Fig. 2. Fourier projection of $Rb_2C_2N_4O_8$ along the *c* axis.

1. Kamlet, M. J., Oesterling, R. E. and Adolph, H. G. *J. Chem. Soc.* **1965** 5838.
2. Lippincott, E. R., Kenney, T. E., Nanney, T. R. and Weiffenbach, C. K. *J. Chem. Soc.* **B 1967** 32.
3. Holden, J. R. and Dickinson, C. W. *Am. Cryst. Ass. Winter Meeting, 1967,* Program and Abstracts; *J. Am. Chem. Soc. In press.*
4. Bjørnstad, H. J. and Klewe, B. *To be published.*
5. Dickens, B. *Chem. Commun.* **1967** 246.
6. Bekoe, D. A., Gantzel, P. K. and Trueblood, K. N. *Acta Cryst.* **22** (1967) 657.
7. Hunter, L. *J. Chem. Soc.* **123** (1923) 547.
8. Bhuiya, A. K. and Stanley, E. *Acta Cryst.* **16** (1963) 981.

Received July 1, 1967.

$Rb_2C_2N_4O_8$ crystals are orthorhombic with $a = 7.6_8$ Å, $b = 13.3_0$ Å, $c = 8.8_3$ Å, and 4 formula units in the unit cell. The space group *Pccn* requires the same symmetry of the anion as for the potassium salt. The structure was determined in the *hk*0 projection by Fourier methods and the minimum residual method. The final Fourier map is shown in Fig. 2. The rubidium atoms seem to overlap completely. The *z*-parameters were determined from the 0*kl* projection. The final *R*-value for 166 *hk*0 and 0*kl* reflections (34 accidental extinctions included) was 11 %.

The coordination number of the cation is six and eight for the potassium and the rubidium salt, respectively. In both structures the crystallographic two-fold axis is normal to the carbon-carbon bond. According to the large twist angles of the approximately planar $-C(NO_2)_2^-$ groups, the dihedral $N-C-C-N$ angles being about 60° and .70°, respectively, the double bond character of the $C-C$ bond must be negligible. There are indications of propeller twists of the nitro groups. Differences in coordination of the oxygen atoms may lead to different twist angles, thus destroying the D_2 symmetry. A deviation from this symmetry cannot, however, be stated with certainty because of the considerable overlap of atoms in the projections.

A three-dimensional investigation of these salts is now being undertaken.

Fluorimetric Determination of Boron with Chinizarin in Concentrated Sulfuric Acid

A. HOLME

University of Oslo, Chemical Institute A, Blindern, Oslo 3, Norway

During a systematic investigation of the complex formation in concentrated sulfuric acid between boric acid and a series of hydroxyanthraquinones (1,4-dihydroxy-, 1,5-dihydroxy-, 1,8-dihydroxy-, 1,2,3-trihydroxy-, 1,2,4-trihydroxy-, and 1,2,3,5,6,7-hexahydroxyanthraquinone), it was found that chinizarin (1,4-dihydroxyanthraquinone) was the only reagent producing a fluorescent complex. The present paper describes the fluorimetric determination of boron with chinizarin.

Previous studies on the fluorescence of boron complexes in concentrated sulfuric acid have been published by Marcantonatos, Marcantonatos and Monnier.[1] The basis of fluorospectrophotometry is the principle that in dilute solutions and at a given wavelength the fluorescence intensity is proportional with the concentration of the fluorescent substance.[2,3]

Experimental. Reagents. Chinizarin (K & K Laboratories, USA) was dissolved in concentrated sulfuric acid, precipitated in and

washed with distilled water. This treatment was repeated once. Boric acid (Riedel-De Haën, Germany) and concentrated sulfuric acid, 95 – 97 %, (Merck, Germany) were of reagent-grade quality.

Equipment. Standard and sample solutions were prepared in volumetric flasks. Solutions stored in these flasks were tested for boron; no boron was detected spectrophotometrically by the reaction with quinalizarin.

Instruments. A Zeiss spectrophotometer PMQ II with fluorescence equipment ZFM 4, system A, (mercury lamp, filter 365 nm, 1 cm cells, slit 0.1 mm, sensitivity of the detector 10/II) was used. The instrument was calibrated against a fluorescence standard F 53 (80 % T at 530 nm, slit 0.1 mm, sensitivity of detector 1/II).

The precision of the instrument was determined by a series of 24 individual random observations, and a standard deviation $s \approx 0.1$ (% T) was found.

The apparent fluorescence excitation spectrum.[3] The fluorescence intensity (% T) was measured as a function of the wavelength (nm) at constant slit (0.1 mm). Solutions of chinizarin (Ch) in 96.6 % sulfuric acid fluoresces, the fluorescence maximum varying from 570 nm at 0.200×10^{-4} M Ch to 595 nm at 4.00×10^{-4} M Ch. A mixture of chinizarin and boric acid (B) in 96.6 % sulfuric acid gives a fluorescence maximum at 595 nm when measured against a blank with the same content of chinizarin as in the sample.

The effect of time. A series of solutions containing 2.00×10^{-4} M B and 2.00×10^{-4} M Ch and a series of blanks containing 2.00×10^{-4} M Ch in 96.6 % sulfuric acid were prepared. After 0.5, 1, 2, 3, 4, and 5 h the fluorescence intensities were measured at 595 nm. The differences of the fluorescence intensities between solutions and blanks were found approximately constant in a range from 2 to 3.5 h. Below and above this range the differences decreased.

The effect of heat treatment. A series of solutions 2.00×10^{-4} M B and 2.00×10^{-4} M Ch and a series of blanks 2.00×10^{-4} M Ch were prepared and measured at 595 nm after being temperated for 2 h in a thermostatically controlled bath at 10, 15, 20, 25, 30, 35, and 40°. Variations in the temperature (10 – 40°) had no influence upon the differences of the fluorescence intensities between the solutions and the blanks. All observations were in the range $29.5 \pm 2s$ (% T).
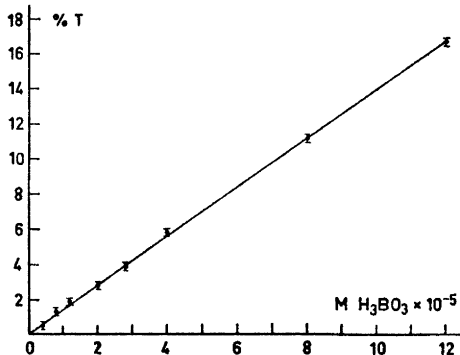

Fig. 1. Calibration curve for the determination of boron with chinizarin.

The effect of concentration of sulfuric acid. A series of seven sulfuric acids with concentrations varying from 88.6 % to 99.4 % were prepared. A solution 2.00×10^{-4} M B and 2.00×10^{-4} M Ch and a blank 2.00×10^{-4} M Ch were prepared for each acid and measured at 595 nm. The difference of the fluorescence intensities between solution and blank was found approximately constant in the range of 91 – 96 % sulfuric acid. For concentrations below and above this range the difference decreased.

Calibration curve. A series of solutions with 0.0400×10^{-4} – 0.800×10^{-4} M B and 2.00×10^{-4} M Ch and a series of blanks 2.00×10^{-4} M Ch in 96.6 % sulfuric acid were prepared and measured at 595 nm after 2 h at room temperature. The resulting curve is reproduced in Fig. 1.

The lower limit of detectability of boron is calculated by the signal to noise ratio.[2] This calculation showed a lower limit of 0.01 ppm boron.

1. Marcantonatos, M., Marcantonatos, A. and Monnier, D. *Helv. Chim. Acta* **48** (1965) 194.
2. Hercules, D. M. *Anal. Chem.* **38** (1966) 29A.
3. Parcer, C. A. and Rees, W. T. *Analyst* **85** (1960) 587.

Received July 3, 1967.