SHORT STRUCTURAL PAPERS

Papers intended for publication under this heading must be in the format prescribed in Notes for Authors, *Acta Cryst.* (1973). **B29**, 154.

Acta Cryst. (1976). B32, 2671

Potassium Hexachlorostannate(IV) and Ammonium Hexachlorostannate(IV)

BY JOHN A. LERBSCHER AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1W5

(*Received* 20 *January* 1976; *accepted* 23 *February* 1976)

Abstract. Cubic, *Fm3m*; $a=9{\cdot}990$ (2), 10·038 (2) Å, for K_2SnCl_6 and $(NH_4)_2SnCl_6$ respectively; $Z=4$; $R=0{\cdot}039$ and 0·034 for 137 and 221 reflexions. K_2PtCl_6-type structure, x(Cl) = 0·2411, 0·2412 (0·2428 and 0·2419 after libration corrections). The K salt undergoes a transition at 262K ($\Delta S=R\ln 2$) to a lower symmetry (possibly tetragonal) form. In the NH_4 salt, H atoms are in 32(*f*), $x=0{\cdot}30$.

Introduction. Unit-cell and intensity data were measured with spherical crystals, a Datex-automated G.E. XRD 6 diffractometer, Mo $K\alpha$ radiation, θ–2θ scan, check-reflexion scaling, and absorption corrections. Of about 260 reflexions with $\theta \leq 45°$, 137 (K salt) and 221 (NH_4 salt) with intensity greater than 3σ above background [$\sigma^2(I)=S+B+(0{\cdot}05S)^2$, where S = scan and B = background count] were used in the refinements. The structures (*Strukturbericht*, **1**, 431, 444; **3**, 121, 479; *Struct. Rep.* **40A**, 150; see also Wyckoff, 1965) were refined by least-squares methods (six parameters), with minimization of $\sum w(F_o-F_c)^2$, with $\sqrt{w}=|F_o|/32$ when $|F_o| \leq 32$, $\sqrt{w}=32/|F_o|$ when $|F_o|>32$. A final difference map for the NH_4 compound contained only two significant positive peaks, 2·8 e Å^{-3} at the Sn position, and 0·9 e Å^{-3} at position 32(*f*): $x=0{\cdot}30$ (Fig. 1), the latter probably corresponding to the hydrogen atoms. Final positional and thermal parameters are in Table 1.*

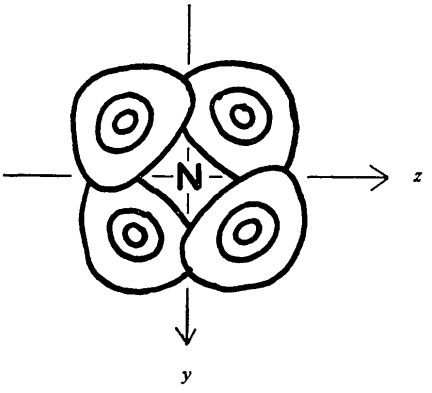

Fig. 1. Part of the difference synthesis for $(NH_4)_2SnCl_6$.

Discussion. The compounds have the K_2PtCl_6-type structure (*Strukturbericht*, **1**, 429, 445, 793; **2**, 496; **3**, 121; *Struct. Rep.* **39A**, 178). The thermal parameters (Table 1) indicate libration of the $SnCl_6^{2-}$ anions, and after correction (Cruickshank, 1956; q^2 taken as 0·15), $x=0{\cdot}2428$ and 0·2419. Sn–Cl = 2·409 (2) and 2·421 (2) Å (2·426 and 2·428 Å after thermal-libration correction), for the K and NH_4 salts respectively. K^+ (NH_4^+) ions have twelve Cl neighbours, three from each of four $SnCl_6^{2-}$ ions, at 3·53 (3·55) Å. In the ammonium compound the H atom is directed towards the centre

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31746 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters*

K (or N) in 8(*c*): ¼,¼,¼
Sn in 4(*a*): 0,0,0
Cl in 24(*e*): *x*,0,0; $x=0{\cdot}2411$ (2) (K salt), 0·2412 (1) (NH_4 salt)
H in 32(*f*): *x*,*x*,*x*; $x=0{\cdot}30$ (NH_4 salt)

		K salt		NH_4 salt	
		U (Å^2)	R.m.s. displ. (Å)	U (Å^2)	R.m.s. displ. (Å)
K (or N)	U	0·0540 (9)	0·232	0·0341 (3)	0·185
Sn	U	0·0242 (4)	0·156	0·0185 (1)	0·136
Cl	U_{11}	0·0219 (7)	0·148	0·0174 (4)	0·132
	$U_{22}=U_{33}$	0·0821 (14)	0·286	0·0410 (4)	0·202
	$U_{12}=U_{23}=U_{13}$	0		0	

of a triangle of Cl atoms from three separate anions, N–H=0·9, H···Cl=2·9 Å; the latter distance seems too long for significant hydrogen-bond interaction.

The studies were undertaken as a result of interest in the phase transition ($\Delta S = R\ln 2$) at 262K for the K salt (Morfee, Staveley, Walters & Wigley, 1960). The structure adopted by A_2BX_6 compounds of this type appears to depend on the ratio of the size of the A cation to the hole available for it in the BX_6 lattice (Brown, 1964); thus a small A cation results in distortion from cubic to tetragonal or lower symmetry. Ratios greater than 0·98 result in cubic structures at any temperature [for $(NH_4)_2SnCl_6$ the ratio is 0·99], ratios less than 0·89 give structures of lower symmetry at room temperature, while ratios in the range 0·89 to 0·98 yield structures which are cubic at room temperature but transform to lower symmetry at lower temperatures (for K_2SnCl_6 the ratio is 0·92).

The thermal parameters of the Cl atom for both the K and NH_4 salts are larger normal to the Sn–Cl bonds (Table 1) but not excessive, so that the structures appear to be truly cubic at room temperature with libration of the $SnCl_6^{2-}$ ions, rather than a superposition of lower-symmetry structures. On cooling in a stream of nitrogen gas, crystals of the NH_4 compound remained cubic, but the K salt underwent a phase change at about 260K. A Weissenberg film exhibited splitting of spots and the appearance of a 035 reflexion (cubic indices), which suggested lower symmetry. Since the low-temperature specimen was no longer a single crystal, determination of the exact symmetry was difficult, but the structure could possibly be like that of tetragonal room-temperature K_2SnBr_6 (*Strukturbericht*, **6**, 121) (Fig. 2), which is cubic above 400K (*Struct. Rep.* **27**, 462), the cation/hole ratio being 0·86.

We thank the National Research Council of Canada for financial support and the University of British Columbia Computing Centre for assistance.

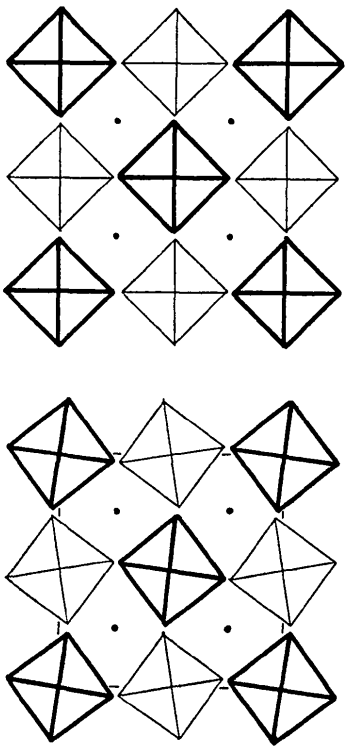

Fig. 2. Structure of room-temperature K_2SnCl_6 (top) and K_2SnBr_6 (bottom).

References

BROWN, I. D. (1964). *Canad. J. Chem.* **42**, 2758–2767.
CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754–756.
MORFEE, R. G. S., STAVELEY, L. A. K., WALTERS, S. T. & WIGLEY, D. L. (1960). *Phys. Chem. Solids*, **13**, 132–144.
WYCKOFF, R. W. G. (1965). *Crystal Structures*, 2nd ed., Vol. III, pp. 339–345. New York: Interscience.

Acta Cryst. (1976). B**32**, 2672

N-Vinyl-2-thiopyrrolidone

BY ALAJOS KÁLMÁN AND GYULA ARGAY
Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525-Budapest, P.O.B. 17, Hungary

AND FERENC CSER
Research Institute for Plastics Industry, Hungária krt. 114, H-1950-Budapest XIV, Hungary

(*Received* 26 *March* 1976; *accepted* 17 *April* 1976)

Abstract. C_6H_9NS, monoclinic, $C2/m$ (from refinement); $a=12{\cdot}316$ (3), $b=6{\cdot}909$ (2), $c=7{\cdot}930$ (2) Å, $\beta=98{\cdot}14$ (2)°; $Z=4$; $V=668{\cdot}0$ Å^3; $D_c=1{\cdot}264$ g cm^{-3}; μ(Mo $K\bar{\alpha}$, $\bar{\lambda}=0{\cdot}7107$ Å)$=3{\cdot}27$ cm^{-1}. The structure of NVTP was solved by heavy-atom and Fourier techniques. An R of 0·056 was obtained for 781 observed