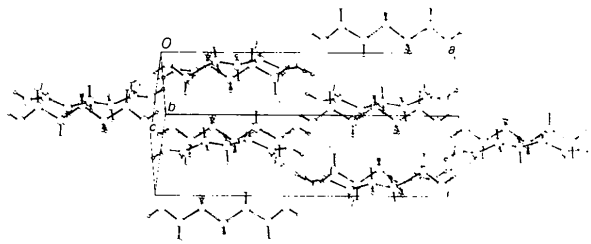


Fig. 4. Molecular packing and H-bonding scheme in the crystal structure of α -ketoglutaric acid.

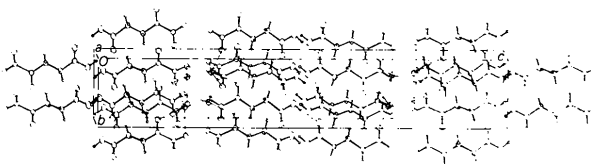


Fig. 5. Packing of the ions in the crystal of sodium hydrogen α -ketoglutarate. The dotted lines are hydrogen bonds.

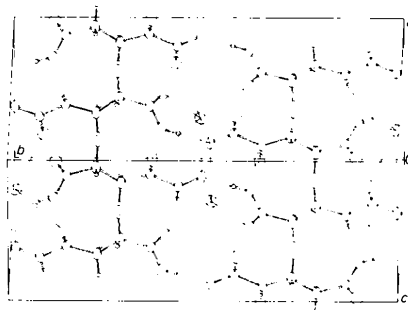


Fig. 6. A view of the crystal structure of potassium hydrogen α -ketoglutarate.

Table 5. *Geometry of the hydrogen bonds for compounds (I), (II) and (III)*

O—H...O	O...O	O—H	H...O	∠O—H...O
Compound (I)				
O(1)—H(1)...O(2)	2.679 (2) Å	0.87 (4) Å	1.81 (4) Å	179 (3)°
O(5)—H(5)...O(4 ⁱⁱ)	2.678 (2)	0.93 (4)	1.76 (4)	167 (3)
Compound (II)				
O(5)—H(5)...O(4 ⁱⁱⁱ)	2.688 (2)	0.87 (4)	1.82 (4)	173 (3)
Compound (III)				
O(5)—H(5)...O(1 ^{iv})	2.511 (2)	0.87 (4)	1.65 (4)	176 (4)

Symmetry code: (i) $1-x, -y, 1-z$; (ii) $-x, -y, 1-z$; (iii) $-x, 1-y, 1-z$; (iv) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Crystals of (II) and (III) consist of α -ketoglutarate monoanions and sodium or potassium cations respectively. The difference between α -ketoglutaric acid and its monosodium and monopotassium salts in the crystalline state is that the anionic form of the ketoglutarate residue in (II) and (III) causes the neighbouring molecules to be linked by Na⁺ (or K⁺) cations and not only by H bonds which nevertheless affect the structure of the basic skeleton in both salts.

In (II) each Na⁺ cation is coordinated to six O atoms that belong to five different glutarate anions. The polyhedron of the six O atoms is a distorted octahedron with the Na...O distances ranging from 2.355 (2) to 2.605 (2) Å. Coordination polyhedra and H bonds are displaced alternately along the *c* direction. Thus the ionic interactions stabilize the structure in three dimensions. The O(1), O(2) and O(3) atoms that coordinate to sodium cations are not involved in H bonding. The centres of H-bonded dimers coincide with the centres of symmetry.

In (III) each K⁺ cation is surrounded by eight O atoms belonging to seven different glutarate ions at distances varying from 2.747 (2) to 3.013 (2) Å. In contrast to (II) all O atoms are involved in coordination bonds. As shown on the packing diagram (Fig. 6) the hydrogen bond O(5)—H(5)...O(1) links the monoprotonated α -ketoglutarate ions head-to-tail along the *b* axis. The packing of these chains is completed through the coordination to the K⁺ cations.

The H bonds in (I) and (II) may be described as normal dimer type, whilst in (III) (where the H bond is shorter) as *B*₂ type according to Speakman's notation (Speakman, 1972; Sime, Speakman & Parthasarathy, 1970).

The geometry of the basic α -ketoglutarate skeleton can best be described in terms of torsion angles (Table 4). In the case of (I) and (II) the groups of atoms C(3), C(4), C(5), O(4) and O(5) are almost in one plane. In contrast, the torsion angle C(3)—C(4)—C(5)—O(5) in (III) is 93.2 (5)° indicating the loss of coplanarity of the carboxyl group with respect to the plane through the C atoms. In general, the C-atom chain of (III) is more planar than that of (I) and (II) [the maximum deviation from the best plane through C atoms is

0.031 (2) Å for C(3) in (III); the respective values for C(3) in (I) and (II) are: 0.25 (1) and 0.24 (1) Å].

The differences in bond lengths in the compounds under consideration do not essentially exceed the limits of 3σ but there is a tendency that should be mentioned: namely, the distance C(3)—C(4) of 1.506 (2) Å in (II) differs to a great extent from that in (III) of 1.522 (3) Å. This difference seems to originate from a hyperconjugation-like effect in the case of (II) and (I) where C(2)—O(3) and O(4)—C(5)—O(5) are approximately coplanar. Another approach is based on the hypothesis given by Tavale, Pant & Biswas (1963) for the series of Na α -ketomonocarboxylates. In Na oxobutyrate there was a difference between bond length C(*sp*³)—C(carbonyl) and the expected value. The authors explained that fact on the assumption of partial enolization. However, the difference in the α -ketoglutarate is not so pronounced as in the α -ketobutyrate [besides, Tavale *et al.* (1963) solved the structure with a limited amount of visually estimated film data]. Furthermore, the final difference-Fourier syntheses for (I), (II) and (III) (as discussed in the *Experimental*) do not indicate any delocalization or disordering of the H atoms.

Despite the extensive discussion (Leiserowitz, 1976; Ciunik, 1980; *Molecular Structures and Dimensions*, 1970–1983) concerning various aspects of stereochemistry of carboxylic acids and their derivatives there is no systematic review covering the whole problem. The paper of Leiserowitz (1976) treats the subject in an exhaustive manner but the author does not consider the anionic forms of the carboxylic acid residues in the crystalline carboxylate, therefore making no suggestion as to the structural relations between anionic and non-anionic forms, their influence on the intramolecular structure of the basic skeleton of the molecule, the interaction between molecules in the crystal lattice *etc.*

Finally, our work was stimulated by trials to isolate the Mn^{II} complexes with α -ketoglutaric acid. Unfortunately, thus far we have not obtained such crystals.

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