Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Rinneite, $K_3Na[FeCl_6]$, at 293, 84 and 9.5 K

Brian N. Figgis *et al.*

Electronic paper
This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Rinneite, $K_3Na[FeCl_6]$, at 293, 84 and 9.5 K

Brian N. Figgis,* Alexandre N. Sobolev, Edward S. Kucharski and Vanessa Broughton

Chemistry Department, University of Western Australia, Nedlands, WA 6907, Australia
Correspondence e-mail: bnf@crystal.uwa.edu.au

Received 12 April 2000
Accepted 19 April 2000

Data validation number: IUC0000118

The crystal structure of tripotassium sodium hexachloroferrate(II) has been determined by X-ray diffraction at 293, 84 and 9.5 K. The accurate and extensive data sets collected should be suitable for charge–density analysis studies.

Comment

Rinneite, $K_3Na[FeCl_6]$, is of interest in inorganic chemistry as it provides a rare example of a high-spin Fe^{II} complex with six monatomic ligands and high-symmetry stereochemistry. We have determined the crystal structure of $K_3Na[FeCl_6]$ by X-ray diffraction at 293, 84 and 9.5 K. It is made up of Na^+ and K^+ cations and $[FeCl_6]^{4-}$ anions. The structural features, including the cation coordination polyhedra, have been described before (Beattie & Moore, 1982) and the present results present no unusual features. The bond lengths and angles for the $[FeCl_6]^{4-}$ ion at the three temperatures are given in Table 1.

The $[FeCl_4]^{3-}$ ion consists of a regular octahedron compressed by 1.22° down a threefold axis, so that the C_3—Fe—Cl angle is 36.42°, with no twist of opposite triangular faces about that axis. The Fe—Cl bond lengths are all equal. The bond lengths and angles at ambient temperature match those of Beattie & Moore [Fe—Cl 2.5100 (5) Å and Cl—Fe—Cl 88.39 (2)°] within the error limits of 3σ and do not vary significantly with temperaure.

Experimental

$K_3Na[FeCl_6]$ was prepared from aqueous solution as described by Boeke (1909). Large single crystals of the somewhat air and moisture sensitive complex were obtained. In an inert atmosphere, one of these was shaved into a small approximate cube by hand using a razor blade and mounted inside a sealed glass capillary tube.

$K_3Na[FeCl_6]$ at 293 K

Crystal data

$K_3Na[FeCl_6]$
M_r = 408.84
Trigonal, $R\bar{3}c$
a = 12.033 (2) Å
c = 13.863 (4) Å
V = 1738.3 (6) Å^3
Z = 6
D_x = 2.343 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 reflections
θ = 15.45–15.45°
μ = 3.736 mm^{-1}
T = 293 (2) K
Cube, very pale yellow
0.40 × 0.40 × 0.40 mm

Data collection

Huber 512 goniometer diffractometer
ω–2θ scans
Absorption correction: spherical (*Xtal*3.4; Hall *et al.*, 1996)
T_{min} = 0.268, T_{max} = 0.282
3808 measured reflections
347 independent reflections
347 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 25.05°
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections
every 100 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.031
S = 1.623
347 reflections
20 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0099P)^2 + 0.5551P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0146 (6)

$K_3Na[FeCl_6]$ at 84 K

Crystal data

$K_3Na[FeCl_6]$
M_r = 408.84
Trigonal, $R\bar{3}c$
a = 11.922 (1) Å
c = 13.761 (2) Å
V = 1693.9 (3) Å^3
Z = 6
D_x = 2.405 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
θ = 17.0–20.5°
μ = 3.834 mm^{-1}
T = 84 (2) K
Prism, very pale yellow
0.49 × 0.35 × 0.33 mm

Data collection

Syntex $P2_1$ diffractometer
ω–2θ scans
Absorption correction: Gaussian (*Xtal* 3.4; Hall *et al.*, 1996)
T_{min} = 0.279, T_{max} = 0.377
37 086 measured reflections
1991 independent reflections
1930 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 50.10°
$h = -25 \rightarrow 25$
$k = -25 \rightarrow 25$
$l = -29 \rightarrow 29$
6 standard reflections
every 100 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.036
S = 1.398
1991 reflections
20 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0106P)^2 + 0.7910P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0047 (2)

$K_3Na[FeCl_6]$ at 9.5 K

Crystal data

$K_3Na[FeCl_6]$
M_r = 408.84
Trigonal, $R\bar{3}c$
a = 11.893 (1) Å
c = 13.735 (2) Å
V = 1682.4 (3) Å^3
Z = 6
D_x = 2.421 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 24.42–29.92°
μ = 3.860 mm^{-1}
T = 9.5 (5) K
Cube, very pale yellow
0.40 × 0.40 × 0.40 mm

Data collection

Huber 512 goniometer diffractometer
ω–2θ scans
Absorption correction: spherical (*Xtal* 3.4; Hall *et al.*, 1996)
T_{min} = 0.257, T_{max} = 0.306
28 510 measured reflections
1983 independent reflections
1981 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 50.15°
$h = -25 \rightarrow 25$
$k = -25 \rightarrow 25$
$l = -29 \rightarrow 29$
3 standard reflections
every 100 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.050
S = 1.459
1983 reflections
20 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0109P)^2 + 3.4848P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.93 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0071 (2)

Table 1
Bond lengths (A) and angles (°) in $K_3Na[FeCl_6]$ at 293, 84 and 9.5 K.

	293 K	84 K	9.5 K
Fe—Cl	2.5124 (5)	2.5009 (2)	2.4973 (2)
Cl—Fe—Cl^{i}	180	180	180
Cl—Fe—Cl^{ii}	88.39 (2)	88.3366(8)	88.330 (8)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-y, x-y, -z$.

Room temperature and the very low temperature data sets were collected on a locally assembled Huber 512 goniometer equipped with a Displex 202D cryogenic refrigerator (Hendricksen *et al.*, 1986; Larsen, 1995). The 84 K data was collected on a Syntex *P*21 diffractometer equipped with a locally developed nitrogen gas stream cooling device. Full spheres of data were collected. For the 9.5 K data collection, the correction for the absorption by the beryllium thermal shields was performed by the *PROFIT* (Streltsov & Zavodnik, 1989) program.

For the determinations at 9.5 and 293 K, data collection: local software; cell refinement: local software. For the determination at 84 K, data reduction: *PROFIT* (Streltsov & Zavodnik, 1989). For all determinations, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1983); software used to prepare material for publication: *SHELXL*97.

The authors thank the Australian Research Council for financial support and Dr J. K. Beattie, University of Sydney, for advice about the preparation of the material.

References

Beattie, J. K. & Moore, C. J. (1982). *Inorg. Chem.* **21**, 1292–1295.
Boeke, H. E. (1909). *Sitz. Acad. Wiss. Berlin*, **34**, 632–638.
Hall, S. R., King, G. S. D. & Stewart, J. M. (1996). Editors. *Xtal*3.4 *User's Manual.* University of Western Australia, Australia.
Hendriksen, K., Larsen, F. K. & Rasmussen, S. E. (1986). *J. Appl. Cryst.* **19**, 390–394.
Larsen, F. K. (1995). *Acta Cryst.* B**51**, 468–482.
Sheldrick, G. M. (1983). *SHELXTL User's Manual*. Revision 3. Nicolet XRD Corporation, Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Siemens (1991). *P*3/*P*4-*PC Software*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Streltsov, V. A. & Zavodnik, V. E. (1989). *Sov. Phys. Crystallogr.* **34**, 824–828.