Note on the structure of dimethylamine–boron trifluoride. By S. Geller* and M. E. Milberg†, *Baker Laboratory of Chemistry, Cornell University, Ithaca, N.Y., U.S.A.*

Complete structure determinations have been reported for the closely related molecular addition compounds of formulae $H_3N–BF_3$ (Hoard, Geller & Cashin, 1951), $H_3CH_2N–BF_3$ (Geller & Hoard, 1950), and $(H_3C)_3N–BF_3$ (Geller & Hoard, 1951). The purpose of this note is to report briefly on intensive but unsuccessful efforts to determine the structure of the remaining member of the series, dimethylamine–boron trifluoride, $(H_3C)_2HN–BF_3$.

The monoclinic unit of structure has

$$a = 7.50, \quad b = 6.06, \quad c = 12.25 \text{A}., \quad \beta = 102°,$$

and contains four stoichiometric molecules. Nearly all of the data obtainable with Cu $K\alpha$ radiation were provided by complete sets of Weissenberg photographs with oscillation about b and c. Reflections of the type $(h0l)$, l odd, and $(0k0)$, k odd, are not observed; thus $C_{2h}^5–P2_1/c$ is uniquely indicated as the probable space group. Only a few 'forbidden' $(0k0)$ spectra can be looked for, but a 26 hr. exposure on a Buerger precision camera set to bring out (010) and (030) failed to reveal either of them. The assumption of a centrosymmetric space group is further supported by the absence of a measurable pyroelectric effect, the molecule itself possessing a considerable permanent dipole moment.

The apparent wealth of information provided by the data at hand would appear to make the deduction of an approximate structure a comparatively simple problem. Presumably the effective size and shape of the molecule, $(H_3C)_2HN–BF_3$, can be estimated with some accuracy from the work on related compounds. The character of

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the Patterson section, $P(X, \frac{1}{2}, Z)$, and the short b translation, when considered together with the symmetry of $P2_1/c$, would seem to delimit the region in which such a molecule (the asymmetric unit) could lie. An additional clue to the orientation of the molecule is provided by $P(X, 0, Z)$, which shows one strong peak interpretable as an intramolecular distance, F–F, N–F, or just possibly C–C, between two atoms having very nearly the same y co-ordinate. Nevertheless, all possibilities suggested by these considerations and by other Patterson syntheses have led to gross inconsistencies. It seems not improbable that the true structure is based on Pc, even though the missing $(0k0)$ spectra and the absence of a pyroelectric effect would still need to be explained in terms of peculiarities of the atomic arrangement.

With the hope that the method of inequalities (Harker & Kasper, 1948) might be of aid in determining some of the phases, the observed amplitudes were put on an absolute basis (Harker, 1948). As all except two of the unitary structure factors were definitely less than 0·5, the method of inequalities is not very useful in this case (cf. Hughes, 1949).

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A preliminary X-ray investigation of potassium- and ammonium-trioxalatochromate. III. By J. N. van Niekerk and F. R. L. Schoening, *National Physical Laboratory, Council for Scientific and Industrial Research, Pretoria, South Africa*

The two compounds examined were (1) $K_3[Cr(C_2O_4)_3].xH_2O$ and (2) $(NH_4)_3[Cr(C_2O_4)_3].xH_2O$. Both compounds form fairly hard dark blue crystals which lose water of crystallization upon exposure to normal atmospheric conditions, decomposing into a light blue crystalline powder. During the X-ray examinations of the crystals they were coated with thin films of Perspex to prevent water loss. Single-crystal oscillation and Weissenberg photographs were taken of both compounds, using Cu $K\alpha$ and Mo $K\alpha$ radiation.

(1) $K_3[Cr(C_2O_4)_3].xH_2O$

The potassium salt crystallizes as thick prismatic needles with well-developed {031} prism faces. The crystals are

monoclinic, belonging to the class $2/m–C_{2h}$, and the unit-cell dimensions are

$$a = 7.71, \quad b = 19.74, \quad c = 10.40 \text{A}.; \quad \beta = 108°0'.$$

The axial ratios

$$a:b:3c = 0.3906:1:1.5805$$

can be compared with those given by Jaeger (1919), namely,

$$c:b:a = 0.3917:1:1.5733, \quad \beta = 72° 5\tfrac{2}{3}'.$$

The density of the crystals, determined by the method of flotation, is 2·16 g.cm.$^{-3}$ (cf. Jaeger's value 2·141 g.cm.$^{-3}$). The unit cell therefore contains four of the above formula

units, and, assuming three water molecules in each formula unit, the calculated density is $2 \cdot 15 \, \text{g.cm.}^{-3}$.

Systematic extinctions occur only for $h0l$ with l odd and $0k0$ with k odd, hence the space group is $P2_1/c-C_{2h}^5$. A close inspection of the hkl reflexions shows, however, that the crystal very nearly belongs to the space group $C2/c-C_{2h}^6$. The reason for this is that out of 215 spectra recorded for a Patterson–Harker section, only 28 weak spectra did not conform to the extinction conditions implied by this space group.

(2) $(NH_4)_3[Cr(C_2O_4)_3].xH_2O$

The ammonium salt generally crystallizes in the form of flat plates. The crystals are triclinic, class $\bar{1}-C_i$, and not monoclinic as reported by Wyrouboff (1900). Referring the crystals to a set of axes approximately similar to those used in the potassium salt, the following unit-cell dimensions were obtained:

$$a' = 7 \cdot 79, \quad b' = 20 \cdot 13, \quad c' = 10 \cdot 73 \, \text{A.};$$
$$\alpha' = 91^\circ 55', \quad \beta' = 112^\circ 36', \quad \gamma' = 89^\circ 18'.$$

This triclinic unit cell and the general appearance of the photographs resemble very closely the corresponding data of the potassium salt. The unit cell as given above is,

however, centred on the C face, and the following set of transformations

$$a = a', \quad b = \tfrac{1}{2}a' + \tfrac{1}{2}b', \quad c = c'$$

gives the primitive triclinic cell with dimensions

$$a = 7 \cdot 79, \quad b = 10 \cdot 90, \quad c = 10 \cdot 73 \, \text{A.};$$
$$\alpha = 98^\circ 10', \quad \beta = 112^\circ 36', \quad \gamma = 67^\circ 22'.$$

An independent set of measurements confirmed these values.

The density, determined by the method of flotation, is $1 \cdot 79 \, \text{g.cm.}^{-3}$. Assuming two formula units, each with three water molecules, in the unit cell, the calculated density is $1 \cdot 81 \, \text{g.cm.}^{-3}$.

There are no systematic extinctions, hence the space group is either $P1-C_1^1$ or $P\bar{1}-C_i^1$. An examination of the external crystal form and the close similarity between the two structures, as obtained from detailed structural work now in progress, suggest that the space group is $P\bar{1}-C_i^1$.

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An experimentally determined atomic scattering-factor curve for chromium.

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While investigating the structure of

$$(NH_4)_3[Cr(C_2O_4)_3].2H_2O$$
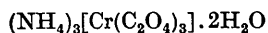
by the method of double Fourier synthesis, a projection was obtained in which very nearly all the atoms in the structure were resolved. Using atomic scattering-factor values for carbon as given by Robertson (1935), and reducing the corresponding oxygen and nitrogen values given by James & Brindley (1931) by the same ratio as that by which Robertson's values for carbon differ from those of James & Brindley, the possibility then arises of determining a set of atomic scattering-factor values for chromium in the trioxalato complex.

The intensities of the 124 spectra used for obtaining this projection were carefully estimated by eye by comparing them with a set of previously calibrated intensity spots of approximately the same size. The intensities of a number of these spectra were measured on a Geiger-counter spectrometer in order to find their approximate absolute values. A conversion factor was then calculated by which all the eye-estimated intensities were multiplied, to express the intensities of all the spectra on an approximately absolute scale.

By using atomic scattering-factor values for oxygen, nitrogen and carbon as described above, and values for chromium as previously described by us (van Niekerk & Schoening, 1951), structure factors were calculated for all spectra with $\sin \theta/\lambda \leqslant 0 \cdot 25$. It was estimated that for these low-order spectra the true f values for chromium would not differ appreciably from the theoretical values. These calculated structure factors were then compared

with the observed ones, and it was found that on multiplying the observed intensities of the low-order spectra by a further factor of $1 \cdot 2$, excellent agreement was obtained. All spectra were now multiplied by this factor, thus expressing them all on an absolute scale.

Considering spectra with $\sin \theta/\lambda > 0 \cdot 25$, structure factors were calculated using that f factor for chromium which gave the best fit between observed and calculated values in each individual case. These f values for chromium were plotted against $\sin \theta/\lambda$, and the points were found to fall approximately on a smooth curve. The best average curve was then drawn through these points. Using the f values obtained from this curve, the structure factors for all 200 spectra, including absent spectra, were recalculated. The agreement between observed and calculated structure factors was excellent, and seemed to confirm the procedures adopted in deriving a set of f values for chromium in this particular complex. The following table gives the atomic scattering-factor values for chromium finally obtained by the methods outlined above:

$\sin \theta/\lambda$ (A.$^{-1}$)	0	0·1	0·2	0·3	0·4	0·5
f	24·0	21·0	17·1	13·2	9·3	6·5
$\sin \theta/\lambda$ (A.$^{-1}$)	0·6	0·7	0·8	0·9	1·0	1·1
f	4·7	3·5	2·6	2·1	1·8	1·6

During the investigation Mo $K\alpha$ radiation was used throughout.

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