

The Crystal Structure of Larderellite, $\text{NH}_4\text{B}_5\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$

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The crystal structure of larderellite has been determined by three-dimensional X-ray diffraction analysis; it crystallizes in the monoclinic space group $P2_1/c$. The unit cell, containing four stoichiometric units $\text{NH}_4\text{B}_5\text{O}_8 \cdot 2\text{H}_2\text{O}$, has the dimensions: $a = 9.47$, $b = 7.63$, $c = 11.65$ Å, $\beta = 97^\circ 5'$. The structure was obtained by means of the symbolic addition method. Refinement was carried out by three-dimensional least-squares methods, yielding a final R value of 0.119. The structure of larderellite is characterized by infinite chains $[\text{B}_5\text{O}_7(\text{OH})_2]_n^-$; the chains, two per cell, are linked by the ammonium ions and by hydrogen bonds.

Introduction

Larderellite is a hydrated ammonium borate first described by Bechi (1853) as one of the components of some incrustations originated by fumaroles in the Larderello geothermal area (Tuscany). Owing to insufficient pure material, the different chemical formulae proposed for it until a few years ago have been considered as uncertain in the mineralogical literature. Moreover, the determination of the density and a single-crystal X-ray study were infeasible because the crystals present in the available samples were too minute in size.

The cell data and space group of the crystal were determined by Marinelli (1959) who found a natural sample of larderellite made up of relatively large crystals. His data were confirmed by Clark (1960), who also reported an accurate determination of density made by R. K. Carron and the results of new chemical analyses carried out by W. T. Schaller and A. C. Vlisidis. On the basis of the density value and the symmetry requirements of the space group, Clark suggested that the most probable chemical formula for larderellite is $\text{NH}_4\text{B}_5\text{O}_8 \cdot 2\text{H}_2\text{O}$.

Christ (1960) in his study on the crystal chemistry of hydrated borates pointed out that, on the basis of its composition, larderellite probably contains the pentaborate ion $[\text{B}_5\text{O}_6(\text{OH})_4]^-$, known to exist in the compound $\text{NH}_4\text{B}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ and in its potassium relative $\text{KB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ (Zachariasen, 1937; Zachariasen & Plettinger, 1963). Clark (1960) agreed with this hypothesis and thus attributed to larderellite the structural formula $\text{NH}_4\text{B}_5\text{O}_6(\text{OH})_4$. However, until now nobody has succeeded in synthesizing larderellite, in spite of its great similarity, according to the above classification, to the synthetic ammonium pentaborate from which it should differ only by two water molecules of crystallization.

Taking this fact into account we considered the structural formula proposed for larderellite to be doubtful and that it was necessary to try to definitely establish its crystal structure.

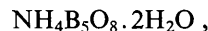
Experimental

The morphology, optical properties and X-ray crystallography of larderellite are fully described by Marinelli (1959):

$$\begin{aligned} a &= 9.47 \pm 0.01 \text{ \AA}, \\ b &= 7.63 \pm 0.01 \\ c &= 11.65 \pm 0.01, \\ \beta &= 97^\circ 05' \pm 15'. \end{aligned}$$

Space group : $P2_1/c$.

$U = 835 \text{ \AA}^3$. With four stoichiometric units,



in the unit cell the calculated density is $D_c = 1.877 \text{ g.cm}^{-3}$. The measured density is $D_m = 1.905 \pm 0.044 \text{ g.cm}^{-3}$ (from Clark 1960).

The mineral occurs in small rhombus-shaped crystals plated on {100} with [010] parallel to the short diagonal and [001] parallel to the long diagonal of the rhombi. The crystals present a perfect {001} cleavage.

Intensity data were collected by the multiple-film equi-inclination Weissenberg technique with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

From a rhombus-shaped crystal 0.013 mm thick and with short diagonal and long diagonal dimensions of 0.079 mm and 0.128 mm respectively, layers 0 through 4 along the b axis and layers 0 and 1 along the c axis were recorded. Owing to the smallness of the crystal very long exposures (nearly two weeks for each layer) were necessary.

The intensities were visually estimated by comparison with a calibrated film strip. Corrections for Lorentz and polarization factors were made, but no absorption correction was applied because of the low linear absorption coefficient ($\mu = 16.5 \text{ cm}^{-1}$ for Cu $K\alpha$ radiation) and the very small dimensions of the specimen.

Phase determination

By the use of the following values for ϵ , as dictated by the space group, the normalized structure factors $|E_h|$

were calculated (Karle & Hauptman, 1956) by means of a program incorporated in the *X-ray '63 System* (Stewart, 1964): $\varepsilon=2$ for $h0l$ and $0k0$ reflexions; otherwise $\varepsilon=1$.

The structure was solved by obtaining the values of the phases directly from the structure factor magnitudes by means of the symbolic addition procedure. The origin of the unit cell was specified by assigning phases to three linearly independent reflexions having large $|E|$ values. Letters a and b were assigned to two additional reflexions; at a later stage it appeared necessary to designate the sign of another reflexion with a third symbol c in order to facilitate the application of the Σ_2 formula (Hauptman & Karle, 1953):

$$sE_h \sim s \Sigma_h E_k E_{h-k} \quad (1)$$

where s means 'sign of'. The letter assignments and the three origin specifying signs are shown in Table 1.

Table 1. *The assignments for the application of the Σ_2 phase determination formula*

| h | k | l | $ E $ | Sign |
|-----|-----|------------|-------|------|
| 2 | 2 | $\bar{3}$ | 2.48 | + |
| 7 | 1 | 7 | 2.26 | + |
| 4 | 1 | $\bar{4}$ | 2.24 | + |
| 8 | 3 | $\bar{10}$ | 2.03 | a |
| 4 | 4 | $\bar{1}$ | 2.01 | b |
| 8 | 2 | $\bar{2}$ | 2.45 | c |

The application of the method was facilitated by the preparation of lists of the reflexion combinations in (1) by means of the *SORTE* program (Bednowitz, 1968).

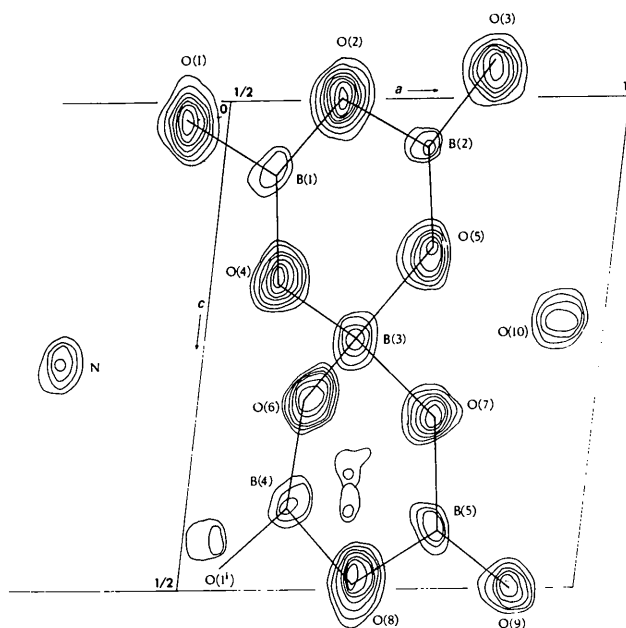


Fig. 1. Sections from the three-dimensional E map viewed along $[010]$, with the sixteen heavy atoms of the asymmetric unit. The contours are at equally spaced intervals on an arbitrary scale.

As the phase determination progressed there were several indications that $a=-$ and $c=+$ and probably $b=-$. Signs were thus attributed to 138 of the largest $|E|$'s. A three-dimensional E map was computed which clearly showed the positions for the sixteen heavy atoms of the asymmetric unit. Sections from this map are shown in Fig. 1.

The refinement

Coordinates of the sixteen heavy atoms as read from the E map were refined by the full-matrix least-squares program of Busing, Martin & Levy adapted to the *X-ray '63 System*; the function minimized was $\Sigma(|F_o| - |F_c|)^2$. Individual scale factors for each layer were varied during the refinement; their starting values were determined by means of the common reflexions. After three refinement cycles with isotropic temperature factors the value of the residual $R = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|$ dropped from 0.28 to 0.138.

A three-dimensional Fourier difference synthesis was calculated in order to locate the hydrogen atoms: the synthesis showed smearing of the electron density around the nitrogen atom of the ammonium ion, so that no further efforts were made to locate the hydrogen atoms of this ion. The positions where the hydrogen atoms of the hydroxyl groups and of the water molecule should be situated, on the basis of stereochemical considerations, were found to be in areas of positive electronic density; therefore we assigned to these hydrogen atoms the corresponding coordinates and introduced them with an isotropic thermal parameter of 5 \AA^2 into the subsequent refinement. Three more refinement cycles, in which the positional and thermal parameters of the hydrogen atoms were maintained constant, led to the final value of the residual $R=0.119$.

The shifts of parameters in the last cycle were less than one tenth of the corresponding estimated standard deviations.

The atomic scattering factors used in the structure-factor calculations were taken from *International Tables for X-ray Crystallography* (1962).

The observed and calculated structure factors are compared in Table 2. Table 3 gives the final positional and thermal parameters with their standard deviations.

Description and discussion of the structure

The principal structural features of larderellite are illustrated in Fig. 2, where the structure is described in terms of boron coordination triangles and tetrahedra. The basic structural unit is the double ring, built up from one BO_4 tetrahedron and four planar BO_3 triangles, which was first found by Zachariasen (1937) as an isolated ion in $\text{KB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. In larderellite these structural units are connected to form infinite chains in which each unit is obtained from the preceding one through the operation of a screw diad axis; two symmetry equivalent infinite chains run through a single unit-cell.

Table 2. *Observed and calculated structure factors*

| M | K | L | FC | FC | H | K | L | FC | FC | H | K | L | FO | FC | H | K | L | FO | FC | H | K | L | FO | FC |
|-----|-----|---|-------|-------|-----|---|---|------|------|-----|---|----|-------|-------|----|----|----|------|------|----|---|----|------|------|
| 2 | 0 | 0 | 64.1 | 57.4 | 4 | 1 | 1 | 64.2 | 56.9 | -4 | 1 | 10 | 17.1 | 20.3 | -5 | 2 | 8 | 17.7 | 16.8 | -3 | 3 | 6 | 12.5 | 11.2 |
| 3 | 0 | 0 | 27.8 | 25.6 | 5 | 1 | 1 | 18.4 | 17.8 | -3 | 1 | 10 | 11.1 | 11.7 | -4 | 2 | 8 | 23.6 | 24.3 | -2 | 3 | 6 | 32.2 | 31.6 |
| 4 | 0 | 0 | 12.8 | 12.9 | 6 | 1 | 1 | 25.7 | 24.2 | -1 | 1 | 10 | 21.1 | 23.6 | -1 | 2 | 8 | 16.6 | 16.6 | -1 | 3 | 6 | 9.0 | 10.9 |
| 5 | 0 | 0 | 52.7 | 55.2 | 7 | 1 | 1 | 25.7 | 35.7 | 0 | 1 | 11 | 12.1 | 14.1 | -1 | 2 | 8 | 19.4 | 18.8 | 0 | 3 | 6 | 11.7 | 11.2 |
| 6 | 0 | 0 | 22.1 | 15.4 | 9 | 1 | 1 | 10.2 | 8.2 | 1 | 1 | 10 | 11.1 | 11.4 | 0 | 2 | 8 | 11.3 | 10.3 | 1 | 3 | 6 | 13.1 | 9.9 |
| 7 | 0 | 0 | 31.6 | 27.6 | -11 | 1 | 2 | 14.6 | 11.4 | 3 | 1 | 10 | 16.9 | 20.5 | 1 | 2 | 8 | 7.5 | 7.4 | 2 | 3 | 6 | 22.3 | 23.2 |
| 8 | 0 | 0 | 22.8 | 17.0 | -17 | 1 | 2 | 16.0 | 4.9 | -8 | 1 | 11 | 10.2 | 9.1 | 2 | 2 | 8 | 15.6 | 20.9 | 5 | 3 | 6 | 26.1 | 26.0 |
| 9 | 0 | 0 | 24.3 | 22.6 | -6 | 1 | 2 | 7.1 | 5.7 | -6 | 1 | 11 | 13.0 | 15.4 | 4 | 3 | 6 | 12.9 | 14.7 | 7 | 3 | 6 | 10.1 | 7.4 |
| 10 | 0 | 0 | 8.2 | 9.0 | -5 | 1 | 2 | 9.0 | 10.0 | -4 | 1 | 11 | 16.5 | 19.3 | 8 | 2 | 8 | 14.8 | 10.9 | 8 | 3 | 6 | 18.5 | 15.2 |
| 11 | 0 | 0 | 14.0 | 16.0 | -4 | 1 | 2 | 19.8 | 19.7 | -2 | 1 | 11 | 26.3 | 30.0 | 9 | 2 | 8 | 7.5 | 7.8 | 9 | 3 | 6 | 20.7 | 15.7 |
| -12 | 0 | 2 | 15.0 | 22.8 | -3 | 1 | 2 | 20.1 | 24.0 | -1 | 1 | 11 | 7.1 | 11.8 | -9 | 2 | 9 | 12.1 | 9.6 | -8 | 3 | 7 | 8.3 | 8.2 |
| -11 | 0 | 2 | 32.1 | 43.0 | -2 | 1 | 2 | 33.8 | 36.7 | 0 | 1 | 11 | 9.4 | 10.5 | -6 | 2 | 9 | 19.0 | 20.6 | -6 | 3 | 7 | 7.4 | 6.7 |
| -10 | 0 | 2 | 46.4 | 55.6 | -1 | 1 | 2 | 37.4 | 44.8 | 1 | 1 | 11 | 12.3 | 14.7 | -5 | 2 | 9 | 21.5 | 23.9 | -4 | 3 | 7 | 24.8 | 24.4 |
| -9 | 0 | 2 | 21.3 | 19.4 | 0 | 1 | 2 | 27.7 | 34.8 | 1 | 1 | 11 | 16.5 | 16.3 | -4 | 2 | 9 | 30.3 | 32.7 | -3 | 3 | 7 | 11.0 | 8.5 |
| -8 | 0 | 2 | 66.9 | 56.3 | 1 | 1 | 2 | 33.4 | 31.6 | -7 | 1 | 12 | 7.5 | 4.5 | -3 | 2 | 9 | 12.5 | 12.4 | -2 | 3 | 7 | 8.0 | 10.1 |
| -7 | 0 | 2 | 10.0 | 7.6 | 2 | 1 | 2 | 55.2 | 46.4 | 0 | 1 | 12 | 12.3 | 14.4 | -2 | 2 | 9 | 13.6 | 18.6 | 0 | 3 | 7 | 10.0 | 11.2 |
| -6 | 0 | 2 | 59.1 | 49.9 | 3 | 1 | 2 | 20.7 | 19.8 | 1 | 1 | 12 | 17.5 | 17.5 | -1 | 2 | 9 | 25.8 | 25.2 | 1 | 3 | 7 | 22.6 | 24.2 |
| -5 | 0 | 2 | 5.3 | 2.5 | 4 | 1 | 2 | 64.2 | 58.9 | 3 | 1 | 12 | 7.9 | 9.5 | 1 | 2 | 9 | 20.5 | 26.3 | 2 | 3 | 7 | 10.2 | 8.4 |
| 0 | 0 | 2 | 31.1 | 46.3 | 5 | 1 | 2 | 23.5 | 19.2 | -1 | 1 | 13 | 12.3 | 13.1 | 2 | 2 | 9 | 12.5 | 13.8 | 3 | 3 | 7 | 25.2 | 26.8 |
| 1 | 0 | 2 | 13.0 | 18.5 | 6 | 1 | 2 | 23.0 | 22.8 | 0 | 1 | 13 | 8.4 | 7.3 | 3 | 2 | 9 | 23.6 | 26.8 | 4 | 3 | 7 | 8.8 | 8.3 |
| 2 | 0 | 2 | 14.3 | 14.0 | 7 | 1 | 2 | 19.6 | 20.3 | 3 | 1 | 13 | 9.4 | 5.6 | 5 | 2 | 9 | 16.3 | 17.0 | 5 | 3 | 7 | 8.1 | 8.9 |
| 3 | 0 | 2 | 68.9 | 52.0 | 8 | 1 | 2 | 11.1 | 10.8 | -4 | 1 | 14 | 6.1 | 5.2 | 6 | 2 | 9 | 7.9 | 8.1 | 7 | 3 | 7 | 19.5 | 16.0 |
| 4 | 0 | 2 | 33.6 | 31.1 | 11 | 1 | 2 | 11.7 | 9.9 | -2 | 1 | 14 | 9.8 | 9.2 | 7 | 2 | 9 | 7.5 | 10.5 | 8 | 3 | 7 | 19.6 | 16.7 |
| 5 | 0 | 2 | 31.3 | 28.6 | -11 | 1 | 3 | 18.6 | 20.0 | -1 | 1 | 14 | 8.1 | 7.2 | 8 | 2 | 9 | 14.4 | 11.8 | 9 | 3 | 7 | 19.4 | 17.5 |
| 6 | 0 | 2 | 22.8 | 17.7 | -9 | 1 | 3 | 17.5 | 18.6 | 0 | 2 | 0 | 65.9 | 61.2 | -8 | 2 | 10 | 11.1 | 11.4 | -9 | 3 | 8 | 14.9 | 13.1 |
| 7 | 0 | 2 | 23.1 | 18.0 | -7 | 1 | 3 | 15.9 | 21.0 | 2 | 2 | 0 | 117.3 | 113.0 | -3 | 2 | 10 | 9.8 | 10.2 | -6 | 3 | 8 | 20.8 | 20.8 |
| 8 | 0 | 2 | 26.8 | 25.3 | -6 | 1 | 3 | 28.6 | 33.0 | 2 | 2 | 0 | 11.7 | 11.7 | -2 | 10 | 0 | 21.5 | 19.2 | -3 | 3 | 8 | 11.5 | 10.8 |
| 9 | 0 | 2 | 11.8 | 11.8 | -4 | 1 | 3 | 14.6 | 13.8 | 4 | 2 | 0 | 26.1 | 22.3 | -1 | 10 | 0 | 9.2 | 10.0 | -3 | 3 | 8 | 12.0 | 10.7 |
| -10 | 0 | 4 | 15.5 | 16.2 | -3 | 1 | 3 | 14.4 | 14.1 | 6 | 2 | 0 | 5.8 | 8.3 | 0 | 2 | 10 | 12.9 | 13.6 | -2 | 3 | 8 | 37.9 | 38.3 |
| -9 | 0 | 4 | 15.5 | 17.1 | -2 | 1 | 3 | 10.4 | 10.0 | 7 | 2 | 0 | 5.8 | 6.5 | 2 | 2 | 10 | 12.9 | 14.6 | -1 | 3 | 8 | 18.5 | 16.2 |
| -8 | 0 | 4 | 12.5 | 12.5 | -1 | 1 | 3 | 24.7 | 24.7 | -8 | 2 | 0 | 23.6 | 24.1 | 3 | 2 | 10 | 13.6 | 18.1 | 0 | 3 | 8 | 23.5 | 23.5 |
| -7 | 0 | 4 | 26.8 | 26.8 | 0 | 1 | 3 | 14.6 | 13.8 | -10 | 2 | 0 | 19.8 | 18.8 | -8 | 2 | 11 | 15.2 | 17.5 | 1 | 3 | 8 | 10.9 | 10.0 |
| -6 | 0 | 4 | 10.3 | 9.5 | 1 | 1 | 3 | 13.2 | 11.9 | -9 | 2 | 1 | 29.7 | 24.3 | -7 | 2 | 11 | 10.2 | 7.7 | 2 | 3 | 8 | 23.0 | 23.4 |
| -5 | 0 | 4 | 41.1 | 52.6 | 3 | 1 | 3 | 12.3 | 9.8 | -8 | 2 | 1 | 35.9 | 29.5 | -6 | 2 | 11 | 13.6 | 13.3 | 3 | 3 | 8 | 20.7 | 21.8 |
| -4 | 0 | 4 | 6.5 | 9.0 | 4 | 1 | 3 | 34.1 | 29.9 | -5 | 2 | 1 | 8.0 | 6.3 | -3 | 2 | 11 | 12.5 | 16.1 | 4 | 3 | 8 | 7.5 | 6.0 |
| -3 | 0 | 4 | 25.1 | 31.8 | 5 | 1 | 3 | 38.7 | 35.2 | -3 | 2 | 1 | 12.9 | 11.7 | -2 | 3 | 11 | 15.7 | 15.7 | 5 | 3 | 8 | 24.1 | 18.9 |
| -2 | 0 | 4 | 129.8 | 135.8 | 6 | 1 | 3 | 36.4 | 34.6 | -2 | 2 | 1 | 136.7 | 147.0 | -1 | 2 | 11 | 15.2 | 19.2 | 6 | 3 | 8 | 9.7 | 6.9 |
| -1 | 0 | 4 | 34.1 | 33.0 | -9 | 1 | 4 | 20.7 | 18.4 | -1 | 2 | 1 | 31.7 | 40.4 | 0 | 2 | 11 | 11.3 | 14.4 | -8 | 3 | 9 | 19.0 | 20.7 |
| 0 | 0 | 4 | 15.0 | 10.0 | -8 | 1 | 4 | 15.5 | 14.6 | 0 | 2 | 1 | 14.2 | 7.1 | 3 | 2 | 11 | 11.7 | 13.3 | -7 | 3 | 9 | 13.9 | 12.2 |
| 1 | 0 | 4 | 18.9 | 38.5 | -7 | 1 | 4 | 13.6 | 14.6 | 1 | 2 | 1 | 8.4 | 7.5 | 5 | 2 | 11 | 7.1 | 8.8 | -6 | 3 | 9 | 12.1 | 13.4 |
| 2 | 0 | 4 | 9.2 | 7.0 | -6 | 1 | 4 | 29.2 | 27.8 | 2 | 2 | 1 | 29.2 | 64.0 | 6 | 2 | 11 | 15.2 | 16.6 | -5 | 3 | 9 | 10.5 | 13.0 |
| 3 | 0 | 4 | 26.8 | 21.8 | -4 | 1 | 4 | 79.2 | 65.4 | 3 | 2 | 1 | 80.0 | 66.0 | -7 | 2 | 12 | 8.8 | 7.5 | -4 | 3 | 9 | 8.9 | 12.9 |
| 4 | 0 | 4 | 15.5 | 11.3 | -3 | 1 | 4 | 19.8 | 17.6 | 4 | 2 | 1 | 15.9 | 15.3 | -6 | 2 | 12 | 13.3 | 11.2 | -3 | 3 | 9 | 11.4 | 8.9 |
| 5 | 0 | 4 | 20.3 | 17.3 | -1 | 1 | 4 | 9.4 | 11.8 | 5 | 2 | 1 | 10.4 | 9.5 | -4 | 2 | 12 | 13.6 | 16.9 | -2 | 3 | 9 | 33.4 | 36.5 |
| 6 | 0 | 4 | 20.5 | 17.1 | 0 | 1 | 4 | 18.6 | 20.1 | 6 | 2 | 1 | 25.5 | 23.5 | -2 | 2 | 12 | 10.6 | 13.6 | -1 | 3 | 9 | 18.7 | 20.6 |
| 7 | 0 | 4 | 12.0 | 12.0 | 1 | 1 | 4 | 11.7 | 12.5 | 7 | 2 | 1 | 36.2 | 36.2 | -1 | 2 | 12 | 9.1 | 9.1 | 0 | 3 | 9 | 11.3 | 10.6 |
| -8 | 0 | 4 | 13.8 | 15.8 | 2 | 1 | 4 | 25.3 | 21.7 | 8 | 2 | 1 | 10.0 | 12.0 | 1 | 2 | 12 | 19.6 | 19.7 | 1 | 3 | 9 | 18.9 | 21.0 |
| -9 | 0 | 4 | 18.0 | 20.7 | 3 | 1 | 4 | 44.9 | 46.2 | 9 | 2 | 1 | 19.8 | 17.6 | 3 | 2 | 12 | 12.5 | 11.8 | 2 | 3 | 9 | 26.4 | 32.2 |
| -10 | 0 | 4 | 12.0 | 14.0 | 4 | 1 | 4 | 24.0 | 22.3 | 10 | 2 | 1 | 13.6 | 11.8 | -5 | 2 | 13 | 11.3 | 12.1 | 4 | 3 | 9 | 11.2 | 10.8 |
| -11 | 0 | 4 | 17.5 | 20.1 | 5 | 1 | 4 | 8.8 | 7.8 | -10 | 2 | 1 | 14.0 | 14.0 | -2 | 3 | 13 | 13.5 | 12.5 | -8 | 3 | 10 | 23.2 | 21.7 |
| -12 | 0 | 4 | 33.3 | 39.6 | 6 | 1 | 4 | 16.3 | 15.2 | -9 | 2 | 1 | 21.9 | 18.1 | 3 | 2 | 13 | 10.0 | 8.0 | -5 | 3 | 10 | 8.5 | 10.9 |
| -13 | 0 | 4 | 26.3 | 32.0 | 8 | 1 | 4 | 19.2 | 18.3 | -8 | 2 | 2 | 47.4 | 39.4 | -1 | 2 | 14 | 10.6 | 9.9 | -3 | 3 | 10 | 22.5 | 24.9 |
| -14 | 0 | 4 | 14.8 | 13.6 | 9 | 1 | 4 | 12.3 | 11.9 | -3 | 2 | 2 | 32.2 | 29.1 | 1 | 3 | 0 | 23.6 | 31.4 | -1 | 3 | 10 | 18.2 | 19.4 |
| -15 | 0 | 4 | 9.3 | 10.4 | 11 | 1 | 4 | 10.2 | 10.5 | -2 | 2 | 2 | 64.5 | 71.3 | 2 | 3 | 0 | 11.6 | 11.1 | 1 | 3 | 11 | 17.0 | 15.1 |
| -16 | 0 | 4 | 8.6 | 8.6 | 12 | 1 | 4 | 11.7 | 11.7 | 1 | 2 | 2 | 13.2 | 13.2 | 3 | 3 | 0 | 13.7 | 11.0 | 0 | 3 | 11 | 9.5 | 13.5 |
| 0 | 0 | 4 | 33.6 | 30.5 | -6 | 1 | 5 | 41.6 | 43.1 | 2 | 2 | 2 | 21.9 | 23.6 | 4 | 3 | 0 | 8.7 | 6.6 | 5 | 3 | 10 | 7.3 | 8.7 |
| 1 | 0 | 4 | 35.3 | 28.1 | -4 | 1 | 5 | 33.4 | 30.8 | 2 | 2 | 2 | 20.5 | 23.6 | 5 | 3 | 0 | 10.0 | 10.9 | -8 | 3 | 11 | 17.6 | 15.5 |
| 2 | 0 | 4 | 14.3 | 12.0 | -2 | 1 | 5 | 17.3 | 19.8 | 3 | 2 | 2 | 48.2 | 43.4 | 6 | 3 | 0 | 16.3 | 13.7 | -7 | 3 | 11 | 14.8 | 10.8 |
| 3 | 0 | 4 | 48.4 | 40.3 | 3 | 1 | 5 | 20.5 | 17.8 | -10 | 2 | 2 | 31.7 | 30.8 | 7 | 3 | 0 | 31.0 | 27.0 | 0 | 3 | 11 | 12.1 | 11.1 |
| 4 | 0 | 4 | 47.6 | 42.3 | 0 | 1 | 5 | 23.4 | 23.8 | 7 | 2 | 2 | 12.5 | 9.4 | -7 | 3 | 1 | 21.9 | 17.7 | 1 | 3 | 11 | 12.9 | 11.8 |
| 5 | 0 | 4 | 26.3 | 24.8 | 1 | 1 | 5 | 34.1 | 34.7 | 8 | 2 | 2 | 12.9 | 12.1 | -5 | 3 | 1 | 16.4 | 17.2 | 2 | 3 | 11 | 12.5 | 11.0 |
| 6 | 0 | 4 | 31.3 | 30.0 | 2 | 1 | 5 | 21.7 | 21.0 | -8 | 2 | 3 | 34.9 | 30.8 | -4 | 3 | 1 | 18.2 | 17.2 | -2 | 3 | 12 | 12.0 | 15.1 |
| 7 | 0 | 4 | 19.0 | 18.0 | 3 | 1 | 5 | 9.4 | 6.1 | -7 | 2 | 3 | 14.4 | 13.5 | -1 | 3 | 1 | 26.0 | 32.5 | 1 | 3 | 12 | 10.9 | 9.0 |
| 8 | 0 | 4 | 17.3 | 16.3 | 4 | 1 | 5 | 12.1 | 12.2 | 6 | 2 | 3 | 31.1 | 30.8 | 0 | 3 | 1 | 13.8 | 12.5 | 0 | 3 | 12 | 10.3 | 10.3 |
| -9 | 0 | 4 | 15.0 | 18.1 | 5 | 1 | 5 | 14.4 | 14.6 | -3 | 2 | 3 | 44.7 | 46.8 | 1 | 3 | 1 | 12.3 | 16.4 | -5 | 3 | 13 | 8.0 | 5.7 |
| -10 | 0</ | | | | | | | | | | | | | | | | | | | | | | | |

Table 2 (cont.)

| H | A | L | FC | FC | F | K | L | FC | FC | H | K | L | F | FC | H | K | L | FC | FC | H | F | L | FC | FC |
|----|---|---|------|------|-----|---|---|------|------|----|---|----|------|------|----|---|----|------|------|----|---|---|------|------|
| -7 | 4 | 4 | 14.4 | 17.4 | 8 | 4 | 5 | 12.6 | 8.4 | 5 | 4 | 5 | 5.1 | 9.7 | -4 | 4 | 12 | 10.9 | 16.4 | 2 | 6 | 1 | 15.4 | 16.6 |
| -6 | 4 | 4 | 16.6 | 14.3 | -2 | 4 | 5 | 11.5 | 17.4 | 7 | 4 | 5 | 15.1 | 16.2 | -1 | 4 | 12 | 9.4 | 15.1 | 3 | 6 | 1 | 18.3 | 21.3 |
| -5 | 4 | 4 | 13.1 | 15.6 | -4 | 4 | 5 | 13.4 | 12.4 | 7 | 4 | 5 | 14.2 | 11.5 | 4 | 4 | 12 | 16.5 | 9.7 | 4 | 6 | 1 | 18.7 | 26.4 |
| -4 | 4 | 4 | 12.7 | 11.3 | -3 | 4 | 5 | 14.7 | 12.4 | -9 | 4 | 5 | 10.2 | 11.7 | -4 | 4 | 13 | 9.5 | 10.1 | 5 | 6 | 1 | 14.2 | 15.3 |
| -3 | 4 | 4 | 16.7 | 15.1 | 7 | 4 | 5 | 10.1 | 6.7 | -5 | 4 | 9 | 11.5 | 14.1 | 4 | 4 | 13 | 12.5 | 11.5 | 6 | 6 | 1 | 9.7 | 13.9 |
| -2 | 4 | 4 | 15.7 | 17.2 | 1 | 4 | 5 | 22.4 | 23.4 | -4 | 4 | 9 | 14.3 | 13.5 | 1 | 5 | 5 | 42.5 | 45.5 | 7 | 7 | 5 | 10.8 | 9.3 |
| -1 | 4 | 4 | 13.4 | 17.4 | 3 | 4 | 5 | 7.7 | 8.2 | 3 | 4 | 5 | 34.3 | 31.7 | 4 | 5 | 5 | 21.3 | 15.8 | 3 | 7 | 5 | 17.5 | 15.4 |
| 1 | 4 | 4 | 5.6 | 7.2 | 5 | 4 | 5 | 18.7 | 22.7 | 1 | 4 | 5 | 35.7 | 42.5 | 5 | 5 | 5 | 27.5 | 27.2 | 5 | 7 | 5 | 7.0 | 11.0 |
| 2 | 4 | 4 | 12.9 | 11.6 | -10 | 4 | 7 | 18.2 | 15.7 | 2 | 4 | 9 | 16.1 | 11.2 | -6 | 5 | 1 | 9.5 | 2.9 | -7 | 7 | 1 | 15.4 | 12.6 |
| 4 | 4 | 4 | 21.4 | 19.4 | -6 | 4 | 7 | 13.1 | 19.5 | 4 | 4 | 5 | 16.4 | 16.5 | -4 | 5 | 1 | 8.5 | 10.5 | -7 | 7 | 1 | 11.9 | 14.4 |
| 5 | 4 | 4 | 16.5 | 16.9 | -4 | 4 | 7 | 12.9 | 11.3 | -3 | 4 | 15 | 11.5 | 11.4 | -1 | 5 | 1 | 16.3 | 9.1 | 2 | 7 | 1 | 25.5 | 27.8 |
| 6 | 4 | 4 | 14.4 | 7.9 | -2 | 4 | 7 | 16.3 | 23.7 | -7 | 4 | 15 | 16.7 | 15.9 | 7 | 5 | 1 | 26.5 | 23.0 | 9 | 8 | 9 | 15.2 | 13.4 |
| 7 | 4 | 4 | 14.2 | 14.2 | -1 | 4 | 7 | 13.1 | 16.2 | -6 | 4 | 15 | 12.4 | 12.5 | 7 | 5 | 1 | 29.9 | 32.5 | 1 | 8 | 5 | 18.0 | 19.6 |
| 8 | 4 | 4 | 16.0 | 11.3 | 7 | 4 | 7 | 17.1 | 14.8 | -3 | 4 | 16 | 3.3 | 11.2 | 5 | 5 | 1 | 9.1 | 11.0 | 2 | 8 | 5 | 14.8 | 15.3 |
| -8 | 4 | 5 | 25.0 | 19.1 | 1 | 4 | 7 | 16.2 | 17.5 | -1 | 4 | 16 | 16.4 | 22.1 | 2 | 6 | 5 | 12.5 | 12.5 | 3 | 8 | 5 | 9.5 | 5.7 |
| -6 | 4 | 5 | 25.6 | 17.9 | 2 | 4 | 7 | 3.2 | 4.5 | 3 | 4 | 12 | 11.9 | 12.7 | 4 | 6 | 5 | 29.9 | 28.7 | 4 | 8 | 5 | 16.3 | 12.7 |
| -4 | 4 | 5 | 29.7 | 23.1 | 3 | 4 | 7 | 29.5 | 24.2 | 4 | 4 | 10 | 5.5 | 7.2 | 4 | 5 | 5 | 28.9 | 25.9 | 6 | 8 | 5 | 5.8 | 6.2 |
| -2 | 4 | 5 | 23.7 | 23.7 | 5 | 4 | 7 | 14.2 | 9.3 | -2 | 4 | 11 | 11.5 | 7.7 | 7 | 5 | 5 | 11.5 | 15.5 | -4 | 8 | 5 | 10.3 | 13.3 |
| -1 | 4 | 5 | 9.1 | 6.8 | 8 | 4 | 7 | 15.2 | 13.7 | -4 | 4 | 11 | 10.4 | 17.4 | -7 | 6 | 1 | 8.9 | 9.8 | -2 | 8 | 1 | 23.9 | 23.6 |
| C | 4 | 5 | 41.3 | 42.2 | -6 | 4 | 8 | 12.8 | 12.6 | -3 | 4 | 11 | 11.8 | 11.7 | -7 | 5 | 1 | 25.7 | 28.5 | -1 | 8 | 1 | 13.6 | 12.3 |
| 1 | 4 | 5 | 13.4 | 12.7 | -2 | 4 | 8 | 34.5 | 34.5 | -2 | 4 | 11 | 15.7 | 15.4 | -5 | 6 | 1 | 16.9 | 15.9 | 5 | 8 | 1 | 8.6 | 12.2 |
| 2 | 4 | 5 | 17.2 | 19.4 | -1 | 4 | 5 | 16.4 | 16.4 | -1 | 4 | 11 | 7.9 | 9.7 | -4 | 4 | 1 | 37.1 | 31.6 | 2 | 8 | 1 | 15.9 | 14.1 |
| 3 | 4 | 5 | 13.5 | 14.2 | 0 | 4 | 8 | 16.7 | 18.5 | 0 | 4 | 11 | 7.8 | 9.4 | -2 | 6 | 1 | 36.6 | 31.4 | 3 | 8 | 1 | 11.9 | 14.7 |
| 4 | 4 | 5 | 14.8 | 16.2 | 1 | 4 | 8 | 13.6 | 12.5 | 5 | 4 | 11 | 19.6 | 17.5 | -1 | 6 | 1 | 16.7 | 13.1 | 1 | 9 | 5 | 7.7 | 4.7 |

Table 3. Positional parameters in fractional coordinates and isotropic temperature factors

The significant figures of the standard deviations are in parentheses.

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> |
|-------|-------------|-------------|-------------|--------------------------|
| O(1) | 0.4562 (9) | 0.2012 (15) | 0.0219 (7) | 1.07 (17) Å ² |
| O(2) | 0.6369 (10) | 0.4037 (15) | -0.0036 (8) | 1.27 (17) |
| O(3) | 0.8215 (9) | 0.5942 (15) | -0.0357 (8) | 1.26 (18) |
| O(4) | 0.5997 (9) | 0.3232 (15) | 0.1879 (7) | 1.34 (18) |
| O(5) | 0.7736 (9) | 0.5426 (15) | 0.1583 (7) | 1.07 (17) |
| O(6) | 0.6205 (9) | 0.5779 (15) | 0.3047 (7) | 1.01 (17) |
| O(7) | 0.8069 (9) | 0.3614 (15) | 0.3275 (7) | 1.25 (17) |
| O(8) | 0.7350 (9) | 0.5005 (15) | 0.4926 (7) | 1.22 (18) |
| O(9) | 0.9322 (9) | 0.3067 (15) | 0.5088 (8) | 1.41 (18) |
| O(10) | 0.9552 (10) | 0.1128 (17) | 0.2295 (8) | 1.90 (20) |
| B(1) | 0.5656 (16) | 0.3091 (28) | 0.0710 (12) | 1.31 (28) |
| B(2) | 0.7487 (17) | 0.5111 (29) | 0.0448 (14) | 1.70 (31) |
| B(3) | 0.7000 (16) | 0.4533 (26) | 0.2431 (12) | 0.92 (26) |
| B(4) | 0.6314 (16) | 0.5935 (28) | 0.4192 (13) | 1.25 (27) |
| B(5) | 0.8246 (15) | 0.3909 (25) | 0.4418 (12) | 0.82 (25) |
| N | 0.3219 (13) | 0.4393 (20) | 0.2658 (10) | 1.93 (25) |
| H(1) | 1.056 | 0.089 | 0.260 | 5.00 |
| H(2) | 0.899 | 0.208 | 0.267 | 5.00 |
| H(3) | 0.941 | 0.338 | 0.597 | 5.00 |
| H(4) | 0.911 | 0.671 | -0.026 | 5.00 |

Table 4. Boron-oxygen bond lengths and angles in larderellite

Triangularly coordinated boron

| | Distance | E.s.d. | | Angle | E.s.d. |
|---------------------|----------|---------|------------------------------|--------|--------|
| B(1)-O(1)* | 1.390 Å | 0.020 Å | O(1)-B(1)-O(2) | 116.9° | 1.1° |
| O(2)* | 1.371 | 0.020 | O(1)-B(1)-O(4) | 122.1 | 1.4 |
| O(4) | 1.364 | 0.017 | O(2)-B(1)-O(4) | 121.1 | 1.4 |
| B(2)-O(2)* | 1.401 | 0.020 | O(2)-B(2)-O(3) | 114.2 | 1.2 |
| O(3) | 1.384 | 0.021 | O(2)-B(2)-O(5) | 122.4 | 1.4 |
| O(5) | 1.336 | 0.019 | O(3)-B(2)-O(5) | 123.1 | 1.5 |
| B(4)-O(6) | 1.331 | 0.017 | O(1 ¹)-B(4)-O(6) | 124.2 | 1.4 |
| O(8)* | 1.410 | 0.019 | O(1 ¹)-B(4)-O(8) | 114.2 | 1.2 |
| O(1 ¹)* | 1.405 | 0.019 | O(6)-B(4)-O(8) | 121.6 | 1.4 |
| 3(5)-O(7) | 1.340 | 0.016 | O(7)-B(5)-O(8) | 121.4 | 1.2 |
| O(8)* | 1.376 | 0.019 | O(7)-B(5)-O(9) | 118.8 | 1.4 |
| O(9) | 1.364 | 0.017 | O(8)-B(5)-O(9) | 119.8 | 1.1 |
| Average | 1.373 | | | 120.0 | |

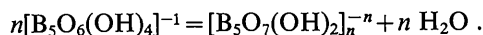
Tetrahedrally coordinated boron

| | Distance | E.s.d. | | Angle | E.s.d. |
|-----------|----------|---------|----------------|--------|--------|
| B(3)-O(4) | 1.466 Å | 0.020 Å | O(4)-B(3)-O(5) | 111.1° | 1.0° |
| O(5) | 1.447 | 0.019 | O(4)-B(3)-O(6) | 108.2 | 1.1 |
| O(6) | 1.456 | 0.020 | O(4)-B(3)-O(7) | 108.7 | 1.4 |
| O(7) | 1.496 | 0.018 | O(5)-B(3)-O(6) | 110.6 | 1.4 |
| | | | O(5)-B(3)-O(7) | 109.0 | 1.1 |
| | | | O(6)-B(3)-O(7) | 109.3 | 1.0 |
| Average | 1.466 | | | 109.5 | |

* Oxygen atoms bonded to two boron atoms in the trigonal state.

Assignment of the hydrogen atoms was carried out assuming, according to Christ's (1960) third rule, that the oxygen atoms O(3) and O(9), not shared between two boron atoms in the polyion, represent hydroxyl groups, and that the single unattached oxygen atom O(10) represents a water molecule. Thus the structural formula for larderellite is: $\text{NH}_4\text{B}_5\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$.

The infinite chains found in larderellite consist of the polymerization product of the insular polyions $[\text{B}_5\text{O}_6(\text{OH})_4]^{-1}$, according to the schematic reaction:



Successive chains along [001] are linked through ammonium-oxygen bonds and through hydrogen bonds *via* the water molecules to form sheets parallel to (100); the sheets are linked by additional hydrogen bonds.

Interatomic distances and angles are presented in Tables 4, 5 and 6 and in Fig. 3. In these Tables and Figure the atoms of the different asymmetric units are related to the atoms of the fundamental unit as follows:

| | | | | |
|------|---------|-------|------------------|-----------------|
| i | atom at | $1-x$ | $\frac{1}{2}+y$ | $\frac{1}{2}-z$ |
| ii | atom at | x | $1+y$ | z |
| iii | atom at | $1-x$ | $-\frac{1}{2}+y$ | $\frac{1}{2}-z$ |
| iv | atom at | $1-x$ | $1-y$ | $-z$ |
| v | atom at | $1-x$ | $1-y$ | $1-z$ |
| vi | atom at | $2-x$ | $-\frac{1}{2}+y$ | $\frac{1}{2}-z$ |
| vii | atom at | $2-x$ | $\frac{1}{2}+y$ | $\frac{1}{2}-z$ |
| viii | atom at | x | $\frac{1}{2}-y$ | $\frac{1}{2}+z$ |

Table 5. Ammonium-oxygen bond lengths

The estimated standard deviations are 0.02 Å.

| | |
|---|--------|
| $\text{NH}_4\text{-O}(3^{\text{iv}})$ | 2.86 Å |
| $\text{NH}_4\text{-O}(10^{\text{i}})$ | 2.94 |
| $\text{NH}_4\text{-O}(6^{\text{iii}})$ | 2.95 |
| $\text{NH}_4\text{-O}(8^{\text{v}})$ | 2.97 |
| $\text{NH}_4\text{-O}(6)$ | 3.00 |
| $\text{NH}_4\text{-O}(4)$ | 3.02 |
| $\text{NH}_4\text{-O}(4^{\text{i}})$ | 3.05 |
| $\text{NH}_4\text{-O}(1^{\text{viii}})$ | 3.28 |
| $\text{NH}_4\text{-O}(5^{\text{iii}})$ | 3.31 |
| $\text{NH}_4\text{-O}(2^{\text{iv}})$ | 3.35 |

Table 6. Distances shorter than 3.0 Å between oxygen atoms not bonded to the same boron atom

| | |
|---|--------|
| $\text{O}(10) \cdots \text{O}(7)$ | 2.70 Å |
| $\text{O}(10) \cdots \text{O}(5^{\text{vi}})$ | 2.79 |
| $\text{O}(9) \cdots \text{O}(10^{\text{viii}})$ | 2.63 |
| $\text{O}(3) \cdots \text{O}(9^{\text{vi}})$ | 2.83 |

Bond lengths and angles in the boron-oxygen infinite chains are given in Table 4 and in Fig. 3. In larderellite the average B-O distance in the triangles is 1.373 Å and in the tetrahedron 1.466 Å, in excellent agreement with the results previously found in other borates by various workers.

We have examined the variation of the bond lengths of the trigonal B-O bonds in the light of the treatment of Coulson & Dingle (1968), who explain differences

in bond length by differences in π -bond order. The π -bond order is clearly less for B-O bonds where an oxygen atom is linked to two boron atoms in the trigonal state. In larderellite there are chains of four

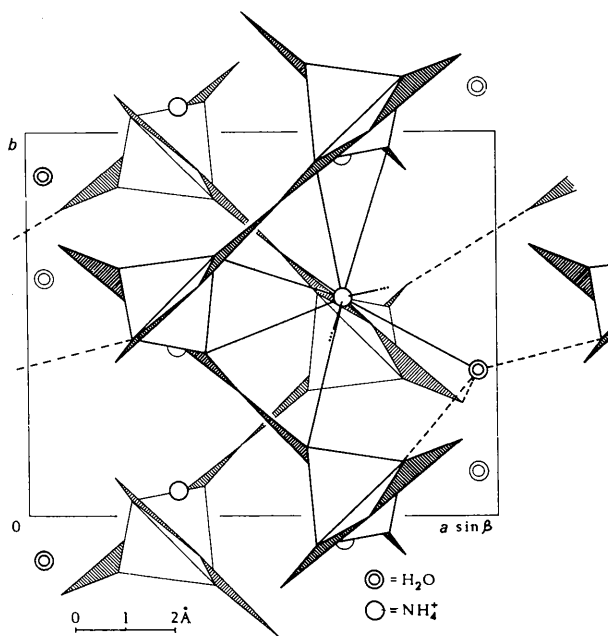


Fig. 2. The crystal structure of larderellite viewed along [001]. The dashed lines represent hydrogen bonds. The continuous lines represent $\text{NH}_4\text{-O}$ bonds; those ending with dots indicate that the bond is associated with an oxygen atom translated one unit in the [001] direction.

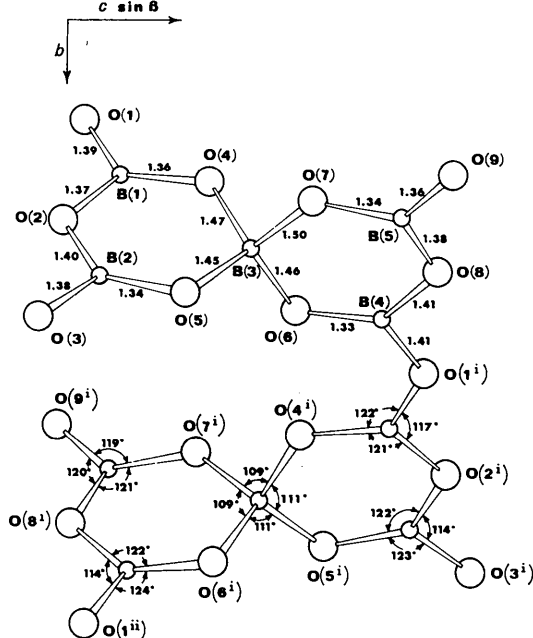


Fig. 3. Bond lengths and angles in the borate chain. The chain is viewed along [100].

loss of one water molecule; this also is well explained by the crystal structure.

All the programs used throughout the work, apart from the *SORTE* program, are collected in the *X-ray '63 System*. The computations were carried out at the Centro Nazionale Universitario di Calcolo Elettronico (Pisa).

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The Crystal and Molecular Structure of Cobalt(III) Tris(*O*-ethylxanthate)

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Cobalt(III) tris(*O*-ethylxanthate) crystallizes in the rhombohedral space group $R\bar{3}$, with two molecules in the unit cell, $a = 9.65 \text{ \AA}$, $\alpha = 100^\circ 48'$. The crystal structure has been determined by two-dimensional Patterson and Fourier syntheses and refined with three-dimensional data by anisotropic least-squares methods, with a final agreement index for the observed reflexions, $R_1 = 0.090$. Each molecule is made up of three ethylxanthic ligands coordinated to a cobalt atom through the sulphur atoms; the molecule has trigonal symmetry C_3-3 . The intermolecular interactions are of the van der Waals type. Mean bond lengths: Co-S, 2.277; S-C, 1.673; C-O, 1.359 Å. The $\cdots\text{S}_2\text{C}=\text{OR}$ form makes only a minor contribution to the structure of the xanthic radical.

Introduction

Recently the refinement of the structure of cobalt(III) tris(*N,N*-diethyldithiocarbamate) (Merlino, 1968) has been completed in our laboratory, as part of a research programme developed with the aim of gaining information on metal-sulphur bonds and on the structure of xanthic and dithiocarbamic ligands.

The results obtained confirm that the resonance form $\cdots\text{S}_2\text{C}=\text{NR}_2$ makes an important contribution to the molecular structure. Chatt, Duncanson & Venanzi (1956*a,b*) explained the importance of this resonance form by the strong electron releasing effect of the $-\text{NR}_2$ group and the ability of the sulphur atoms to accept electrons; they observe that the resonance form $\cdots\text{S}_2\text{C}=\text{OR}$ would make only a minor contribution to the structure of the xanthates, because of the smaller mesomeric effect of the $-\text{OR}$ group relative to the $-\text{NR}_2$ group.

An indication of this is given by the comparison of the C-N = 1.33 Å distance in nickel diethyldithiocarbamate (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965), nickel di-*n*-propyldithiocarbamate (Peyronel & Pignedoli, 1967) and zinc diethyldithiocarbamate (Bonamico, Mazzone, Vaciago & Zambonelli, 1965), with the distance C-O = 1.38 Å found in nickel ethylxanthate, whose structure was determined from two-dimensional data (Franzini, 1963) and the distances C-O = 1.33 and 1.42 Å (average 1.38 Å) found in zinc ethylxanthate (Ikeda & Hagihara, 1966). However these comparisons are not conclusive and it seemed useful to investigate the Co^{III} ethylxanthate crystal structure, the determination of which is the subject of this paper.

Experimental

The X-ray crystallography of cobalt(III) tris(*O*-ethylxanthate) was studied by Derenzini (1938); he