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Thermal Expansion of α-NH_4HgCl_3

BY J. SADANANDAM AND S. V. SURYANARAYANA

Department of Physics, University College of Science, Osmania University, Hyderabad 500 007, *India*

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Abstract

α-NH_4HgCl_3 belongs to the tetragonal system with the space group P_4/mmm. Earlier X-ray studies indicate that this crystal can be described as a layer structure, the layers being perpendicular to the tetragonal axis. With a Rigaku camera, modified for work at high temperatures, the temperature variation of the lattice parameters and thermal-expansion coefficients of this crystal were determined. The coefficient of expansion, at room temperature, along the tetragonal axis is less than that in the perpendicular direction.

In this laboratory, a general programme of study of the temperature variation of the lattice parameters and thermal expansion using X-ray methods on some mixed halides of the general formula ABX_3 has been undertaken.

Ammonium trichloromercurate(II) exists in the two polymorphic forms α and β (Beljaev & Mironov, 1952). α-NH_4HgCl_3 is obtained from a melt of equimolar mixtures of NH_4Cl and $HgCl_2$. β-NH_4HgCl_3 is obtained from equimolar aqueous solutions of the same materials. The α form crystallizes in the tetragonal system with space group P_4/mmm, while the β form occurs in the orthorhombic system with space group *Pnma*.

α-NH_4HgCl_3 was prepared by heating (*ca* 523 K) a sealed glass tube containing stoichiometric quantities of mercury(II) chloride and ammonium chloride. The tube was then cooled and opened and the product ground. A comparison with ASTM data (Swanson, McMurdie, Morris & Evans, 1967) of the observed d spacings of a photograph of this sample taken at room temperature confirmed the formation of the α phase. The chemical analysis also confirmed the same, the impurities being Si, Al, Cu, Ag, Ba, Ca, Na and Mn found as traces.

Six photographs taken at different temperatures between 302 and 364 K were obtained using a Rigaku X-ray camera 114·6 mm in diameter, modified for work at high temperatures (Sadanandam & Suryanarayana, 1979). The photograph taken at about 383 K did not correspond to the one that had been obtained earlier. Above this temperature, it was observed that the colour of the sample changed from white to brown. Photographs at 383 K were repeated on more than one sample and it was confirmed that the change is of a chemical nature.

The lattice parameters were evaluated by Cohen's (1935) least-squares treatment. A comparison of the lattice parameters of α-NH_4HgCl_3 at room temperature is given in Table 1.

Table 1. *Comparison of the lattice parameters of* α-NH_4HgCl_3 *at room temperature*

a (Å)	c (Å)	Reference
4·194	7·927	Hermsen (1938)
4·1977	7·9353	Swanson *et al.* (1967)
4·1969	7·9369	Present work

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With Jette & Foote's (1935) method, the maximum error limits evaluated are ± 0.001 Å and ± 0.002 Å in a and c respectively. However, repeated measurements of the films have indicated a difference of ± 0.0002 Å in a and c. The higher statistical error might be due to the small number of unambiguous reflections used in the calculations. The data on the lattice parameters of this compound at different temperatures are given in Table 2.

Table 2. *Lattice parameters of* α-NH_4HgCl_3 *at different temperatures*

Temperature (K)	a (Å)	c (Å)
302	4·1969	7·9369
322	4·2022	7·9402
336	4·2027	7·9419
350	4·2066	7·9451
359	4·2076	7·9501
364	4·2088	7·9552

The a/T data have been subjected to least-squares treatment, and the temperature variation of a may be represented by:

$$a_T = 4{\cdot}1920 + 1{\cdot}8413 \times 10^{-4} T.$$

The coefficient of expansion, along the a direction (α_a) as evaluated using the above equation, comes out as $43{\cdot}9 \times 10^{-6}\ K^{-1}$.

The c/T data between 302 and 350 K have been subjected to a least-squares treatment and the following expression represents the variation of c with temperature:

$$c_T = 7{\cdot}9319 + 1{\cdot}6588 \times 10^{-4} T.$$

However, the values of the c parameter obtained at 359 and 364 K could not be included in this fit, as the data follow neither a straight line nor a regular curve with respect to earlier data. An average value of the coefficient of expansion along c has been evaluated between 302 and 350 K and it comes out as $20{\cdot}9 \times 10^{-6}\ K^{-1}$. However, since the c/T curve did not show any continuous variation for the whole range of temperatures studied and in view of the difficulty of obtaining data above 364 K, no further inferences can be made about the variation of α_c with T in the high-temperature range except to mention that the value of the c parameter shows an increasing trend in this temperature range, indicating that α_c increases above 353 K. The statistical errors in α_a and α_c are 1·5 and 1·75% respectively.

One obvious fact that comes out from these results is that the value of α_c is very much smaller than that of α_a at room temperature. Further, α_a is temperature independent, and α_c increases at higher temperatures. X-ray studies on this compound (Hermsen, 1938) revealed that the structure consists of layers of $HgCl_6$ octahedra linked together into $(HgCl_3)_n^{-n}$ layers. Of the six Cl atoms forming the octahedra, two Cl(2) atoms are much closer to the Hg atom than the Cl(1) atoms; Hg–Cl(2) = 2·33 Å and Hg–Cl(1) = 2·96 Å. The former is bonded to only one Hg atom, and the latter to four Hg atoms. From these facts Sagisawa, Kiriyama & Kiriyama (1975) inferred that Cl(2) is much more covalently bound than Cl(1). This picture of the structure is in agreement with the present data on the thermal-expansion behaviour: namely, that α_c is smaller than α_a; that is, the numerical value of the coefficient is smaller along the direction of the shorter bond length than that in a perpendicular direction along which the Hg–Cl(1) distance is larger.

The situation is complicated when we look at the data on the temperature variation of α_a and α_c. While α_a is constant over the temperature range studied, α_c increases above *ca* 353 K and at these highest temperatures α_c is greater than α_a. This observation does not conform to the available structural data on α-NH_4HgCl_3. Hence, the authors feel that it is necessary to refine the structure of this compound at different temperatures to understand the peculiar thermal-expansion behaviour. Such a study is in progress in this laboratory.

A comparison of the photograph taken at 383 K with those taken at lower temperatures indicated that the sample transformed to a system of lower symmetry. From a comparison of the d spacings of the transformed sample with the data of ASTM (Swanson & Eleanor, 1953), it was confirmed that the original sample of α-NH_4HgCl_3 decomposed to $HgCl_2$ at 383 K. The lattice parameters of $HgCl_2$ were evaluated and are compared in Table 3.

Table 3. *Lattice parameters of* $HgCl_2$ *(transformed at* 383 K *from* α-NH_4HgCl_3*)*

a (Å)	b (Å)	c (Å)	Reference
5·975	12·761	4·334	Swanson *et al.* (1953)
5·894	12·712	4·399	Present work

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