

perhaps best viewed in Fig. 3. The bond distances for C(13)–N(1), N(1)–N(2), N(2)–C(3), and C(3)–C(19) (Fig. 4) are all indicative of bond orders between one and two.

Table 7. Deviations (Å) of atoms from various mean planes calculated for compound II

The atoms included in the plane calculation are indicated with an asterisk.

(a) Plane of the five-membered ring containing two nitrogen and three carbon atoms

N(1)*	0.031 (3)	C(4)*	0.024 (4)	C(11)	–1.397 (4)
N(2)*	–0.015 (3)	C(12)*	–0.032 (4)	C(13)	0.349 (4)
C(3)*	–0.008 (3)	C(5)	–1.232 (4)	C(19)	0.008 (4)

(b) Plane of the five-membered ring, all carbon atoms

C(4)*	–0.046 (4)	C(12)*	0.032 (4)	C(8)	–0.104 (5)
C(5)*	0.043 (4)	N(1)	–1.213 (3)	C(9)	–0.079 (5)
C(6)*	–0.024 (4)	C(3)	–1.400 (3)	C(10)	–0.027 (4)
C(11)*	–0.006 (4)	C(7)	–0.068 (4)	O(25)	0.170 (3)

(c) Plane of the benzo moiety

C(6)*	–0.001 (4)	C(10)*	0.004 (4)	C(12)	–0.018 (4)
C(7)*	0.004 (4)	C(11)*	–0.003 (4)	O(25)	0.166 (3)
C(8)*	–0.004 (5)	C(4)	–0.106 (4)		
C(9)*	0.000 (5)	C(5)	0.031 (4)		

(d) Plane of the phenyl group bonded to N(1)

C(13)*	–0.008 (4)	C(16)*	–0.008 (5)	N(1)	–0.048 (3)
C(14)*	0.006 (4)	C(17)*	0.006 (4)	N(2)	0.182 (3)
C(15)*	0.002 (4)	C(18)*	0.002 (4)	C(12)	–0.069 (4)

(e) Plane of the phenyl group bonded to C(3)

C(19)*	0.000 (3)	C(22)*	0.006 (5)	N(2)	0.282 (3)
C(20)*	0.001 (4)	C(23)*	–0.005 (5)	C(3)	0.021 (3)
C(21)*	–0.004 (4)	C(24)*	0.002 (4)	C(4)	–0.199 (4)

Dihedral angles: *a*–*b*, 115.5; *a*–*d*, 13.3; *a*–*e*, 13.0; *b*–*c*, 2.0°.

The second feature is the nature of the two fused (*cis*) five-membered ring systems. Both rings are nearly planar (Table 7) but each has assumed a slight amount of ‘envelope’ conformation: for the heterocyclic ring, atom C(12) is the flap of the envelope; for the ring containing all carbon atoms, it is atom C(4). If the two rings are treated as planes, one finds that the dihedral angle between the two is 115.5°. However, the torsion angles for N(1)–C(12)–C(4)–C(5) and C(3)–C(4)–C(12)–C(11) are 122.9 and –111.7°, respectively, and, in conjunction with the torsion angles associated with each individual ring, more clearly indicate the geometry about the two bridgehead atoms.

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## The Crystal and Molecular Structure of Rubidium Tetrathiocyanatobismuthate(III)

BY Z. GALDECKI, M. L. GŁÓWKA AND B. GOLIŃSKI

*Institute of General Chemistry, Technical University, 90-924 Łódź, Poland*

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The crystal structure of Rb[Bi(SCN)<sub>4</sub>] has been determined by inspection of Patterson two-dimensional (*h0l*) and (*hk0*) syntheses. Refinement was carried out by the full-matrix least-squares method, including anisotropic thermal parameters, to a final *R* of 0.076. The refinement was based on three-dimensional intensities of 648 reflexions obtained with Cu *K*α radiation and measured using a non-integrating Zeiss photometer. The space group is *P*2<sub>1</sub>2<sub>1</sub>2 with *a* = 11.24, *b* = 7.65, *c* = 6.52 Å and *Z* = 2. Each Bi atom is surrounded by four S atoms which form a trigonal bipyramid with bismuth at the centre. The fifth corner is occupied by the lone pair of the central atom. There are two types of SCN groups and these are slightly bent [S(1)–C(1)–N(1) = 165.5° and S(2)–C(2)–N(2) = 173.7°]. The bismuth–sulphur distances are 2.70 for S(1) and 2.87 Å for S(2). The Bi–N(2) distance (2.74 Å) corresponds to the sum of the ionic Bi radius and the van der Waals N radius, which suggests a weak interaction.

### Introduction

The crystal structure of rubidium tetrathiocyanatobismuthate(III) has been determined as part of the programme of study of the structures of complex compounds with cations of Group V. We were par-

ticularly interested in the coordination of bismuth, in the structure of the SCN group and in the stereochemical influence of the lone pair of the Bi atom. In addition, the problems of the crystal chemistry of complexes of bismuth(III) have not so far been thoroughly examined.

### Experimental

Orange, well formed crystals of  $\text{Rb}[\text{Bi}(\text{SCN})_4]$  were obtained by Cygański (1963). The title compound crystallizes in the form of rhombic plates and prisms with bounding faces  $\{100\}$ ,  $\{110\}$  and  $\{001\}$ . Unit-cell dimensions were calculated from high-order reflexions on oscillation and Weissenberg photographs. The absence of the symmetry centre was also indicated by the evident piezoelectric effect.

#### Crystal data

$\text{Rb}[\text{Bi}(\text{SCN})_4]$ ,  $M=526.8$ ; orthorhombic, space group  $P2_12_12$ ;  $Z=2$ ;  $a=11.24 \pm 0.01$ ,  $b=7.65 \pm 0.01$ ,  $c=6.52 \pm 0.01$  Å;  $V=560.6$  Å<sup>3</sup>.  $D_m=3.03$  g cm<sup>-3</sup> (by the pycnometric method in water),  $D_c=3.11$  g cm<sup>-3</sup>;  $F(000)=472$ ;  $\mu(\text{Cu } K\alpha)=438$  cm<sup>-1</sup>.

The intensity data were recorded on multiple-film equi-inclination Weissenberg photographs taken around  $[001]$  up to the fifth layer and around  $[010]$  up to the second. Nickel-filtered copper radiation was used. The relative intensities of  $hk0$  and  $h0l$  reflexions were estimated visually, then all the three-dimensional intensities were measured with a non-integrating Zeiss photometer using a procedure described by Wallwork & Standley (1954) and modified by the authors of the present paper (Gałdecki & Główska, 1976). The set of intensities was scaled and corrected in the usual manner. Because of considerable absorption the crystals were shaped into spheres with radius 0.013 cm and a spherical absorption correction was made (*International Tables for X-ray Crystallography*, 1962). The approximate scale factor was calculated by Wilson's (1942) method. In total, 648 independent  $|F|$  values were obtained and taken into refinement. These data were processed using the X-RAY 70 System (Stewart, Kundell & Baldwin, 1970) and the IBM 360/50 computer.

#### Structure determination and refinement

We started to examine the structure with two-dimensional Patterson and Fourier syntheses because of their centrosymmetry. The positions of the bismuth, rubidium and sulphur atoms were determined from Patterson projection on the  $(001)$  and  $(010)$  planes. On the basis of the Bi and Rb parameters, the signs of

$F_{hko}$  and  $F_{h0l}$  values were calculated and difference Fourier projections were prepared. Several two-dimensional syntheses were carried out to find the positions of the other atoms.

The structure was then refined using a full-matrix least-squares program with an initial  $R$  of 0.16. After two cycles of isotropic three-dimensional refinement ( $R=0.097$ ), and a further three cycles with anisotropic temperature factors, the conventional  $R$  value over all 648 reflexions was 0.076. The final shifts of the parameters were smaller than  $0.3\sigma$ . The following weighting scheme was employed:  $w=1/(15+|F|+0.005|F|^2)$ . The scattering factors were those given by Doyle & Turner (1968).

### Results and discussion

The final parameters are listed in Table 1.\*

Each Bi atom is surrounded by four S atoms which form the trigonal bipyramid, if the fact that the lone pair of the Bi atom occupies the fifth corner is taken into account (Gillespie & Nyholm, 1957). The mean Bi-S distance is 2.785 Å which agrees well with those found in  $\text{RbBi}_3\text{S}_5$  by Schmitz & Bronger (1974) and in  $\text{BiSCl}$  (Doenges, 1950). The value 2.785 Å is intermediate between the sums of the ionic and covalent radii (Pauling, 1973, pp. 217, 279).

The trigonal bipyramid is distorted in that the angles  $\text{S}(1)\text{-Bi-S}(1)$  ( $92.6^\circ$ ) and  $\text{S}(2)\text{-Bi-S}(2)$  ( $158.2^\circ$ ) are reduced below the ideal values and the Bi atom is shifted towards the corner not occupied by coordinating atoms, a 'swing' coordination being formed (Gillespie & Nyholm, 1957). Beside four S atoms in the nearest vicinity of bismuth, there are two symmetrically equivalent nitrogen atoms  $\text{N}(2)$ . The distances of these atoms, however, are too great to correspond to chemical bonds, being equal to the sum of the ionic Bi radius and the van der Waals N radius (Pauling, 1973, pp. 249, 479), and suggest weak interaction.

There are two types of SCN groups having different

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31548 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic coordinates* ( $\times 10^4$ ) *and anisotropic thermal parameters* ( $\times 10^3$ ) *with estimated standard deviations in parentheses*

The form of the temperature factor expression is

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Bi	0	0	858 (3)	21 (1)	23 (1)	18 (1)	1 (1)	0	0
Rb	0	5000	6833 (9)	52 (3)	32 (3)	23 (3)	-5 (3)	0	0
S(1)	3402 (9)	6012 (13)	6277 (19)	26 (5)	28 (5)	16 (4)	7 (4)	-6 (4)	-1 (4)
S(2)	3990 (8)	1632 (12)	8312 (20)	26 (4)	22 (4)	21 (4)	2 (3)	1 (4)	2 (4)
N(1)	3908 (25)	3637 (47)	3069 (67)	9 (12)	58 (19)	41 (15)	13 (13)	-1 (15)	31 (19)
N(2)	1584 (30)	2343 (50)	-775 (64)	24 (15)	59 (22)	69 (25)	72 (17)	9 (17)	35 (21)
C(1)	3620 (24)	4761 (51)	4233 (68)	7 (12)	76 (25)	77 (25)	86 (16)	14 (14)	30 (25)
C(2)	2552 (32)	2032 (55)	-1258 (68)	30 (19)	74 (24)	58 (21)	-101 (20)	-35 (20)	50 (22)

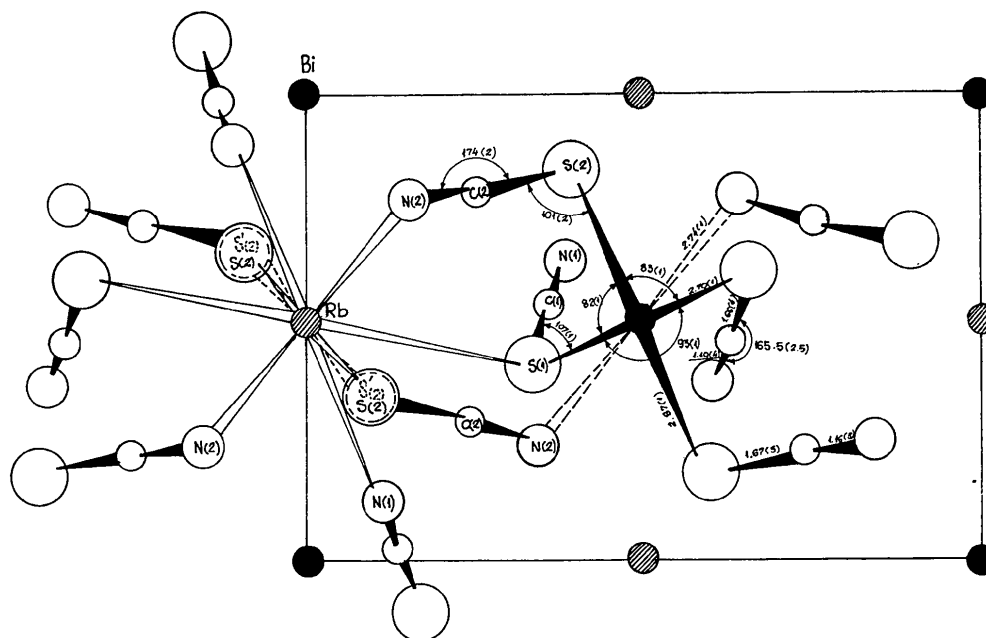


Fig. 1. The structure of  $\text{Rb}[\text{Bi}(\text{SCN})_4]$ , projection along the (001) axis.

bond lengths and angles. They are slightly bent,  $\text{S}(1)\text{--C}(1)\text{--N}(1) = 165.5$ ,  $\text{S}(2)\text{--C}(2)\text{--N}(2) = 173.7^\circ$ . Similar deviation from rectilinearity was observed by Scolaudi (1953). Interatomic N–C distances in thiocyanate groups show a predominance of the mesomeric form  $\text{S}\text{--C}\equiv\text{N}$ . This is also confirmed by coordination of the SCN groups by means of sulphur and not nitrogen.

The rubidium ion is surrounded by two N(1) atoms at 3.042, two N(2) atoms at 3.120, two S(1) atoms at 3.918, two S(2) atoms at 3.587 and two S(2) atoms at 3.755 Å (Fig. 1).

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