Structure of the Hexathionate Ion in the *trans*-Dichloro-dien-cobalt(III) Salt

OLAV FOSS and KJARTAN MARØY

Chemical Institute, University of Bergen, Bergen, Norway

In the potassium barium salt, $K_2Ba(S_6O_6)_2$, the sulphur chain of the hexathionate ion has a *cis-cis* configuration as in the S_8 ring of orthorhombic sulphur.[1] It has now been found that the extended *trans-trans* rotational isomer occurs in the crystals of *trans*-dichloro-dien-cobalt(III) hexathionate monohydrate.

This salt, $(Coen_2Cl_2)_2S_6O_6.H_2O$, is orthorhombic, with the unit cell dimensions:[2] a = 12.12 Å, b = 19.13 Å, c = 6.43 Å, and two formula units per unit cell. The space group is $C_{2v}^8 - Pba2$, which requires that the hexathionate ions and the water molecules lie on twofold axes of symmetry.

The intensities of 149 observed $hk0$ reflections out of 187 attainable with Fe$K\alpha$ radiation were estimated visually from zero-layer Weissenberg photographs, taken of a prism {110} with edges 0.08 × 0.09 mm (μr approx. 0.7). The cobalt x and y coordinates were found from the $hk0$ Patterson map, the Co-Co $2x,2y$ vector being also the centre vector of the centro-symmetric cation and the peak therefore large. Using cobalt as a searcher atom, the two chlorine atoms were located by means of the vector convergence method.[3] The cobalt and chlorine contributions gave the probable signs of one fourth (37) of the strongest $hk0$ reflections, and a Fourier synthesis based on these indicated the positions of the three sulphur atoms of the asymmetric unit and thereby the signs of 40 additional reflections; none of the signs changed later. The second Fourier map allowed the location of the lighter atoms, and Fourier refinement and next Fourier difference refinement were then carried out.

The $hk0$ Fourier map is shown in Fig. 1, and the x and y coordinates of the heavier atoms are listed in Table 1, together with the temperature constants B used in the calculation of structure factors. The B values, assigned on the basis of the differ-

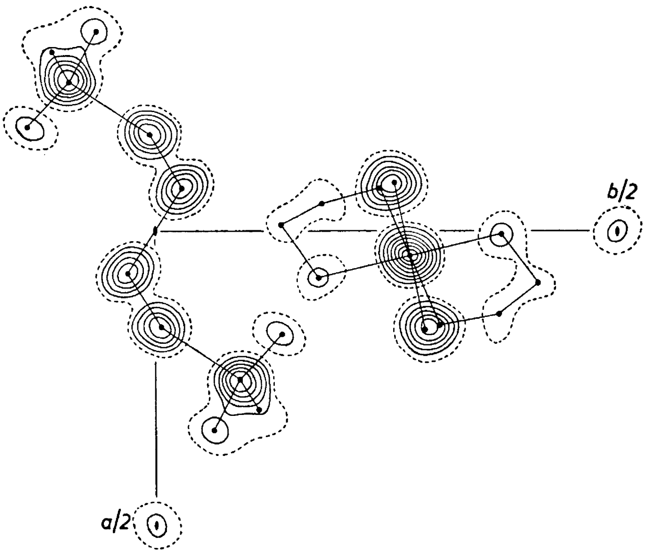

Fig. 1. Electron density projection of *trans*-dichloro-dien-cobalt(III) hexathionate monohydrate along the c axis. Contours are at intervals of 4 e · Å^{-2} for the cobalt and chlorine atoms and 3 e · Å^{-2} for the other atoms, beginning with 4 e · Å^{-2} (dashed).

ence maps, indicate an increased thermal vibration of atoms at the middle of the sulphur chain relative to the ends. Ignoring contributions from the 17 hydrogen atoms of the asymmetric unit, the reliability index *R* is 0.10 for the *hk*0 data.

Table 1. Atomic coordinates, in fractions of cell edges, and temperature constants *B*, in Å^2. Origin on a twofold axis.

	x	y	B
Co	0.0410	0.2757	3.5
Cl_1	0.1660	0.2930	
Cl_2	—0.0840	0.2584	
S_1	0.2530	0.0917	3.0
S_2	0.1638	0.0050	3.5
S_3	0.0722	—0.0289	4.0

The z coordinates of the atoms will be determined later from a projection along the a axis. The middle sulphur-sulphur bond of the hexathionate ion lies across the twofold axis and the length is independent of the sulphur z coordinate; the x and y coordinates of S_3 give a length of 2.07 ± 0.02 Å for this bond.

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3. Beevers, C. A. and Robertson, J. H. *Acta Cryst.* **3** (1950) 164.

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