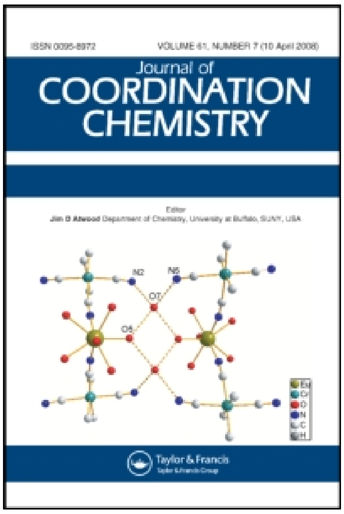

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Supramolecular interactions in the X-ray crystal structure of potassium tris(oxalato)ferrate(III) trihydrate

Peter C. Junk[a]
[a] School of Chemistry, Monash University, Clayton, Vic, Australia

To cite this Article Junk, Peter C.(2005) 'Supramolecular interactions in the X-ray crystal structure of potassium tris(oxalato)ferrate(III) trihydrate', Journal of Coordination Chemistry, 58: 4, 355 — 361
To link to this Article: DOI: 10.1080/00958970512331334250
URL: http://dx.doi.org/10.1080/00958970512331334250

Journal of Coordination Chemistry
Vol. 58, No. 4, 10 March 2005, 355–361

Supramolecular interactions in the X-ray crystal structure of potassium tris(oxalato)ferrate(III) trihydrate

PETER C. JUNK*

School of Chemistry, Monash University, Clayton, Vic, 3800, Australia

(Received 19 July 2004; Revised 11 October 2004; In final form 16 November 2004)

Potassium tris(oxalato)ferrate(III) trihydrate crystallises in the monoclinic space group $P2_1/c$ with $a = 7.7422(10)$, $b = 19.9168(10)$, $c = 10.3457(10)$ Å, $\beta = 107.846(10)^\circ$, $V = 1518.5(3)$ Å^3, for $Z = 4$. The overall structure is comprised of $[Fe(C_2O_4)_3]^{3-}$ octahedral units linked through potassium ions and hydrogen bonding between water molecules and oxalate anions giving a three-dimensional supramolecular network.

Keywords: Iron(III); Oxalate; Supramolecular; Hydrogen bonding

1. Introduction

The coordination and binding capacity of the oxalate ($C_2O_4^{2-}$) ion has made it ubiquitous in synthetic and naturally-occurring chemistry, e.g. in the iron-containing complex humboltine and in molybdenum-containing compounds important in biochemistry as well as in chromium oxalate complexes in the tanning industry [1]. In particular, the tris-oxalato metallate ions $[M(C_2O_4)_3]^{3-}$ of the transition metals and aluminium have been extensively studied in wide-ranging applications and many X-ray crystal structures of these ions have appeared in the literature; the tris(oxalate)ferrate(III) ion has been structurally authenticated in many systems (a Cambridge Crystallographic Database search for the resulted in eight such hits for alkali metal salts of the $[Fe(C_2O_4)_3]^{3-}$ ion) [2], but it came as a surprise to find that for simple cationic species, e.g. the alkali metal tris(oxalate)ferrates, there were only a limited number of examples in the literature [3]. Thus, three examples of $[NH_4]_3[Fe(C_2O_4)_3] \cdot 3H_2O$ [4], three of the $[K_{3-x}Na_x][Fe(C_2O_4)_3] \cdot xH_2O$ system [5], $Na_3[Fe(C_2O_4)_3] \cdot nH_2O$ [6] and $Li_4Cl[Fe(C_2O_4)_3] \cdot 9H_2O$ [7] are the only representatives of these systems. Surprisingly, the only structural reference to the well-known $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ was as a powder X-ray crystallographic study, or space group determinations on single crystals [8]. Thus, we now report herein, the single crystal

---

*E-mail: peter.junk@sci.monash.edu.au

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970512331334250

X-ray structure determination of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ and its supramolecular interactions in the three-dimensional network.

2. Experimental

2.1. *Synthesis*

$K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ was synthesised according to a literature method [9]. Bright green X-ray quality crystals were isolated by slow cooling of the reaction mixture.

2.2. *Crystal structure determination*

A crystal of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ was mounted on a glass fibre using epoxy resin, and data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with total reflections and unique data listed in table 1. The position of the heavy atoms were found using the Patterson method and refined on F^2 using SHELXL97–2 [10] with X-SEED [11] as a graphics interface. All non-hydrogen atoms were located and refined with anisotropic thermal parameters. Hydrogen atoms were placed in optimal positions and refined with fixed thermal parameters. Crystal data and a summary of data collection appear in table 1, while selected bond distances and angles appear in table 2; hydrogen bonding parameters are in table 3.

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 244090. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223 336-033; E-mail: deposit@ccdc.cam.ac.uk).

3. Discussion

$K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with the one whole molecule of the complex in the asymmetric unit. In the $[Fe(C_2O_4)_3]^{3-}$ anion,

Table 1. Crystal data and summary of data collection.

Compound	$[K_3(Fe(C_2O_4)_3)]\cdot 3H_2O$
Formula	$C_6H_6FeK_3O_{15}$
Formula wt.	491.26
Space group	$P2_1/c$
a, Å	7.7422(10)
b, Å	19.9168(10)
c, Å	10.3457(10)
β, °	107.846(10)
V, Å^3	1518.5(3)
Z	4
D_c, g cm^{-3}	2.149
μ, mm^{-1}	1.90
Diffractometer	Enraf-Nonius CAD4
Reflections collected	2856
Unique reflections	2652 ($R_{int} = 0.066$)
T, K	296
R [$I > 2\sigma(I)$]	0.0409
$wR2$ (all data)	0.1210

Table 2. Selected bond distances (Å) and angles (°) for $[K_3(Fe(C_2O_4)_3)]\cdot 3H_2O$.

Fe(1)–O(1)	1.981(2)	K(2)–O(3)#3	2.666(3)
Fe(1)–O(2)	2.031(2)	K(2)–O(4)#3	3.034(3)
Fe(1)–O(5)	1.986(2)	K(2)–O(6)	3.144(2)
Fe(1)–O(6)	2.031(2)	K(2)–O(7)#1	2.703(2)
Fe(1)–O(9)	2.010(2)	K(2)–O(8)	3.331(3)
Fe(1)–O(10)	2.001(2)	K(2)–O(8)#2	2.732(2)
K(1)–O(1)#2	3.058(2)	K(2)–O(11)#6	2.814(3)
K(1)–O(2)#1	3.150(2)	K(22)–O(13)	3.089(6)
K(1)–O(4)#7	2.829(2)	K(2)–O(15)	2.947(4)
K(1)–O(5)#1	2.900(2)	K(3)–O(2)	2.946(2)
K(1)–O(6)#2	3.002(2)	K(3)–O(3)#3	2.766(3)
K(1)–O(8)	2.871(2)	K(3)–O(4)	3.271(3)
K(1)–O(13)	2.737(4)	K(3)–O(4)#5	2.793(2)
K(1)–O(14)#7	2.793(4)	K(3)–O(7)#1	2.700(2)
		K(3)–O(8)#1	2.998(3)
		K(3)–O(11)#4	3.219(3)
		K(3)–O(12)#4	2.771(3)
		K(3)–O(14)	2.637(3)
O(1)–Fe(1)–O(2)	80.38(9)	O(2)–Fe(1)–O(10)	87.15(9)
O(1)–Fe(1)–O(5)	162.98(11)	O(5)–Fe(1)–O(6)	80.41(9)
O(1)–Fe(1)–O(6)	89.10(9)	O(5)–Fe(1)–O(9)	100.82(10)
O(1)–Fe(1)–O(9)	92.41(10)	O(6)–Fe(1)–O(9)	89.66(9)
O(1)–Fe(1)–O(10)	102.18(10)	O(5)–Fe(1)–O(10)	90.84(10)
O(2)–Fe(1)–O(5)	89.49(9)	O(6)–Fe(1)–O(10)	164.45(10)
O(2)–Fe(1)–O(6)	105.46(10)	O(9)–Fe(1)–O(10)	79.31(9)
O(2)–Fe(1)–O(9)	163.02(9)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+2$, $-z+1$; #2 $-x+2$, $-y+2$, $-z+1$; #3 $-x+2$, $-y+2$, $-z+2$; #4 $-x+1$, $y+1/2$, $-z+3/2$; #5 $-x+1$, $-y+2$, $-z+2$; #6 $-x+2$, $y+1/2$, $-z+3/2$; #7 x, y, $z-1$.

Table 3. Hydrogen bond distances (Å) and angles (°) for $[K_3(Fe(C_2O_4)_3)]\cdot 3H_2O$.

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(14)–H(14A)···O(15)#11	0.996(10)	2.24(3)	2.940(5)	126(3)
O(13)–H(13B)···O(15)	0.999(10)	1.84(3)	2.778(5)	156(5)
O(13)–H(13A)···O(9)#2	1.000(10)	1.93(3)	2.782(4)	141(4)
O(14)–H(14B)···O(10)#5	0.999(10)	1.84(3)	2.776(4)	155(7)
O(15)–H(15B)···O(12)#4	1.005(11)	1.90(6)	2.812(5)	149(10)

Symmetry transformations used to generate equivalent atoms: #2 $-x+2$, $-y+2$, $-z+1$; #4 $-x+1$, $y+1/2$, $-z+3/2$; #5 $-x+1$, $-y+2$, $-z+2$; #11 x, $-y+5/2$, $z+1/2$.

the iron(III) centre is distorted from regular octahedral geometry with the three oxalato ligands being bound in a bidentate fashion (figure 1, table 2). The Fe–O bond lengths on two oxalate ligands are asymmetric while on the third the Fe–O bond distances are closer to symmetric (table 2).

The three potassium ions do not exist as discrete ions in the lattice, but rather are coordinated by either water molecules of solvation or oxygen atoms of the oxalate ions. The ion K(1) is eight coordinate and has a geometry most closely described [12] as a dodecahedron (figure 2a). The eight-fold coordination arises from two water molecules and six oxygens of the oxalate ligands, with the water molecules situated in *cis* B vertices (B1 and B2 positions) [13] of the dodecahedron. The K–O distances vary considerably from K(1)–O(13) 2.737(4) Å to K(1)–O(2) of 3.150(2) Å. The K–O(water) distances (2.737(4) and 2.793(4) Å) are at the lower end of this range. K(2) and K(3) are both nine coordinate with polyhedra most closely matching [12]

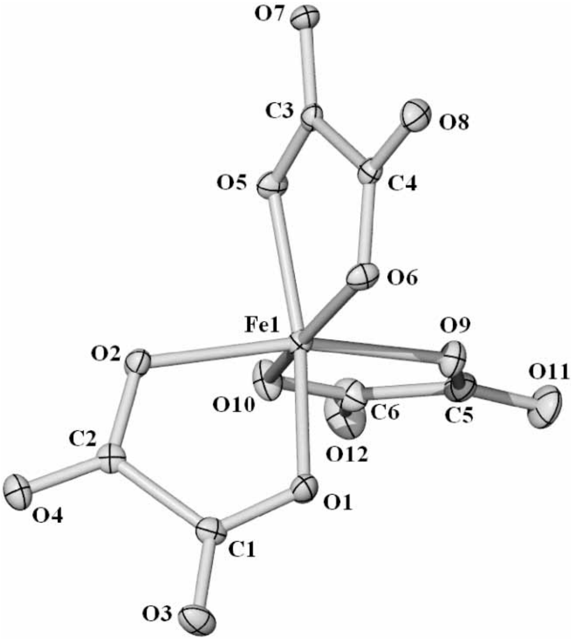

Figure 1. The octahedral coordination geometry about iron in $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$.

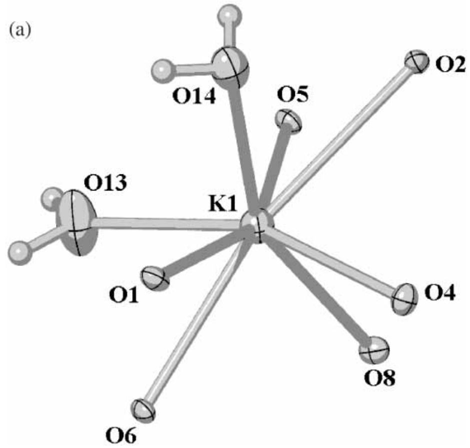

Figure 2. (a) The dodecahedral geometry about eight-coordinate K(1) in $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$. (b) The double trigonal prismatic geometry about nine-coordinate K(2) in $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$. (c) The double trigonal prismatic geometry about nine-coordinate K(3) in $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$.

a double trigonal prism with the coordination sites being made up by two water molecules and seven oxalate oxygens for K(2) and one water molecule and eight oxalate oxygens for K(3) (figures 2b and 2c). The K(2)–O distances range from 2.666(3) to 3.331(3) Å (table 2) with the K–O(water) distances being midway in this range (K(2)–O(13) 3.089(6) and K(2)–O(15) 2.947(4) Å); the K(3)–O distances are in the range 2.637(3) to 3.219(3) Å with K(3)–O(water) being the shortest of these. The

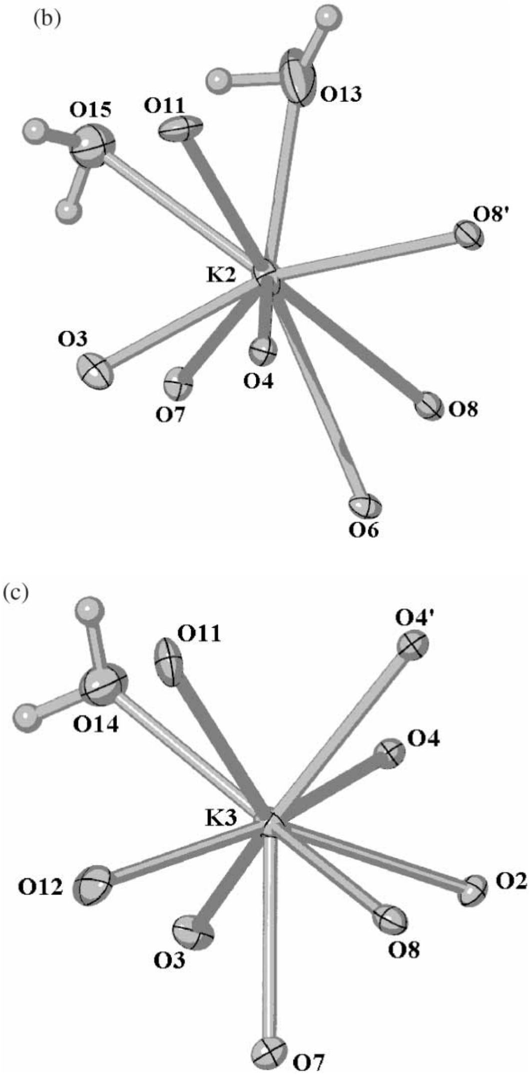

Figure 2. Continued.

binding of the potassium ions to the oxalate oxygen atoms is so extensive that each $[Fe(C_2O_4)_3]^{3-}$ unit is shrouded by 12 potassium ions which effectively hold the anionic fragments together in a three-dimensional array (figure 3) such that all oxygen atoms of the oxalate groups except O(1), O(9) and O(10) are bound by at least one potassium ion. Hydrogen bonding is also prevalent in the three-dimensional structure and contributes to the solid network (figure 3, table 3). Of the O(oxalate) atoms not bound to potassium ions (see above) both O(9) and O(10) are involved in hydrogen bonding, leaving O(1) as the only hydrogen bond acceptor in the network solid not bound by a counter ion or involved in H-bonding.

Finally, the X-ray crystal structure of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ is isomorphous to $[NH_4]_3[Fe(C_2O_4)_3] \cdot 3H_2O$ [4], $[K_{3-x}Na_x][Fe(C_2O_4)_3] \cdot xH_2O$ [5] and $K_3[M(C_2O_4)_3] \cdot 3H_2O$ (M = Al [14], V [15] and Cr [8, 14a,c].

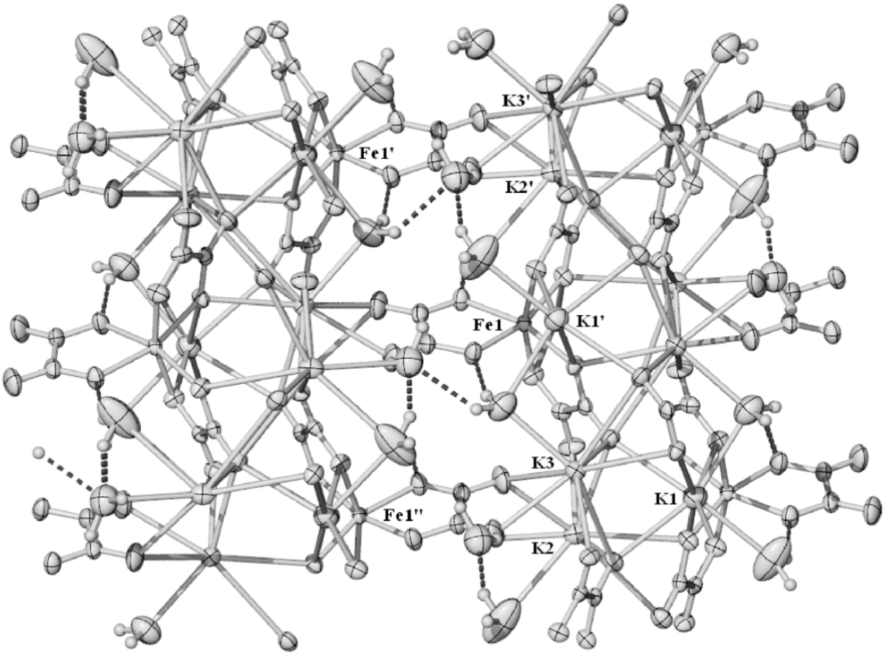

Figure 3. Packing diagram of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ showing the extended three-dimensional structure with extensive hydrogen bonding.

4. Conclusion

Potassium tris(oxalato)ferrate(III) trihydrate is comprised of potassium-shrouded $[Fe(C_2O_4)_3]^{3-}$ octahedral units linked through a network of potassium ions and hydrogen bonds giving a three-dimensional supramolecular network.

References

[1] C.O. Oldham, *Comprehensive Coordination Chemistry*, G. Wilkinson, P.D. Gilland, J.A. McCleverty (Eds.), Vol. 2, p. 443, Pergamon, Oxford (1987).

[2] K.V Krishnamurty, G.M. Harris, *Chem. Rev.* **61**, 213 (1961); (b) A Cambridge Crystallographic Database search for the tris-oxalato-ferrate(III) ion resulted in 30 hits for various cations.

[3] A Cambridge Crystallographic Database search for the resulted in eight such hits for alkali metal salts of the $[Fe(C_2O_4)_3]^{3-}$ ion.

[4] (a) E.H. Merrachi, B.F. Mentzen, F. Chassagneux, *Revue de Chimie Minerale* **23**, 329 (1986); (b) E.H. Merrachi, B.F. Mentzen, F. Chassagneux, J. Bouix, *Revue de Chimie Minerale* **24**, 56 (1987); (c) E.H. Merrachi, F. Chassagneux, B.F. Mentzen, *Powder Diffraction* **3**, 96 (1988).

[5] (a) R. Wartchow, *Z. Kristallogr. – New Crystal Structures* **212**(2), 83 (1997); (b) R. Wartchow, *Z. Kristallogr.* **212**, 57 (1997); (c) S. Henneicke, R. Wartchow, *Z. Kristallogr.* **212**, 56 (1997).

[6] Z. Yu, W. Qiang-Jin, X. Wei-Wen, Z. Lin-Na, Z. Zi-Ying, Fu. Gui-Xiang, *Chinese J. Struct. Chem. (Jiegou Huaxue)* **13**, 216 (1994).

[7] J.P. Declercq, J. Feneau-Dupont, J. Ladriere, *Polyhedron* **12**, 1031 (1993).

[8] (a) J. Van Niekerk, F.R.L. Schoening, *Acta Crystallogr.* **4**, 35 (1951); (b) J. Van Niekerk, F.R.L. Schoening, *Acta Crystallogr.* **4**, 381 (1951); (c) J. Van Niekerk, F.R.L. Schoening, *Acta Crystallogr.* **5**, 196 (1952).

[9] J.C. Bailar, Jr., E.M. Jones, *Inorg. Synth.* **1**, 35 (1939).

[10] G. M. Sheldrick, *SHELXL-97*, University of Gottingen (1997).

[11] L.J. Barbour, *J. Supramol. Chem.* **1**, 189 (2001).

[12] M. Johnson, J.C. Taylor, G.W. Cox, *J. Applied Crystallogr.* **13**, 188 (1980).

[13] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th edn., p. 17, Wiley Interscience, New York (1999).

[14] (a) R.D. Gillard, S.H. Laurie, P.R. Mitchell, *J. Chem. Soc. A* 3006 (1969); (b) P. Herpin, *Bull. Soc. Franc. Miner. Crist.* **81**, 245 (1958); (c) D. Taylor, *Aust. J. Chem.* **31**, 1455 (1978).

[15] R.H. Fenn, A.J. Graham, R.D. Gillard, *Nature (London)* **213**, 1012 (1967).