Crystal structure of potassium tris(oxalato)ferrate(III) trihydrate doped with sodium, $K_{2.9}Na_{0.1}Fe(C_2O_4)_3 \cdot 3H_2O$

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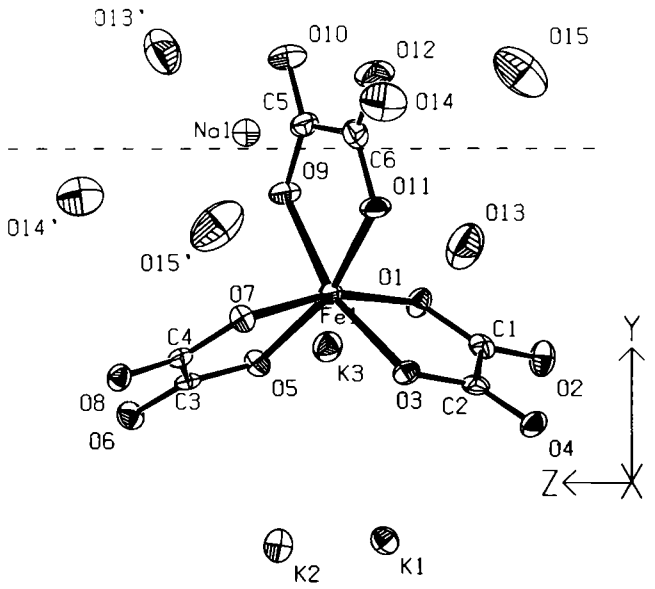

Source of material: The preparation of two phases of a trisoxalatoferrate(III) is described in ref. 1. Sodium oxalate was added to favour the formation of the cubic anhydrous phase. But crystals of the monoclinic trihydrate were formed, too. They contain sodium only as an impurity. An ICP-AES analysis yielded for the cations the relation Fe : K : Na = 1 : 2.93(5) : 0.12(2) in the trihydrate.

The crystal structure of the sodium-doped trihydrate is the same as that of the pure potassium compound (see ref. 2). The refinement of the oxygen positions of the water molecules is much improved. The disorder which seems to be present in this class of compounds (see refs. 3, 4, 5) is observed in the title compound, too, at least in part: The occupation factor of K(3) is less than 1 and a difference peak is observed in the channel of the water molecules (O(13), O(14), O(15) near O(15)). The channel axis running through 3/4,1/4,1/2 in the *c*-direction is marked by a dashed line in the figure. The position of the difference peak was used to put the sodium atom on it with a refined occupation factor of 0.1. In this model it is unsatisfactory that the distance between Na(1) and O(15) is too short (1.6 Å). Taylor (see ref. 3) therefore assumed a disorder for O(15) too. But in spite of the large anisotropic displacement parameters of O(15) the lowering of the occupation factor of this atom did not improve the refinement here.

The next highest difference peak located between O(13) and O(14) may indicate a hydrogen atom but no further hydrogen atoms could be detected. The third difference peak corresponds to Taylor's Ow(3*). Both peaks were not considered here in the refinement. The setting of the structure agrees with ref. 2 but differs from that of other authors: For comparison the data of ref. 3 and 5 have to be transformed by 1/2–*x*, *y*, 1/2–*z* or origin-shifted by 1/2, 1/2, 0, those of ref. 4 transformed by *x*, 1/2–*y*, *z* or origin-shifted by 0, 0, 1/2. On large crystals the following faces were observed: {0,1,0}, {1,1,0} and {$\bar{1}$,1,1}. The crystals are elongated in the *c*-direction and are flat in the *b*-direction.

Table 1. Parameters used for the X-ray data collection

Crystal:	yellow-green crystal of irregular shape, size 0.08 x 0.13 x 0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	19.00 cm^{-1}
Diffractometer:	Siemens-Stoe
Scan mode:	ω/2θ, learnt profile
$T_{measurement}$:	298 K
$2\theta_{max}$:	46.1°
$N(hkl)_{unique}$:	2118
Criterion for I_o:	$I_o > 2\,\sigma(I_o)$
$N(param)_{refined}$:	232
Programs:	SHELXL-93, PLATON, X-RED, X-SHAPE

Table 2. Final atomic coordinates and displacement parameters (in $Å^2$)

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
Na(1)	4*e*	0.107(4)	0.871(3)	0.264(1)	0.390(2)	0.038(6)

Table 3. Final atomic coordinates and displacement parameters (in $Å^2$)

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	4*e*		0.2639(1)	0.13078(4)	0.2506(1)	0.0251(4)	0.0223(4)	0.0261(4)	–0.0003(4)	0.0088(3)	–0.0010(5)
K(1)	4*e*		0.4749(2)	–0.07395(7)	0.1621(1)	0.0330(7)	0.0372(9)	0.035(1)	0.0013(7)	0.0126(7)	0.0038(7)
K(2)	4*e*		0.0391(2)	–0.07804(8)	0.3374(2)	0.0291(7)	0.053(1)	0.037(1)	–0.0019(7)	0.0130(7)	–0.0022(8)

Table 3. (Continued)

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(3)	4e	0.893(4)	0.7580(2)	0.08683(7)	0.2557(2)	0.0433(9)	0.0436(9)	0.0389(9)	−0.0013(9)	0.0171(7)	−0.003(1)
C(1)	4e		0.0286(8)	0.0870(3)	0.0014(7)	0.028(4)	0.029(4)	0.030(4)	−0.008(3)	0.014(3)	0.007(3)
C(2)	4e		0.2147(8)	0.0551(3)	0.0117(7)	0.034(4)	0.018(3)	0.034(5)	−0.007(3)	0.013(3)	0.002(3)
C(3)	4e		0.2765(7)	0.0582(3)	0.4868(6)	0.027(3)	0.014(3)	0.032(4)	−0.001(3)	0.014(3)	−0.004(3)
C(4)	4e		0.4759(8)	0.0779(3)	0.4993(7)	0.029(3)	0.019(3)	0.028(4)	0.002(3)	0.010(3)	−0.005(3)
C(5)	4e		0.2397(8)	0.2702(3)	0.2946(6)	0.042(4)	0.027(4)	0.036(4)	0.006(3)	0.002(3)	−0.005(3)
C(6)	4e		0.3708(8)	0.2625(3)	0.2101(6)	0.053(4)	0.037(4)	0.029(4)	−0.009(4)	0.010(3)	0.004(3)
O(1)	4e		0.0299(5)	0.1233(2)	0.1052(4)	0.025(2)	0.041(3)	0.029(3)	0.005(2)	0.006(2)	−0.008(2)
O(2)	4e		−0.1011(5)	0.0770(2)	−0.0981(4)	0.029(2)	0.062(3)	0.029(3)	−0.009(2)	0.007(2)	−0.004(2)
O(3)	4e		0.3374(5)	0.0655(2)	0.1261(4)	0.026(2)	0.028(2)	0.032(3)	0.003(2)	0.010(2)	−0.004(2)
O(4)	4e		0.2356(5)	0.0229(2)	−0.0835(4)	0.047(3)	0.032(3)	0.033(3)	−0.003(2)	0.022(2)	−0.008(2)
O(5)	4e		0.1623(5)	0.0732(2)	0.3723(4)	0.019(2)	0.034(3)	0.030(3)	0.000(2)	0.005(2)	0.006(2)
O(6)	4e		0.2412(5)	0.0301(2)	0.5817(4)	0.037(2)	0.037(3)	0.033(3)	0.001(2)	0.019(2)	0.004(2)
O(7)	4e		0.4929(5)	0.1101(2)	0.3966(4)	0.020(2)	0.035(3)	0.029(3)	−0.001(2)	0.008(2)	0.005(2)
O(8)	4e		0.5982(5)	0.0615(2)	0.5999(4)	0.025(2)	0.036(2)	0.026(3)	0.003(2)	0.002(2)	−0.004(2)
O(9)	4e		0.1828(5)	0.2138(2)	0.3269(4)	0.040(2)	0.024(2)	0.046(3)	−0.001(2)	0.020(2)	−0.003(2)
O(10)	4e		0.1984(7)	0.3257(2)	0.3234(5)	0.079(4)	0.029(3)	0.068(4)	0.010(3)	0.022(3)	−0.007(3)
O(11)	4e		0.3937(6)	0.2019(2)	0.1774(4)	0.064(3)	0.021(2)	0.044(3)	−0.010(2)	0.029(2)	−0.003(2)
O(12)	4e		0.4454(8)	0.3116(2)	0.1792(5)	0.121(5)	0.036(3)	0.072(4)	−0.029(3)	0.053(4)	−0.008(3)
O(13)	4e		0.6233(7)	0.1696(3)	0.0294(5)	0.091(4)	0.101(5)	0.063(4)	0.011(4)	0.025(3)	−0.022(3)
O(14)	4e		0.7928(7)	0.2890(3)	0.1646(6)	0.080(4)	0.071(4)	0.102(4)	−0.002(3)	0.032(3)	0.004(4)
O(15)	4e		0.9061(8)	0.3133(3)	−0.0608(7)	0.089(4)	0.121(6)	0.130(6)	0.025(4)	0.065(4)	0.053(5)

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