On the Crystal Structure of Cesium Bismuth Iodide

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In connection with solubility studies [1] of BiO_3-BiOI in 1 M and 3 M (H,Na) (ClO_4,I) as a function of $[H^+]$ and $[I^-]$, the structure of cesium bismuth iodide has been investigated and a preliminary report is given in this note.

Crystals were prepared by allowing a solution of cesium nitrate to diffuse into a solution of 14 g sodium iodide and approximately 0.8 g bismuth(III) oxide in 4.3 M acetic acid.[2]

Weissenberg photographs corresponding to the reflections $0kl-5kl$ and $hk0$ have been recorded, using $CuK\alpha$ radiation. The crystals are of hexagonal symmetry and from the systematically absent reflections, the space group was determined to be either No. 186 — $P6_3mc$, No. 190 — $P\bar{6}2c$, or No. 194 — $P6_3/mmc$.[3] The cell dimensions, as calculated from the Weissenberg data, are $a = b = 8.3_9$ Å and $c = 21.0_5$ Å. The volume of the unit cell is thus approximately 1290 Å³. Assuming a cell content of two formula units,[2] a calculated density of 4.70 g/cm³ is obtained, which seems reasonable.

From three-dimensional Patterson calculations, based on the $0kl-5kl$ intensities, the bismuth atoms were found to occupy the four-fold position $4(f)$ in $P6_3/mmc$ (No. 194) with $z = 0.155$. The positions of the iodine and cesium atoms were then deduced from successive electron density calculations. A preliminary three-dimensional least squares refinement of the structure was performed giving an R value of 0.21, and the resulting parameters are

Table 1.

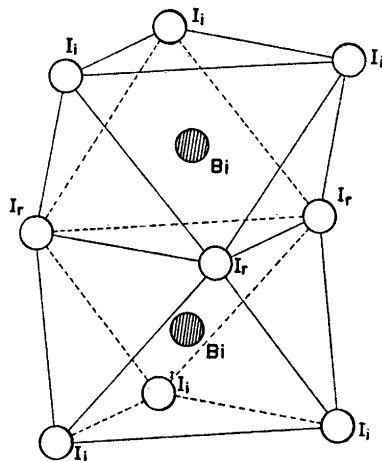| Atom	Position	x	y	z	B (in Å²)
Bi	$4(f)$	1/3	2/3	0.155	−0.141
I_i	$12(k)$	0.161	0.322	0.081	1.339
I_r	$6(h)$	0.508	0.016	1/4	0.944
Cs_1	$2(b)$	0	0	1/4	2.712
Cs_2	$4(f)$	1/3	2/3	−0.081	2.831

Fig. 1. The $Bi_2I_9^{3-}$ ion in the crystals of $Cs_3Bi_2I_9$.

listed in Table 1. Since the linear absorption coefficient is as high as 1450.7 cm⁻¹ no significance can be assigned to the temperature factors until an absorption correction has been performed.

From the structure determination it was found that the crystals contain $[Bi_2I_9]^{3-}$ ions which may be described in terms of two distorted octahedra joined by a common face. The bismuth atoms lie on one six-fold inversion axis and one three-fold rotation axis, the rotation plane and the inversion centre being situated halfway between the two bismuth atoms. The six-fold inversion axis generates the positions of six iodine atoms, I_i, and the three-fold rotation axis the positions of three iodine atoms, I_r (cf. Fig. 1). The distance between the bismuth atoms is 4.0_3 Å and the bismuth-iodine distances are 2.9_4 Å $(Bi-I_i)$ and 3.2_4 Å $(Bi-I_r)$. The distance between the planes through the I_i-triangles is 7.1_3 Å.

A complete three-dimensional refinement, based on intensities corrected for absorption effects, is in progress, and a detailed presentation of the structure of $Cs_3Bi_2I_9$ will soon be published in Acta Chem. Scand.

1. Yen, Ai-chen, and Dyrssen, D. *Acta Chem. Scand. To be published.*
2. Cavalca, L., Nardelli, M. and Braibanti, A. *Gazz. Chim. Ital.* 23 (1954) 1239.
3. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1952, 2nd Ed.
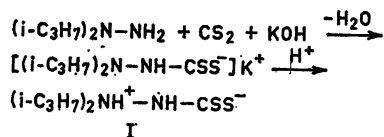
N-Isothiocyanatoamines

V. Conversion of N-Isothiocyanatodiisopropylamine to Seleno- and Tellurothiocarbazic Acid Derivatives

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Recently,[1] the synthesis and infrared spectra of several dithio- and diselenocarbazic acids have been described and their dipolar structure established. *N,N*-Diisopropyldithiocarbazic acid (I), which became of interest in connection with our studies on *N*-isothiocyanatodiisopropylamine,[2] proved to be readily available from N,N-diisopropylhydrazine and carbon disulfide by a closely related method.

$$(\text{i-}C_3H_7)_2N-NH_2 + CS_2 + KOH \xrightarrow{-H_2O}$$
$$[(\text{i-}C_3H_7)_2N-NH-CSS^-]K^+ \xrightarrow{H^+}$$
$$(\text{i-}C_3H_7)_2NH^+-NH-CSS^-$$
$$\text{I}$$

Replacement of carbon disulfide in this synthesis by CSSe or CSTe would furnish the title compounds. Both these starting materials, however, are unstable and dif-

ficult to prepare. To circumvent these preparative difficulties, we decided to investigate the reaction between *N*-isothiocyanatodiisopropylamine and H_2Se or H_2Te. The first reaction proceeds according to the following scheme.

$$(\text{i-}C_3H_7)_2N-NCS + H_2Se \longrightarrow$$
$$(\text{i-}C_3H_7)_2NH^+-NH-CSSe^-$$
$$\text{II}$$
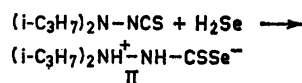
The assignment to I and II of the dipolar structures shown followed from their infrared spectra (KBr). In the high frequency region, the strong bands originating from the NH^+ stretching vibrations were observed in the $2500-3000$ cm^{-1} range and the NH stretching vibrations are (as a result of the neighbouring positive charge) characteristically[1] around 3100 cm^{-1}. The lower frequency regions were nearly identical, apart from two absorptions in the regions $1000-1050$ cm^{-1} and $600-700$ cm^{-1}. These bands have been assigned to the antisymmetrical and symmetrical CSS^- stretching vibrations for dithiocarbazic acids.[1] Consistently with this, we assign the bands at 1048 and 1017 cm^{-1} in I and II, respectively, to the antisymmetrical CXS^- vibrations and the bands at 680 or 650 and 660 or 624 cm^{-1} to the corresponding symmetrical modes.

If an ethanolic solution of II is oxidized for some time with air, the corresponding diselenide (III) is formed.

$$\left[(\text{i-}C_3H_7)_2N-NH-C{\overset{S}{\underset{Se}{\lessgtr}}}\right]_2$$
$$\text{III}$$
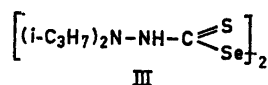
By treating *N*-isothiocyanatodiisopropylamine with hydrogen telluride we obtained, instead of the expected tellurothiocarbazic acid, the tellurium analogue of III (IV). The reason for the failure to observe the intermediate tellurothiocarbazic acid is at present obscure, especially if the strongly reducing properties of hydrogen telluride are taken into account. It cannot *a priori* be decided whether III and IV have the diselenide and ditelluride structures, respectively, instead of being disulfides, though chemical reasoning argues for the former alternative. However, the infrared spectra support the