

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF NOVEL LAYERED IRON ARSENATE-OXALATE
(NH₄)₃K₃[Fe₂(HAsO₄)₂(C₂O₄)₄]·2H₂ON. Ouerfelli^{1,2}, H. Chebbi^{1,3}, M. Faouzi Zid¹¹Université de Tunis El Manar, Faculté des Sciences de Tunis, Laboratoire de Matériaux et Cristallographie, Tunis, Tunisia²Université de Tunis Carthage, Institut Préparatoire aux Etudes d'Ingénieur de Bizerte, Bizerte, Tunisia³Université de Monastir, Institut Préparatoire aux Etudes d'Ingénieurs de Monastir, Monastir, Tunisia
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A new open-framework structure of iron arsenate-oxalate (NH₄)₃K₃[Fe₂(HAsO₄)₂(C₂O₄)₄]·2H₂O (**I**) is synthesized by slow evaporation and structurally characterized by single crystal X-ray diffraction methods. It crystallizes in the triclinic space group $P\bar{1}$ (No. 2), with $a = 10.154(4)$ Å, $b = 10.430(4)$ Å, $c = 15.085(7)$ Å, $\alpha = 96.81(3)^\circ$, $\beta = 105.04(43)^\circ$, $\gamma = 93.93(3)^\circ$, $V = 1523.7(11)$ Å³ and $Z = 2$. Its crystal structure consists of two crystallographically independent bishydrogenarsenato tetraoxalato diiron(III) anions, both located on centres of inversion, while the potassium and ammonium cations and water molecules are located in general positions. These moieties are connected through N—H...O and O—H...O hydrogen bonds to form infinity of layers parallel to the (101) plane, thus leading to a two-dimensional open framework.

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In chemistry, the importance to synthesize new open-framework materials has attracted increasing attention. The incorporation of oxalate anions into the iron-phosphate frameworks expands the structural complexity and properties through their coordinating propensities and geometries. According to the literature, many researches on metal—oxalate hybrid compounds are carried out due to their original structures and potential applications as co-precipitation precursors [1, 2], in heterogeneous catalysis [3, 4] (in sorption and ionic exchange processes), in conductivity and magnetism [5–7], and as Li-ion batteries [8–10]. However, few iron oxalate-phosphates [11] have been reported to date. The oxalate anion is a key bridging element in several molecular magnetic materials. To our knowledge (C₄N₂H₁₂)₂[Fe₄(HAsO₄)₆(C₂O₄)₂] [12] is the first example of iron arsenate-oxalate with the (C₃N₂H₁₂)₃[Fe₆(AsO₄)₂(HAsO₄)₆(C₂O₄)₃] with the organic cation [13] has recently been synthesized. Here we report the synthesis and crystal structure of the first iron arsenate-oxalate with the inorganic cation: (NH₄)₃K₃[Fe₂(HAsO₄)₂(C₂O₄)₄]·2H₂O (**I**).

Experimental. Synthesis of (NH₄)₃K₃[Fe₂(HAsO₄)₂(C₂O₄)₄]·2H₂O (I**).** Crystals of **I** were obtained by slow evaporation. The compound was synthesized from a mixture of potassium nitrate, iron nitrate, and diammonium oxalate respectively (3:1:3 molar ratio), dissolved in deionized water. This solution was acidified by arsenic acid until the pH = 1. After three weeks, the evaporation of the final mixture at a temperature of 12 °C led to the formation of parallelepiped green crystals identified at the title compound. A single crystal obtained in this way was chosen for X-ray diffraction studies.

X-ray crystallography. The X-ray diffraction analysis of compound **I** was performed on an automated four-circle Enraf-Nonius CAD-4 diffractometer with a graphite monochromated MoK_α radiation source ($\lambda = 0.71073 \text{ \AA}$).

The crystallographic data of **I**: $\text{C}_8\text{H}_{18}\text{As}_2\text{Fe}_2\text{K}_3\text{N}_3\text{O}_{26}$, $FW = 974.12$, $T = 293 \text{ K}$, crystal size $0.198 \times 0.121 \times 0.110 \text{ mm}$, triclinic, $P\bar{1}$, $a = 10.154(4) \text{ \AA}$, $b = 10.430(4) \text{ \AA}$, $c = 15.085(7) \text{ \AA}$, $\alpha = 96.81(3)^\circ$, $\beta = 105.04(4)^\circ$, $\gamma = 93.93(3)^\circ$, $V = 1523.7(11) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 2.132 \text{ g/cm}^3$, $\mu(\text{MoK}_\alpha) = 3.758 \text{ mm}^{-1}$, a total of 6612 reflections ($\theta_{\text{min}}/\theta_{\text{max}} = 1.41/26.96^\circ$), 3051 observed reflections ($I \geq 2\sigma(I)$), 448 parameters. $\text{GOOF} = 1.015$, $R_1 = 0.0572$, $wR_2 = 0.1409$ ($I \geq 2\sigma(I)$), $wR_2 = 0.1818$ (all data), max./min. diff. peak $1.12/-1.31 \text{ e/\AA}^3$.

The structure was solved by direct methods using the SHELXS-97 program [14] and refined by full-matrix least squares based on F^2 . Non-hydrogen atoms were refined anisotropically. The N—H hydrogen atoms of ammonium groups and the O—H hydrogen atoms of water molecules were positioned with the idealized geometry (N—H = 0.85 \AA and O—H = 0.82 \AA) and refined with fixed isotropic displacement parameters according to the riding model $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{O})$ while the hydroxyl group in $(\text{HAsO}_4)^{2-}$ anions was restrained using the HFIX 147 instruction in SHELXL-97 [14]. CIF file containing complete information about the structure of **I** was deposited with the Cambridge Crystallographic Data Center (No.1050388); the file is freely available upon request from the following web site: http://www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. The crystal structure of the title complex $(\text{NH}_4)_3\text{K}_3[\text{Fe}_2(\text{HAsO}_4)_2(\text{C}_2\text{O}_4)_4] \cdot 2\text{H}_2\text{O}$ consists of two crystallographically independent bishydrogenarsenato tetraoxalato diiron(III) anions, both located on centres of inversion, while the potassium and ammonium cations and water molecules are located in general positions (Fig. 1).

The structure of the title compound can be described by infinity of layers parallel to the (101) plane, forming a two-dimensional open framework built of FeO_6 , HAsO_4 , C_2O_4 , K, and NH_4 moieties (Fig. 2).

These layers were formed by centrosymmetric mixed cyclic units $[\text{Fe}_2(\text{HAsO}_4)(\text{C}_2\text{O}_4)_4]^{6-}$, isolated from each other by water molecules, potassium and ammonium cations. These moieties are connected through N—H...O and O—H...O hydrogen bonds (Fig. 3). The $[\text{Fe}_2(\text{HAsO}_4)_2(\text{C}_2\text{O}_4)_4]^{6-}$ complex is built of two corner-sharing tetrahedra HAsO_4 and two alternating FeO_6 octahedra. Two oxalates act as bis-bidentate ligands to each FeO_6 octahedron. It shows a distorted octahedral coordination for both Fe1 and Fe2, indicating a wide range of O—O bond lengths ($2.604(8)$ — $3.059(8) \text{ \AA}$ for Fe1,

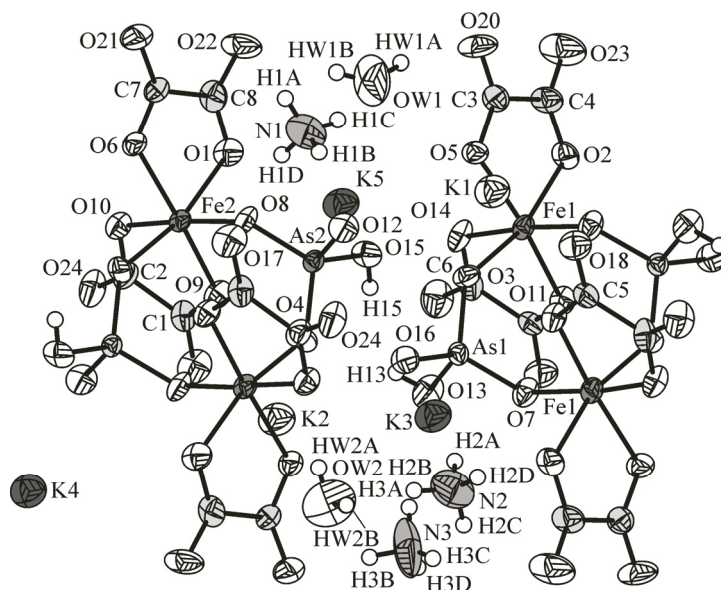


Fig. 1. Crystal structure of **I** with the atom numbering scheme

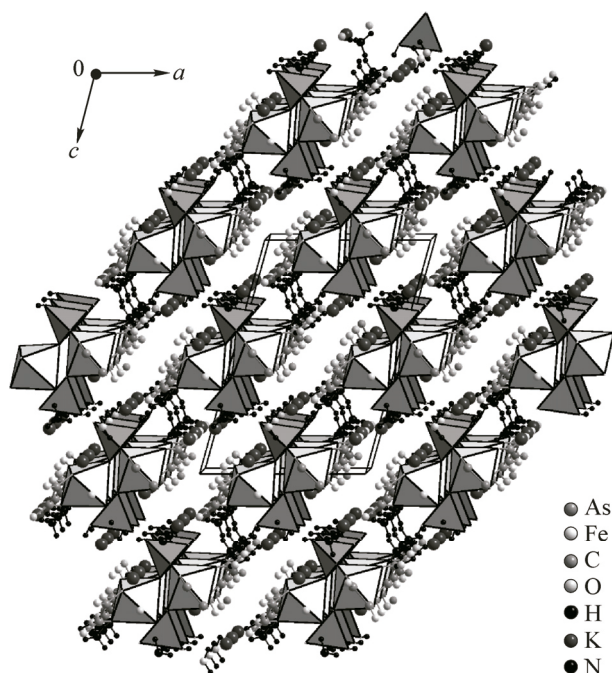


Fig. 2. View of the two-dimensional framework structure of **I**

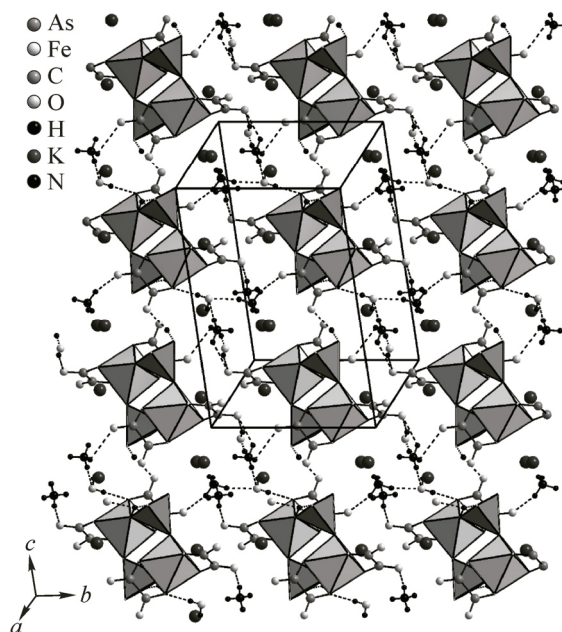


Fig. 3. View towards the (101) plane of the crystal structure of **I**. The dotted lines indicate the N—H...O and O—H...O hydrogen bonds

2.600(9)—3.037(9) Å for Fe2), and small O—Fe—O bond angles (79.5(2)° for Fe1, 79.3(2)° for Fe2) subtended by the oxalate ligands. This is confirmed by $DI_o = 4\%$ and $DI_a = 5$ to 6% for both octahedra (Table 1). The As atoms have tetrahedral coordination with As—O distances in the range of 1.651(5)—1.719(6) Å (av. 1.687 and 1.682 Å for As1 and As2, respectively). AsO₄ are regular tetrahedral; their DI parameters do not exceed 3%. The distorted FeO₆ octahedra have Fe—O distances ranging from 1.953(6) to 2.070(6) Å ($DI_d = 2\%$). These are typical values of the iron octahedral coordination [15—18]. Oxygen atoms are bonded to Fe atoms through As—O—Fe linkages.

A remarkable structural feature of this compound is the absence of covalent intracranial —Fe—O—Fe— interactions. Carbon atoms are bonded to iron atoms through regular C—O linkages with a C—O distance in the range of 1.221(11)—1.304(10) Å (av. C—O = 1.257 Å) and an average O—C—O bond angle of 126.1°. The K⁺ cations partially occupy their sites and they are inserted in the interlayer space. The K—O distances vary from 2.732(10) to 3.428(7) Å.

Table 1

Distortion indices (DI) for the coordination polyhedra around Fe and As in **I**

	As1	As2	Fe1	Fe2		As1	As2	Fe1	Fe2		As1	As2	Fe1	Fe2
DI_d	0.014	0.006	0.015	0.016	DI_a	0.030	0.029	0.057	0.053	DI_o	0.020	0.016	0.040	0.039

$$DI_d = \sum_{i=1}^{n_1} (|d_i - d_m|) / n_1 d_m; \quad DI_a = \sum_{i=1}^{n_2} (|a_i - a_m|) / n_1 a_m; \quad \text{and} \quad DI_o = \sum_{i=1}^{n_2} (|o_i - o_m|) / n_1 o_m.$$

d , a , and o signify the Fe/As—O bond distance, the O—Fe/As—O angle, and the O—O edge within the relevant polyhedron; index i indicates individual values, index m the mean value for the polyhedron. n_1 and n_2 are 4 and 6 for the arsenate tetrahedra; 6 and 12 for the iron octahedra.

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