Synthesis, Infrared, and *X*-Ray Study of Di-μ-thiocyanato-1κ*N*,*S*′:2κ*N*′,*S*-bis-[bis(2,2′-bipyridine)di-isothiocyanatobismuth(III)]: a Case of Eight-co-ordinated Bismuth†

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The synthesis, i.r., and *X*-ray structural characterization of the complex $[Bi(CNS)_3(bipy)_2]_2$ (bipy = 2,2′-bipyridine) are described. Crystals are triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.935(1)$, $b = 14.487(4)$, $c = 9.916(2)$ Å, $\alpha = 92.29(2)$, $\beta = 119.81(1)$, $\gamma = 99.71(1)$°; $R = 0.0315$. The complex molecules consist of dimeric units in which bismuth is eight-co-ordinated by seven nitrogens belonging to two bipyridyl molecules and to three thiocyanate groups, the last co-ordination site being provided by a sulphur atom of an adjacent molecule which acts as a bridge connecting two polyhedra forming centrosymmetric dimers. The i.r. ν(CN) frequencies are consistent with μ-*N*,*S* and terminally *N*-bonded thiocyanate groups.

Although pure bismuth(III) thiocyanate does not appear as isolable compound, various complexes formally containing the $Bi(CNS)_3$ ‡ unit can be obtained. These mainly include adducts with bi- and tri-dentate nitrogen donors of the type $Bi(CNS)_3{\cdot}L$ [L = 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 2,2′:6′,2″-terpyridine (terpy), and similar terdentates][1,2] while one example of 1:2 stoicheiometry is provided by $Bi(CNS)_3(phen)_2$ which has been proposed as a suitable material for the gravimetric estimation of bismuth.[3]

Infrared studies on these compounds,[1,2] while primarily evidencing a rather complicated bonding behaviour of the thiocyanate groups, could not unambiguously establish the co-ordination numbers and stereochemistries as well as whether there exists a definite preference of bismuth towards the thiocyanate donor sites (S- *versus* N-). The compounds may show remarkable differences in their i.r. thiocyanate absorption patterns in spite of similarities in stoicheiometry and in the chelating ligand and, in addition, they show evidence for the simultaneous presence of differently bonded groups.

No crystallographic studies appear to have been reported as yet on bismuth thiocyanate compounds and in this work, which was undertaken also in the belief that single-crystal *X*-ray characterization would be valuable for the interpretation of spectroscopic data, we describe the structure of the hitherto unreported 1:2 adduct $[Bi(CNS)_2(bipy)_2]_2$.

Experimental

Preparation of the Complex.—The compound $Bi(NO_3)_3{\cdot}5H_2O$ (0.25 mmol) was dissolved in methanolic 7 mol dm^{-3} NH_4NCS (5 cm^3) and slowly added, without stirring, to a solution of the ligand bipy in the same thiocyanate medium, 1 mmol in 10 cm^3. On standing at room temperature the system afforded well formed yellow needles which were filtered off and washed with methanol (Found: C, 39.55; H, 2.30; N, 14.45. Calc. for $C_{23}H_{16}BiN_7S_3$: C, 39.70; H, 2.30; N, 14.10%), m.p. 195—198 °C (decomp.).

The complex is highly insoluble in water–methanol and acetone but can be dissolved in the presence of high concentrations of thiocyanate ions forming anionic bismuth(III) thiocyanato species. The compound $[Bi(CNS)_3(bipy)_2]_2$ (like the corresponding phen adduct) can be obtained under a wide range of experimental conditions, the particular procedure given here being the one which affords good-quality crystals.

Infrared spectra were recorded in the 4 000—180 cm^{-1} region on Nujol mulls between CsI plates or as KBr pellets using a Perkin-Elmer 1190 spectrophotometer.

X-Ray Crystallography.—A crystal of approximate dimensions 0.07 × 0.13 × 0.71 mm was mounted on an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation.

Crystal data. $C_{23}H_{16}BiN_7S_3$, $M = 695.6$, triclinic, space group $P\bar{1}$, $a = 9.935(1)$, $b = 14.487(4)$, $c = 9.916(2)$ Å, $\alpha = 92.29(2)$, $\beta = 119.81(1)$, $\gamma = 99.71(1)$°, $U = 1\,208(1)$ Å^3, $D_m = 1.87$ g cm^{-3}, $Z = 2$, $D_c = 1.91$ g cm^{-3}, $F(000) = 668$, $\lambda = 0.7107$ Å, $\mu = 75.52$ cm^{-1}.

Scan speed range 0.63—3.30° min^{-1}, θ range 3.0—25.0°, scan mode ω—2θ. Number of measured reflections 4 539, observed [with $I > 2\sigma(I)$] 3 085; number of refined parameters 157. The intensities of half the reflection sphere were collected, monitoring the intensity of one reflection every 2 h as a check of the crystal alignment and instrument stability: no significant changes were observed. The structure amplitudes were obtained after the usual Lorentz and polarization correction; an absorption correction was not applied.

Solution and refinement of the structure. The structure was solved by the heavy-atom technique and refined by full-matrix isotropic and anisotropic least squares. Hydrogen atoms, placed at the calculated positions, were introduced in the last refinement cycle as fixed contributors: the indices obtained were $R = 0.0315$ and $R' = 0.0334$. The weighting scheme used was $w = 0.0326\,[\sigma^2(F_o) + 0.0394\,F_o{}^2]^{-1}$. During the final refine-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

‡ In formulae, the thiocyanate group is written CNS to indicate ionic as well as unspecified or unknown modes of bonding.

Table 1. Atomic co-ordinates (× 10^4) for $[Bi(CNS)_3(bipy)_2]_2$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Bi	672.3(3)	3 014.2(2)	1 553.3(3)
S(1)	44(3)	5 250(2)	−2 623(3)
S(2)	−5 051(3)	1 786(2)	−1 974(4)
S(3)	−3 272(3)	877(2)	2 396(4)
N(1)	3 711(7)	3 364(4)	2 515(7)
N(2)	2 677(7)	3 502(4)	4 580(7)
N(3)	1 642(7)	1 475(4)	2 166(7)
N(4)	490(8)	1 991(5)	−698(8)
N(5)	1 234(9)	4 307(5)	−24(9)
N(6)	−2 039(11)	2 879(7)	−659(11)
N(7)	−802(8)	2 198(5)	2 642(8)
C(1)	4 197(9)	3 229(6)	1 477(9)
C(2)	5 754(10)	3 297(7)	1 926(11)
C(3)	6 854(12)	3 493(8)	3 471(12)
C(4)	6 399(11)	3 623(6)	4 549(11)
C(5)	4 809(8)	3 557(5)	4 025(8)
C(6)	4 280(8)	3 747(5)	5 157(8)
C(7)	5 319(9)	4 141(5)	6 716(9)
C(8)	4 764(10)	4 298(6)	7 714(10)
C(9)	3 146(10)	4 030(6)	7 121(10)
C(10)	2 132(9)	3 656(5)	5 562(9)
C(11)	2 132(10)	1 216(6)	3 587(10)
C(12)	2 841(11)	447(7)	4 033(11)
C(13)	3 059(12)	−56(8)	2 985(12)
C(14)	2 555(11)	206(7)	1 536(11)
C(15)	1 842(9)	976(6)	1 125(9)
C(16)	1 249(10)	1 279(6)	−427(10)
C(17)	1 405(14)	851(9)	−1 616(14)
C(18)	755(15)	1 148(9)	−3 076(15)
C(19)	−52(15)	1 796(9)	−3 354(15)
C(20)	−120(12)	2 246(7)	−2 113(12)
C(21)	735(8)	4 711(5)	−1 078(8)
C(22)	−3 295(10)	2 405(6)	−1 209(10)
C(23)	−1 850(8)	1 635(5)	2 496(8)

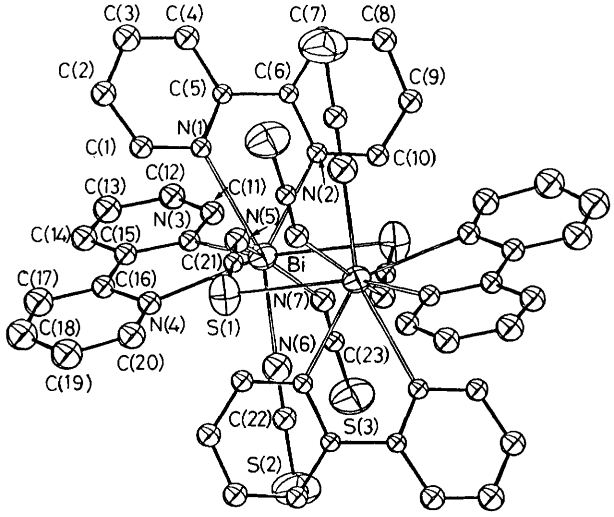

Figure. Perspective view of the dimer

ment zero weight was assigned to five reflections (2 0 0, 2 2 0, 2 −4 1, 2 −2 1, −1 7 3) which may be affected by counting errors or extinction. The atomic scattering factors used, corrected for anomalous dispersion, were taken from ref. 4; all the calculations were performed using a GOULD 32/77 computer and SHELX 76,[5] ORTEP,[6] and PARST[7] programs. The final atomic co-ordinates for non-hydrogen atoms are in Table 1.

Table 2. Selected bond distances (Å) and angles (°)*

Bi–S(1$^{\text{I}}$)	3.016(3)	Bi–N(1)	2.620(7)
Bi–N(2)	2.624(5)	Bi–N(3)	2.553(7)
Bi–N(4)	2.542(8)	Bi–N(5)	2.648(9)
Bi–N(6)	2.453(8)	Bi–N(7)	2.408(9)
S(1)–C(21)	1.631(8)	S(2)–C(22)	1.589(9)
S(3)–C(23)	1.593(9)	N(5)–C(21)	1.145(11)
N(6)–C(22)	1.154(12)	N(7)–C(23)	1.151(11)
N(6)–Bi–N(7)	80.5(3)	N(5)–Bi–N(7)	154.2(3)
N(5)–Bi–N(6)	80.3(3)	N(4)–Bi–N(7)	112.7(3)
N(4)–Bi–N(6)	74.5(3)	N(4)–Bi–N(5)	78.3(2)
N(3)–Bi–N(7)	75.2(2)	N(3)–Bi–N(6)	116.6(3)
N(3)–Bi–N(5)	129.3(3)	N(3)–Bi–N(4)	63.4(2)
N(2)–Bi–N(7)	78.2(2)	N(2)–Bi–N(6)	147.4(3)
N(2)–Bi–N(5)	110.4(2)	N(2)–Bi–N(4)	136.9(2)
N(2)–Bi–N(3)	81.3(2)	N(1)–Bi–N(7)	131.3(2)
N(1)–Bi–N(6)	146.7(3)	N(1)–Bi–N(5)	71.7(2)
N(1)–Bi–N(4)	82.4(2)	N(1)–Bi–N(3)	71.6(2)
N(1)–Bi–N(2)	62.6(2)	S(1$^{\text{I}}$)–Bi–N(7)	83.8(2)
S(1$^{\text{I}}$)–Bi–N(6)	81.5(3)	S(1$^{\text{I}}$)–Bi–N(5)	76.4(2)
S(1$^{\text{I}}$)–Bi–N(4)	147.7(2)	S(1$^{\text{I}}$)–Bi–N(3)	148.8(2)
S(1$^{\text{I}}$)–Bi–N(2)	72.0(1)	S(1$^{\text{I}}$)–Bi–N(1)	108.1(2)
Bi–N(1)–C(5)	121.7(6)	Bi–N(1)–C(1)	120.0(5)
S(2)–C(22)–N(6)	178.0(1)	Bi–N(2)–C(10)	120.0(5)
Bi–N(2)–C(6)	120.6(5)	Bi–N(3)–C(15)	120.2(5)
Bi–N(3)–C(11)	120.3(5)	Bi–N(4)–C(20)	120.5(6)
Bi–N(4)–C(16)	120.7(5)	Bi–N(5)–C(21)	148.0(8)
Bi–N(6)–C(22)	140.4(8)	Bi–N(7)–C(23)	150.2(6)
S(1)–C(21)–N(5)	177.3(8)		

* Symmetry equivalent position: I $-x$, 1 $-y$, $-z$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Description of the Structure.—The complex molecule is depicted in the Figure and the bond distances and angles are reported in Table 2. The bismuth is eight-co-ordinated by seven nitrogens belonging to two bipyridyl molecules and to three thiocyanate groups, the last co-ordination site being provided by the S(1) atom of one adjacent group which acts as a bridge connecting two polyhedra forming centrosymmetric dimers. The co-ordination around the metal cannot be described in terms of a regular polyhedron but atoms N(1), N(2), N(4), N(6), and N(7) are roughly located on a pentagonal plane [bismuth is out of this plane by 0.492(1) Å]; with respect to this plane, a pseudo-apical position could be occupied by N(3) while both N(5) and S(1) ($\bar{x}$, 1 − y, $\bar{z}$) are found on the other side. The last three atoms define a plane perpendicular to the former one [90.9(2)°], with bismuth lying out of the plane by 0.323(1) Å. No evident gaps can be seen in the co-ordination sphere thus pointing to a non-stereoactive role of the bismuth lone pair. Eight-co-ordinated bismuth is rare; one example is present in bismuth thiophosphate[8] [Bi–S 2.68(1)—3.30(1) Å] in which the bismuths are six- and eight-co-ordinated; this polyhedron is described as a very irregular trigonal prism with two extra positions.

In the present compound the two bipyridyl molecules show different behaviour: the ligand with N(3) and N(4) is more strongly bonded with similar distances 2.542(8) and 2.553(7) Å, the two rings are slightly tilted forming a dihedral angle of 5.3(3)°, and bismuth deviates from the N(3), C(15), C(16), N(4) chelate-ring plane by 0.447(1) Å. The second molecule is more loosely co-ordinated with Bi–N 2.620(7) and 2.624(5) Å;

Table 3. Bismuth–nitrogen bond distances (Å) in relevant compounds

(1) $[BiCl_3(C_{11}H_{12}O_3N_4S)_3]$[a]		2.90(1)
(2) $3BiCl_3{\cdot}4tsc$[b]		2.54(4), 2.71(1)
(3) $[Bi(S_2CNEt_2)X_2(py)_2]$[c]	X = Cl	2.794(8), 2.698(8), 2.668(7)
	X = I	2.86(1), 2.71(1), 2.72(1)
(4) $[Bi(S_2CNEt_2)I_2(bipy)]$[d]		2.61(1), 2.56(1)
(5) $[Bi(S_2CNEt_2)I_2(terpy)]$[d]		2.63(2), 2.61(2), 2.61(2)
(6) $[C_5H_5NCSNEt_2]_2[BiCl_5(py)]$[e]		2.615(8)
(7) $[Bi\{N(Ph){=}NC(S){=}NNHPh\}_3]$[f]		2.746(10),2.706(8),2.678(9)
(8) $[Bi(Hdapt)Cl_2]{\cdot}dmso{\cdot}H_2O$[g]		2.67(1), 2.47(1), 2.35(1)
(9) $[Bi(dapt)Cl]{\cdot}dmso$[g]		2.47(2), 2.47(2), 2.48(2)
(10) $[Bi\{OCBu^t{=}CN{=}CCBu^t(O)\}_3]$[h]		2.54(3)
(11) $[Bi(dapt)(OH)]{\cdot}dmso$[i]		2.44(1), 2.49(1), 2.46(1)
(12) $[Bi(dapts)(N_3)]{\cdot}0.5dmso$[i]		2.58(2), 2.46(2), 2.25(2)[j]

tsc = Thiosemicarbazide, py = pyridine, H_2dapt = 2,6-diacetylpyridine bis(2-thenoylhydrazone), dmso = dimethyl sulphoxide, H_2dapts = 2,6-diacetylpyridine bis(thiosemicarbazone).

[a] 3-(*p*-Aminobenzenesulphonamido)-6-methoxypyridazine; M. Belicchi Ferrari, L. Calzolari Capacchi, L. Cavalca, and G. Fava Gasparri, *Acta Crystallogr., Sect. B*, 1972, **28**, 1169. [b] L. P. Battaglia, A. Bonamartini Corradi, M. Nardelli, and M. E. Vidoni Tani, *J. Chem. Soc., Dalton Trans.*, 1978, 583. [c] C. L. Raston, G. L. Rowbottom, and A. H. White, *ibid.*, 1981, 1379. [d] Ref. 9. [e] C. L. Raston, G. L. Rowbottom, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 1389. [f] M. L. Niven, H. M. N. H. Irving, L. R. Nassimbeni, and A. T. Hutton, *Acta Crystallogr., Sect. B*, 1982, **38**, 2140. [g] L. P. Battaglia, A. Bonamartini Corradi, G. Pelosi, P. Tarasconi, and C. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1989, 671. [h] C. A. Stewart, J. C. Calabrese, and A. J. Arduengo III, *J. Am. Chem. Soc.*, 1985, **107**, 3397. [i] L. P. Battaglia, A. Bonamartini Corradi, C. Pelizzi, G. Pelosi, and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, in the press. [j] Bi–N(N_3).

the two rings are mutually bent with a dihedral angle of 12.5(2)° and the chelate ring is coplanar with bismuth. The angles at the metal involving each of these ligands [62.6(2) and 63.4(2)°] are the smallest in the co-ordination polyhedron as a result of the bite of the ligands and of their symmetrical chelation; these values are close to the 62.5(3)° found in $[Bi(S_2CNEt_2)I_2(bipy)]$ and to 62.8(5) and 62.7(5)° in $[Bi(S_2CNEt_2)I_2(terpy)]$.[9] The bismuth–nitrogen bond distances are spread over a rather large range: 2.408(9)—2.648(9) Å (Table 2). The longest, Bi–N(5), is justified considering the bridging action of this thiocyanate group. The two remaining Bi–N (terminal NCS) bond lengths are in fact shorter [2.453(8) and 2.408(9) Å] and comparable to those corresponding to strong interactions. Table 3 reports the values of the Bi–N bond distances in bismuth complexes studied until now, and our values compare well with those observed; it is worthy of note that the shorter values were found in the presence of polydentate ligands having in-plane high chelating power, *e.g.* in **(8)**, **(9)**, **(11)**, and **(12)**; the unusually short distance of 2.25(2) Å in **(12)** concerns one azide group in the axial site of a pentagonal pyramid. The 3.016(3) Å interaction of the metal with atom S(1) can be considered as a 'long bond' and is comparable with those found with more loosely bonded or bridging ligands: $[Bi_2(O_2CMe)_6(tu)_3]{\cdot}H_2O$ (tu = thiourea),[10] 3.132(5) and 3.152(6); $[Bi(O_2CMe)_3(tu)_3]$,[10] 3.020(2), 3.038(2), and 3.124(2); $[Bi_2(pcdt)_6]{\cdot}EtOH$ (pcdt = 1-pyrrolidinecarbodithioate),[11] 3.017(8); $[\{Bi(tu)(pcdt)_2Cl_2\}_2]$,[11] 3.017(4) Å. The thiocyanate groups are close to linearity. Unusually, the Bi–N–C angles for N-terminal groups [140.4(8) and 150.2(6)°] deviate from linearity thus becoming similar to the value of 148.0(7)° observed for the bridging group. In this respect, worthy of note is the similar behaviour of the thiocyanate co-ordination in some lead(II) complexes whose structure has recently been reported:[12] Pb–N–C angles (terminal N-thiocyanates) 136(1)—121(2)° in $Pb(SCN)_2{\cdot}2phen$.

Infrared Spectra.—Analysis of the i.r. data is restricted to absorptions due to the thiocyanate groups: 2 080ms, 2 015s (br) [ν(CN)]; 805vw [ν(CS)?]; 483w (br) and 457w cm^{-1} [δ(NCS)]. The main feature appears to be the two ν(CN) bands which are imputed to μ-*NS* and to terminally N-bonded groups, respectively. Interfering bands due to bipy occur in the ν(CS) and δ(NCS) ranges; however, consistent with the observed structure are the assigned δ(NCS) absorptions, the one at 483 cm^{-1} being imputable to terminal N-thiocyanate groups. The ν(CN) of the bridging groups is near to the lowest limit of reported frequencies for μ-*NS* type of bonding (see for instance refs. 13 and 14). While it has been recognized that ν(CN), besides depending on the type of bonding (the main electronic factor), is also sensitive to steric and crystal-packing requirements (see for instance refs. 13 and 14), we note that accepted empirical criteria for deciding on the thiocyanate bonding mode mainly result from transition-metal complexes and that a generalized lowering of ν(CN) is found with the heaviest Group 5 element thiocyanates.[1,2,15] Owing to their similarity, a similar structure can in principle be expected for the adducts $[Bi(CNS)_3(bipy)_2]$ and $Bi(CNS)_3(phen)_2$. We were unable to obtain crystals of the latter suitable for *X*-ray analysis. Its i.r. spectrum allowed only the safe assignment of the ν(CN) internal modes of the thiocyanate groups (2 089s and 2 040s cm^{-1}) and these findings are not in contrast with the above hypothesis.

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