Synthetic and Structural Studies on Bismuth(III) Thiocyanate and Selenocyanate Complexes†

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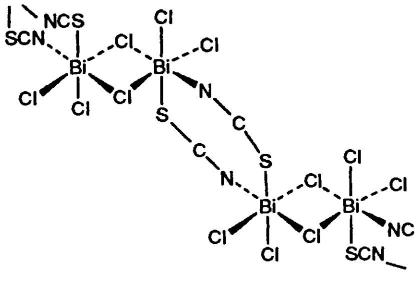
The reaction between either $BiCl_3$ or $Bi(NO_3)_3·5H_2O$ and 3 equivalents of KSCN afforded a yellow material which has not been fully characterised but which reacts as a source of $Bi(SCN)_3$ **A**. Compound **A** and 2 equivalents of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ afforded the green complex $[Bi(SCN)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ which has been characterised by X-ray crystallography and consists of trigonal-pyramidal bismuth centres co-ordinated to one SCN group through sulfur, and two $Mo(CO)_3(\eta\text{-}C_5H_5)$ fragments with additional intermolecular Bi ••• NCS interactions resulting in a one-dimensional polymer. The reaction between **A** and [K(18-crown-6)]SCN (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) afforded an orange and a yellow crystalline material both of which have been characterised by X-ray crystallography and shown to be isomers. In the orange compound a potassium cation is located between two potassium cations co-ordinated by 18-crown-6 ligands and an octahedral $[Bi(SCN)_6]^{3-}$ anion is present. These ions are organised into two-dimensional sheets in which each $[Bi(SCN)_6]^{3-}$ anion is surrounded by four $K[K(18\text{-crown-}6)]_2$ units and *vice versa*. In the yellow compound the structure has the same basic cationic and anionic units but the thiocyanatobismuth anion has four *S*-bonded and two *trans N*-bonded thiocyanate ligands with the anions arranged in parallel columns separated (within columns) by potassium cations. The remaining two potassium cations are co-ordinated by 18-crown-6 ether ligands and are positioned between the columns. The reaction between $BiCl_3$ and 3 equivalents of KSeCN afforded dark red crystals of a complex formulated as $Bi(SeCN)_3$. The reaction between $Bi(SeCN)_3$ and 2 equivalents of $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ afforded $[Bi(SeCN)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$. The reaction of $[N(PPh_3)_2][BiCl_4]$ and 4 equivalents of KSeCN afforded a dark red crystalline compound $K[N(PPh_3)_2]_2[Bi(SeCN)_6]$ the structure of which was also established by X-ray crystallography and comprises isolated $[N(PPh_3)_2]^+$ cations and columns of $[Bi(SeCN)_6]^{3-}$ anions separated by potassium cations in a similar manner to that found in yellow $K[K(18\text{-crown-}6)]_2[Bi(SCN)_4(NCS)_2]$.

The pseudohalides, thiocyanate (SCN) and selenocyanate (SeCN), have an extensive and established chemistry particularly as ligands in transition-metal complexes, but their chemistry in association with the p-block elements is generally much less developed. With particular reference to antimony(III) and bismuth(III), the thiocyanate compounds $Sb(SCN)_3$ and $Bi(SCN)_3$ are not well defined although, in the case of bismuth, complex anions of the form $[Bi(SCN)_4]^-$, $[Bi(SCN)_6]^{3-}$ and $[Bi(SCN)_xX_{6-x}]^{3-}$ (X = halide) have been reported together with some ligand (L) complexes of the type $[Bi(SCN)_3L_3]$ and $[Bi(SCN)_5L]^{2-}$.[1] Selenocyanate complexes of antimony(III) and bismuth(III) are still less well studied although there are some reports of $[Bi(SeCN)_3L_3]$ and $[Bi(SeCN)_6]^{3-}$, particularly the latter.[1]

As with any thiocyanate or selenocyanate complex, there is always the question of whether bonding occurs through the nitrogen or through the sulfur or selenium, the former tending to be found in association with hard-acid centres and the latter with softer acids. Infrared spectroscopic data have been interpreted in terms of both types of bonding for some of the compounds mentioned above,[1] but definitive structural results for antimony and bismuth thiocyanate compounds derived from X-ray crystallography have been described, with one exception, only in the last few years and there are apparently no reports of selenocyanate structures. In $Rb[Bi(SCN)_4]$ **1**,[2] the bismuth is *S*-bonded to four SCN groups arranged in an equatorially vacant, trigonal-bipyramidal or disphenoidal geometry, with two longer contacts to two nitrogen atoms giving an overall geometry close to octahedral. Crystal structures have also been reported for $[Bi_2(phen)_4(NCS)_4(\mu\text{-}NCS)_2]$ **2**[3] (phen = 1,10-phenanthroline) in which the μ-NCS groups are bonded through both N and S (*i.e.* Bi–NCS–Bi) and the terminal thiocyanates are *N*-bonded, $[Bi(C_2H_2N_2S_3)_2(SCN)_3]$ **3**[4] ($C_2H_2N_2S_3$ = 5-amino-1,2,4-dithiazole-3-thione) in which two SCN groups are terminally bound through sulfur and one bridges as in **2**, $[NH_4(18\text{-crown-}6)][BiCl_3(SCN)]$ **4**[5] (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) which contains a polymeric anion with bridging chlorides and thiocyanates as shown, and $[NH_4]_4[Bi(nta)_2(NCS)]$ **5**[6] (nta = nitrilotriacetate) which contains a single *N*-bound, terminal thiocyanate ligand.



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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

A structurally characterised antimony(III) thiocyanate complex is $[Sb(SCN)Ph_2]$[7] which exists as a polymer in which the antimony atoms are four-co-ordinate and where the SCN groups bridge as in **2**–**4**, but in which there are three distinct antimony co-ordination environments, one with two *S*-bonded SCN groups, one with two *N*-bonded groups and one bonded to both nitrogen and sulfur. A number of organobismuth thiocyanate complexes have also been described but none has been structurally characterised.[8]

Herein we describe the results of synthetic and structural studies on some organotransition-metal bismuth thiocyanate complexes and three octahedral complex thiocyanate and selenocyanate anions of bismuth(III).

Results and Discussion

The reaction between 3 equivalents of KSCN and either $Bi(NO_3)_3{\cdot}5H_2O$ or $BiCl_3$ in thf (tetrahydrofuran) afforded a yellow solution from which a yellow powder was obtained after filtration and crystallisation by solvent diffusion of hexane. We were never able to obtain consistent or reproducible analytical data on this yellow solid, although infrared spectra obtained in thf solution were always similar [Table 1, Fig. 1(*a*)]. We presume, however, that it comprises $Bi(SCN)_3$ **A**, at least in part, or some synthetic equivalent thereof, since subsequent reactivity studies revealed that it was certainly a source of $Bi(SCN)_3$ in solution and we will write it as such hereafter.

The reaction between $Bi(SCN)_3$ (generated *in situ*) and 2 equivalents of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ in thf solution led to the immediate formation of a dark green solution from which dark green crystals were obtained after work-up. Analytical and spectroscopic data [Table 1, Fig. 1(*b*)] were consistent with the formula $[Bi(SCN)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **6**, and this was confirmed by X-ray crystallography, the results of which are shown in Figs. 2 and 3. Selected bond distance and angle data are given in Table 2 and atomic positional parameters in Table 3.

The crystal structure of $[Bi(SCN)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **6** consists of a linear polymeric array of molecules in which the bismuth atoms are bridged by weak Bi ··· NCS–Bi contacts [Bi(1)–S(1) 2.804(4), Bi(1)–N(1a) 2.931(19) Å] linking the molecules along the screw axes parallel to the *b* axis of the unit cell (see Fig. 3). This structure may be considered to arise formally by interaction between the Lewis-acidic bismuth centre in **6** and the Lewis-base nitrogen of the thiocyanate of a neighbouring molecule. This interaction [Bi(1)–N(1a)] is essentially *trans* to the Bi–S bond [S(1)–Bi(1)–N(1a) 153.6(4)°] and is consistent with the Lewis-acid function at the bismuth centre being the Bi–S σ* orbital. The polymer (NCS–Bi ··· NCS–Bi) chain is substantially kinked, given the Bi–S–C and C–N ··· Bi angles of 97.3(6) and 138.8(8)°, the latter being rather far from the value of 180° expected for sp hybridisation of the nitrogen lone pair which may be taken as evidence that the N ··· Bi interaction is rather weak. Further indication that this

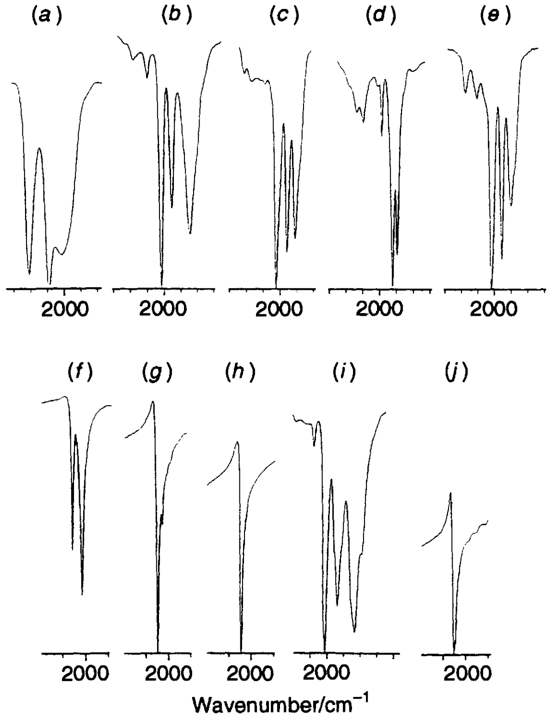

Fig. 1 Infrared spectra for the complexes measured in thf solution in CaF_2 cells unless otherwise stated: (*a*) **A**, (*b*) **6**, (*c*) **7**, (*d*) **8**, (*e*) **9**, (*f*) **10**, (*g*) **11**, (*h*) **12**, (*i*) **13** and (*j*) **14**. The wavenumber scales for spectra (*a*)–(*e*) and (*i*) are calibrated in 50 cm^{-1} divisions, those for (*f*)–(*h*) and (*j*) in divisions of 200 cm^{-1}. The spectra for **10**–**12** and **14** were measured in the solid state as KBr discs

Table 1 Spectroscopic and analytical data for the complexes

			Analysis[b] (%)		
Compound	$\tilde{\nu}(CO)$[a]/cm^{-1}	$\tilde{\nu}(CN)$[a]/cm^{-1}	C	H	N
A $Bi(SCN)_3$		2105s, 2045s, 2008s			
6 $[Bi(SCN)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	2051w, 2008s, 1977m, 1921s	2090w	27.25 (26.95)	1.25 (1.30)	1.85 (1.85)
7 $[Bi(SCN)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$	2046w, 2012s, 1981s, 1956s	2109w, 2089w	28.65 (29.00)	1.45 (1.60)	2.45 (2.25)
8 $[Bi(SCN)\{Co(CO)_3(PPh_3)\}_2]$	1997m, 1962s, 1948s	2070m, 2051m			
9 $[K(18\text{-crown-}6)][Bi(SCN)_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$	2008s, 1977s, 1950m	2090w, 2053w	34.05 (34.25)	3.10 (3.50)	3.10 (2.85)
10 $K[K(18\text{-crown-}6)]_2[Bi(SCN)_6]$		2112s, 2029s[c]	30.20 (29.95)	3.95 (4.00)	6.95 (7.00)
11 $K[K(18\text{-crown-}6)]_2[Bi(SCN)_6]$		2095s, 2054m[c]	29.70 (29.95)	3.90 (4.00)	7.00 (7.00)
12 $Bi(SeCN)_3$		2087s[c]	7.15 (6.90)		8.00 (8.00)
13 $[Bi(SeCN)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	2044w, 2006s, 1970s, 1917s, 1898m				
14 $K[N(PPh_3)_2]_2[Bi(SeCN)_6]$		2106s[c]	48.30 (47.90)	3.20 (3.10)	7.55 (5.75)

[a] Measured in thf solution unless otherwise stated. [b] Calculated values in parentheses. [c] Measured as KBr discs.

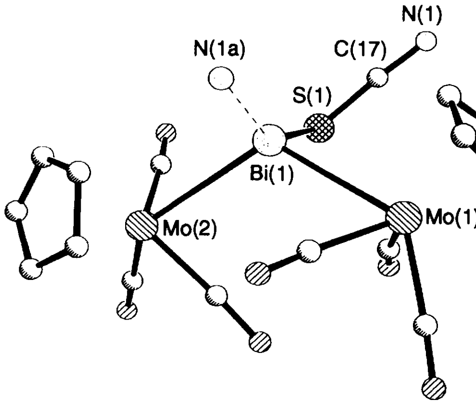

Fig. 2 Molecular structure of [Bi(SCN){Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **6** showing atom labelling and the Bi ··· N intermolecular interaction. All hydrogen atoms have been omitted for clarity

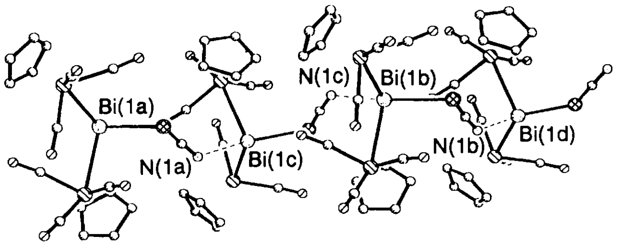

Fig. 3 Part of the crystal structure of [Bi(SCN){Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **6** showing the chain of molecules linked by Bi–SCN ··· Bi interactions. All hydrogen atoms have been omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for complex **6**

Bi(1)–Mo(1)	2.947(2)	Bi(1)–Mo(2)	2.980(2)
Bi(1)–S(1)	2.804(4)	Bi(1)–N(1a)	2.931(19)
Mo(1)–Bi(1)–Mo(2)	116.0(1)	Mo(1)–Bi(1)–S(1)	99.3(1)
Mo(2)–Bi(1)–S(1)	96.5(1)	Mo(1)–Bi(1)–N(1a)	89.5(3)
Mo(2)–Bi(1)–N(1a)	101.9(3)	S(1)–Bi(1)–N(1a)	153.6(4)
Bi(1)–S(1)–C(17)	97.3(6)	S(1)–C(17)–N(1)	171.1(16)
Bi(1)–N(1a)–C(1a)	138.8(8)		

Atoms N(1a) and C(1a) are generated from N(1) and C(1) by symmetry operation $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

Table 3 Atomic coordinates (× 10^4) for complex **6**

Atom	*x*	*y*	*z*
Bi(1)	3437(1)	1992(1)	2435(1)
Mo(1)	4764(1)	2737(1)	4149(1)
Mo(2)	809(1)	2761(1)	1762(1)
S(1)	2917(4)	−292(3)	2761(3)
N(1)	5254(16)	−1233(15)	3212(10)
O(1)	3712(14)	3921(11)	5467(8)
O(2)	2778(11)	1044(10)	4407(7)
O(3)	3622(12)	5017(10)	3230(8)
O(4)	672(18)	222(13)	1141(13)
O(5)	−1624(11)	1942(15)	2090(10)
O(6)	1269(12)	3215(15)	3679(8)
C(1)	4101(15)	3481(13)	4992(9)
C(2)	3450(13)	1676(11)	4254(8)
C(3)	3960(13)	4135(11)	3520(9)
C(4)	6497(15)	2086(21)	3780(10)
C(5)	6778(14)	3175(18)	4136(11)
C(6)	6785(14)	3098(15)	4967(11)
C(7)	6500(13)	2000(18)	5128(11)
C(8)	6305(13)	1347(12)	4360(11)
C(9)	1156(14)	3003(15)	2966(10)
C(10)	−704(15)	2233(17)	1963(12)
C(11)	765(18)	1111(18)	1409(14)
C(12)	−277(19)	3644(28)	577(16)
C(13)	−31(33)	4458(25)	1201(22)
C(14)	1196(33)	4635(17)	1454(13)
C(15)	1686(17)	4010(19)	1014(13)
C(16)	793(28)	3419(19)	470(11)
C(17)	4334(16)	−770(12)	3017(9)

interaction is indeed weak comes from the Bi ··· N distance (*cf.* other Bi^{III}–N bonds *ca.* 2.4 Å, see below). The resultant co-ordination geometry at Bi is essentially of the four-co-ordinate disphenoidal type, with the Mo(CO)$_3$(η-C$_5$H$_5$) fragments (and the bismuth lone pair) in the equatorial plane and the Bi–S and Bi ··· N interactions in the axial sites. We have previously observed and commented in detail upon similar geometries in polymeric species of the general form [BiX(ML$_n$)$_2$] (X = Cl, Br or NO$_3$)[9] and the distortions from idealised angles in **6** are also of the now familiar sort in which, in this case, the S–Bi ··· N angle is significantly reduced from 180°.[10] In this asymmetric case (with respect to the axial groups) the S–Bi–Mo angles are larger than 90° [96.5(1) and 99.3(1)°], while the N ··· Bi–Mo angles are more irregular [89.5(3) and 101.9(3)°]; the angle between the equatorial groups [Mo(1)–Bi(1)–Mo(2)] is 116.0(1)° which is within the usual range.[10]

The reaction between Bi(SCN)$_3$ and 2 equivalents of K[Fe(CO)$_2$(η-C$_5$H$_5$)] also gave a dark green solution from which dark green crystals of [Bi(SCN){Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$] **7** were isolated. Infrared and analytical data [Table 1, Fig. 1(*c*)] were consistent with the anticipated formula although we were unable to obtain X-ray-quality crystals. A similar reaction between Bi(SCN)$_3$ and 2 equivalents of K[Co(CO)$_3$(PPh$_3$)] gave a green solution which resulted in a green powder after work-up, but this contained a mixture of the expected product [Bi(SCN){Co(CO)$_3$(PPh$_3$)}$_2$] **8** and the mononuclear cobalt species [Co(SCN)(CO)$_3$(PPh$_3$)]. An infrared spectrum of reasonably pure **8** is shown in Fig. 1(*d*) for which the pattern of CO absorptions is very similar to those of other complexes of the type [BiX{Co(CO)$_3$(PR$_3$)}$_2$],[11] but we were not able to obtain satisfactory microanalytical data.

We have previously shown that species of the general formula [BiX(ML$_n$)$_2$] (X = halide) readily take up an extra equivalent of halide anion affording anionic complexes of type [BiX$_2$(ML$_n$)$_2$]$^-$ [10] and we were interested to see whether the analogous thiocyanate species would react similarly. Treatment of **7** with 1 equivalent of [K(18-crown-6)]SCN in thf led to no colour change but dark green crystals, obtained after solvent diffusion of hexane, were shown by infrared spectroscopy to be different from **7** and analytical data were consistent with the formula [K(18-crown-6)][Bi(SCN)$_2${Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$] **9**. Of particular significance is the lowering of the ν(CO) bands in **9** by about 5 cm^{-1} compared with those for **7** [Table 1, Fig. 1(*e*)], a feature we have previously encountered in comparing the halide complexes [BiX(ML$_n$)$_2$] and [BiX$_2$(ML$_n$)$_2$]$^-$.[10] Crystals of **9** proved not to be suitable for X-ray diffraction studies and even though two data sets were collected we were unable to obtain a solution.

Our inability fully to characterise Bi(SCN)$_3$ itself, especially in terms of obtaining any X-ray-quality crystals, led us next to consider the possibility of preparing and structurally characterising some thiocyanato anions of bismuth; several such compounds had been mentioned in the literature,[1] as described above, although only **1** had been examined by X-ray crystallography.[2]

The reaction between Bi(SCN)$_3$ and 1 equivalent of [K(18-crown-6)]SCN in MeCN solution followed by crystallisation by solvent diffusion of Et$_2$O resulted in a mixture of well formed orange and yellow crystals. Microanalytical data for both types of crystal were very similar (Table 1) although the solid-state infrared spectra in the ν(CN) region, obtained as KBr discs, were quite different [Table 1, Fig. 1(*f*) and 1(*g*)]. The structures of both types of crystal were determined by X-ray crystallography which revealed that they were in fact isomers with the formula K[K(18-crown-6)]$_2$[Bi(SCN)$_6$] **10** (orange) and **11** (yellow). Views of **10** are shown in Figs. 4 and 5 and of **11** in Figs. 6 and 7; selected bond lengths and angles for the two structures are given in Tables 4 and 6 and atomic positional parameters in Tables 5 and 7.

The crystal structure of complex **10** is complicated and consists of [Bi(SCN)$_6$]$^{3-}$ anions at sites of crystallographic inversion symmetry, one potassium ion at a site of crystallographic C_2 symmetry and two other potassiums (related by symmetry) each of which is complexed by an 18-crown-6 ligand lying in general positions [see Fig. 4; the unique K(18-crown-6) cation is shown]. The co-ordination geometry at bismuth is distorted from regular octahedral [Bi–S 2.829(3), 2.819(3), 2.832(3) Å] and the *cis* S–Bi–S angles fall in two ranges: three are between 92.8(1) and 99.6(1) and three between 80.4(1) and 87.2(1)°. The larger values involve angles between the bonds to S(1), S(2a) and S(3) and also those to S(1a), S(2) and S(3a) (where atom labels suffixed a are generated by the centre of inversion), these sets occupying a pair of opposite faces of the BiS$_6$ octahedron. The remaining S–Bi–S angles are all in the range of lower values. This distortion corresponds to a (slightly irregular) D_{3h} flattening of the octahedral co-ordination environment at bismuth. It is possible that the observed geometry is the result of a dynamic disorder between two (or possibly more) C_{3v} BiS$_6$ geometries which would be expected [from valence shell electron pair repulsion (VSEPR)] if the lone pair were becoming localised on or towards one face of the octahedron, but the displacement ellipsoids do not provide compelling evidence for this.

The crystal structure of complex **10** shows significant contacts between the [Bi(SCN)$_6$]$^{3-}$ anion and the 'isolated' potassium, K(1), which has a distorted octahedral co-ordination environment formed by pairs of two thiocyanate nitrogens and an oxygen of the 18-crown-6 ligand that complexes K(2) [K(1) • • • N(3) 2.858(8), K(1) • • • N(1a) 2.870(7), K(1)–O(6) 2.930(5) Å]. The K(1) • • • N interactions link the [Bi(SCN)$_6$]$^{3-}$ anions forming chains parallel to the crystallographic *b* axis of stoichiometry [KBi(SCN)$_6$]$^{2-}$ (see Fig. 5), in which each K(1) is also ligated by two oxygens of [K(2)(18-crown-6)]$^+$ moieties, and which are further linked into sheets approximately parallel to the crystallographic *ab* plane by inversion symmetry-related N • • • K(1) contacts. These {[KBi(SCN)$_6$]$^{2-}$}$_x$ sheets are sandwiched by [K(2)(18-crown-6)]$^+$ cations as shown for one

Table 4 Selected bond lengths (Å) and angles (°) for complex **10**

Bi–S(1)	2.829(3)	S(1)–C(1)	1.647(7)
Bi–S(2)	2.819(3)	S(2)–C(2)	1.622(8)
Bi–S(3)	2.832(3)	S(3)–C(3)	1.631(8)
K(1) • • • N(3)	2.858(8)	N(1)–C(1)	1.145(9)
K(2) • • • N(1a)	2.970(7)	N(2)–C(2)	1.165(11)
K(1)–O(6)	2.930(5)	N(3)–C(3)	1.162(11)
K(1) • • • N(1a)	2.870(7)		
S(1)–Bi–S(2)	87.2(1)	S(1)–Bi–S(3)	97.8(1)
S(2)–Bi–S(3)	80.4(1)	S(1)–Bi–S(1a)	180.0
S(2)–Bi–S(1a)	92.8(1)	S(3)–Bi–S(1a)	82.2(1)
S(2)–Bi–S(2a)	180.0	S(3)–Bi–S(2a)	99.6(1)
S(3)–Bi–S(3a)	180.0	N(3)–K(1)–O(6)	88.1(2)
Bi–S(1)–C(1)	105.0(3)	Bi–S(2)–C(2)	102.3(3)
Bi–S(3)–C(3)	102.2(3)	S(1)–C(1)–N(1)	176.7(7)
S(2)–C(2)–N(2)	178.0(7)	S(3)–C(3)–N(3)	178.7(7)

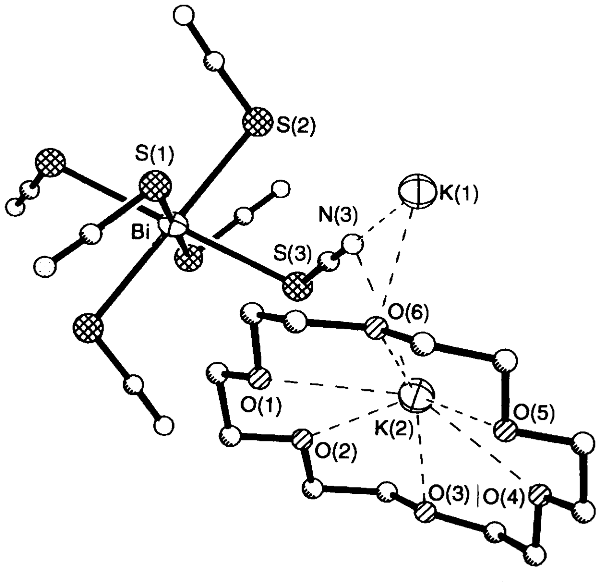

Fig. 4 Molecular structure of K[K(18-crown-6)]$_2$[Bi(SCN)$_6$] **10** showing atom labelling and some of the K • • • N and K • • • O intermolecular interactions. Only one of the [K(18-crown-6)]$^+$ cations is shown. All hydrogen atoms have been omitted for clarity

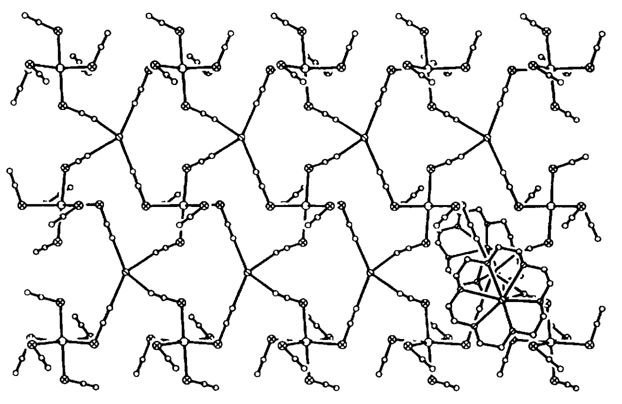

Fig. 5 Part of the crystal structure of K[K(18-crown-6)]$_2$[Bi(SCN)$_6$] **10** showing one sheet of composition {[KBi(SCN)$_6$]$^{2-}$}$_x$ viewed perpendicular to the layer. One pair of [K(18-crown-6)]$^+$ complex cations is shown. All hydrogen atoms have been omitted for clarity

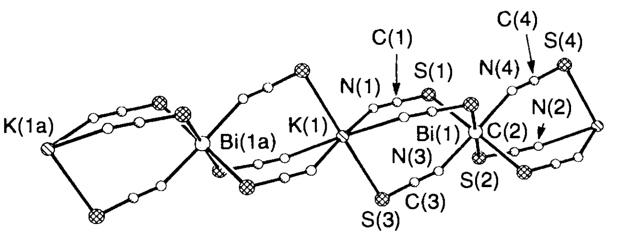

Fig. 6 Part of the crystal structure of K[K(18-crown-6)]$_2$[Bi(SCN)$_4$(NCS)$_2$] **11** showing atom labelling and some of the N • • • K interactions. All hydrogen atoms have been omitted for clarity

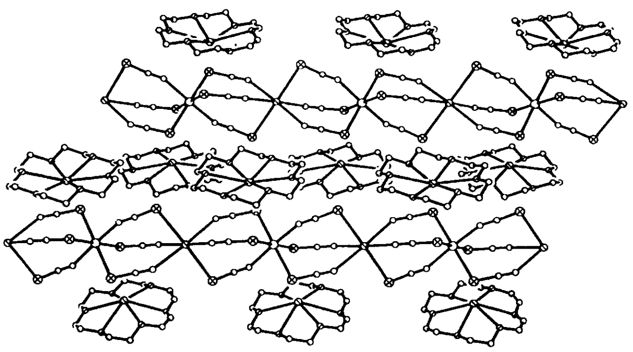

Fig. 7 Part of the crystal structure of K[K(18-crown-6)]$_2$[Bi(SCN)$_4$(NCS)$_2$] **11** showing the molecular chains of composition {[KBi(SCN)$_4$(NCS)$_2$]$^{2-}$}$_x$ and the surrounding [K(18-crown-6)]$^+$ complex cations. All hydrogen atoms have been omitted for clarity

Table 5 Atomic coordinates (× 10^4) for complex **10**

Atom	*x*	*y*	*z*
Bi	0	0	0
K(1)	0	5207(2)	2500
K(2)	1409(1)	5356(2)	1879(1)
S(1)	−136(1)	−251(2)	1356(1)
S(2)	−866(1)	1895(3)	−127(1)
S(3)	482(1)	2884(2)	53(1)
N(1)	547(2)	−2473(7)	1876(3)
N(2)	−1589(3)	164(8)	439(4)
N(3)	255(3)	4020(8)	1270(3)
C(1)	272(3)	−1567(8)	1645(3)
C(2)	−1280(3)	874(9)	209(4)
C(3)	344(3)	3545(8)	762(4)
O(1)	1333(2)	2078(5)	2224(2)
O(2)	1715(2)	3027(5)	1068(2)
O(3)	2227(2)	5746(5)	1064(2)
O(4)	2093(2)	7931(5)	2012(2)
O(5)	1686(2)	6885(5)	3178(2)
O(6)	1022(2)	4350(6)	3078(2)
C(4)	1003(3)	2768(8)	3217(4)
C(5)	908(3)	1912(8)	2598(3)
C(6)	1273(3)	1188(8)	1630(3)
C(7)	1710(3)	1477(7)	1247(3)
C(8)	2069(3)	3308(8)	592(4)
C(9)	2079(3)	4971(7)	462(4)
C(10)	2362(3)	7278(8)	973(4)
C(11)	2514(3)	7958(8)	1634(3)
C(12)	2201(3)	8622(8)	2649(4)
C(13)	1757(3)	8443(8)	3029(4)
C(14)	1251(3)	6750(9)	3553(5)
C(15)	1164(4)	5165(8)	3693(5)

Table 6 Selected bond lengths (Å) and angles (°) for complex **11**

Bi(1)–N(3)	2.44(2)	S(1)–C(1)	1.63(2)
Bi(1)–N(4)	2.34(2)	S(2)–C(2)	1.61(2)
Bi(1)–S(1)	2.812(5)	S(3)–C(3)	1.61(2)
Bi(1)–S(2)	2.825(5)	S(4)–C(4)	1.62(2)
K(1)–N(1^{II})	2.76(2)	C(1)–N(1)	1.14(2)
K(1)–N(2)	2.79(2)	C(2)–N(2)	1.12(2)
K(1)–S(3)	3.317(8)	C(3)–N(3)	1.08(2)
K(1)–S(4^{III})	3.299(8)	C(4)–N(4)	1.14(2)
N(4)–Bi(1)–N(3)	176.9(7)	N(4)–Bi(1)–S(1)	93.2(3)
N(3)–Bi(1)–S(1)	84.7(4)	S(1^{I})–Bi(1)–S(1)	93.3(2)
N(4)–Bi(1)–S(2)	86.2(4)	N(3)–Bi(1)–S(2)	95.8(4)
S(1^{I})–Bi(1)–S(2)	179.24(14)	S(1)–Bi(1)–S(2)	86.2(2)
S(2)–Bi(1)–S(2^{I})	94.3(3)	N(1^{II})–K(1)–N(1^{III})	73.2(7)
N(1^{II})–K(1)–N(2)	176.9(5)	N(1^{III})–K(1)–N(2)	106.4(4)
N(1^{II})–K(1)–N(2^{I})	106.4(4)	N(2)–K(1)–N(2^{I})	73.8(6)
N(1^{II})–K(1)–S(4^{III})	85.4(3)	N(2)–K(1)–S(4^{III})	91.5(4)
N(1^{II})–K(1)–S(3)	93.8(3)	N(2^{I})–K(1)–S(3)	89.3(3)
S(4^{III})–K(1)–S(3)	179.0(2)	C(1)–S(1)–Bi(1)	103.1(6)
C(1)–S(1)–K(3^{VI})	87.5(6)	Bi(1)–S(1)–K(3^{VI})	94.3(2)
N(1)–C(1)–S(1)	179(2)	C(1)–N(1)–K(1^{VII})	147(2)
C(2)–S(2)–Bi(1)	101.9(6)	N(2)–C(2)–S(2)	177(2)
C(2)–N(2)–K(1)	144.7(14)	C(3)–S(3)–K(1)	94.2(7)
N(3)–C(3)–S(3)	175(2)	C(3)–N(3)–Bi(1)	154(2)
C(4)–S(4)–K(1^{VII})	95.9(6)	N(4)–C(4)–S(4)	176(2)
C(4)–N(4)–Bi(1)	157(2)		

Symmetry transformations used to generate equivalent atoms: I $x, -y + \frac{1}{2}, z$; II $x, -y + \frac{1}{2}, z - 1$; III $x, y, z - 1$; IV $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; V $x + \frac{1}{2}, y, -z + \frac{1}{2}$; VI $x - \frac{1}{2}, y, -z + \frac{1}{2}$; VII $x, y, z + 1$.

Table 7 Atomic coordinates (× 10^4) for complex **11**

Atom	*x*	*y*	*z*
Bi(1)	1 228(1)	2 500	1 051(1)
K(1)	1 209(2)	2 500	−3 895(4)
K(2)	2 892(2)	2 500	−10 190(4)
K(3)	4 669(2)	2 500	2 593(4)
S(1)	717(2)	1 120(4)	2 100(4)
C(1)	810(5)	1 290(11)	3 457(13)
N(1)	876(5)	1 389(11)	4 405(11)
S(2)	1 744(2)	1 103(5)	26(4)
C(2)	1 656(5)	1 284(11)	−1 309(13)
N(2)	1 590(6)	1 371(10)	−2 243(11)
S(3)	227(2)	2 500	−2 451(5)
C(3)	474(7)	2 500	−1 221(16)
N(3)	611(8)	2 500	−363(16)
S(4)	2 175(2)	2 500	4 629(4)
C(4)	1 933(6)	2 500	3 385(17)
N(4)	1 789(7)	2 500	2 479(17)
O(1)	3 023(5)	2 500	−7 858(12)
O(2)	3 113(3)	883(6)	−9 045(8)
O(3)	2 978(3)	859(7)	−11 402(7)
O(4)	3 111(4)	2 500	−12 585(10)
O(5)	4 386(6)	2 500	4 880(17)
O(6)	4 333(4)	871(9)	3 644(9)
O(7)	4 564(4)	860(9)	1 322(10)
O(8)	4 372(7)	2 500	194(20)
C(5)	3 159(5)	1 691(10)	−7 337(13)
C(6)	2 962(5)	911(10)	−7 913(12)
C(7)	2 961(5)	94(10)	−9 651(12)
C(8)	3 147(5)	87(11)	−10 804(11)
C(9)	3 146(5)	920(11)	−12 528(12)
C(10)	2 942(5)	1 704(10)	−13 099(13)
C(11)	4 230(6)	1 709(12)	5 298(16)
C(12)	4 413(6)	910(13)	4 819(15)
C(13)	4 461(6)	131(12)	3 034(14)
C(14)	4 365(6)	166(13)	1 880(14)
C(15)	4 462(9)	981(16)	194(21)
C(16)	4 459(12)	1 734(20)	−168(26)

pair of cations in Fig. 5. Further N···K links bind the [K(2)(18-crown-6)]$^+$ moieties to the anionic sheets [K(2)···N(1a) 2.970(7) Å].

Compound **11** is a linkage isomer of **10** in which the bismuth centre is attached to four *S*-bound and two *N*-bonded thiocyanate ligands [Bi–S 2.812(5), 2.825(5); Bi–N 2.34(2), 2.44(2) Å] and which we may represent as [Bi(SCN)$_4$(NCS)$_2$]$^{3-}$ (see Fig. 6). This anion lies at a site of crystallographic mirror symmetry [atoms Bi(1), S(3), C(3), N(3), S(4), C(4) and N(4) lie on the mirror plane as do all the potassium atoms] and the bismuth co-ordination is approximately octahedral with the nitrogens *trans* to one another. Distortions from inversion symmetry at the bismuth centre are relatively small [largest deviation from *trans* angle = 180° being 3.1(7)°]. As in **10** the *cis* X–Bi–X angles fall into two ranges [93.2(3)–95.8(4) and 84.7(4)–86.2(2)°] with those between N(4), S(1) and S(1^{I}) and between N(3), S(2) and S(2^{I}) being greater than 90° and the remainder less than 90°. These distortions hence also lead to a flattened pseudo-D_{3h} co-ordination geometry at bismuth.

The crystal structure of complex **11** consists of chains of stoichiometry [KBi(SCN)$_4$(NCS)$_2$]$^{2-}$ running parallel to the crystallographic *c* axis (see Fig. 6) in which the potassium ions, K(1), are ligated by four nitrogen and two sulfur atoms of bridging thiocyanate ligands [K–S 3.299(8), 3.317(8); K–N 2.79(2), 2.76(2) Å]. These chains are separated by the [K(18-crown-6)]$^+$ complex ions as shown in Fig. 7, which have only weak contacts with the anion chain (K···S distances > 3.68 Å).

Having had some success with the thiocyanate complexes, we then turned our attention to analogous selenocyanate complexes. The reaction between BiCl$_3$ and 3 equivalents of KSeCN in thf solution afforded, after work-up, dark red crystals of a complex formulated as Bi(SeCN)$_3$ **12** primarily on the basis of analytical data (Table 1). A solid-state infrared spectrum is shown in Fig. 1(*h*) which reveals a sharp CN stretch but the crystals were not of a quality suitable for X-ray diffraction which has therefore prevented a more definitive characterisation. In contrast to the thiocyanate system, BiCl$_3$ is a much better starting material than Bi(NO$_3$)$_3$·5H$_2$O in this case.

The reaction between compound **12** and a range of transition-metal carbonylate anions gave rather intractable mixtures but with 2 equivalents of [Bi{Mo(CO)$_3$(η-C$_5$H$_5$)}$_3$][9a] at low temperature in thf a dark green solution resulted, the infrared spectrum of which is shown in Fig. 1(*i*). This is very similar to the spectrum of **6** and is consistent with the formulation [Bi(SeCN){Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **13**. Compound **13** was extremely air sensitive in solution, however, and attempted crystallisation gave only an impure green powder for which we were not able to obtain satisfactory analytical data. No suitable X-ray-quality crystals were obtained.

A much more stable compound was obtained from the reaction between [N(PPh$_3$)$_2$][BiCl$_4$][12] and 4 equivalents of KSeCN which afforded a dark red crystalline compound after work-up. Spectroscopic and analytical data [Table 1, Fig. 1(*j*)] were consistent with the formula K[N(PPh$_3$)$_2$]$_2$[Bi(SeCN)$_6$] **14** which was confirmed by X-ray crystallography the results of which are shown in Figs. 8 and 9. Selected bond lengths and angles are given in Table 8 and atomic positional parameters in Table 9.

Compound **14** is, as with **10** and **11**, a mixed salt. The anion is the selenium analogue of that in **10** and contains a bismuth octahedrally co-ordinated by six selenium atoms [Bi–Se 2.881(3), 2.938(3), 2.941(3), 2.945(3), 2.962(2) and 2.986(2) Å]. In addition the structure contains potassium ions which are co-ordinated to the cyano groups of the anion and isolated [N(PPh$_3$)$_2$]$^+$ cations. The co-ordination geometry at bismuth, however, is severely distorted (much more so than in **10** and **11**, see Fig. 8) and rather irregular with *cis* Se–Bi–Se angles in the range 71–102°. Furthermore, the three largest *cis* Se–Bi–Se angles [101.75(8), 99.90(8) and 98.60(8)°] involve the Se(3, 4, 5) face of the BiSe$_6$ octahedron implying that the primary distortion in this instance is towards a C_{3v} capped-octahedral geometry (as opposed to the D_{3h} distortion in **10** and **11**) consistent with a face-centred localisation of the lone pair, *i.e.* a much more definite stereochemically active role for the lone pair in **14** as opposed to **10** or **11**.

The crystal structure of complex **14** consists of chains of stoichiometry [KBi(SeCN)$_6$]$^{2-}$ running parallel to the crystallographic *a* axis (see Fig. 9) in which the potassium ions, K(1), are ligated by four nitrogen atoms of bridging selenocyanate ligands [K–N 2.51(2), 2.55(2), 2.62(2), 2.66(2) Å], the lower co-ordination number of potassium in this case being associated with shorter K • • • N contacts than in **10** or **11**. These chains are separated by the [N(PPh$_3$)$_2$]$^+$ complex ions which have only very weak contacts with the anion chain.

In conclusion, a word should be said about the infrared spectra of the complexes particularly in the CN stretching region. Numerical data are presented in Table 1 and the ν(CN) absorptions are evident in the spectra shown in Fig. 1, albeit only weakly in the case of the metal complexes. We must, however, exercise some care in relating these spectra to the solid-state structures. First, the spectra for the metal complexes (and **A**) were obtained in thf solution and some dissociation to give free SCN$^-$ and a solvated complex such as [Bi(thf)$_x$(ML$_n$)$_2$]$^+$ (without the metals in the case of **A**) is certainly a possibility, although we are not convinced that this does, in fact, occur; we will return to this matter in a future publication dealing with some related organotransition metal–indium complexes where such dissociation probably does take place.[13] Secondly, when preparing a KBr disc, a degree of bromide for thiocyanate or selenocyanate exchange is possible and we cannot be sure that the spectra obtained are for the complex observed by X-ray crystallography. However, the fact that the spectra for **10** and **11** are different, reproducibly obtained and have no peaks in common suggests that this is unlikely to be a serious problem. In any event, the signals observed in the spectra of all the complexes are useful as a fingerprint of the compound concerned.

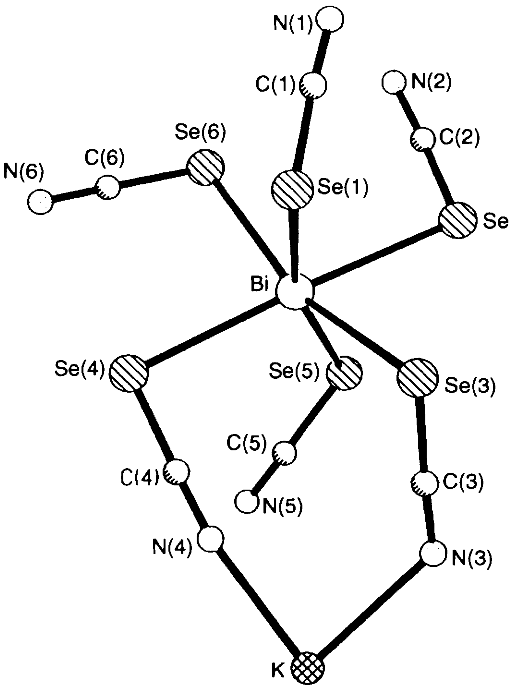

Fig. 8 Molecular structure of the anion and potassium counter ion of K[N(PPh$_3$)$_2$]$_2$[Bi(SeCN)$_6$] **14** showing atom labelling

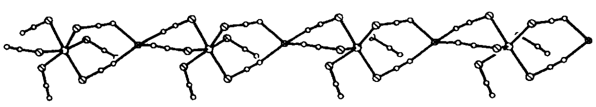

Fig. 9 Part of the crystal structure of K[N(PPh$_3$)$_2$]$_2$[Bi(SeCN)$_6$] **14** showing the molecular chains of composition {[KBi(SeCN)$_6$]$^{2-}$}$_x$

Table 8 Selected bond lengths (Å) and angles (°) for complex **14**

Bi–Se(1)	2.986(2)	Se(1)–C(1)	1.72(2)
Bi–Se(2)	2.938(3)	Se(2)–C(2)	1.71(2)
Bi–Se(3)	2.962(2)	Se(3)–C(3)	1.73(2)
Bi–Se(4)	2.941(3)	Se(4)–C(4)	1.74(2)
Bi–Se(5)	2.945(3)	Se(5)–C(5)	1.72(2)
Bi–Se(6)	2.881(3)	Se(6)–C(6)	1.72(2)
K–N(1$^{\rm I}$)	2.62(2)	C(1)–N(1)	1.17(2)
K–N(2$^{\rm I}$)	2.55(2)	C(2)–N(2)	1.18(2)
K–N(3)	2.66(2)	C(3)–N(3)	1.17(2)
K–N(4)	2.51(2)	C(4)–N(4)	1.17(2)
N(1)–K$^{\rm II}$	2.62(2)	C(5)–N(5)	1.20(2)
N(2)–K$^{\rm II}$	2.55(2)	C(6)–N(6)	1.17(2)
Se(6)–Bi–Se(2)	92.02(9)	Se(6)–Bi–Se(4)	88.80(9)
Se(2)–Bi–Se(4)	175.86(8)	Se(6)–Bi–Se(5)	96.77(8)
Se(2)–Bi–Se(5)	75.98(8)	Se(4)–Bi–Se(5)	99.90(8)
Se(6)–Bi–Se(3)	159.52(8)	Se(2)–Bi–Se(3)	78.73(8)
Se(4)–Bi–Se(3)	101.75(8)	Se(5)–Bi–Se(3)	98.60(8)
Se(6)–Bi–Se(1)	90.98(8)	Se(2)–Bi–Se(1)	90.27(7)
Se(4)–Bi–Se(1)	93.77(7)	Se(5)–Bi–Se(1)	164.39(9)
Se(3)–Bi–Se(1)	71.03(8)	N(4)–K–N(2$^{\rm I}$)	151.2(7)
N(4)–K–N(1$^{\rm I}$)	110.7(7)	N(2$^{\rm I}$)–K–N(1$^{\rm I}$)	93.1(7)
N(4)–K–N(3)	81.8(6)	N(2$^{\rm I}$)–K–N(3)	106.8(7)
N(1$^{\rm I}$)–K–N(3)	107.3(7)	C(1)–Se(1)–Bi	100.5(8)
N(1)–C(1)–Se(1)	177(3)	C(1)–N(1)–K$^{\rm II}$	142(2)
C(2)–Se(2)–Bi	101.2(8)	N(2)–C(2)–Se(2)	171(2)
C(2)–N(2)–K$^{\rm II}$	128(2)	C(3)–Se(3)–Bi	106.6(8)
N(3)–C(3)–Se(3)	177(3)	N(3)–C(3)–K	38(2)
Se(3)–C(3)–K	145.0(12)	C(3)–N(3)–K	126(2)
C(4)–Se(4)–Bi	93.2(8)	N(4)–C(4)–Se(4)	179(2)
C(4)–N(4)–K	166(2)	C(5)–Se(5)–Bi	100.5(9)
N(5)–C(5)–Se(5)	152(3)	C(6)–Se(6)–Bi	96.2(9)
N(6)–C(6)–Se(6)	177(3)		

Symmetry transformations used to generate equivalent atoms: I 1 + *x*, *y*, *z*; II *x* − 1, *y*, *z*.

Table 9 Atomic coordinates (× 10^4) for complex **14**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Bi	3 145(1)	1 043(1)	2 367(1)	C(30)	3 277(16)	1 770(7)	6 730(7)
K	8 302(7)	898(3)	2 344(4)	C(31)	844(15)	1 267(6)	7 214(7)
P(1)	−912(4)	1 464(2)	5 581(2)	C(32)	1 486(16)	937(7)	7 565(8)
P(2)	1 057(4)	1 364(2)	6 515(2)	C(33)	1 298(18)	898(8)	8 105(9)
P(3)	5 310(4)	1 511(2)	8 553(2)	C(34)	547(18)	1 199(8)	8 290(9)
P(4)	7 446(4)	1 614(2)	9 389(2)	C(35)	−82(20)	1 526(9)	7 969(10)
Se(1)	1 726(2)	1 107(1)	1 238(1)	C(36)	66(17)	1 557(7)	7 413(8)
C(1)	340(15)	1 018(9)	1 386(9)	C(37)	1 715(14)	842(6)	6 271(6)
N(1)	−582(14)	938(8)	1 501(9)	C(38)	2 461(15)	904(7)	5 887(7)
Se(2)	2 027(2)	131(1)	2 547(1)	C(39)	2 922(18)	497(8)	5 666(9)
C(2)	846(16)	318(8)	2 827(9)	C(40)	2 605(19)	71(9)	5 830(9)
N(2)	6(14)	488(7)	2 961(8)	C(41)	1 856(18)	−4(9)	6 203(8)
Se(3)	4 185(2)	409(1)	1 617(1)	C(42)	1 369(17)	396(7)	6 423(8)
C(3)	5 639(14)	329(9)	1 911(9)	C(43)	4 419(15)	2 027(6)	8 413(7)
N(3)	6 613(12)	252(7)	2 107(7)	C(44)	3 276(17)	1 985(8)	8 133(8)
Se(4)	4 389(2)	1 942(1)	2 258(1)	C(45)	2 585(19)	2 404(8)	8 059(8)
C(4)	5 706(15)	1 658(8)	2 227(9)	C(46)	3 019(18)	2 821(8)	8 238(8)
N(4)	6 581(13)	1 456(7)	2 209(8)	C(47)	4 138(16)	2 864(7)	8 512(7)
Se(5)	4 458(2)	701(1)	3 424(1)	C(48)	4 861(17)	2 464(7)	8 592(7)
C(5)	5 706(18)	1 041(9)	3 471(10)	C(49)	4 556(14)	1 118(6)	8 958(6)
N(5)	6 523(18)	1 249(10)	3 732(11)	C(50)	4 919(16)	647(7)	9 060(7)
Se(6)	1 400(2)	1 572(1)	2 822(1)	C(51)	4 387(15)	366(7)	9 404(7)
C(6)	1 764(23)	2 120(7)	2 593(10)	C(52)	3 518(18)	549(8)	9 659(8)
N(6)	2 019(19)	2 487(6)	2 415(9)	C(53)	3 201(17)	1 002(8)	9 591(8)
N(7)	−174(12)	1 521(5)	6 184(6)	C(54)	3 719(16)	1 294(7)	9 246(7)
N(8)	6 586(12)	1 634(5)	8 823(5)	C(55)	5 391(16)	1 197(7)	7 919(7)
C(7)	−2 021(14)	1 006(6)	5 561(6)	C(56)	6 215(17)	1 345(8)	7 612(8)
C(8)	−1 867(16)	636(7)	5 938(7)	C(57)	6 292(18)	1 123(8)	7 102(8)
C(9)	−2 728(16)	288(7)	5 904(8)	C(58)	5 549(18)	769(8)	6 935(9)
C(10)	−3 717(18)	320(8)	5 514(8)	C(59)	4 710(17)	615(7)	7 217(8)
C(11)	−3 887(18)	681(7)	5 145(8)	C(60)	4 656(15)	828(6)	7 721(7)
C(12)	−3 040(16)	1 025(7)	5 167(7)	C(61)	8 452(15)	1 129(6)	9 394(7)
C(13)	−1 705(14)	2 014(6)	5 408(7)	C(62)	9 428(14)	1 090(7)	9 806(7)
C(14)	−1 978(17)	2 146(7)	4 865(8)	C(63)	10 160(17)	672(7)	9 806(8)
C(15)	−2 704(16)	2 554(7)	4 739(8)	C(64)	9 872(18)	350(8)	9 374(8)
C(16)	−3 006(19)	2 811(9)	5 139(9)	C(65)	8 968(16)	389(7)	8 981(8)
C(17)	−2 746(18)	2 662(8)	5 661(9)	C(66)	8 237(17)	779(7)	8 994(8)
C(18)	−2 050(16)	2 269(7)	5 850(8)	C(67)	6 720(14)	1 548(6)	9 965(7)
C(19)	−53(15)	1 336(6)	5 058(7)	C(68)	5 875(15)	1 877(7)	10 047(7)
C(20)	−88(17)	880(7)	4 807(8)	C(69)	5 207(17)	1 826(7)	10 453(7)
C(21)	670(18)	799(8)	4 421(8)	C(70)	5 331(17)	1 451(7)	10 779(8)
C(22)	1 405(18)	1 134(8)	4 327(8)	C(71)	6 190(17)	1 117(8)	10 735(8)
C(23)	1 501(17)	1 566(8)	4 577(8)	C(72)	6 849(17)	1 158(7)	10 314(7)
C(24)	756(16)	1 657(7)	4 934(7)	C(73)	8 272(15)	2 164(6)	9 487(7)
C(25)	2 089(15)	1 840(7)	6 543(7)	C(74)	8 489(16)	2 395(7)	9 036(8)
C(26)	1 685(17)	2 297(7)	6 391(7)	C(75)	9 122(17)	2 813(8)	9 083(8)
C(27)	2 524(17)	2 681(8)	6 439(7)	C(76)	9 528(18)	3 005(9)	9 582(9)
C(28)	3 702(17)	2 590(8)	6 618(7)	C(77)	9 344(17)	2 784(8)	10 053(9)
C(29)	4 093(20)	2 148(8)	6 757(8)	C(78)	8 673(15)	2 337(7)	10 018(8)

Experimental

General Considerations.—All experiments were performed under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk techniques. All solvents were dried and distilled over appropriate drying agents immediately prior to use. Infrared spectra were recorded in thf solution in CaF_2 cells or as KBr discs on a Nicolet SXB FTIR spectrophotometer and microanalytical data were obtained at the University of Newcastle.

The complexes $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ were prepared according to refs. 14 and 15, $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ and $K[Fe(CO)_2(\eta\text{-}C_5H_5)]$ by reduction of the corresponding dimers with Na/K in thf and $K[Co(CO)_3(PPh_3)]$ according to ref. 16. The compounds $BiCl_3$, $Bi(NO_3)_3{\cdot}5H_2O$, KSCN, KSeCN, $[N(PPh_3)_2]Cl$ and 18-crown-6 were procured commercially and used without further purification.

Preparations.—$[Bi(SCN)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **6**. The solids $Bi(NO_3)_3{\cdot}5H_2O$ (0.380 g, 0.784 mmol) and KSCN (0.288 g, 2.350 mmol) were dissolved in thf (30 cm^3) and the solution stirred for 18 h at room temperature. This resulted in a yellow solution [containing $Bi(SCN)_3$, see text] and a grey solid (presumably KNO_3). This mixture was then cooled to 0 °C and a filtered solution of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$, prepared by a Na/K reduction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.384 g, 0.784 mmol) in thf (20 cm^3) was added which resulted in the immediate formation of a dark green solution. After stirring for 1 h, the solution was filtered through Celite and the solvent volume of the filtrate reduced to around 10 cm^3 by vacuum. An overlayer of hexane (30 cm^3) was then added and solvent diffusion over a period of days at −25 °C afforded dark green crystals of complex **6** (36%).

Compound **6** was also produced, but in far lower yields, from $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$[9a] (0.166 g, 0.176 mmol) and KSCN (0.034 g, 0.352 mmol) in thf (10 cm^3) at room temperature with subsequent work-up as described above.

$[Bi(SCN)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **7**. A solution of $Bi(SCN)_3$ was prepared in an identical manner to that described for complex **6** using $Bi(NO_3)_3{\cdot}5H_2O$ (1.197 g, 2.467 mmol) and

KSCN (0.718 g, 7.402 mmol). After cooling to 0 °C a filtered solution of $K[Fe(CO)_2(\eta\text{-}C_5H_5)]$, prepared by a Na/K reduction of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.873 g, 2.467 mmol) in thf (25 cm^3), was added which resulted in the immediate formation of a dark brown solution. This solution was stirred for 20 h at room temperature during which time it changed to dark green. It was then filtered through Celite and the solvent from the filtrate removed by vacuum to leave a dark solid. This solid was redissolved in CH_2Cl_2 (10 cm^3) giving a dark green solution and hexane (30 cm^3) was then added as an overlayer. Solvent diffusion at −25 °C over 4 d resulted in dark green crystals of complex **7** (22%).

$[Bi(SCN)\{Co(CO)_3(PPh_3)\}_2]$ **8**. A solution of $Bi(SCN)_3$ was prepared as described for complex **6** from $Bi(NO_3)_3$ (0.324 g, 0.67 mmol) and KSCN (1.195 g, 2.06 mmol) and cooled to 0 °C. To this was added a solution of $K[Co(CO)_3(PPh_3)]$, prepared by reduction of $[Co_2(CO)_8]$ (0.321 g, 0.67 mmol) with KOH followed by refluxing with 2 equivalents of PPh_3, which resulted in a dark green solution which was stirred for 2 d. After filtration through Celite, the volume of the filtrate was reduced to about 10 cm^3 and hexane (30 cm^3) was added as an overlayer. Solvent diffusion at −25 °C over a period of 7 d afforded a dark green powder which was shown by infrared spectroscopy to be a mixture of complexes **8** and $[Co(SCN)(CO)_3(PPh_3)]$.

[K(18-crown-6)]SCN. Potassium thiocyanate (0.476 g, 4.898 mmol) was dissolved in MeOH (10 cm^3) and 18-crown-6 (1.30 g, 4.898 mmol) was added which gave a clear solution which was stirred for 24 h. Diethyl ether (20 cm^3) was then added as an overlayer and solvent diffusion at −25 °C over a period of 2 d resulted in the required product as a white crystalline powder (90%).

$[K(18\text{-crown-}6)][Bi(SCN)_2\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ **9**. A sample of complex **7** (0.103 g, 0.17 mmol) was dissolved in CH_2Cl_2 (15 cm^3) which gave a green solution to which [K(18-crown-6)]SCN (0.060 g, 0.17 mmol) was then added. The resulting solution was stirred for 30 min, with no colour change, and hexane (30 cm^3) was then added as an overlayer. Solvent diffusion over a period of 5 d at −25 °C resulted in dark green crystals of complex **9** (20%).

$K[K(18\text{-crown-}6)]_2[Bi(SCN)_6]$ **10** *and* **11**. The compounds $Bi(NO_3)_3\cdot 5H_2O$ (0.201 g, 0.414 mmol) and KSCN (0.121 g, 1.243 mmol) were dissolved in MeCN (10 cm^3) and stirred for 24 h. The resultant yellow solution was filtered through Celite, [K(18-crown-6)]SCN (0.150 g, 0.414 mmol) was added and the solution stirred for 24 h. Diethyl ether (30 cm^3) was then layered over the solution and solvent diffusion at room temperature over several weeks afforded a mixture of orange crystals of complex **10** and yellow crystals of **11** in low yield.

$Bi(SeCN)_3$ **12**. Samples of $BiCl_3$ (0.267 g, 0.847 mmol) and KSeCN (0.366 g, 2.542 mmol) were placed in a flask, dissolved in thf (10 cm^3) and stirred for 24 h which resulted in a red solution and a grey solid. The red solution was transferred to another flask and Et_2O (30 cm^3) added as an overlayer. Solvent diffusion at room temperature over a period of days afforded red crystals of compound **12** (69%).

$[Bi(SeCN)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **13**. Samples of $[Bi\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$[9a] (0.313 g, 0.332 mmol) and $Bi(SeCN)_3$ (0.087 g, 0.166 mmol) were placed in a flask and dissolved in thf (10 cm^3) at −78 °C. The resulting brown solution was stirred for 30 min and allowed to warm to room temperature during which time it became dark green. Hexane (30 cm^3) was then added as an overlayer and solvent diffusion over several days at −30 °C afforded complex **13** as an impure green powder.

$K[N(PPh_3)_2]_2[Bi(SeCN)_6]$ **14**. This compound was synthesised by two methods.

(*a*) The solids $[N(PPh_3)_2][BiCl_4]$[11] (0.167 g, 0.188 mmol) and KSeCN (0.108 g, 0.751 mmol) were dissolved in MeCN (5 cm^3) which gave a yellow-orange solution. This was stirred for 18 h which resulted in a red solution and a grey solid. The solution was transferred to a separate flask and Et_2O (20 cm^3) added as an overlayer. Solvent diffusion over 2 d at room temperature afforded dark red crystals of complex **14** (58%).

(*b*) The salts $[N(PPh_3)_2][BiCl_4]$[11] (0.383 g, 0.431 mmol), $[N(PPh_3)_2]Cl$ (0.494 g, 0.861 mmol) and KSeCN (0.372 g, 2.583 mmol) were dissolved in MeCN (10 cm^3) and stirred for 18 h which resulted in a red solution and a grey solid. The solution was transferred to another flask and Et_2O (30 cm^3) added as an overlayer. Solvent diffusion over a period of 4 d afforded dark red crystals of complex **14** (83%).

X-Ray Crystallography of Complexes **6**, **10**, **11** *and* **14**.—Many of the details of the structure analyses carried out are listed in Table 10. X-Ray diffraction measurements were made at room temperature (295 K) using Siemens four-circle P3m diffractometers on single crystals mounted in thin-walled glass capillaries with graphite-monochromated Mo-Kα X-radiation (λ = 0.710 73 Å). Cell dimensions for each analysis were determined from the setting-angle values of centred reflections.

For each structure analysis the intensity data were collected by Wyckoff ω scans for unique portions of reciprocal space and corrected for Lorentz, polarisation, crystal decay and long-term intensity fluctuations, on the basis of the intensities of three check reflections repeatedly measured during data collection. Corrections for X-ray absorption effects were applied on the basis of azimuthal scan data. In the case of complex **6** data collected for $2\theta > 40°$ had to be discarded because of a machine malfunction which led to seriously inaccurate intensities. The structures were solved by heavy-atom (Patterson and Fourier difference) methods, and refined by full-matrix least squares against F (for **6** and **10**) or F^2 (for **11** and **14**). Except where noted below, all non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints or restraints. For **6** the displacement ellipsoids in the $Mo(CO)_3(\eta\text{-}C_5H_5)$ fragment centred on Mo(2) are indicative of substantial librational motion and perhaps disorder. In the structure of **10** Bi lies at a centre of inversion and K(1) on a crystallographic two-fold axis; only the bismuth, potassium and sulfur atoms were assigned anisotropic displacement parameters. In **11** the bismuth, potassium and two thiocyanate groups [of S(3) and S(4)] lie on crystallographic mirror planes of symmetry; the carbon and oxygen atoms of the 18-crown-6 ligand were assigned isotropic displacement parameters. In the structure of **14** only the bismuth, potassium, phosphorus and selenium atoms were assigned anisotropic displacement parameters. Weak similarity constraints were applied to the geometries of the SeCN ligands requiring that they have similar Se–C, C–N and Se $\cdots$ N distances (a total of 45 restraints). Despite this one selenocyanate group is apparently bent at carbon [Se(5)–C(5)–N(5) 152(3)°], presumably as a result of a disorder that was not readily modelled. All hydrogen atoms were constrained to ideal geometries with C–H 0.96 Å and assigned fixed isotropic displacement parameters. An isotropic extinction correction was applied in the case of **6**, parameter x refined to 0.000 17(2) where $F_c = F_c^{uncorr}/(1 + 0.002xF_c^2/\sin 2\theta)^{\frac{1}{4}}$.

Final difference syntheses showed no chemically significant features, the largest being close to the metal atoms. Refinements converged smoothly to residuals given in Table 10. Calculations were made with programs of the SHELXTL-PLUS[17] and SHELXL 93[18] packages as implemented on a Siemens R3m/V structure determination system. Complex neutral-atom scattering factors were taken from ref. 19.

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

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Table 10 Details of structure analyses of compounds **6**, **10**, **11** and **14**

	6	**10**	**11**	**14**
Formula	$C_{17}H_{10}BiMo_2NO_6S$	$C_{30}H_{48}BiK_3N_3O_6S_3$	$C_{30}H_{48}BiK_3N_3O_6S_3$	$C_{78}H_{60}BiKN_8P_4Se_6$
M	757.2	1203.4	1203.4	1955.6
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group (no.)	$P2_1/c$ (14)	$C2/c$ (15)	$Pnma$ (62)	$P2_1/n$ (14)
a/Å	11.310(6)	26.430(9)	29.072(12)	11.582(3)
b/Å	11.604(6)	8.782(6)	14.828(6)	28.079(10)
c/Å	16.801(8)	20.360(9)	11.719(6)	24.587(7)
β/°	107.53(4)	96.01(3)	90	99.61(2)
U/Å^3	2103(2)	4699(4)	5052(4)	7884(4)
Z	4	4	4	4
D_c/g cm^{-3}	2.39	1.70	1.58	1.65
$F(000)$	1400	2408	2408	3800
μ(Mo-Kα)/cm^{-1}	96.5	43.4	40.4	51.9
Crystal dimensions (mm)	1.0 × 0.9 × 0.75	0.4 × 0.5 × 0.6	0.56 × 0.51 × 0.51	0.5 × 0.45 × 0.35
2θ range/°	3–55	3–40	3–50	3–45
Scan width (ω/°)	0.9	1.6	1.0	1.0
Total data	5462	4513	4633	10 912
Unique data	4817	2110	4633	10 310
'Observed' data, N_o	3296	1768	3752	8277
Observation criterion [$F_o^2 > n\sigma(F_o^2)$]	2	2	0	0
Minimum, maximum transmission coefficient	0.021, 0.057	0.349, 0.629	0.052, 0.085	0.064, 0.099
R_{merg}	0.050	0.018	0	0.085
Disordered atoms	None	None	None	(one SeCN group)
Least-squares variables, N_v	248	145	191	453 (45 restraints)
R	0.052[a]	0.029[a]	0.066[b]	0.069[b]
R'	0.060[a]	0.038[a]	0.136[b]	0.132[b]
S	1.23[a]	1.35[a]	0.93[b]	0.95[b]
g	0.0010	0.0005	0.077	0.068
Final difference map features (e Å^{-3})	+2.2, −1.6	+0.6, −0.7	+0.6, −0.8	+1.2, −0.8

[a] $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$; $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, $\sigma_c^2(F_o)$ = variance in F_o due to counting statistics. [b] Residuals calculated for reflections with $F^2 > 2\sigma(F^2)$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^4)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N - N_v)]^{\frac{1}{2}}$; $R = \Sigma|F_o - F_c|/\Sigma|F_o|$; $\Delta = F_o^2 - F_c^2$; $N = N_o$ + restraints; $w = [\sigma_c^2(F_o^2) + (gP)^2]^{-1}$, $\sigma_c^2(F_o^2)$ = variance in F_o^2 due to counting statistics, $P = [\max.(F_o^2,0) + 2F_c^2]/3$.

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