Acta Cryst. (1975). B31, 2339

Dipotassium Silver Triiodide

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(*Received* 7 *April* 1975; *accepted* 11 *April* 1975)

Abstract. K_2AgI_3, orthorhombic, *Pnma*, $a=10{\cdot}01$ (1), $b=4{\cdot}78$ (1), $c=19{\cdot}32$ (2) Å, $D_c=4{\cdot}07$ g cm^{-3}, $Z=4$, $R=0{\cdot}062$ for 595 reflexions. The I^- ions form three distinct geometrical units in the structure, tetrahedra, square pyramids and square prisms. The tetrahedra are face-shared and one out of every three contains an Ag^+ ion. Square prisms accommodate the K^+ ions.

Introduction. Needle-like crystals of K_2AgI_3 were isolated from a solid reaction mixture of KI and AgI heated to 130°C. The cell constants at 20°C were determined by least-squares refinement of the angular settings of 25 high-order reflexions. Systematic absences for $hk0$: $h=2n+1$ and $0kl$: $k+l=2n+1$ indicate either *Pnma* or $Pna2_1$. As the crystals were deliquescent, a crystal, $0{\cdot}06\times0{\cdot}06\times0{\cdot}12$ mm, was mounted in a Lindemann glass tube for data collection. With graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å), 649 reflexions were collected on a Philips PW1100 diffractometer over the range $3\leq\theta\leq22°$. The ω–2θ scan technique was employed, the scan width being $1{\cdot}2°\theta$ and scan speed $0{\cdot}04°\theta$ s^{-1}. The intensities of three reflexions measured periodically indicated no crystal decomposition. The background was counted for half the scanning time on both sides of each reflexion. 54 reflexions were considered to be unobserved according to the criterion $I<1{\cdot}65\sigma(I)$ where $\sigma(I)=[(0{\cdot}02S)^2+S+B]^{1/2}$, S=scan count and B=background count. Lorentz and polarization but no absorption corrections ($\mu=130{\cdot}0$ cm^{-1}) were made. Scattering factors for Ag^+, I^- and K^+ were those of Cromer & Mann (1968).

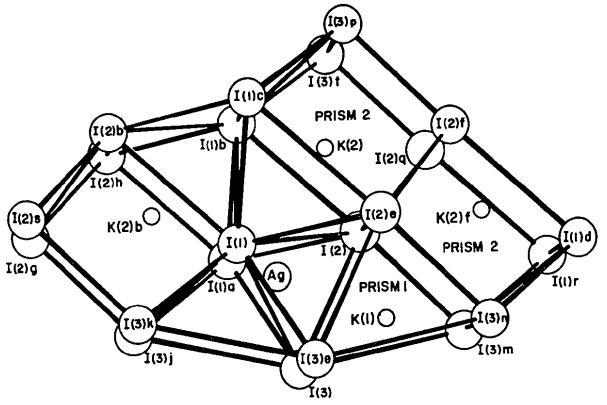

Fig. 1. The structure as viewed a few degrees from the [010] projection. The symmetry code for the atoms is given in Table 2.

The distribution of E values indicated the space group *Pnma*. This was verified by the final structural results. The structure was solved by direct methods with the Karle–Hauptman $\sum_2$ relationship. With the program *PHASE* of X-RAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), 122 reflexions with $E>1{\cdot}1$ could be phased and the subsequent E map revealed all the atoms. After several cycles of isotropic and anisotropic temperature refinement with unit weighting, R converged to 0·062. Final atomic and thermal parameters are given in Table 1. Bond lengths and angles are listed in Table 2. The labelling scheme for the atoms is shown in Fig. 1.*

Discussion. A stereoscopic illustration (Fig. 2) shows the structural features of this compound. The I^- ions form three distinct geometrical units in the structure, tetrahedra, square pyramids and square prisms.

There are three face-shared tetrahedra which have a common edge [I(1) and I(1)*a* in Fig. 1] along **b**. The central tetrahedron contains an Ag^+ ion while the other two are empty. Square pyramids are stacked above and below each of these tetrahedra and columns of alternating tetrahedra and pyramids parallel to **b** are thus formed.

Each K^+ ion is contained in a square prism and lies just above the centre of one of the square faces. There

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31046 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional and thermal parameters*

Values are $\times10^4$. Anisotropic temperature factors are of the form:

$$T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	4895 (3)	2500 (0)	4013 (2)	262 (19)	292 (22)	320 (20)	0	35 (16)	0
I(2)	8807 (3)	7500 (0)	4294 (2)	199 (19)	446 (25)	240 (19)	0	−6 (15)	0
I(3)	6884 (3)	7500 (0)	2226 (2)	260 (19)	426 (24)	199 (17)	0	−17 (15)	0
Ag	6280 (5)	7500 (0)	3646 (2)	327 (25)	538 (33)	354 (26)	0	12 (20)	0
K(1)	9223 (12)	2500 (0)	2880 (6)	281 (67)	494 (88)	285 (66)	0	−50 (57)	0
K(2)	7526 (13)	2500 (0)	5403 (6)	292 (69)	634 (99)	200 (64)	0	17 (55)	0

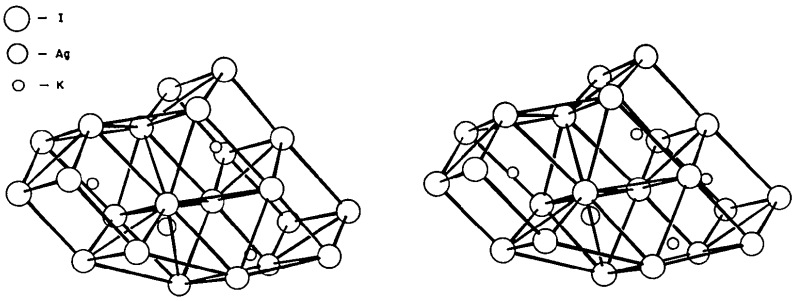

Fig. 2. A stereoscopic illustration of the structure.

are two sets of square prisms which differ in their orientation in the cell. In the one instance the prisms share triangular faces (prism 1 in Fig. 1) and are stacked to form columns parallel to **b**. Each of these prisms contains a K^+ ion. In the second orientation, the prisms share square faces with each other to form columns also parallel to **b** (prism 2 in Fig. 1). Two such columns are linked by shared triangular faces of adjacent prisms. In each of these columns every alternate prism contains a K^+ ion.

The figures were drawn with *ORTEP* (Johnson, 1965).

Table 2. *Bond lengths* (Å) *and angles* (°)

Symmetry code

a	x,	$y+1$,	z	*k*	$x-0{\cdot}5$, $0{\cdot}5-y$, $0{\cdot}5-z$
b	$1-x$,	$1-y$,	$1-z$	*m*	$0{\cdot}5+x$, $1{\cdot}5-y$, $0{\cdot}5-z$
c	$1-x$,	$-y$,	$1-z$	*n*	$0{\cdot}5+x$, $0{\cdot}5-y$, $0{\cdot}5-z$
d	$1+x$,	y,	z	*p*	$1{\cdot}5-x$, $y-0{\cdot}5$, $0{\cdot}5+z$
e	x,	$y-1$,	z	*q*	$2-x$, $2-y$, $1-z$
f	$2-x$,	$1-y$,	$1-z$	*r*	$1+x$, $1+y$, z
g	$x-1$,	y,	z	*s*	$x-1$, $y-1$, z
h	$1-x$, $0{\cdot}5+y$,		$1-z$	*t*	$1{\cdot}5-x$, $0{\cdot}5+y$, $0{\cdot}5+z$
j	$x-0{\cdot}5$, $1{\cdot}5-y$,		$0{\cdot}5-z$		

(*a*) Tetrahedra

1. I(1)—I(1)*a*	4·783 (10)	I(3)—I(3)*j*	5·118 (7)
I(1)—I(3)	4·649 (6)	I(3)—I(1)*a*	4·648 (6)
I(1)—I(3)*j*	4·532 (6)	I(1)*a*–I(3)*j*	4·532 (6)
2. I(1)—I(1)*a*	4·783 (10)	Ag—I(3)	2·809 (6)
I(1)—I(2)	4·622 (6)	Ag—I(1)*a*	2·854 (5)
I(1)—I(3)	4·649 (6)	I(1)—Ag—I(1)*a*	113·8 (2)
I(2)—I(1)*a*	4·622 (6)	I(1)—Ag—I(2)	109·0 (1)
I(2)—I(3)	4·435 (6)	I(1)—Ag—I(3)	110·3 (1)
I(1)*a*–I(3)	4·648 (6)	I(2) Ag I(1)*a*	109·0 (1)
Ag—I(1)	2·854 (5)	I(2)—Ag—I(3)	103·9 (2)
Ag—I(2)	2·823 (6)	I(1)*a*–Ag—I(3)	110·3 (1)
3. I(1)—I(1)*a*	4·783 (10)	I(2)—I(1)*a*	4·622 (6)
I(1)—I(2)	4·622 (6)	I(2)—I(1)*b*	4·944 (6)
I(1)—I(1)*b*	4·506 (6)	I(1)*a*–I(1)*b*	4·506 (6)

(*b*) Square pyramids

1. I(1)—I(3)	4·649 (6)	I(3)—I(3)*e*	4·783 (10)
I(1)—I(3)*e*	4·649 (6)	I(3)*e* –I(3)*k*	5·118 (7)
I(1)—I(3)*j*	4·532 (6)	I(3)*k*–I(3)*j*	4·783 (10)
I(1)—I(3)*k*	4·532 (6)	I(3)*j*—I(3)	5·118 (7)
2. I(1)—I(3)	4·649 (6)	I(2)—I(3)	4·435 (6)
I(1)—I(3)*e*	4·649 (6)	I(3)—I(3)*e*	4·783 (10)
I(1)—I(2)	4·622 (6)	I(3)*e* –I(2)*e*	4·435 (6)
I(1)—I(2)*e*	4·622 (6)	I(2)*e* –I(2)	4·783 (10)
3. I(1)—I(2)	4·622 (6)	I(2)—I(2)*e*	4·783 (10)
I(1)—I(2)*e*	4·622 (6)	I(2)*e* –I(1)*c*	4·944 (6)
I(1)—I(1)*b*	4·506 (6)	I(1)*c* –I(1)*b*	4·783 (10)
I(1)—I(1)*c*	4·506 (6)	I(1)*b*–I(2)	4·944 (6)

Table 2 (*cont.*)

(*c*) Square prisms

1	I(2)—I(3)	4·435 (6)	I(2)—K(1)–I(3)	75·6 (2)
	I(3)—I(3)*e*	4·783 (10)	I(2)—K(1)–I(2)*e*	81·7 (3)
	I(3)*e* –I(2)*e*	4·435 (6)	I(2)—K(1)–I(3)*m*	72·0 (2)
	I(2)*e* –I(2)	4·783 (10)	I(2)—K(1)–I(3)*n*	124·3 (4)
	I(2)—I(3)*m*	4·256 (6)	I(2)—K(1)–I(3)*e*	128·8 (4)
	I(2)*e* –I(3)*n*	4·256 (6)	I(3)—K(1)–I(2)*e*	128·8 (4)
	I(3)—I(3)*m*	5·118 (7)	I(3)—K(1)–I(3)*e*	83·9 (3)
	I(3)*e* –I(3)*n*	5·118 (7)	I(3)—K(1)–I(3)*m*	91·2 (2)
	I(3)*m*–I(3)*n*	4·783 (10)	I(3)—K(1)–I(3)*n*	155·8 (4)
	K(1) –I(3)	3·578 (10)	I(2)*e* –K(1)–I(3)*e*	75·6 (2)
	K(1) –I(3)*e*	3·578 (10)	I(2)*e* –K(1)–I(3)*m*	124·3 (4)
	K(1) –I(3)*m*	3·585 (10)	I(2)*e* –K(1)–I(3)*n*	72·0 (2)
	K(1) –I(3)*n*	3·585 (10)	I(3)*e* –K(1)–I(3)*m*	155·8 (4)
	K(1) –I(2)	3·654 (10)	I(3)*e* –K(1)–I(3)*n*	91·2 (2)
	K(1) –I(2)*e*	3·654 (10)	I(3)*m*–K(1)–I(3)*n*	83·6 (3)
2.	I(2)—I(3)*m*	4·256 (6)	I(2)*e* –I(2)*f*	4·344 (5)
	I(3)*m*–I(3)*n*	4·783 (10)	I(3)*m*–I(1)*d*	4·532 (6)
	I(3)*n*–I(2)*e*	4·256 (6)	I(3)*n*–I(1)*d*	4·532 (6)
	I(2)*e* –I(2)	4·783 (10)	I(1)*d*–I(2)*f*	4·944 (6)
	I(2)—I(2)*f*	4·344 (5)		
3.	I(2)—I(2)*e*	4·783 (10)	I(2)—K(2)–I(2)*e*	87·5 (3)
	I(2)*e* –I(1)*c*	4·944 (6)	I(2)—K(2)–I(2)*f*	74·4 (2)
	I(1)*c* –I(1)*b*	4·783 (10)	I(2)—K(2)–I(1)*b*	89·1 (2)
	I(1)*b*–I(2)	4·944 (6)	I(2)—K(2)–I(1)*c*	155·0 (4)
	I(2)—I(2)*f*	4·344 (5)	I(2)—K(2)–I(3)*p*	123·3 (3)
	I(2)*e* –I(2)*f*	4·344 (5)	I(2)*e* –K(2)–I(2)*f*	74·4 (2)
	I(1)*b*–I(3)*p*	4·532 (6)	I(2)*e* –K(2)–I(1)*b*	155·0 (4)
	I(1)*c* –I(3)*p*	4·532 (6)	I(2)*e* –K(2)–I(1)*c*	89·1 (2)
	I(2)*f* –I(3)*p*	4·256 (6)	I(2)*e* –K(2)–I(3)*p*	123·3 (3)
	K(2) –I(2)	3·456 (10)	I(2)*f* –K(2)–I(1)*b*	128·2 (2)
	K(2) –I(2)*e*	3·456 (10)	I(2)*f* –K(2)–I(1)*c*	128·2 (2)
	K(2) –I(1)*b*	3·587 (10)	I(2)*f* –K(2)–I(3)*p*	71·4 (2)
	K(2) –I(1)*c*	3·587 (10)	I(1)*b* –K(2)–I(1)*c*	83·6 (3)
	K(2) –I(2)*f*	3·718 (14)	I(1)*b*–K(2)–I(3)*p*	78·6 (2)
	K(2) –I(3)*p*	3·570 (13)	I(1)*c* –K(2)–I(3)*p*	78·6 (2)

References

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