Stereochemistry of Some Organic Derivatives of Group Vb Elements. Part V.[1] Crystal and Molecular Structure of Bis(isocyanato)triphenylantimony

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Crystals of the title compound are monoclinic, space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 11{\cdot}920(3)$, $b = 12{\cdot}693(8)$, $c = 12{\cdot}270(3)$ Å, $\beta = 90{\cdot}22(1)°$. The structure was solved by the heavy-atom method and refined by least-squares procedures to R 0.039 for 1643 observed diffractometer data. The NCO groups are *N*-bonded to antimony which has a trigonal bipyramidal configuration, with the N atoms axial. Mean molecular dimensions include: Sb–N 2·124(4), N–C 1·128(7), C–O 1·188(7), Sb–C 2·119(6) Å; N–Sb–N 178·6(6), Sb–N–C 145·4, and 152·2(6)°.

THE ability of the pseudohalide ions NCX$^-$ (X = O, S, or Se) to bond through the N or X atoms has given rise to considerable interest [2-5] in the structure and bonding of their metal derivatives. Apart from *X*-ray crystallographic studies, numerous i.r. spectroscopic studies have been devoted to the elucidation of the bonding mode of these ions, and in particular, that of the thiocyanate ion. Co-ordination of the NCX$^-$ ion through N should result in a decrease in C–N and an increase in C–X bond order. Opposite effects are expected if the bonding is through X. Thus the bonding mode can be ascertained by i.r. spectroscopy if the internal vibrational modes of the co-ordinated NCX ligand can be described in terms of pure ν(NC) and ν(NX) modes. Experimental evidence [2-4] suggests that this is more or less so for NCS and NCSe ligands. In the case of NCO, however, there is considerable mixing of the ν(CN) and ν(CO) modes. The interpretation of the vibrational spectra of the cyanates is also complicated owing to the Fermi resonance interaction between the ν(CO) frequency and the first overtone of the δ(NCO) frequency. Thus, vibrational spectroscopic data do not provide reliable criteria for determining the mode of bonding of this ion.

A number of organometallic cyanates [4,5] of main-group II, III, and IV elements which have been characterized, have all, by analogy with organic isocyanates, been considered to be *N*-bonded. Organometallic cyanates of anitimony(V) [6,7] and bismuth(V) [8,9] have been characterized recently and herein we report the *X*-ray analysis of the [Ph$_3$Sb(NCO)$_2$] structure.

EXPERIMENTAL

Small plate-like crystals were obtained from chloroform–light petroleum. A crystal of dimensions *ca.* 0·19 × 0·15 × 0·05 mm was used.

Crystal Data.—C$_{20}$H$_{15}$N$_2$O$_2$Sb, $M = 437{\cdot}1$, Monoclinic, $a = 11{\cdot}920(3)$, $b = 12{\cdot}693(8)$, $c = 12{\cdot}270(3)$ Å, $\beta = 90{\cdot}22(1)°$, $U = 1856$ Å^3, $D_m = 1{\cdot}565$, $Z = 4$, $D_c = 1{\cdot}572$, $F(000) = 864$. Space group $P2_1/n$ (C^5_{2h}), from systematic absences: $h0l$ for $h + l$ odd, $0k0$ for k odd. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 15·3 cm^{-1}.

Crystallographic Measurements.—Unit-cell and space-group data were obtained from rotation, Weissenberg, and precession photographs taken with Cu-K_α radiation ($\lambda = 1{\cdot}4918$ Å). Accurate cell parameters were obtained by a least-squares procedure applied to the setting angles of 12 high-order reflexions measured on a Hilger and Watts four-circle diffractometer. The intensities of all reflexions with 2θ (Mo-K_α) $< 46°$ (minimum interplanar spacing 0·91 Å) were measured with the diffractometer by the θ—2θ scan technique. Integrated intensities were obtained from scans through 80 steps of 0·01° s^{-1}, with background counts of 20 s at each end of the scans. The variation in intensity of 3 reflexions monitored every 100 reflexions was within ±1% from the mean. Corrections for Lorentz and polarization factors were applied but not for absorption. Of 2317 independent reflexions, 1643, having a net count $I > 3\sigma(I)$ {where $\sigma(I) = [S + 4(b_1 + b_2) + (0{\cdot}05I)^2]^{1/2}$ and S, b_1, and b_2 are the scan, first, and second background counts, respectively} were taken as observed.

Structure Determination.—The co-ordinates of the antimony atom were determined from a three-dimensional Patterson synthesis. An electron-density distribution map, phased with the antimony contributions, revealed the entire

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structure. The nitrogen and oxygen atoms were tentatively distinguished on the basis of peak heights. With all the non-hydrogen atoms included in the structure–factor calculations R was 0·33.

Refinement.—Two initial cycles of full-matrix least-squares refinement, in which positional and isotropic thermal parameters of non-hydrogen atoms together with overall scale factor were refined, reduced R to 0·082. The function minimized was $\Sigma w(F_o - F_c)$; scattering factors were taken from ref. 10. The antimony atom and the atoms of the isocyanate group were then allowed to vibrate anisotropically and in one cycle of full-matrix least-squares calculations R became 0·054. Two cycles of least-squares refinement using a block-diagonal approximation to the matrix, with all non-hydrogen atoms allowed to vibrate anisotropically and allowance for anomalous dispersion of antimony, reduced R to 0·046. Calculated hydrogen co-ordinates for the 15 hydrogen atoms were then included, but not refined, in three further cycles of block-diagonal least-squares calculations at which point the refinement had converged with R 0·039 for 1643 observed reflexions [R' (= $\Sigma w\Delta^2/\Sigma wF_o^2$) 0·034] and the ratio of the shift-to-σ was $<0·14$. A final difference synthesis showed a generally flat topography. After the refinement had converged, the isocyanate was theoretically altered to cyanate by interchanging the nitrogen and oxygen atoms. Two cycles of full-matrix anisotropic refinement converged at a higher value of R (0·042) and with anomalous thermal parameters, indicating that this mode of bonding is incorrect.

Final fractional co-ordinates of all atoms are in Table 1, and bond lengths, angles, and their respective estimated standard deviations calculated from the co-ordinates of Table 1, in Table 2. Some shorter intra- and inter-molecular contacts are listed in Table 3. Final observed structure amplitudes and calculated structure factors, thermal parameters, and details of mean-plane calculations are listed in Supplementary Publication No. SUP 21303 (28 pp., 1 microfiche) *.

TABLE 1

Atomic (fractional) co-ordinates, with estimated standard deviations in parentheses

Atom	x	y	z
Sb	0·21756(3)	0·20725(3)	0·13119(3)
C(11)	0·0854(5)	0·2946(4)	0·2031(4)
C(12)	0·0514(6)	0·2722(6)	0·3077(5)
C(13)	−0·0373(7)	0·3352(7)	0·3505(6)
C(14)	−0·0887(6)	0·4115(6)	0·2925(5)
C(15)	−0·0550(6)	0·4310(6)	0·1895(5)
C(16)	0·0328(6)	0·3719(5)	0·1436(5)
C(21)	0·3853(5)	0·2626(5)	0·1443(4)
C(22)	0·4080(6)	0·3693(5)	0·1214(5)
C(23)	0·5187(7)	0·4045(5)	0·1250(5)
C(24)	0·6019(7)	0·3320(7)	0·1499(6)
C(25)	0·5799(6)	0·2289(6)	0·1721(6)
C(26)	0·4698(6)	0·1927(5)	0·1698(5)
C(31)	0·1865(5)	0·0653(5)	0·0472(4)
C(32)	0·1335(5)	0·0660(5)	−0·0527(4)
C(33)	0·1127(6)	−0·0300(5)	−0·1082(4)
C(34)	0·1467(6)	−0·1217(6)	−0·0648(5)
C(35)	0·2004(9)	−0·1233(6)	0·0317(7)
C(36)	0·2204(8)	−0·0306(6)	0·0910(6)
N(1)	0·1975(4)	0·2919(4)	−0·0170(4)
C(1)	0·2416(5)	0·3416(5)	−0·0820(4)
O(1)	0·2853(4)	0·3922(4)	−0·1510(3)
N(2)	0·2411(5)	0·1208(5)	0·2775(3)
C(2)	0·2840(6)	0·1063(5)	0·3567(4)
O(2)	0·3254(7)	0·0906(5)	0·4436(4)

TABLE 2

Bond distances (Å) and angles (°)

(*a*) Non-phenyl-group atoms

(i) Distances

Sb–N(1)	2·125 4)	N(1)–C(1)	1·146(7)
Sb–N(2)	2·122(4)	C(1)–O(1)	1·186(7)
Sb–C(11)	2·123(5)	N(2)–C(2)	1·111(7)
Sb–C(21)	2·124(6)	C(2)–O(2)	1·189(8)
Sb–C(31)	2·109(6)		

(ii) Angles

N(1)–Sb–N(2)	178·6(6)	Sb–N(1)–C(1)	145·4(5)
N(1)–Sb–C(11)	90·6(2)	Sb–N(2)–C(2)	152·2(6)
N(1)–Sb–C(21)	90·0(2)	N(1)–C(1)–O(1)	178·4(5)
N(1)–Sb–C(31)	89·7(2)	N(2)–C(2)–O(2)	177·8(10)
N(2)–Sb–C(11)	90·8(2)	C(11)–Sb–C(21)	119·8(2)
N(2)–Sb–C(21)	89·2(2)	C(21)–Sb–C(31)	118·8(2)
N(2)–Sb–C(31)	89·7(2)	C(31)–Sb–C(11)	121·4(2)

(*b*) Phenyl-group atoms

(i) Distances

C(11)–C(12)	1·377(8)	C(13)–C(14)	1·350(11)
C(11)–C(16)	1·372(8)	C(14)–C(15)	1·350(9)
C(12)–C(13)	1·425(11)	C(15)–C(16)	1·406(10)
C(21)–C(22)	1·408(9)	C(23)–C(24)	1·389(11)
C(21)–C(26)	1·377(9)	C(24)–C(25)	1·363(12)
C(22)–C(23)	1·392(10)	C(25)–C(26)	1·390(10)
C(31)–C(32)	1·375(8)	C(33)–C(34)	1·345(10)
C(31)–C(36)	1·387(9)	C(34)–C(35)	1·344(11)
C(32)–C(33)	1·412(9)	C(35)–C(36)	1·401(11)

(ii) Angles

Sb–C(11)–C(12)	120·1(5)	C(12)–C(13)–C(14)	122·8(7)
C(12)–C(11)–C(16)	120·5(6)	C(13)–C(14)–C(15)	119·2(7)
C(16)–C(11)–Sb	119·4(4)	C(14)–C(15)–C(16)	120·3(6)
C(11)–C(12)–C(13)	116·8(6)	C(15)–C(16)–C(11)	120·4(5)
Sb–C(21)–C(22)	119·0(4)	C(22)–C(23)–C(24)	118·1(6)
C(22)–C(21)–C(26)	121·4(6)	C(23)–C(24)–C(25)	122·8(7)
C(26)–C(21)–Sb	119·5(4)	C(24)–C(25)–C(26)	119·7(7)
C(21)–C(22)–C(23)	119·1(6)	C(25)–C(26)–C(21)	118·9(8)
Sb–C(31)–C(32)	120·6(4)	C(32)–C(33)–C(34)	120·2(6)
C(32)–C(31)–C(36)	118·8(6)	C(33)–C(34)–C(35)	120·2(7)
C(36)–C(31)–Sb	120·7(4)	C(34)–C(35)–C(36)	121·5(7)
C(31)–C(32)–C(33)	120·2(5)	C(35)–C(36)–C(31)	119·1(7)

TABLE 3

Intramolecular non-bonded distances $<3·5$ Å

Sb · · · C(12)	3·054	N(2) · · · C(11)	3·024
Sb · · · C(16)	3·041	N(2) · · · C(12)	2·992
Sb · · · C(22)	3·066	N(2) · · · C(21)	2·983
Sb · · · C(26)	3·048	N(2) · · · C(26)	3·169
Sb · · · C(32)	3·048	N(2) · · · C(31)	2·983
Sb · · · C(36)	3·058	N(2) · · · C(36)	2·998
N(1) · · · C(11)	3·018	C(1) · · · C(21)	3·405
N(1) · · · C(16)	2·967	C(1) · · · C(22)	3·202
N(1) · · · C(21)	3·004	C(1) · · · Sb	3·136
N(1) · · · C(22)	3·181	C(2) · · · C(21)	3·497
N(1) · · · C(31)	2·987	C(2) · · · C(26)	3·379
N(1) · · · C(32)	3·001	C(2) · · · Sb	3·148

Intermolecular contacts $<3·5$ Å

O(2) · · · C(15^{I})	3·346	O(1) · · · C(23^{III})	3·495
O(2) · · · C(16^{II})	3·426	O(1) · · · C(33^{IV})	3·351

The superscripts refer to the following equivalent positions:

I $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ III $1 - x, 1 - y, -z$
II $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ IV $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

The molecular geometry and atom-numbering scheme are shown in Figure 1 and the arrangement of the molecules in the unit cell in Figure 2.[11]

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

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DISCUSSION

This structure analysis establishes that [$Ph_3Sb(NCO)_2$] is a non-ionic isocyanate as inferred from spectroscopic data.[7] The co-ordination geometry at antimony (Figure 1) is that of a trigonal bipyramid with little distortion of the C_3SbN_2 skeleton and with the nitrogen atoms of the isocyanate groups axial. The N(1)–Sb–N(2) angle is 178·6(6)°, the N–Sb–C angles are close to 90° [range 89·7—90·6(2)°], and the C–Sb–C angles are in the range 118·8—121·4(2)°. The Sb, C(11), C(21), and C(31) atoms are coplanar.

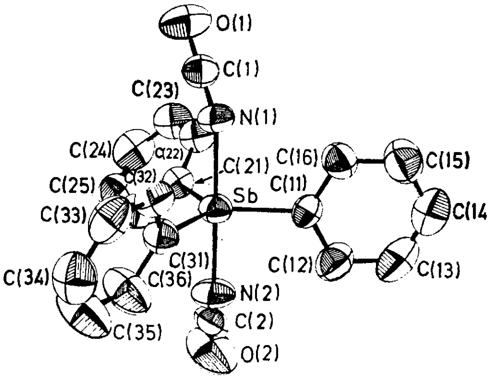

FIGURE 1 A view of the molecule showing the numbering system used; ellipsoids are drawn at the 50% level

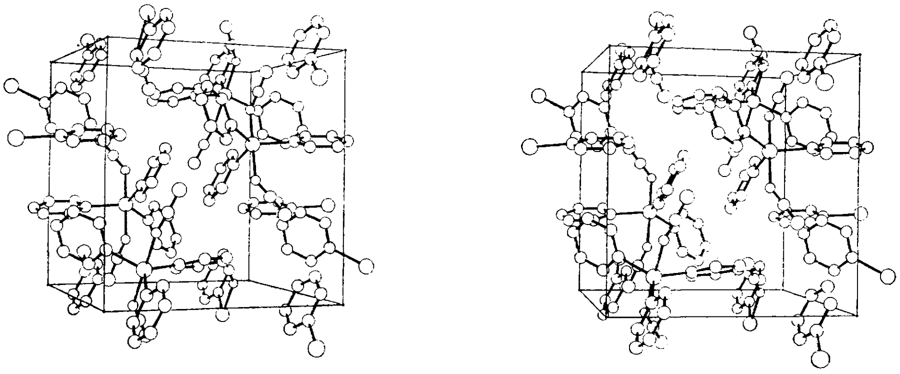

FIGURE 2 Stereoview of the contents of a unit cell; the origin is at the bottom left-hand corner nearer the viewer with *a* along, *c* up, and *b* into the page

The Sb–N(1) and Sb–N(2) bond lengths [2·125(4) and 2·122(4) Å] are internally consistent but are significantly shorter than the Sb–N distance [2·236(8) Å] in μ-oxo-bis(triphenylazidoantimony).[12]

The isocyanate groups are essentially linear [N(1)–C(1)–O(1) 178·4(5), N(2)–C(2)–O(2) 177·2(10)°]. The difference in the Sb–N–C angles [Sb–N(1)–C(1) 145·4(5), Sb–N(2)–C(2) 152·2(6)°] undoubtedly has its origin in the reduction to a minimum of steric interaction between the phenyl rings and the N–C–O groups. The present values are similar to that reported from an electron-diffraction study of trimethylsilyl isocyanate [150(3)°],[13] but much different M–N–C angles were found in AgNCO (128·2°),[14] [$(C_5H_5)Cr(NO)_2NCO$] [180·0(4)],[15] and HNCO [132·3(3)°].[16] The N–C and C–O distances in AgNCO and HNCO are not significantly different from each other (mean 1·19 Å). In [$Ph_3Sb(NCO)_2$] these bonds are significantly different [means: N–C 1·129(7), C–O 1·188(8) Å]; in [$(C_5H_5)Cr(NO)_2NCO$] they are also significantly different [N–C 1·126(5) and C–O 1·179(5) Å] and agree well with those found here even though the M–N–C angles are quite different.

The mean Sb–C(Ph) bond length [2·119(6) Å] is very similar to mean values reported for other trigonal bipyramidal phenyl–antimony derivatives.[12,17–19]

The phenyl rings are individually planar and are rotated about their Sb–C bonds so as to minimize intra- and inter-molecular phenyl interactions. Phenyl rings (1) and (3) (Figure 1) are rotated through 88 and 70°, respectively, in the same sense, while ring (2) is rotated 45° in the opposite direction from the plane through C(11), C(21), and C(31). The orientation of the NCO groups about the N–Sb–N axis effectively minimizes intra- and inter-molecular interactions; both N–C–O groups are inclined in the direction of phenyl ring (2) which has a rotation angle 45° out of the C(11), C(21), C(31) plane. The shortest intermolecular contacts occur between the terminal oxygen atoms and neighbouring phenyl rings, O(1) · · · C(33) 3·351 and O(2) · · · C(15) 3·346 Å. These and all other intermolecular contacts correspond to, or are greater than, van der Waals interactions.

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