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Review Paper

Structural Studies of the Pseudohalides of the s and p-Block Elements

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Contents

1. Introduction

The purpose of this review is to present a survey of the structures of the pseudohalide derivatives of all the s and p block elements. The original definition of pseudohalides by Birckenbach and Kellerman[1] encompassed the ions: CN^-, NCO^-, NCS^-, $NCSe^-$, $NCTe^-$ and N_3^-. No structural data are available for tellurocyanate, $NCTe^-$, which has been prepared only recently[2]; added to the original list, for the present purposes, are fulminate CNO^-, cyanamide NCN^{-2}, and thionylimide, NSO^-. Of these pseudohalides, cyanide bears the closest chemical resemblance to the halides proper: on relaxing sufficiently the demand of chemical similarity, almost any species X^- could, to some extent, be regarded as a pseudohalide. Nevertheless, fulminate is sufficiently similar to cyanide, and cyanamide and thionylimide are sufficiently similar to azide to justify inclusion.

The great majority of the structures discussed herein have been determined by unambiguous methods: in the solid state by neutron or X-ray diffraction, in the vapour phase by electron diffraction or by rotational spectroscopy, either Raman or microwave. Almost inevitably a number of the simpler structures were determined many years ago, before the introduction of the sector method of electron diffraction, or before the introduction of the least squares method to the refinement of structures deduced from diffraction experiments.

Bond lengths are quoted throughout in Ångstroms, bond angles in degrees: estimated standard deviations are given in parentheses. Older structures generally have no errors quoted. Except where explicitly stated otherwise, structural parameters for solid state compounds are the mean values of structurally equivalent but crystallographically non-equivalent parameters.

2. Pseudohalides of Hydrogen

A. Hydrogen Cyanide and Fulminic Acid

In the vapour phase both hydrogen cyanide, HCN, and its N-oxide fulminic acid, HCNO, are linear molecules. For hydrogen cyanide, microwave spectroscopy has given[3] the bond lengths r(H–C), 1.063(1)Å; and r(C–N), 1.155(1)Å: distances found[4] in a microwave study of fulminic acid are r(H–C) 1.027(1)Å; r(C–N), 1.161(15)Å; and r(N–O), 1.207(15)Å. The rather large uncertainties in the C–N and N–O distances of fulminic acid are a consequence of the closeness of the nitrogen atom to the centre of mass: however the partitioning of the C···O distance in fulminic acid (r(N–O)/r(C–N) = 1.040) is the same as in methyl fulminate[5] (r(N–O), 1.2189(4)Å; r(C–N), 1.1671(6) Å; r(N–O)/r(C–N) = 1.044).

The short N–O distance in fulminic acid (and methyl fulminate), may be compared with those in *cis*-azobenzene dioxide[6], 1.264(4)Å, and trimethylamine N-oxide[7], 1.388(5)Å. For neither hydrogen cyanide[3] nor trimethylamine[8] does the formation of the N-oxide significantly alter the rest of the geometry.

The structure of hydrogen cyanide has also been determined[9] in the solid phase; the linear molecules form infinite linear chains. The repeat distance along the chain is 4.34Å, and a Fourier refinement led to a

TABLE I. Geometrical Parameters for Isocyanic and Isothiocyanic Acids.

Compound	r(H–N)Å	r(N–C)Å	r(C–X)Å[a]	<(H–N–C)°	Ref.
HNCO	0.987(10)	1.207(10)	1.171(10)	128.1(0.5)	10
HNCS	0.989(3)	1.216(7)	1.560(3)	135.0(0.2)	11

[a] X = O or S.

C–N distance of 1.154Å, while from a least squares refinement a value of 1.19(15)Å was obtained. Whatever the precise value of r(C–N) in solid hydrogen cyanide, this gives for the C(–H)· · ·N distance a value of 3.15–3.19Å, so placing the H· · ·N distance in the range 2.09–2.13Å.

B. Isocyanic Acid and Isothiocyanic Acid

Microwave studies of isocyanic acid[10], HNCO, and isothiocyanic acid[11], HNCS, have yielded the ground-state geometrical parameters set out in Table I. The N–C–X (X = O, S) fragment of each molecule was assumed to be linear.

In isocyanic acid, the C–O distance, 1.171Å, is typical of double-bond distances between singly-connected oxygen and doubly-connected carbon, being comparable with the value 1.1619(5) observed[12] in carbon dioxide, but is shorter than the typical distance between singly-connected oxygen and triply connected carbon; for example, in acetaldehyde the C–O distance is 1.2155(20)Å[13]. The C–S distance in isothiocyanic acid 1.560Å is similarly close to that found in carbon disulphide 1.5529(50)Å[14], but substantially shorter than that observed[15] in thiourea, 1.720(9)Å.

Likewise, the C–N distances in these two acids, 1.207Å and 1.216Å are shorter than the C–N distance, 1.27Å, found between doubly-connected nitrogen and triply-connected carbon in dimethyl glyoxime[16].

An X-ray study[17] of crystalline HNCO revealed linear NCO fragments with r(N–C) of 1.18(2)Å and r(C–O) of 1.18(2)Å: the hydrogen atoms were not found, but the molecules appear to be joined by N· · ·H–N hydrogen bonds with the N· · ·N distance approximately 3.07Å.

C. Hydrazoic Acid

A microwave study of gaseous hydrazoic acid has yielded[18] the following geometrical parameters, by making the assumption that the N_a–N_b–N_c fragment is linear: r(H–N_a), 0.975(15)Å; r(N_a–N_b), 1.237(2)Å; r(N_b–N_c), 1.133(2)Å; and <(H–N_a–N_b), 114.1(0.5)°. The N_b–N_c distance differs little from the corresponding N–N distance, 1.1286(2)Å in the isoelectronic nitrous oxide[19], nor is the N_a–N_b distance appreciably different from the N–N bond lengths in azomethane[20] 1.24Å and azobenzene, 1.243(3)Å[21]. The angle at N_a of 114.1° is however markedly different from the corresponding angles in isocyanic and isothiocyanic acids, 128.1° and 135.0° respectively.

If we regard isocyanic and hydrazoic acids as CO and N_2 complexes respectively of the fragment HN, then the angles observed at N_a in these compounds are consistent with the view that CO is a better π-bonding group than N_2, as found in transition metal complexes of CO and N_2.

Alternatively, the structures of HNCO and HN_3 may be compared using the approach of Sidgwick and Powell[22]. Removal of groups surrounding the atom N_a in closed shell configurations and their subsequent replacement as two electron donors leads to the conclusion that whereas in HN_3, N_a is surrounded by eight electrons, in HNCO it is surrounded by only six, so that a wider inter-bond angle is expected in HNCO.

D. Cyanamide

The unsubstituted molecule carbodiimide HN=C=NH appears to be unknown, only its isomer cyanamide H_2NCN having been isolated. This is more properly regarded as a cyanide of Group V and will be discussed in Section 7.

E. Thionylimide

Thionylimide has been studied by microwave spectroscopy[23], and found to have a *cis*-planar structure with r(H–N), 1.03Å; r(N–S), 1.51Å; r(S–O), 1.45Å; <(H–N–S), 116°; and <(N–S–O), 121°. The S–O distance and the interbond angle at sulphur may be compared with the corresponding parameters in the isoelectronic sulphur dioxide[24], 1.431(2)Å and 118.5(1.0)° respectively.

3. Pseudohalides of Group I

A. Cyanides

The cyanides of sodium, potassium, rubidium and caesium are dimorphic: the high temperature forms of NaCN[25], KCN[26] and RbCN[27] crystallise in a 6:6 sodium chloride structure, while the high temperature form of CsCN[27] crystallises with an 8:8 caesium chloride arrangement. The behaviour of the cyanide ion as an apparently spherical entity can be rationalised by assuming either disorder or rotation of the CN^- groups. An X-ray study[28] of NaCN was unable to distinguish between these possibilities, but in a later neutron study[29] on KCN, the data were consistent only with rotating cyanide groups.

In a further neutron study[30] of cubic KCN at 180° K, free rotation of the cyanide groups was ruled out: no preferred orientation of the cyanide groups could be established and the authors suggest that they undergo rapid interchanges between a number of equivalent orientations separated by only a low activation barrier. A sophisticated analysis of the cyanide group motion in NaCN, studied by neutron diffraction, has appeared[31].

At low temperatures, rotation of the cyanide groups ceases and the symmetry of the crystals is reduced. NaCN[25] and KCN[26] adopt an orthorhombic modification of the sodium chloride structure in which all the cyanide groups are parallel, while CsCN[27] forms a rhombohedral modification of the caesium chloride structure with the cyanide group lying along the three-fold axis.

Only a single crystalline modification of LiCN is known: this forms an orthorhombic structure[32] in which each lithium ion is coordinated by the nitrogens of three cyanide ions and the carbon of a fourth, at the vertices of a somewhat distorted tetrahedron. No rotation of cyanide ions occurs. The C–N distances observed are, in LiCN[32], 1.15 Å, in NaCN[25], 1.05 Å, and in KCN[29], 1.16(1) Å: these are closely comparable with that found in hydrogen cyanide[3], 1.155(1) Å. The change in coordination from 4:4 in LiCN *via* 6:6 in NaCN, KCN and RbCN to 8:8 in CsCN is noteworthy.

The only structurally characterised hydrated cyanide of Group I is sodium cyanide dihydrate[33], $NaCN \cdot 2H_2O$. In this the cyanide ions have r(C–N) of 1.07 Å, appear to be ordered and are hydrogen bonded to water molecules with N · · · (H)O of 2.81 Å: $NaCN \cdot 2H_2O$ is essentially isostructural with $NaBr \cdot 2H_2O$[34].

B. Cyanates and Azides

Probably the most thoroughly studied of the Group I pseudo-halides are the azides[35]. Sodium azide crystallises in two modifications; β-NaN_3 has a rhombohedrally distorted NaCl structure[36], in which the linear and symmetrical azide groups lie along the three-fold axes with r(N–N) 1.173(12) Å, while α-NaN_3 although monoclinic is very closely similar to the β form: in α-NaN_3 the N–N distance[36] is 1.167(13) Å. Lithium azide is monoclinic and isostructural with α-NaN_3[36], with r(N–N) of 1.162(14) Å. In lithium and sodium azides the azide groups are all parallel, but evidence was found for extensive libration of the azide ions yielding corrections to the N–N distance of 0.007 Å in LiN_3 and α-NaN_3 and 0.005 Å in β-NaN_3.

The azides of potassium, rubidium and caesium are isostructural[37] crystallising in a tetragonal modification of the 8:8 CsCl structure, with linear azide groups lying along the edges of the CsCl type cell, related by the four fold rotation axis. The central nitrogen atoms of eight azide groups are disposed about each metal ion at the vertices of a tetragonally compressed cube: the closest neighbours of each metal ion are the terminal nitrogen atoms of eight azide ions which approximately describe a square antiprism. The N–N distances are: in KN_3, 1.18(1) Å; in RbN_3, 1.17(11) Å; and in CsN_3, 1.17(7) Å[37].

Lithium azide monohydrate is markedly different in structure from the anhydrous material[38]. It contains two types of lithium ion: those of type I are octahedrally coordinated by the terminal nitrogen atoms of six azide groups and each pair of adjacent lithiums is joined by two linear and symmetrical bidentate azide ions, so forming an infinite network. The lithium ions of the second type are octahedrally coordinated by six water molecules. In the azide groups, the N–N distance is 1.174(2) Å. This structure is remarkable, not least as it provides a rate example of a molecular species of a first row atom, *i.e.* $Li(OH_2)_6^+$, with a coordination number which is greater than four.

The cyanates of the Group I elements, so far as they have been investigated, appear to be isostructural with the corresponding azides. Sodium cyanate is rhombohedral, isostructural with β-NaN_3[39]; the NCO group is strictly linear with r(C–O) of 1.13 Å, and r(C–N) of 1.21 Å. Sodium fulminate, NaCNO, appears to be essentially isostructural[40].

TABLE II. Structural Relationships Between Some Pseudohalides of the Alkali Metals, Thallium and Ammonium.

Structure	Space Group	Compounds	Ref.
6:6 NaCl structure	Fm3m	NaCN (H.T.), KCN (H.T.), RbCN (H.T.)	25, 26, 27
Orthorhombic modification of NaCl	Imm2	NaCN (L.T.), KCN (L.T.)	25, 26
Rhombohedral modification of NaCl	R3m	β-NaN_3, NaNCO, NaCNO	36, 39, 40
8:8 CsCl structure	Pm3m	CsCN (H.T.), TlCN	27, 88
Tetragonal modification of CsCl	P4/mcm	NH_4CN	151
Tetragonal modification of CsCl	I4/mcm	KNCO, RbNCO, CsNCO, TlNCO	41
		KN_3, RbN_3, CsN_3, TlN_3	37
Rhombohedral modification of CsCl	R3m	CsCN (L.T.)	27
Orthorhombic modification of CsCl	Pmna	NH_4N_3	152

The cyanates of potassium, rubidium and caesium are all tetragonal[41], crystallising in space group I 4/mcm, and appear to be isostructural with the analogous azides.

C. Thiocyanates

The only Group I thiocyanate whose structure has been investigated is the potassium salt which crystallises with an orthorhombic structure markedly different from that of any other Group I pseudohalide[40,42]. The NCS group is linear, with r(N–C) 1.15Å and r(C–S) 1.79Å. It should perhaps be emphasised that this is not a modern determination, and that although the general features of the structure are probably correct, undue weight should not be placed on the values of the geometrical parameters obtained: in particular the C–S distance derived is exceptionally long and may result from a slight misplacement of the carbon and/or sulphur atoms.

The structural relationships between a number of pseudo-halides of the Group I metals, and a few ammonium and thallium(I) pseudo-halides, are summarised in Table II.

4. Pseudohalides of Group II

A. Group IIA

Like those of Group I, the pseudohalides of Group IIA appear to be largely ionic in character: only the azides and the cyanamides have been subject of detailed structural investigations.

(i) Azides

Strontium azide is orthorhombic[43] and contains linear azide ions having r(N–N) of 1.163(24)Å; the azide ions undergo extensive thermal motion and the authors estimated a librational correction of +0.007Å. Each strontium ion is surrounded by eight azide ions whose central nitrogen atoms describe an approximate square antiprism, as do also the eight nearest neighbours (terminal nitrogens). Calcium azide crystallises in the same space group and with closely similar cell dimensions, and seems to be virtually identical in structure with the strontium salt[44].

Barium azide crystallises with a quite different monoclinic structure[45]: the nearest neighbours of each barium ion are the terminal nitrogen atoms of nine different azide ions, which adopt a tri-capped trigonal prismatic arrangement. The unit cell contains two crystallographically distinct azide ions and in one r(N_a–N_b) is 1.168(2)Å, and r(N_b–N_C) is 1.164(2)Å; in the other r(N_a–N_b) is 1.178(2)Å and r(N_b–N_c) is 1.157(2)Å; neither differs significantly from linearity. As with a number of other ionic azides[37], evidence was found for appreciable rigid-bar type torsional motion of the azide ions, but in this example no librational corrections were estimated.

A number of hydrated azides of the Group IIA metals exist, but their crystallographic study has not progressed[44,46,47] beyond the determination of cell dimensions and, in some cases, of a tentative space group. In view of the remarkable structural changes which accompany the hydration of lithium azide[36,38], further structural investigation of these hydrates would surely be worthwhile.

(ii) Cyanamides

In both $CaCN_2$ and $SrCN_2$, discrete linear NCN^{-2} ions can be discerned. Calcium cyanamide crystallises in a rhombohedrally distorted form of the CsCl structure[48], and so is closely related structurally to β-NaN_3: the NCN^{-2} ion is strictly linear and symmetrical, having r(C–N) of 1.224(16)Å. Although the structure can be related to the 8:8 CsCl arrangement, the extent of the rhombohedral distortion is such that each calcium ion is closely coordinated by only six nitrogen atoms, belonging to six different cyanamide ions, in a trigonal antiprismatic arrangement. The coordination of the cyanamide ions by calcium is, of course, similar.

In strontium cyanamide[49], there are two sets of cyanamide ions, populated in the ratio 3:1. The members of the smaller set must either be freely rotating about carbon in parallel planes or be disordered within these planes: the electron density of the two nitrogen atoms of this set of anions is distributed uniformly throughout a toroidal region around the carbon atoms. The C–N distance derived for the ordered or stationary set of cyanamide ions is 1.28(7)Å; this does not differ significantly from the value found[48] for the calcium salt.

B. Group IIB

By contrast with the elements of Group IIA, zinc, cadmium and mercury exhibit a great variety of structural types amongst their pseudohalides, both in binary compounds and in complexes.

(i) Cyanides

The binary cyanides of zinc and cadmium crystallise in the anti-cuprite structure: while it is probable that the M–C–N–M fragments are linear, the carbon and nitrogen atoms were not placed accurately[50,51]. Mercury(II) cyanide, on the other hand, has been the subject[52] of an accurate 3-dimensional neutron study. The structure consists of essentially linear molecules, but each mercury atom is bonded weakly to two nitrogen atoms in addition to the carbon atoms of two cyanide groups: the principal structural parameters for mercury(II) cyanide are set out in Table III, along with those of a number of other cyano-mercury(II) species.

The cyanide species $K_2M(CN)_4$ (M = Zn, Cd, Hg) are all isostructural[53]: while discrete tetrahedral $M(CN)_4^{-2}$ ions can readily be recognised, the struc-

TABLE III. Selected Geometrical Parameters for Cyano-Mercury(II) Compounds.

Compound	r(Hg–C)Å	r(C–N)Å	r(R–Hg)Å	<(R–Hg–C)°	<(Hg–C–N)°	Method	Ref.
$Hg(CN)_2$	2.015(3)	1.137(3)	2.015(3)	175.0(2.0)	177.0(3.0)	N	52
CH_3HgCN	2.01(5)	1.18(7)	2.15(5)	180(6.0)	175(15)	X	55
	2.05(1)	1.14(1)	2.08(2)	180(2.0)	180(3)	N	
$Hg(CN)_2 \cdot KI$	2.079(96)	1.046(139)	2.079(96)	176.5(2.5)	171(8)	X	56
$(NCHg)_2O$[a]	2.02(4)	1.28(6)	2.04(3)	158	173	X	57
	1.97(4)	1.18(6)	1.99(3)	*ca.* 180	*ca.* 180		
$NCHgNO_3$	2.063(9)[b]	1.128(13)	2.063(9)[b]	180	180	X	58
$Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$	2.04(8)[c]	1.156[d]	2.04(8)[c]	177(4)	174(5)	X	59
$2Hg(CN)_2 \cdot Zn(NO_3)_2 \cdot 7H_2O$	2.06(3)	1.11(4)	[e]	174.1(1.2)	175.9(2.6)	X	60
	1.97(3)	1.18(4)	[e]	[e]	177.9(2.8)		

[a] Two types of Hg: see text. [b] C,N not distinguished. [c] Orientation of CN assumed by authors. [d] Values assumed by authors. [e] Two CN environments within $Zn(OH_2)_4(NCHgCN)_2$ molecules: first row of values refers to $(CN)_I$, second to $(CN)_{II}$; see text.

ture nevertheless bears a startling resemblance to the AB_2O_4 spinel structure, with CN^- ions in the oxygen sites, Zn^{+2}, Cd^{+2} or Hg^{+2} ions in the tetrahedral A site and K^+ ions in the octahedral B site. The zinc complex has more recently been studied by neutron diffraction and the authors considered[54] four possible models for the cyanide geometry: they were able to reject models involving (i) rotating cyanide ions, (ii) disordered cyanide ions, and (iii) cyanide ions whose coordination is Zn–N–C–K–C–N–Zn, i.e. bonded to zinc *via* nitrogen. The best fit to the neutron diffraction data was obtained for a structure involving the cyanide bonded to zinc *via* the carbon atoms, thus K–N–C–Zn–C–N–K: the C–N bond distance, corrected for thermal motion, was found to be 1.157(9)Å.

All the other cyanide species of Group IIB which have been investigated structurally are mercury derivatives, whose principal geometrical parameters are set out in Table III.

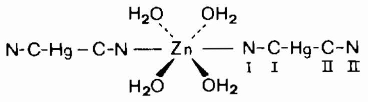
Methylmercury(II) cyanide has been investigated both by X-ray and by neutron diffraction[55]. The overall accuracy of the structure derived from the neutron data is higher, but none of the differences between the neutron and the X-ray structures is significant. The methyl group was found to be rotating about the H_3C–Hg bond: no significant intermolecular interactions were observed. The neutron diffraction studies of $Hg(CN)_2$[52], CH_3HgCN[55] and $K_2Zn(CN)_4$[54] are important as they demonstrate quite unambiguously that the cyanide ligand coordinates to metals (at least in Group IIB) *via* carbon rather than *via* nitrogen.

The stoichiometrically similar compounds $Hg(CN)_2 \cdot KI$ and $Hg(CN)_2 \cdot HgO$ are in fact entirely different structurally. The structure of $Hg(CN)_2 \cdot KI$ consists[56] of essentially linear $Hg(CN)_2$ molecules lying approximately normal to sheets of iodide, ions such that the mercury is coordinated by two cyanide ions at 2.08Å and four more distant iodide ions at 3.38Å. The four coordinating iodide ions describe a square giving the mercury tetragonally compressed octahedral geometry. $Hg(CN)_2 \cdot HgO$, by contrast, consists of bis(cyanomercury(II))oxide, $O(HgCN)_2$, molecules[57]: the molecules are planar and contain two distinct types of mercury atom. The first type, Hg_I, exhibits an O–Hg_I–C angle of 158° (no errors were quoted by the author for interbond angles) and is bonded intermolecularly to two oxygen atoms at 2.53Å, with an O···Hg_I···O angle of 101°, giving the mercury atom Hg_I deformed tetrahedral geometry. The second type, Hg_{II}, has an O–Hg_{II}–C angle of approximately 180°, and takes part in intermolecular bonds with four nitrogen atoms, two at 2.84Å and 2.96Å, so taking on approximately octahedral geometry. The molecules are linked by the Hg_I···O interactions into columns, which are themselves linked together by the Hg_{II}···N bonds.

Cyanomercury(II) nitrate, $NCHgNO_3$, which is formally similar to bis(cyanomercury(II))oxide, exhibits yet another kind of structure[58]. The mercury atoms and the cyanide groups are formed into infinite, strictly linear cationic chains: –Hg–(C–N)–Hg–(C–N)–Hg–, with nitrate groups placed between the chains in a disordered arrangement. Within the chains, the carbon and nitrogen atoms of the cyanide groups were not distinguished: their separation was 1.128(13)Å and their average distance from the mercury atoms was 2.063(9)Å.

In the double salt $Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$, approximately linear chains –Hg–C–N–Ag–N–C–Hg–C–N–Ag– are found[59]. By fixing the C–N distance at 1.156Å and assuming that the cyanide groups are ordered with the carbon end coordinated to the mercury, the authors were able to derive mean parameters as follows: r(Hg–C) 2.04(8)Å; r(Ag–N) 2.11(6)Å; <(C–Hg–C) 177(4)°; <(N–Ag–N) 163(2)°; <(Hg–C–N) 174(5)° and <(Ag–N–C) 173(6)°. Both the mercury and the silver make a number of fairly close contacts with oxygen atoms in their equatorial planes.

By contrast with the infinite chains observed in the double salt of mercury(II) cyanide and silver nitrate, in the double salt with zinc nitrate, $2Hg(CN)_2 \cdot Zn(NO_3)_2 \cdot 7H_2O$, molecular species $Zn(OH_2)_4(Hg(CN)_2)_2^{+2}$ are discernible[60] in which mercury(II) cyanide molecules act as ligands, coordinating onto zinc *via* the nitrogen of one cyanide group thus:



so that there are two distinct HgCN groupings HgC_IN_I and $HgC_{II}N_{II}$ within the molecule. The geometrical parameters derived for the two distinct HgCN fragments do not differ significantly. The $Zn–N_I$ distance found was 2.13(2)Å with a $(Zn–N_I–C_I)$ angle of 173.5(2.6)°: the overall Zn–Hg distance is 5.30Å. In the cadmium analogue $Hg(CN)_2 \cdot Cd(NO_3)_2 \cdot xH_2O$, the Cd–Hg distance is 5.41Å, suggesting the presence of Hg–C–N–Cd chains[60]: however no evidence was found for the occurrence of carbon and nitrogen atoms along the Cd–Hg axis. The author has suggested that the structure may consist of independent $Hg(CN)_2$ molecules and cadmium ions surrounded by a disordered array of oxygen atoms.

(ii) Thiocyanates

No thiocyanate derivatives of zinc appear to have been characterised structurally. Two cadmium thiocyanates have been examined. In $K_2Cd(SCN)_4 \cdot 2H_2O$, the cadmium atoms are octahedrally coordinated by four sulphur atoms at a distance of 2.66Å, and by two nitrogen atoms at 2.45Å, there being two distinct types of NCS group in the asymmetric unit[61]: the dimensions of the thiocyanate groups are poorly determined, as the carbon and nitrogen atoms are placed with only limited accuracy. Octahedral cadmium atoms coordinated by 4S + 2N are found[62] also in $Cd(NCS)_2(etu)_2$, where etu denotes ethylenethiourea. The cadmiums are surrounded by two sulphur atoms from etu, two sulphur atoms from NCS, and two nitrogen atoms from NCS, the octahedra being thereby linked into infinite chains. In the NCS groups the dimensions found are: N–C, 1.19(10)Å; C–S, 1.55(5)Å; <(S–C–N), 165(9)°; and <(Cd–S–C), 109.1(44)°.

A substantial number of mercury(II) thiocyanate species have been structurally investigated: the principal geometrical parameters derived from the more accurate structure determinations are collected in Table IV. In mercury thiocyanate $Hg(SCN)_2$ the mercury exhibits approximately octahedral coordination, being surrounded by two sulphur atoms at 2.381Å and four nitrogen atoms at 2.81Å[63]. Distorted octahedral mercury is found[64] also in *cis*-$Hg(SCN)_2$(*o*-phen)$_2$ in which the mercury–sulphur distances are 2.58 and 2.62Å. Molecular mercury(II) thiocyanate occurs[65] also in $M^IHg(SCN)_3$ ($M^I = K^+$ or NH_4^+), which consist of M^+ and SCN^- ions and $Hg(SCN)_2$ molecules; the mercury is four coordinate, with two sulphur atoms at 2.47Å (K^+ salt) and 2.52Å (NH_4^+ salt) within the $Hg(SCN)_2$ molecule, and two further at 3.29Å belonging to SCN^- ions: for both the K^+ and NH_4^+ salts the carbon and nitrogen atoms of the thiocyanate are placed only with limited accuracy.

The thiocyanate groups act as bidentate bridging ligands in $CoHg(SCN)_4$[66], so that mercury is coordinated by four sulphur atoms and cobalt by four nitrogen atoms: in each case the metal coordination polyhedron is a rather distorted tetrahedron. Isostructural are $ZnHg(SCN)_4$[67], $CdHg(SCN)_4$[67], and $CoHg(SeCN)_4$[68]. The copper complex $CuHg(SCN)_4$ while stoichiometrically analogous to the foregoing, adopts a quite different structure in which the copper, instead of being tetrahedral, has tetragonally distorted octahedral coordination[69]: the mercury atom is still tetrahedrally coordinated by four sulphur atoms and the copper is coordinated by two axial sulphur atoms at a distance of 3.00Å, and by four equatorial nitrogen atoms at 1.94Å. The copper–ethylenediamine salt $Cu(en)_2Hg(SCN)_4$ similarly contains[70] tetrahedral mercury, coordinated by four sulphur atoms, and tetragonal copper, now coordinated by four equatorial nitrogen atoms (from ethylenediamine) at 2.07Å and two axial nitrogens (from SCN) at 2.58Å and 2.81Å: the two other distances from copper to nitrogen of SCN are very

TABLE IV. Principal Geometrical Parameters for Isothiocyanates for Mercury(II).

Compound	r(Hg–S)Å	r(S–C)Å	r(C–N)Å	<(Hg–S–C)°	<(S–C–N)°	r(Hg···X)Å	r(N···Y)Å	Ref.
$Hg(SCN)_2$	2.381(6)	1.62(2)	1.18(3)	97.6(0.5)	177.5(1.3)	2.81(1)[a]	–	63
$CoHg(SCN)_4$	2.558(4)	1.635(14)	1.20(2)	97.4(0.5)	177.9(1.7)	–	1.921(16)[b]	66
$CuHg(SCN)_4$[c]	2.63	1.66	1.20	92.4	160.3	–	–	69
	2.53	1.82	1.21	98.4	169.1	–	1.94[d]	
$Cuen_2Hg(SCN)_4$	2.55	1.57	1.34	102.1	163.2	–	2.58[e] 2.81	70

[a] 4 Hg···N distances of 2.81(1)Å. [b] 4 N···Co distances of 1.921(16)Å. [c] Two types of SCN group. [d] 4 N···Cu distances of 1.94Å. [e] 2 N···Cu distances of 2.58 and 2.81Å.

TABLE V. Geometrical Parameters for Azides of Group IIB.

Compound	$r(M\text{–}N_a)$Å	$r(N_a\text{–}N_b)$Å	$r(N_b\text{–}N_c)$Å	$<(M\text{–}N_a\text{–}N_b)^\circ$	$<(N_a\text{–}N_b\text{–}N_c)^\circ$	Coordination Number of Metal	Ref.
$Zn(N_3)_2(NH_3)_2$	1.988(10)	1.19(2)	1.16(2)	128(2)	176(2)	4	72
$Zn(N_3)_2(py)_2$[a]	1.937(10)	1.161(18)	1.132(10)	128.9(1.0)	175.0(1.5)	4	73
$Cd(N_3)_2(py)_2$[a]	2.344(16)	1.167(20)	1.141(21)	135(1)	179.1(1.7)	6	74
α-$Hg(N_3)_2$	2.09(2)	1.19(3)	1.16(3)	115(2)	174(2)	7	75

[a] py = pyridine.

long, 3.60Å and 4.06Å, and are too long to be significant in the coordination of the copper. In the two copper compounds the overall structure is dominated by the steric requirements of the tetragonal copper(II) ion.

Both ClHgSCN and BrHgSCN consists of molecules containing linear two coordinate mercury[71]: the Hg–S distances are 2.31Å and 2.38Å respectively. These distances are very close to that observed[63] in $Hg(SCN)_2$ in which the mercury coordination was 2S + 4N. It may be significant that Hg–S distances in those species containing four-coordinate mercury lie in the fairly narrow range 2.53–2.63Å. It is unfortunate that no Hg–N distances were quoted for *cis*-$Hg(SCN)_2$(*o*-phen)$_2$; in view of the observed[64] Hg–S distances (2.58 and 2.62Å) more precise specification of the mercury coordination polyhedron would be welcome.

(iii) Azides

The binary azides of zinc and cadmium are structurally uncharacterised: some complexes of these azides with amines have been investigated and the principal geometrical parameters for these are collected in Table V. Both the bis-ammonia and bis-pyridine adducts of zinc azide, $Zn(N_3)_2(NH_3)_2$[72] and $Zn(N_3)_2(py)_2$[73] exist as monomeric molecules containing four-coordinate zinc. The geometrical differences between the $Zn\text{–}N_3$ fragments in these two molecules are insignificant: the Zn–N (amine) distances are 2.017(10)Å and 2.031(10)Å. By contrast, $Cd(N_3)_2(py)_2$ contains[74] six coordinate cadmium: each cadmium atom is coordinated by two pyridines which occupy *trans* positions in an approximate octahedron, and by four azide groups which serve to link the CdN_6 octahedra into a three-dimensional framework. The mean Cd–N (azide) distance is 2.344Å and the mean Cd–N(pyridine) distance is 2.349Å.

In α-$Hg(N_3)_2$ discrete molecules can be discerned[75] containing approximately linearly coordinated mercury: the N–Hg–N angle is 175(1)°, and the mean $Hg\text{–}N_a\text{–}N_b$ angle is 115(2)°, with a dihedral angle of 43° between the two azide groups. The Hg–N distance has a mean value of 2.09(2) and there are five other nitrogen–mercury distances in the range 2.67–3.16Å. The effective coordination number of the mercury is seven; the coordination polyhedron about mercury is a monocapped trigonal prism with the directly-bonded N–Hg–N fragment lying in the diagonal of the capped rectangular face.

(iv) Other pseudohalides

The only other pseudohalogen derivatives of the Group IIB metals which have been investigated are the tetra-fulminatometallate anions, $M(CNO)_4^{-2}$: no X-ray study has been performed but the vibrational spectra of these ions are fully in accord with T_d symmetry[76] implying linear M–C–N–O chains.

5. Pseudohalides of Group III

There appears to be no structural information on the pseudohalides of scandium, yttrium, lanthanum or gallium. Only relatively few studies have been made of the pseudohalides of boron, aluminium, indium and thallium. Perhaps more than in any other group, the compounds of Group III are almost wholly covalent among the lighter elements of the group and almost wholly ionic among the heavier: in view of this, all the pseudohalides of boron and aluminium will be discussed together, followed by those of indium and thallium.

A. Boron and Aluminium

Three isothiocyanate derivatives, all of boron, have been studied, and the geometrical data for the pseudohalide fragments are collected in Table VI. In ammonia–isothiocyanatoborane[77], NH_3BH_2NCS the B–N bond distance, 1.534(8)Å is closely comparable with that found in ammonia–triborane-7, $NH_3B_3H_7$, (1.581(3)Å)[78], whereas in tetra-B-isothiocyanatotetra-N-t-butylborazocine, $(Me_3CNBNCS)_4$[79] and 6-isothiocyanatodecaborane-14, 6-$B_{10}H_{13}NCS$[80], the B–N distances are 1.431(11)Å and 1.435(6)Å respectively: the shorter distances have been taken to indicate π-interaction between the nitrogen atom of the isothiocyanate group and the boron to which it is attached[79,80]. However, the B–N–C angle seems to be independent of any $p_\pi \rightarrow p_\pi$ interaction involving the isothiocyanate

TABLE VI. Selected Geometrical Parameters for Boron Isothiocyanates.

Compound	r(B–N)Å	r(N–C)Å	r(C–S)Å	<(B–N–C)°	<(N–C–S)°	r(B···C)Å	Ref.
$NH_3 \cdot BH_2NCS$	1.534(8)	1.137(8)	1.627(6)	177.5(0.6)	179.2(0.5)	2.670	77
$(Me_3CNBNCS)_4$	1.431(11)	1.172(10)	1.560(8)	176.4(0.8)	177.3(0.7)	2.602	79
6-$B_{10}H_{13}NCS$	1.435(6)	1.149(5)	1.581(4)	171.0(0.6)	178.1(0.6)	2.576	80

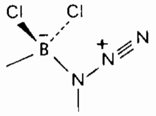
group, and is close to 180° in each compound. If it is assumed that the lowest of the B–N–C angles, 171° in 6-$B_{10}H_{13}NCS$, is limited by the non-bonded B···C interaction, then adoption of Bartell's[81] non-bonded radius for carbon, 1.25Å, yields a non-bonded radius of 1.33Å for boron: this is entirely reasonable in view of the values for C, 1.25Å; N, 1.14Å; O, 1.13Å; F, 1.08Å. That the B···C distances do not determine the B–N–C angle in the other two *iso*thiocyanatoboranes may be a consequence of the effect of crystal forces on this angle: it is known[82] that such forces can cause substantial perturbations to those inter-bond angles whose deformation force constants are low, such as M–N=C or M–O–M′.

In ammonia–isothiocyanatoborane the N–C distance is much shorter, 1.137Å and the C–S distance is much longer, 1.627Å, than the corresponding distances in isothiocyanic acid[11], 1.216Å and 1.560Å respectively. This was ascribed by the authors[77] to an important contribution to the structure from the form

$$B\text{–}\overset{+}{N}{\equiv}C\text{–}S^-$$

However the N–C bond is distinctly short, 1.149Å in 6-$B_{10}H_{13}NCS$[80], although the lengthening of the C–S bond is far less marked than in $NH_3 \cdot BH_2NCS$, so that such a rationalisation seems not to be wholly satisfactory.

For each of boron and aluminium, a single molecular azide derivative has been structurally characterised. The structure of $(BCl_2N_3)_3$ consists[83] of B_3N_3 rings made up of BCl_2 groups and one terminal nitrogen atoms of each azide group. The boron atoms are approximately tetrahedral, while the ring nitrogen atoms are planar: the mean N_a–N_b and N_b–N_c distances are 1.260(10)Å and 1.088(10)Å respectively, and the N_a–N_b–N_c angle is 178.5(1.1)°. In the $(Me_3AlN_3AlMe_3)^-$ anion, studied[84] as its potassium salt, the azide group is again bonded to two other atoms, here aluminium, through the same terminal nitrogen. The Al_2N_3 fragment is planar with N_a–N_b and N_b–N_c distances of 1.21(2)Å and 1.13(2)Å respectively and an angle N_a–N_b–N_c of 178(1)°. In the boron compound, the B–N–B angle is 127.5(0.6)°, while the corresponding angle in the aluminium species is 127(1)°: an angle close to 120° might have been expected in each of these compounds, and it seems that the opening of the angle to *ca.* 127° is more probably steric than electronic in origin. Although in $(BCl_2N_3)_3$, the N_a–N_b is significantly longer than that in hydrazoic acid[18] (1.260(10)Å *vs.* 1.237(2)Å) and the N_b–N_c significantly shorter (1.088(10)Å *vs.* 1.133(2)Å), a difference which might be attributed to contributions from



this is not reflected in the azide group dimensions of the $(Al_2Me_6N_3)^-$ ion, which differ insignificantly from those in HN_3. The compounds $M^I(Al_2Me_6X)$ have also been prepared[85] for X = NCS and NCSe: vibrational spectra indicate structures similar to that of the azide analogue with the pseudohalide bonded to aluminium through sulphur or selenium.

B. *Indium and Thallium*

The only pseudohalogen derivatives of indium which have been structurally investigated are the tricyanide, $In(CN)_3$, and the trithiocyanate, $In(SCN)_3$[86]. The tricyanide appears[86] from powder photography to be isostructural with indium trichloride[87]: this implies an ionic structure consisting of essentially close-packed (freely-rotating?) cyanide groups with the indium atoms in octahedral interstices. The trithiocyanate appears from powder photography to be cubic and the authors suggest a structure containing bridging SCN groups in which the angle In–S–C is about 109° and C–N···In about 180°. Complete structure determinations would be welcome for both these pseudohalides.

The thallium pseudohalides which have been characterised structurally are all derivatives of thallium(I), TlX, and are all isostructural with the corresponding pseudohalides of the larger alkali metals (see Table II). Thallium cyanide crystallises in the cubic 8:8 CsCl structure[88], presumably with freely rotating cyanide groups. Thallium azide crystallises in the same tetragonally distorted form of the CsCl structure as the azides of potassium, rubidium and caesium[37]: the azide group is linear and symmetrical with an N–N distance of 1.16(24)Å. The large standard deviation on this distance is probably a reflection of the difficulty of placing accurately light nitrogen atoms in the presence of the very heavy thallium atom if using X-ray data alone.

Thallium cyanate is similarly isostructural with the cyanates of potassium, rubidium and caesium[41], which are themselves isostructural with the corresponding azides. Thallium thiocyanate is isostructural with the potassium salt[42,89].

6. Pseudohalides of Group IV

Very many compounds with a pseudohalogen bonded to carbon have been structurally characterised[90]: in general the structural interest has attached principally to the rest of the carbon framework, and consequently only a few of the simpler examples will be discussed here.

A. Cyanides and Fulminates

The principal geometrical parameters of the cyanides of the Group IV elements are set out in Table VII, together with those of fulminates. It may be noted that substitution of hydrogen by halogen in CH_3CN does not lead to the expected shortening of the C–C and C–N distances[19,91,92]. Methyl substitution giving Me_3CCN leaves the C–N distance essentially unchanged but causes an increase in the ≡C–C≡ distance from 1.458 Å to 1.495 Å[93], an increase which is exactly paralleled in the corresponding acetylenes. Methyl cyanide forms 1 : 1 adducts with boron trihalides: in the boron trifluoride adduct, the nitrogen–boron distance is 1.635 Å, with all the skeletal atoms in a straight line[94]. The C–C distance is unchanged, but the C–N distance is decreased to 1.124 Å, presumably because the unshared electron pair on nitrogen is somewhat antibonding in character: the adducts with boron trichloride and boron tribromide appear[95] to be isostructural.

Silyl cyanide has been studied in the vapour both by electron diffraction[96] and by microwave spectroscopy[97]: the structures obtained are identical. In the solid state silyl cyanide appears[98] to form continuous chains with a short Si–C distance and a long Si···N distance.

It is noteworthy that in both the silyl and germyl derivatives, the M–C distance (M = Si or Ge) is significantly greater in the cyanides[96,97,99] than in the isoelectronic acetylenes[100,101,102], whereas in the corresponding methyls, the C–C distances are identical[19,103].

Trimethylgermyl cyanide forms long chains in the solid state[104]. The Ge–C and C–N distances are normal, being 1.98(6) Å and 1.15(13) Å respectively: there is a long distance intermolecular interaction, N→Ge, of 3.57 Å which is reflected in the CH_3–Ge–CH_3 angle of 114.8(1.4)°. Infinite chains are also found in trimethyltin cyanide[105] but now the $SnMe_3$ groups are planar, the cyanide groups are end-over-end disordered, and each atom of the cyanide group is 2.49(2) Å distant from the next tin atom in the chain, indicating a much stronger N→Sn interaction. Both trimethylgermyl cyanide in chloroform solution[106] and trimethylsilyl cyanide in the vapour phase[107] appear to consist of equilibrium mixtures of the normal C-bonded cyanide and the N-bonded isocyanide: no isocyanide of a group IV element other than carbon has been isolated. Both triethyltin cyanide and trimethyllead cyanide appear to be isostructural with trimethyltin cyanide, but only the heavy atoms could be located in these structures[108]: if it is assumed that the C–N distance is the same in all three compounds, the mean value of the M–C and M–N distances is for Et_3SnCN

TABLE VII. Geometrical Parameters for Cyanides and Fulminates of Group IV.

Compound	r(M–C)Å[a]	r(C–N)Å	r(N···M)Å[b]			Phase[c]	Method[d]	Ref.
CH_3CN	1.458(1)	1.157(1)	–			V	R	19
CF_3CN	1.461	1.153	–			V	R	91
CCl_3CN	1.460	1.158[e]	–			V	R	92
CMe_3CN	1.495(15)	1.159(1)	–			V	R	93
CH_3CNBF_3	1.458	1.124	–	r(N–B)	1.635 Å	S	X	94
SiH_3CN	1.848(2)	1.158(2)	–			V	E	96
	1.847(5)	1.158(2)	–			V	R	97
GeH_3CN	1.919(1)	1.155(1)	–			V	R	99
Me_3GeCN	1.98(6)	1.15(13)	3.57			S	X	104
Me_3SnCN	2.49(2)[f]	1.09(2)	2.49(2)[f]			S	X	105
$Me_2Si(CN)_2$	1.86(3)	1.14(2)	3.48(3) 3.97(2)			S	X	109
$Me_2Ge(CN)_2$	1.96(2)	1.12(2)	3.28(2) 3.84(2)			S	X	109
$Me_2Sn(CN)_2$	2.27(7)	1.09(12)	2.68(11)			S	X	109
MeCNO	1.4414(4)	1.1671(6)	–	r(N–O)	1.2189(4) Å	V	R	112
Me_3CCNO	1.458(10)	1.169[e]	–	r(N–O)	1.217 Å[e]	V	R	113

[a] M = C, Si, Ge or Sn. [b] Intermolecular distance in solid. [c] V = Vapour, S = Solid. [d] E = Electron diffraction; R = Microwave spectroscopy; X = X-ray diffraction. [e] Value assumed by authors. [f] Cyanide groups disordered.

2.44 Å, and for Me_3PbCN 2.59 Å, comparable with the 2.49 Å observed for Me_3SnCN[105].

In the structures of $Me_2Si(CN)_2$ and $Me_2Ge(CN)_2$, discrete molecules can be recognised[109]. In each, one cyanide nitrogen makes a short contact with a neighbouring molecule, so forming infinite chains: the other $N \cdots M$ distance is greater than the van der Waals contact distance, so that these structures are rather similar to that of Me_3GeCN[104]. The observed CH_3–M–CH_3 angles are for M = Si, 120.2(1.0)°, and for M = Ge, 120.9(0.8)°. By contrast, in $Me_2Sn(CN)_2$ the two $N \cdots Sn$ interactions are now equivalent[109]: the Sn–C distance is 2.27(7) Å, while the $Sn \cdots N$ distance is 2.68(11) Å, and the CH_3–Sn–CH_3 angle is now 148.7 (2.5)°, so that this structure approaches the ionic situation containing $(CH_3)_2Sn^{+2}$ groups and detached cyanide ions. The limiting condition of such a structure would have linear $(CH_3)_2Sn^{+2}$ ions (isoelectronic and isostructural with $(CH_3)_2Tl^+$ [110] and $(CH_3)_2Hg$[111]), with octahedral coordination of the tin completed by four cyanide groups. It may be noted that the NC–M–CN angle in $Me_2Sn(CN)_2$ is 85.3(3.7)°; in $Me_2Ge(CN)_2$, 100.9(0.7)°; and in $Me_2Si(CN)_2$, 101.1(1.0)°. $Me_2Pb(CN)_2$ appears[109] to be isostructural with the tin analogue.

Of the Group IV elements, only carbon forms isolable, molecular N-bonded isocyanides. In the simplest of these, methyl isocyanide[19], the C–N distance is 1.424 Å and the N=C distance 1.166 Å: the C–N=C angle is 180°, conferring C_{3v} symmetry on the molecule as a whole.

Two fulminates of carbon have been studied by microwave spectroscopy: both are symmetric tops. In methyl fulminate, CH_3CNO, the three skeletal bonded distances were determined explicitly[112] as C–C, 1.4414(6) Å, C–N 1.1671(6) Å and N–O 1.2189(4) Å. The C–C distance is slightly shorter than that observed in the parent compound CH_3CN[19], while the C–N distance is slightly larger: in view of the small uncertainties in these two determinations, the differences between corresponding distances are significant. It is of interest that the change in the C–N distance induced by N-oxidation is in the opposite sense to that induced[94] by N-coordination to boron trifluoride.

In t-butyl fulminate, $(CH_3)_3CCNO$, not all the independent geometrical parameters could be found explicitly[113]: by making plausible assumptions about the structure of the $(CH_3)_3C$–group and setting r(C–N) at 1.169 Å and r(N–O) at 1.217 Å, the ≡C–C≡ distance was found to be 1.458(10) Å. The ratio r(N–O)/r(C–N) in this structure is 1.041, from the assumed values: this may be compared with observed values of 1.040 in fulminic acid[4] and 1.044 in methyl fulminate[112]. The frequency of skeletal deformation δ(C–C–N) in $(CH_3)_3CCNO$ was deduced as 86 ± 20 cm^{-1}.

Several salts of cyanoform, containing the $C(CN)_3^-$ anion, have been structurally investigated. These are of interest in that in the sodium[114], copper(II)[115] and ammonium[116] salts, the central carbon atom of the anion is not pyramidal as expected but essentially planar. The ammonium salt crystallises in a monoclinic modification of the CsCl structure: the anion exhibits C_{3v} symmetry with linear C–C–N fragments and a mean $C–\hat{C}–C$ angle of 119.6(1.0)°. The deviation from planarity implied by this is felt by the authors to be real[116]. The sodium salt by contrast has 6-fold coordination of the cation rather than 8-fold as found in the ammonium salt. The mean C–C–C angle is 120°, and the mean C–C–N angle 179.0°: the authors feel[114] that any deviations from planarity in this case are due to crystal packing effects. The copper salt[115] also contains a strictly planar anion. The most accurate bond distances were obtained for the sodium salt[114]: corrected for libration, the mean C–C distance is 1.408(2) Å and the mean C–N 1.153(3) Å.

B. Isocyanates and Isothiocyanates

The principal geometrical parameters of the simpler isocyanates and isothiocyanates of Group IV are set out in Table VIII. It will be noted that in general the N–C and C–O distances in the isocyanates are close to those in HNCO[10], 1.207 Å and 1.171 Å respectively, while the N–C and C–S distances in the isothiocyanates are close to those in HNCS[11], 1.216 Å and 1.560 Å. In particular, in an isocyanate the N–C distance is greater than the C–O distance.

Methyl isocyanate has been studied both by microwave spectroscopy[117] and by electron diffraction[118]: the microwave structure cannot be regarded as a uniquely accurate structure, only as a "best-fit" to the observed spectrum whose interpretation is complicated by extensive interaction between the molecular vibrations and both the overall and the internal rotations of the molecule. In the electron diffraction study of CH_3NCO[118], it was found that the peaks in the radial distribution curve assigned to the N=C and C=O distances overlap, so that these distances are strongly correlated: it seems probable that the alternative assignment, with r(N–C) 1.202 Å and r(C–O) 1.168 Å is more appropriate. Such a reversal will not affect the C–N=C angle which is determined largely by the non bonded C(methyl)$\cdots$O distance; this is unchanged by the reversal of the N–C and C–O distances.

Methyl isothiocyanate likewise has been studied by both electron diffraction[118] and microwave methods[117]: as with CH_3NCS, the microwave structure is only a "best-fit", for similar reasons. Subject to this limitation on the accuracy of the microwave study, the two structures are in reasonable agreement.

Two silyl isocyanates, SiH_3NCO and Me_3SiNCO, and one isothiocyanate SiH_3NCS, have been investigated by both microwave spectroscopy and electron diffraction. That apparently different structures result from the two techniques is readily understood in terms

TABLE VIII. Geometrical Parameters of Group IV Isocyanates and Isothiocyanates.

Compound	r(M–N) Å[a]	r(N–C) Å	r(C–Z) Å[b]	r(M···C) Å	<(M–N–C)°	Method[c]	Ref.
CH_3NCO	1.450(4)	1.168(5)	1.202(5)	2.464(8)	140.3(0.4)	E	118
	1.437	1.207	1.171	2.486	140(1)	R	117
SiH_3NCO	1.703(4)	1.216(9)	1.164(8)	2.833(6)	151.7(1.2)	E	121
	1.699	1.150	1.179	–	180	R	119
Me_3SiNCO	1.76(2)	1.20(1)	1.18(1)	2.86	150(3)	E	124
	1.690	1.16[d]	1.179[d]	–	180	R	123
SiF_3NCO	1.648(10)	1.190[d]	1.168(25)	2.799(12)	160.7(1.2)	E	125
$SiCl_3NCO$	1.646(8)	1.219(7)	1.139(8)	2.679	138.0(0.4)	E	127
$SiCl_2(NCO)_2$	1.687(4)	1.217(5)	1.146(5)	2.698	136.0(1.0)	E	127
$SiCl(NCO)_3$	1.684(5)	1.213(5)	1.144(5)	2.767	145.0(2.0)	E	127
$Si(NCO)_4$	1.688(3)	1.209(2)	1.165(2)	2.777	146.4	E	128
GeH_3NCO	1.831(4)	1.190(7)	1.182(7)	2.858	141.3(0.4)	E	130
CH_3NCS	1.479(8)	1.192(6)	1.597(5)	2.525(16)	141.6(0.4)	E	118
	1.452	1.216	1.561	2.562	147.5(1.0)	R	117
SiH_3NCS	1.704(6)	1.197(7)	1.563(6)	2.873(6)	163.8(2.6)	E	121
	1.714(10)	1.211(10)	1.560[d]	–	180	R	120
Me_3SiNCS	1.78(2)	1.18(1)	1.56(1)	2.89	154(2)	E	124
$Si(NCS)_4$	1.673(10)	1.198(12)	1.510(13)	2.865	172.5(0.8)	X	129
Me_3SnNCS	2.15(6)	1.15(7)	1.64(7)[e]	3.29	173(5)	X	132
$Me_2Sn(NCS)_2$	2.139(13)	1.174(14)	1.571(3)[f]	3.28	163.5(1.7)	X	133

[a] M = C, Si, Ge or Sn. [b] Z = O or S. [c] E = Gas phase electron diffraction; R = Microwave spectroscopy; X = X-ray diffraction. [d] Value assumed by authors. [e] Intermolecular S···Sn distance 3.13(2) Å. [f] Intermolecular S···Sn distance 3.21(1) Å.

of the experiments. Structure determination by microwave spectroscopy depends on the observation and assignment of rotational transitions within a given vibrational state, and the experimentally derived moments of inertia apply to that particular vibrational state. Electron diffraction, on the other hand, measures interatomic distances directly, averaged over all the thermally populated vibrational states. If a molecule such as SiH_3NCO has a low frequency skeletal bending vibration, δ(Si–N–C), then several excited states of this mode will be populated at the temperature of the experiment: these have probability maxima displaced from the linear configuration, so that the structure observed, averaged over all the bent excited states as well as the linear ground state, appears to be bent. The microwave structures in Table VIII all refer to vibrational ground states.

The most extensively studied of the isocyanates and isothiocyanates are SiH_3NCO and SiH_3NCS, which were shown by microwave spectroscopy[119,120] to have linear ground vibrational states. The electron diffraction data for these two compounds have been used to determine potential functions for the skeletal bending mode δ(Si–N–C)[121]: for the isocyanate the best function found was a mixed harmonic–quartic function with an energy minimum at an Si–N–C angle of 159° (observed 152°), while for the isothiocyanate, the best function found was purely harmonic, with the energy minimum at an Si–N–C angle of 180°. The skeletal bending frequencies deduced from these potentials were 20 cm^{-1} for silylisocyanate and 100 cm^{-1} for silylisothiocyanate, which may be compared (Table IX) with frequencies derived from the l-doubling constants, 30 cm^{-1} and 54 cm^{-1} [119,120] and from shrinkage calculations, 69 cm^{-1} and 113 cm^{-1} [122].

Trimethylsilyl isocyanate has been shown to be linear at nitrogen in its ground vibrational state[123]: in view of the similarity between its electron diffraction structure and that of trimethylsilyl isothiocyanate[124], it seems likely that this latter compound also has a linear ground state.

The skeletal bending frequency δ(Si–N–C) in Me_3SiNCO was deduced[123] as 64 ± 15 cm^{-1}, comparable with the estimates for SiH_3NCO.[119,120,122]

No distinction could be made, from electron diffraction data, between a purely harmonic potential and a harmonic–quartic function[125] for SiF_3NCO: the best harmonic potential yielded a skeletal frequency of 97 cm^{-1}: it seems probable that SiF_3NCO, $SiCl_3NCO$[125,126,127] and $SiCl_3NCS$[126] all have linear ground states. Although no estimates of skeletal bending frequencies are available for $SiCl_2(NCO)_2$[127], $SiCl(NCO)_3$[127] and $Si(NCO)_4$[128], there seems to be no reason for ruling out linear Si–N–C–O fragments in the vibrational ground states of these molecules. An X-ray study[129] of crystalline $Si(NCS)_4$ has revealed an Si–N–C angle of 172.5°: this is quite possibly a perturbation from the minimum energy linear configuration, arising from intermolecular forces.

Although germyl isocyanate might plausibly be

TABLE IX. Skeletal Bending Frequencies in Isocyanates, Isothiocyanates and Fulminates.

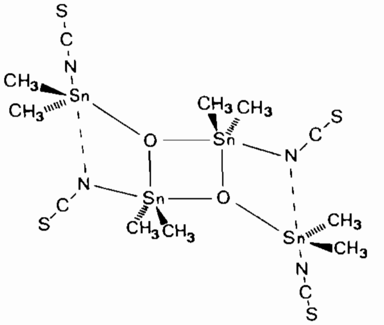
Compound	Vibration	Frequency (cm^{-1})	Method	Ref.
SiH_3NCO	δ(Si–N–C)	20	Potential function[a]	121
		30	l-doubling	119
		69	Shrinkage	122
SiH_3NCS	δ(Si–N–C)	100	Potential function[b]	121
		54	l-doubling	120
		113	Shrinkage	122
Me_3SiNCO	δ(Si–N–C)	64 ± 15	Vibrational satellites in microwave spectrum	123
SiF_3NCO	δ(Si–N–C)	97	Potential function[b]	125
$SiCl_3NCO$	δ(Si–N–C)	29	Combination bands in infrared spectrum	126
$SiCl_3NCS$	δ(Si–N–C)	24	Combination bands in infrared spectrum	126
Me_3CCNO	δ(C–C–N)	86 ± 20	Vibrational satellites in microwave spectrum	113

[a] Harmonic–quartic function. [b] Harmonic function.

thought from its electron diffraction structure[130] to have a linear Ge–N–C–O skeleton in its ground state, its microwave spectrum indicates that this is not so[131]: for an assumed value of 1.81 Å for the Ge–N distance, the Ge–N–C angle was deduced from the rotational constants to be 143°. Germyl isothiocyanate appears from its vibrational spectra to have a non-linear Ge–N–C–S skeleton[221].

Both Me_3SnNCS[132] and $Me_2Sn(NCS)_2$[133] are associated in the solid state, with weak intermolecular interactions between sulphur and tin. In the trimethyl tin compound, the Me_3Sn group is planar within experimental error, and the S···Sn–N–C–S group is approximately linear, giving the tin trigonal bipyramidal coordination. The Sn–N distance, 2.15 Å, is not unusually long (*cf.* Sn···N distance of 2.68 Å in $Me_2Sn(CN)_2$[109]), while the Sn···S distance, 3.13 Å is closely comparable with the short non-bonded Sn···S distance, 3.16 Å, in dimethyldithiocarbamatotrimethylstannane, $Me_3SnSCSNMe_2$[134, 135], but appreciably longer than its bonded Sn–S distance, 2.47 Å. In $Me_2Sn(NCS)_2$ the tin atoms are six-coordinate[133]: the Sn–N distances are 2.139 Å and the Sn···S, 3.20 Å, so that as with Me_3SnNCS, distinct and discrete molecules can be recognised in the structure. The tin coordination is somewhat distorted from the regular octahedron which would obtain for a completely ionic structure, having a CH_3–Sn–CH_3 angle of 148.9(0.9)° and an N–Sn–N angle of 86.6(0.5)°: these are virtually identical with the corresponding angles in $Me_2Sn(CN)_2$[109], CH_3–Sn–CH_3, 148.7° and NC–Sn–CN, 85.3°, strongly suggesting that the character of the bonds involving tin is essentially identical in the two compounds.

The structure of $(Me_2SnNCS)_2O$ consists of dimeric molecules[136]:



The whole structure has 2/m symmetry: the endocyclic tin atoms (those in Sn_2O_2 ring) have trigonal bipyramidal coordination. Weak inter-dimer bonds between sulphur and the exocyclic tin atoms give these tins very distorted octahedral coordination. The "bonded" Sn–N distances are Sn(endocyclic)–N 2.39(8) and Sn(exocyclic)–N 2.06(4) Å: the "non-bonded" Sn···N distance is 2.84(4) Å. The dimensions of the two crystallographically distinct N–C–S fragments are the same within experimental error: (endocyclic values first) N–C, 1.17(7) and 1.10(7); C–S, 1.61(6) and 1.64(5); N–C–S, 177.2(4.0)° and 179.9(8.0)°. The exocyclic Sn–N–C angle is 169.4(3.0)°; in an isolated dimer molecule this angle, and the corresponding angles in isolated Me_3SnNCS and $Me_2Sn(NCS)_2$ molecules would probably all be 180°.

Although no simple isocyanate of tin has been structurally investigated, the structure has been determined of $Me_3SnNCO \cdot Me_3SnOH$[137]: this consists of infinite OSnNSnOSnNSn chains, the N being that of the isocyanate group, and the O that of hydroxide. The two distinct Me_3Sn groups in the structure are both planar within experimental error. The two Sn–N distances are

2.43(5)Å and 2.75(5)Å, but the two Sn–O distances are 2.14(5)Å and 2.15(5)Å. This may indicate that the structure should be regarded as made up of $Me_3SnOH \cdot Me_3SnNCO$ molecules, so that the Sn–N distance of 2.43Å is "intramolecular", while that of 2.75Å is "intermolecular".

$Pb(NCS)_2(etu)_2$ (etu = ethylenethiourea) is isostructural[138] with the cadmium analogue[62].

Of the Group IV elements only carbon forms monomeric S-bonded normal thiocyanates: these are discussed with the other pseudohalides of sulphur.

C. Azides

Methyl azide has been investigated by both electron diffraction[108] and microwave spectroscopy[139]: while the microwave structure is only a best fit to the observed spectrum, the close correspondence between the two structures indicates that the skeleton is bent and fairly rigid.

In silyl azide, the $Si–N_a–N_b$ angle is 123.8(1.0)°[140] as found by electron diffraction. This is much smaller than the angles at N found by electron diffraction[121] for the analogous SiH_3NCO, 151.7°, and SiH_3NCS 163.8°: that silyl azide is bent at N_a in its vibrational ground state is suggested both by its vibrational spectra[141] and its unanalysed microwave spectrum[142]. Germyl azide has been investigated only by electron diffraction[130]: in view of the several results for silyl azide there seems no reason to suppose that germyl azide differs appreciably in its geometry from methyl azide. The principal structural parameters of methyl, silyl and germyl azides are summarised in Table X. The $N_a–N_b$ distance is always significantly longer than the $N_b–N_c$ distance, as found also for HN_3[18].

The structures of a number of organic azides have been described: possibly the most interest attaches to the structure of $C(N_3)_3^+ \; SbCl_6^-$[143]. This salt contains approximately planar propeller-like cations in which the three azide groups, although crystallographically different, do not differ significantly in their dimensions: the values quoted in Table X are mean values. The mean $N_a–N_b–N_c$ angle is 163.2°: as with other molecular pseudohalides in the solid state, the deviation from linearity observed here is most probably a reflection of the effect of intermolecular forces acting to deform an interbond angle, for which deformation the restoring force constant is very low (it has been calculated[121] that to alter the Si–N–C angle in SiH_3NCO from 180° to 140° requires the expenditure of no more than 1 kcal/mol).

The only tin azide to have been studied is $Me_3SnN_3 \cdot Me_3SnOH$, which appears to be isostructural[137] with $Me_3SnNCO \cdot Me_3SnOH$.

The α phase of lead(II) azide forms a complex structure, which has been the subject of a very careful three-dimensional neutron study[144]. Four distinct azide environments can be discerned in the structure: in three of these, the two terminal nitrogens of the azide group are each coordinated to two lead atoms, while in the fourth, one terminal nitrogen is coordinated to three lead atoms and the other to only one. In each of the 2 + 2 coordinate azides the two N–N distances are fairly similar, ranging from 1.160(8)Å to 1.193(8)Å with an average of 1.171Å. In the 3 + 1 azide group the N–N distance involving four-coordinate nitrogen is 1.213(10)Å, while that involving two-coordinate nitrogen is 1.147(13)Å. The overall structure is built of layers of symmetric (2 + 2) azide groups, lead atoms, and asymmetric (3 + 1) azide groups. Each lead atom is coordinated by eight nitrogens at the vertices of a distorted square antiprism: a similar arrangement is found in the azides of potassium, rubidium, caesium and thallium[27], and of strontium[43].

D. Carbodiimides and Cyanamides

Two organic carbodiimides have been investigated by X-ray methods. In bis-*p*-tolyl carbodiimide, $(p\text{-}CH_3C_6H_4N)_2C$, the dihedral angle between CNC planes is 88°[145], so that the structure is unambiguously allene-like: in bis-*p*-nitrophenyl carbodiimide, (*p*-

TABLE X. Geometrical Parameters of Some Group IV Azides and Carbodiimides.

Compound	$r(M–N_a)$Å[a]	$r(N_a–Y)$Å[b]	$r(Y–Z)$Å[c]	$r(M\cdots Y)$Å	$<(M–N_a–Y)$°	Method[d]	Ref.
CH_3N_3	1.468(5)	1.216(4)	1.130(5)	2.290(6)	116.8(0.3)	E	118
	1.46	1.24	1.13	2.30	117	R	139
$C(N_3)_3^{+}$[e]	1.336(11)	1.390(11)	1.051(10)	2.361	120(1)	X	143
SiH_3N_3	1.719(8)	1.304(11)	1.125(8)	2.674(10)	123.8(1.0)	E	140
GeH_3N_3	1.845(6)	1.250(9)	1.140(7)	2.684	119(2)	E	130
$(p\text{-}CH_3C_6H_4N)_2C$	1.430(4)	1.214(5)	–	2.37_6	127.8(0.3)	X	145
$(p\text{-}NO_2C_6H_4N)_2C$	1.399(8)	1.211(9)	–	2.38_6	132.0(0.6)	X	146
$(SiH_3N)_2C$	1.696(4)	1.206(5)	–	2.809(4)	150.6(1.2)	E	140
$(GeH_3N)_2C$	1.813(5)	1.184(8)	–	2.807	138(1)	E	130
$(Me_3Sn)_2CN_2$[f]	2.47(1)	1.24(2)	–	3.24	117.6(0.4)	X	147

[a] M = C, Si, Ge or Sn. [b] Y = N_b or C. [c] Z = N_c. [d] E = Gas phase electron diffraction; R = Microwave spectroscopy; X = X-ray diffraction. [e] As $SbCl_6^-$ salt. [f] Infinite structure, see text.

$NO_2C_6H_4N)_2C$, the dihedral angle is 113.5°, but the authors felt[146] that the deviation from the 90° expected for an allene-like structure was due principally to intermolecular forces.

Disilyl carbodiimide is found, by electron diffraction[140], to have an Si–N–C angle of 150.6°, and a dihedral angle of 102°: by analogy with silyl isocyanate and silyl isothiocyanate, it seems probable that the ground vibrational state of disilyl carbodiimide has a linear SiNCNSi group, and that the structure observed reflects the low frequency high amplitude skeletal deformations. Digermyl carbodiimide has a Ge–N–C angle, 138° almost identical[130] with that in germyl isocyanate, 141.3°: the authors felt that in this example, an allene-like structure was the best description.

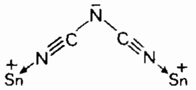
No discrete molecules can be recognised in crystalline $(Me_3Sn)_2CN_2$[147]. The structure consists of an infinite helical network of planar Me_3Sn groups and linear, symmetrical NCN groups. Each tin has trigonal bipyramidal geometry, with equatorial methyl groups and axial nitrogen atoms: the N–Sn–N angle is 173(2)° and the deviation from linearity is ascribed by the authors to intermolecular forces. The nitrogen atoms are all identical and have planar trigonal coordination by C + 2Sn. The Sn_2NCNSn_2 fragments have D_2 symmetry with a dihedral angle, between the Sn_2N planes, of 68°. The Sn–N distance 2.47(1) Å, is similar to the 2.49 Å observed[105] in the ionic Me_3SnCN, where the CN groups are disordered. The authors[147] consider the structure of $(Me_3Sn)_2CN_2$ to be intermediate between carbodiimide, cyanamide and ionic structures.

Somewhat analogous, at least in stoichiometry, to $(Me_3Sn)_2CN_2$ are the dicyanamides $Me_3SnC_2N_3$ and $Me_2Sn(C_2N_3)_2$[148]. Dicyanamides are often written in the form $RN(CN)_2$, but in these two tin derivatives, no coordination of the central nitrogen of the ligands to tin occurs. In each compound the NCNCN groups are planar: the SnNC and NCN angles are close to 180°, but the CNC angle is 129.6(1.1)° in the trimethyl tin compound, and 124.2(0.8)° in the dimethyl tin species.

$Me_3SnC_2N_3$ consists of infinite chains of strictly planar Me_3Sn groups and NCNCN groups, so that the tin atoms have trigonal bipyramidal coordination. $Me_2Sn(C_2N_3)_2$ consists of two dimensional sheets of approximately octahedral tin atoms joined by planar NCNCN groups, with the $SnMe_2$ groups normal to the sheets.

The central C–N distances are 1.263(15) Å and 1.289(10) Å in the trimethyl and dimethyl compounds respectively, the outer C–N distances 1.116(14) Å and 1.132(9) Å, and the Sn–N distances are 2.335(9) Å and 2.289(6) Å.

The form



is a major contributor to the structures of these dicyanamides.

$PbCN_2$ is quite definitely a cyanamide derivative[149]. The structure consists of a spiral PbNPbN chain with cyano groups attached to the intra-chain nitrogen atoms. The C–N(chain) distance is 1.25(6) Å, while the C–N(terminal) distance is 1.17(8) Å, not significantly shorter. The intra-chain nitrogen forms two bonds to lead with a mean Pb–N distance of 2.42(5) Å; both nitrogens make long Pb···N contacts between spirals.

E. Thionylimides

The only structurally characterised thionylimide of Group IV is the methyl derivative, CH_3NSO[150]. By adopting the N–S and S–O distances and the N–S–O angle from $HNSO$[23], a *cis*-planar structure consistent with the microwave spectrum was derived, having a C–N distance of 1.47 Å and a C–N–S angle of 122°.

7. Pseudohalides of Group V

By comparison with Group IV, rather few pseudohalides of Group V have been structurally investigated, or indeed chemically characterised. While the ammonium pseudohalides might plausibly be included with those of Group I, they are discussed here, followed by molecular pseudohalides.

A. Ammonium Pseudohalides

Ammonium cyanide crystallises[151] in a tetragonal (P4/mcm) modification of the 8:8 CsCl structure (*cf.* Table II): the cyanide groups are in fixed orientations, but the carbon and nitrogen atoms are disordered. The C–N distance is 1.09 Å.

Ammonium azide exists as an orthorhombic (Pmna) modification of the CsCl structure[152] (*cf.* Table II): the N–N distances are reported as 1.16 Å and 1.17 Å, but this difference is probably insignificant.

Ammonium thiocyanate crystallises in a monoclinic structure peculiar to itself[153], containing linear SCN^- ions with the S–C distance 1.59 Å and the C–N distance 1.25 Å. Ammonium silver thiocyanate, $NH_4Ag(SCN)_2$, consists[154] of ammonium ions, thiocyanate ions and AgSCN molecules: in the SCN^- ions, the distances are S–C, 1.707 Å and C–N 1.095 Å. $NH_4Hg(SCN)_3$ similarly consists[65] of NH_4^+ ions, SCN^- ions and $Hg(SCN)_2$ molecules: in the SCN^- ion the distances are S–C, 1.65 Å and C–N 1.09 Å.

B. Cyanides

Geometrical parameters for the Group V cyanides of the form X_2MCN are collected in Table XI. Of the compounds studied in the vapour phase, only PF_2CN has been investigated by both electron diffraction[155] and microwave spectroscopy[156]. The differences be-

TABLE XI. Geometrical Parameters for Group V Cyanides X_2MCN.

Compound	r(M–C)Å[a]	r(C–N)Å	<(M–C–N)°	<(X–M–X)°[b]	r(N···M)Å[c]	Method[d]	Ref.
NH_2CN	1.346(5)	1.160(5)	180[e]	113.5(0.1)	–	R	158
NF_2CN	1.386(9)	1.158(4)	173.9(2.2)	102.8(0.5)	–	R	157
PF_2CN	1.792(9)	1.165(5)	180[e]	97.9(0.3)	–	E	155
	1.815(5)	1.157(3)	171.2(0.8)	99.2(0.2)	–	R	156
$P(CN)_3$	1.788(20)	1.149(30)	171.6(3.0)	93.5(2.0)	2.85	X	159
Me_2AsCN	2.01(4)	1.16(7)	180(4)	105(2)	3.18	X	160
$MeAs(CN)_2$	1.98(3)	1.12(4)	175(2)	93.7(2.0)[f]	2.94	X	161
$As(CN)_3$	1.93(4)	1.11(5)	175(3)	90.5(2.0)	2.74	X	161, 162

[a] M = N, P or As. [b] X = H, F, CN or Me. [c] Shortest intermolecular r(N···M) in solid. [d] E = Electron diffraction; R = Microwave spectroscopy; X = X-ray diffraction. [e] Value assumed by authors. [f] Mean C–As–C angle.

tween these two structures for PF_2CN are just significant, in particular the differences in r(P–C). This is probably a reflection of the assumption in the electron diffraction study that the PCN fragment is linear, while it appears from the microwave study to be bent, with the CN group tilted away from the fluorines. Since the P···N and C–N distances are well determined in the electron diffraction experiment, being well separated peaks in the radial distribution curve, this assumption of linearity for PCN causes the P–C distance, which is overlapped by P–F, to be too short. This in turn will increase the refined value of the vibrational amplitude of the P–C distance; the authors note[155] that this amplitude is larger than expected.

In NF_2CN[157], the NCN fragment is bent, with the CN tilted away from the fluorines: NCN was assumed to be linear in a study of NH_2CN[158]. That the N–C (single) bond is longer in NF_2CN by some 0.040 Å than that in NH_2CN is surprising: substitution of hydrogen by halogen normally causes a slight shortening of nearby bonds. It seems unlikely that neglect of any NCN bending in NH_2CN could cause a large apparent change in the N–C distance, and it must be concluded that this difference is real.

Phosphorus tricyanide, $P(CN)_3$ consists of pyramidal molecules[159], each of whose CN groups engages in N···P interactions with neighbouring molecules. Within the molecule the PCN fragment is bent: this may be real or it may be a packing effect. The shortest intermolecular N···P distance is 2.85 Å: the other two are 2.96 Å and 2.97 Å.

The three cyanoarsines of Table XI have essentially similar structures in the crystal. Me_2AsCN consists of pyramidal molecules arranged into infinite, approximately linear, chains in which the molecules are joined by N···As interactions[160]. The structure is very similar to that of Me_3GeCN[104]: the cyanide groups are ordered as also are the methyl groups. No rotation of the Me_2As groups about the As–C bond occurs. In both $McAs(CN)_2$[161] and $As(CN)_3$[161,162], only one cyanide group engages in a close interaction with a neighbouring arsenic atom. Whereas in Me_2AsCN, there is a backbone AsCNAsCN with two methyl groups per arsenic, in $MeAs(CN)_2$ the same backbone has one methyl and one cyanide side group per arsenic, and $As(CN)_3$ has two cyanide side groups. With increasing cyanide substitution, the N···As distance becomes steadily smaller: 3.18 Å in Me_2AsCN, 2.94 Å in $MeAs(CN)_2$ and 2.74 Å in $As(CN)_3$. This may reflect an increase, with cyanide substitution, in the effective nuclear charge of arsenic. Were analogous derivatives of antimony and bismuth to be investigated it seems probable that these would mirror the trend found in the heavier Group IV cyanides, where the cyanide groups become progressively more ionic on descending the group.

A Group V cyanide not of the general type X_2MCN is nitrosyl cyanide ONCN. If it is assumed that the molecule is planar the following structure can be deduced[163] from the microwave spectrum: r(O–N), 1.228(5) Å; r(N–C)(central), 1.401(5) Å; r(C–N) (terminal), 1.170(5) Å; <(O–N–C), 114.7(1.0)°; and <(N–C–N), 172.5(3.0)° such that the CN group is tilted away from the NO group. This tilt is in the same sense as the tilts in NF_2CN[157] and PF_2CN[156].

C. Isocyanates, Isothiocyanates and Carbodiimides

As well as PF_2CN, several other PF_2 pseudohalides have been investigated by electron diffraction: the results of these studies are summarised in Table XII. Both PF_2NCO and PF_2NCS appear[164] from the electron diffraction experiments to be bent at nitrogen with <(P–N–C) 130.6° in PF_2NCO and 140.5° in PF_2NCS. The low frequency skeletal bend δ(P–N–C) was identified, from combination bands in the vibrational spectra, at 105 cm^{-1} in the isocyanate and 85 cm^{-1} in the isothiocyanate. Shrinkage corrections to the PNC angle calculated from the vibrational data led to corrected values for this angle of approximately 135° for PF_2NCO and approximately 144° for PF_2NCS. Unlike their SiI_3 analogues[121] therefore, these pseudohalides appear to be little different from the methyl[117,118] or, indeed, the hydrogen[10,11] species.

TABLE XII. Geometrical Parameters of N-bonded Pseudohalides of the PF_2 Group.

Compound	r(P–N)Å	r(N–C)Å	r(C–X)Å[a]	<(P–N–C)°	r(P···C)Å	δ(P–N–C)cm^{-1}	Ref.
PF_2NCO	1.683(6)	1.256(6)	1.168(5)	130.6(0.8)	2.67	105	162
PF_2NCS	1.686(7)	1.221(6)	1.553	140.5(0.7)	2.74	81	162
$(PF_2N)_2C$	1.680(6)	1.240(5)	–	132.8(0.5)	2.68	b	163

[a] X = O or S. [b] Not reported.

In $(PF_2N)_2C$, the PNC angle, as determined in the electron diffraction experiment[165], is 132.8(0.5)°. By analogy with PF_2NCO and PF_2NCS, the author suggests that the shrinkage-corrected angle is about 138°, although no assignment of δ(P–N–C) can be made from the vibrational spectra. The dihedral angle between PNC planes is 55 ± 15°, indicating that the compound ought to be regarded as an allene-like carbodiimide.

The only other Group V isothiocyanate whose structure is known is phosphonitrilic isothiocyanate, $N_3P_3(NCS)_6$[166]. This consists of planar hexagonal N_3P_3 rings, with two N-bonded NCS groups on each phosphorus, with a mean N_{exo}–P–N_{exo} angle of 100(1)°. The average P–N–C angle is 152(10)°, with individual values ranging from 135° to 165°, indicating how readily this angle can be deformed, at least between certain limits, by intermolecular forces within the crystal. The average N–C–S angle is 175(2)°, and its deviation from linearity may be real or it may be another consequence of intermolecular forces. The N_{exo}–P distance is 1.63(1)Å: this is much shorter than a 'single-bonded' N–P distance (P–N in $H_3NPO_3^-$ is 1.77(2)Å[167]) and the authors suggest some π-interaction between the nitrogen of the thiocyanate and the d-orbitals of phosphorus. The N–C and C–S distances are unexceptional, being 1.12(4)Å and 1.59(4)Å respectively.

D. Azides

Only one structural study of a Group V azide has been reported. Antimony(V) azide tetrachloride is dimeric $[SbCl_4N_3]_2$[168]: the dimeric molecule is centrosymmetric and is based on a four membered Sb_2N_2 ring. The antimony atoms are octahedrally coordinated by four chlorines and the N_a atoms of two azide groups in *cis* positions. The N_a–N_b and N_b–N_c distances are 1.231(22)Å and 1.132(26)Å respectively, and the mean N_a–N_b–N_c angle is 177.9(2.0)°. The azide groups are not coplanar with the $Sb_2(N_a)_2$ ring, but are tilted out of this plane by some 25°.

8. Pseudohalides of Group VI

All the structurally characterised pseudohalides of the Group VI elements can be regarded either as cyanides, or as normal thiocyanates or selenocyanates. The classification which has been adopted first conseders all those species containing only isolated Group VI atoms, then those containing aggregates of such atoms. While perhaps somewhat arbitrary, this seems the simplest and most obvious division.

The S-bonded normal thiocyanates of carbon are included in this group, considered as cyanides of sulphur. While again this may appear to be somewhat arbitrary, these compounds have far more in common structurally with the rest of the Group VI species than with the isothiocyanates of Group IV.

A. Pseudohalides Containing Isolated Group VI Atoms

The principal geometrical parameters for this class of pseudohalides are collected in Table XIII. It may be noted that all the sulphur species have a bond-angle at sulphur of around 99°, those of selenium slightly smaller: this is fairly typical of 2-connected sulphur

TABLE XIII. Selected Geometrical Parameters for Pseudohalides of Group VI, Containing only Isolated Group VI Atoms.

Compound	r(M–Z)Å[a]	r(Z–C)Å	r(C–N)Å	<(M–Z–C)°	<(Z–C–N)°	Method[b]	Ref.
$S(CN)_2$	1.701(2)	1.701(2)	1.157(2)	98.4(0.2)	175.0(0.2)	R	169
MeSCN	1.820[c]	1.684	1.156[c]	99.9	180[c]	R	170
	1.818[c]	1.689	1.157[c]	99.6	180[c]	R	117
$CH_2(SCN)_2$	1.808(6)	1.677(9)	1.194(12)	98.2(0.4)	176.4(1.0)	X	171
$(CH_2SCN)_2$	1.80(1)	1.63(1)	1.18(2)	99.4(0.7)	172.3(1.3)	X	172
CF_3SeCN	1.984(20)	1.854(16)	1.152(20)	92.2(2.0)	180[c]	E	173
p-$NCSeC_6H_4SeCN$	1.916(19)	1.837(23)	1.149(28)	94.4(0.9)	171.8(3.0)	X	174

[a] M = CN, CH_3, CH_2, CF_3 or C_6H_4; Z = S or Se. [b] E = Electron Diffraction; R = Microwave Spectroscopy; X = X-ray diffraction. [c] Value assumed by authors.

or selenium. Unlike the N-bonded isothiocyanates[77,79,80,120,121,124,129,164,166], the normal thiocyanates exhibit no unusual bond angles.

Sulphur(II) cyanide, $S(CN)_2$, has C_{2v} symmetry: the SCN groups are bent, with the two CN fragments tilted away from one another[169].

Two independent microwave studies have been made of methyl thiocyanate, MeSCN[117,170]. Neither has provided a complete structure determination: plausible assumed values for certain of the parameters have led to values for the remainder. The two studies give essentially identical structures.

In $CH_2(SCN)_2$, the SCN fragments are bent[171], as in $S(CN)_2$, with the CN groups tilted away from one another. The molecule has C_2 symmetry, and pairs of neighbouring molecules in the crystal are linked together by pairs of weak N···S interactions. The SCN groups of neighbouring molecules overlap, giving an N···S distance of 3.17(1)Å. The ethane derivative $(CH_2SCN)_2$ crystallises with its molecules centrosymmetric, in the *anti* conformation[172]. The SCN groups are bent, but the authors did not feel that this was significant: it should be noted, however, that this is a fairly early determination (1958), reported before the occurrence of bent pseudohalide fragments in vapour phase molecules had been recognised[156,157,163,169,192,193]. Intermolecular interactions, at an N···S distance of 3.28Å, again occur in pairs.

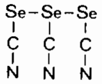
In an electron diffraction study of gaseous CF_3SeCN, the simplifying assumption was made[173] that the SeCN fragment is linear: if this assumption were relaxed, SeCN would almost certainly turn out to be slightly bent. In *p*-diselenocyanatobenzene, $NCSeC_6H_4SeCN$, the SeCN fragments are found to be bent[174]. Each selenium atom makes close contacts with two nitrogen atoms, at distances of 3.06Å and 3.32Å; each Se···N interaction is approximately colinear with an Se–C bond, so that the selenium attains an approximately square planar coordination, as expected for a twelve valence-electron AX_4E_2 system[175].

B. Pseudohalides Containing Arrays of Group VI Atoms

Of the species $X(YCN)_2$ where X, Y = S, Se, all but $S(SeCN)_2$ have been structurally characterised: their principal geometrical parameters are set out in Table XIV. The species with Y = S, $S(SCN)_2$[176] and $Se(SCN)_2$[177] both have approximately linear SCN groups: however, the latter is not a very recent structure, and the placing of the light atoms may not be of the highest accuracy.

The structure of $Se(SeCN)_2$ was originally refined by Fourier methods[178]: the authors felt that the placing of the carbon and nitrogen atoms was, in presence of three selenium atoms, somewhat uncertain. This structure was later refined[175] by least squares methods, using the original data, and it is the results of this refinement which appear in Table XIV. An attempt[174] to refine the structure of $Se(SCN)_2$ by least squares methods was unsuccessful because of inadequate data.

The triselenocyanate ion $(SeCN)_3^-$, analogous to the triiodide ion I_3^-, has been characterised in a number of salts. In each of these the anion has the same basic structure



which differs in detail from salt to salt (Table XV). In the potassium salt, the anion has no symmetry[179],

TABLE XIV. Geometrical Parameters for the Compounds $X(YCN)_2$ (X,Y = S,Se).

X	Y	r(X–Y)Å	r(Y–C)Å	r(C–N)Å	<(Y–X–Y)°	<(X–Y–C)°	<(Y–C–N)°	Dihedral angle (°)[a]	Ref.
S	S	2.12	1.69	1.21	102	99	180	87	176
Se	S	2.21	1.69	1.13	101	104	180	79	177
Se	Se	2.301(8)	1.921(45)	1.005(54)	103.2(0.4)	94.3(1.4)	167(5)	94	174

[a] Angle between YXY and XYC planes.

TABLE XV. Structures of the Triselenocyanate Ion in Various Salts.

Compound	r(Se–Se)Å	r(Se–C)Å	r(C–N)Å	<(Se–Se–Se)°	<(Se–Se–C)°	<(Se–C–N)°	Tilt angle[a]	Ref.
$K(SeCN)_3\cdot{}^1/_2H_2O$	2.669(4)	1.84(3)	1.12(4)	176.0(0.3)	91.6(0.6)	178.7(2.0)	57.4	179
$Rb(SeCN)_3\cdot{}^1/_2H_2O$	2.656(3)	1.81(3)	1.17(3)	176.9(0.3)	92.0(0.5)	178.7(2.1)	65	180
$Cs(SeCN)_3$	2.650(3)	1.816(20)	1.178(27)	178.3(0.1)	92.3(0.4)	177.8(1.4)	43.9	181

[a] See text.

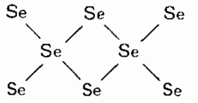
TABLE XVI. Geometrical Parameters for Thiourea Complexes of Tellurium Pseudohalides.

Compound[a]	r(Te–Y)Å[b]	r(Y–C)Å	r(C–N)Å	r(Te–L)Å[c]	<(Te–Y–C)°	<(Y–C–N)°	Ref.
$\mathrm{(etu)_2Te(SCN)_2}$	2.684(7)	1.673(21)	1.13(3)	2.651(6)	96.3(0.8)	178(2)	183
$\mathrm{(etu)_2Te(SeCN)_2}$	2.809(3)	1.814(21)	1.14(3)	2.676(6)	95.9(0.9)	176(2)	183
$\mathrm{(trtu)_2Te(SeCN)_2}$	2.834(2)	1.799(22)	1.152(31)	2.670(5)	100.9(0.6)	178.5(1.7)	184
$\mathrm{(tmtu)_2Te(SeCN)_2}$	2.815(3)	1.809(20)	1.163(27)	2.728(4)	99.8(0.7)	176.9(1.9)	184

[a] etu = ethylenethiourea; trtu = trimethylenethiourea; tmtu = tetramethylthiourea. [b] Y = S or Se. [c] L = Sulphur atom of thiourea ligand.

in the rubidium salt it lies on a mirror plane through the central SeCN fragment[180], and in the caesium salt, it lies on a two fold axis[181]. The tilt angle, the angle between planes defined by (a) a terminal SeCN fragment and the central Se atom and (b) the central SeCN fragment and a terminal Se atom, is the only parameter to vary significantly between the several salts: it is probable that the tilt angle is the most readily deformed of all the angles in the anion and that its actual value is largely dependent on intermolecular, rather than intramolecular forces.

Superficially similar to the alkali metal triselenocyanates, is potassium selenium triselenocyanate, which has been studied crystallographically as its hemihydrate, $\mathrm{KSe(SeCN)_3 \cdot {}^1/_2H_2O}$[182]. This should properly be written $\mathrm{K_2Se_2(SeCN)_6 \cdot H_2O}$, as the anion exists based on an approximately planar $\mathrm{Se_8}$ unit:



The mean terminal Se–Se distance is 2.407(2)Å while the mean bridging Se–Se distance is 3.177(2)Å. The four-coordinate selenium atoms are approximately square planar (having twelve valence shell electrons). Each of the other six selenium atoms bears a CN group; these are all on the same side of the $\mathrm{Se_8}$ plane, with SeCN units approximately normal to this plane, although the Se–Se–C angles were not reported in detail.

By contrast with the derivatives of sulphur and selenium, neither the thiocyanate nor the selenocyanate of tellurium has been isolated in uncomplexed form. However these have both been prepared in the form of complexes with sulphur donors: $\mathrm{L_2Te(SCN)_2}$ where L is ethylenethiourea (etu), and $\mathrm{L_2Te(SeCN)_2}$, where L is etu, trimethylenethiourea (trtu) or tetramethylthiourea (tmtu). In each of these complexes the tellurium is square planar with the ligands in the trans arrangement. The principal geometrical parameters of these complexes are recorded in Table XVI. The Se–C distance in the selenocyanates[183, 184] is appreciably shorter than the corresponding distance in $\mathrm{CF_3SeCN}$[173]: it might have been expected that the shorter distance would occur in the fluorine substituted compound.

9. Pseudohalides of Group VII

By far the most extensively studied of the Group VII pseudohalides are the cyanides: apart from these, only a few other derivatives, all of chlorine, have been investigated.

A. Cyanides

The cyanides of fluorine, chlorine, bromine and iodine have been investigated in the vapour phase by microwave spectroscopy[3], and all save that of fluorine in the crystalline state by X-ray diffraction[185, 186, 187]. The molecules are all linear and the interatomic distances are set out in Table XVII. It is noteworthy that in the highly accurate vapour phase structures, there is no change in the C–N distance on changing from the highly electronegative fluorine to the feebly electronegative iodine.

In the solid state, the molecules form linear chains, being held together by N···X interactions: the same trend is found on descending the group as was found in the Group IV and Group V cyanides, namely that the N···X distance becomes shorter (despite the increasing size of X) and the X–C and N···X distances approach one another, as the whole structure becomes progressively more ionic in character.

This propensity towards chain-formation is little affected by the interpolation of electron conducting groups between cyanide and the halogen. For example cyanoiodoacetylene, I–C≡C–CN, forms linear chains[188] with an I–C distance of 1.79Å, C–N of 1.20Å, and N···I of 2.93Å. *p*-Iodocyanobenzene, $\mathrm{IC_6H_4CN}$, forms similar chains[189], in which the N···I distance is 3.18Å.

B. Other Pseudohalides

An electron diffraction study of chlorine isocyanate was unable to distinguish between two possible planar structures[190]. Both had r(Cl–N) of 1.700(2)Å: one possibility had r(N–C), 1.151(6)Å; r(C–O), 1.225 (6)Å; <(Cl–N–C), 123.1(0.5)° and <(N–C–O) 180°, while the other had r(N–C), 1.227(5)Å; r(C–O) 1.156(6)Å (the usual way round); <(Cl–N–C), 118.2 (0.6)°; and <(N–C–O), 171.0(2.1)°, such that the CO fragment was bent away from the chlorine. Only the expected values of the N–C and C–O distances

TABLE XVII. Molecular Structures of Halogen Cyanides.

Vapour Phase

Compound	r(X–C) Å	r(C–N) Å	Ref.
FCN	1.262(1)	1.159(1)	3
ClCN	1.631(1)	1.159(1)	3
BrCN	1.789(1)	1.158(1)	3
ICN	1.994(1)	1.159(1)	3

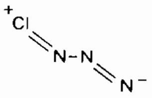
Solid Phase

Compound	r(X–C) Å	r(C–N) Å	r(N· · ·X) Å	Ref.
ClCN	1.57	1.16	3.01	185
BrCN	1.79	1.15	2.87	186
ICN	2.03	1.18	2.73	187

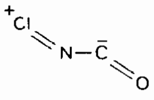
allowed a choice to be made. That the structure was planar, but with NCO weakly bent, was suggested also by a study of the vibrational spectra[191].

A microwave study[192] has provided a structure fully in accord with the second of the electron diffraction possibilities. The *trans*-planar structure has r(Cl–N), 1.703(11) Å, r(N–C) 1.218(12) Å, r(C–O) 1.165(8) Å; <(Cl–N–C) 119.4(1.0)° and <(N–C–O) 171.6 (1.5)°: none of these parameters differs significantly from those of the second electron diffraction model.

Chlorine azide similarly has a *trans* planar structure[193] with r(Cl–N_a), 1.745(5) Å; r(N_a–N_b), 1.252 (10) Å; r(N_b–N_c), 1.133(10) Å; <(Cl–N_a–N_b), 108.7 (0.5)°; and <(N_a–N_b–N_c), 171.9(0.5)°. The N_a–N_b–N_c angle is identical with the N–C–O angle found[192] in the isocyanate. The authors suggest[193] that the structure of chlorine azide may be understood in terms of the form



The analogous form for the isocyanate would be



Unlike HNSO[23] and MeNSO[150], ClNSO is nonplanar[194]. The dihedral angle between the ClNS and NSO planes is 35.5(3.5)°: if it were zero, then the molecule would have the *cis*-planar structure found for HNSO and MeNSO. The other geometrical parameters are: r(Cl–N), 1.696(3) Å; r(N–S), 1.559(4) Å; r(S–O), 1.445(4) Å; <(Cl–N–S), 116.3(0.4)°; and <(N–S–O), 116.0(0.6)°. These must, for the time being, be regarded as the standard dimensions for a thionylimide group, with which others may be compared. The example of the halogen cyanides[3] suggests that the dimensions of the NSO group may be unaffected by changes in substituent, or at least by changes in substituent electronegativity.

10. Inter-Pseudohalogens

Just as the halogens form compounds amongst themselves, such as ICl, so also do the pseudohalogens, forming compounds such as NCN_3, cyanogen azide.

If sulphur(II) dicyanide, discussed earlier[169], is now regarded as cyanogen thiocyanate, then structures are known for four cyanogen pseudohalides: the cyanide (cyanogen)[195, 196, 197], the isocyanate[198], the azide[199] and the thiocyanate.

Cyanogen itself has been studied both in the vapour phase, by rotational Raman spectroscopy[195] and by high resolution infrared spectroscopy[196], and in the solid state by X-ray diffraction[197]. When the C–N distance was fixed at 1.157 Å, the distance found in a microwave study of cyanoacetylene[200], the rotational data yielded[195] a C–C distance of 1.380 Å. The infrared spectrum[196] yields r(C–C), 1.389(30) Å and r(C–N), 1.154(17) Å. The molecule is linear in the vapour phase. In the crystalline state, at −95 °C[197], the molecules lie across centres of symmetry and have r(C–N), 1.130(15) Å; r(C–C), 1.37(2) Å; and <(C–C–N), 179.6(0.3)°. The nitrogen atoms lie in approximate hexagonal close packing: no particularly short intermolecular distances were noted.

Cyanogen isocyanate, NCNCO, is planar[198]. By making a number of assumptions, namely that the NCN and NCO fragments are linear, that the NCO fragment has the same dimensions as in $HNCO$[10], and that the terminal N–C distance is 1.164 Å, as found[199] in the azide, the remaining N–C distance, r(NC–NCO) was found to be 1.283 Å, and the C–N–C angle to be 140°. The skeletal bending frequency δ(C–N–C) was found to be 144 ± 40 cm^{-1}.

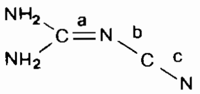
Cyanogen azide, NCN_3, is also planar[199]: in determining the structure the only assumption made was that the N_3 group was linear. The parameters obtained were: r(N–C) (terminal), 1.164(5)Å; r(C–N_a)(central), 1.312(20)Å; r(N_a–N_b), 1.252(10)Å; r(N_b–N_c), 1.133(10)Å; <(C–N_a–N_b), 120.2(1.0)°; and <(N_a–C–N), 176.0(2.0)°, such that the CN group is tilted away from the azide group. This tilt is similar to that observed in NCSCN[169] and in other pseudohalides.

The triselenocyanate ion, $(SeCN)_3^-$, discussed earlier[179, 180, 181] may be regarded as a pseudohalogen analogue of ions such as triiodide I_3^-. The doubly bridging SeCN groups in the $Se_2(SeCN)_6^{-2}$ ion[182] are analogous to bridging iodine in species such as $AlICl_6$[201] and I_2Cl_6[202].

11. Polymeric Pseudohalogens

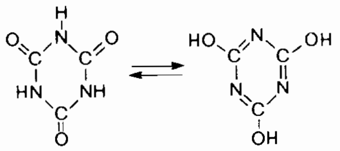
Polymers of HCN and its Derivatives

Dicyandiamide is the dimer of NH_2CN and has the form[203]:



the C–N distances designated a, b, c are 1.36Å, 1.28Å and 1.22Å respectively; the C–N–C angle is 120(4)°.

The majority of polymerised cyanides are trimers and are based on planar C_3N_3 rings: the parent compound of this series is cyanuric acid $(HNCO)_3$, and the remainder are all derivatives of its enol form.



The principal structural parameters for a number of cyanuric compounds, and for *sym*-triazine $(HCN)_3$, are collected in Table XVIII.

Cyanuric acid has been studied by X-ray diffraction both at 100°K and at 295°K[204]. The principal effect of lowering the temperature is to reduce the uncertainties in the parameters; on lowering the temperature, the Debye-Waller temperature factors are reduced, and more diffraction maxima have significant intensity. A low temperature neutron diffraction study has also been undertaken[205].

The major difference observed between the X-ray and neutron studies is the N–H distance, 0.90Å determined by X-rays and 1.033Å determined by neutrons. Neutrons are scattered by atomic nuclei, so that the neutron diffraction experiment yields an internuclear distance: X-rays are scattered by electrons: in the case of hydrogen atoms, the centroid of the electron cloud is not coincident with the nucleus but is always closer to the neighbouring atom, so that the X-ray bond distance to hydrogen almost invariably appears to be too short.

In cyanuric fluoride[206], chloride[207] and amide[207], the bond distance from carbon to the substituent is in each case longer than that found in the parent monomers[3, 158]. D_{3h} molecular symmetry was assumed for each of these compounds.

Cyanuric azide has the usual C_3N_3 ring[208]: in the azide group r(N_a–N_b) is 1.26Å; r(N_b–N_c), 1.11Å; and <(C–N_a–N_b) is 114°. The tricyanomelamine anion $(NCN \cdot CN)_3^{-3}$ is a polymerisation product[209] of the dicyanamide $N(CN)_2^-$, ion.

Sym-triazine, the trimer of hydrogen cyanide, has been studied both by Raman spectroscopy[211] and by X-ray diffraction[212]. In deriving a structure from the rotational data, it was assumed that the C–H distance was 1.084Å, somewhat longer than that in HCN itself[3]: in addition it was assumed that the molecule was planar. The only major difference between the vapour

TABLE XVIII. Principal Structural Parameters of Cyanuric Acid and its Derivatives.

Compound	r(C–N)Å	<(C–N–C)°	<(N–C–N)°	Method[a]	Ref.
$(HNCO)_3$	1.372(1)	124.7(0.1)	115.3(0.1)	XL	204
	1.373(6)	124.5(0.5)	115.2(0.5)	X	204
	1.370	124.6	115.4	N	205
$(FCN)_3$	1.333(9)	113(1)	127(1)	E	206
$(ClCN)_3$	1.33(2)	115(3)	125(3)	E	207
$(NH_2CN)_3$	1.34(1)	117(3)	123(3)	E	207
$(N_3CN)_3$	1.35	113	127	X	208
$(NCN \cdot CN)_3^{-3}$	1.34	114	126	X	209
$(C_6H_5CN)_3$	1.335(7)	115.5(1.0)	124.5(1.0)	X	210
$(HCN)_3$	1.338(1)	113(1)	127.5(1.0)	R	211
	1.319(5)	113.2(0.4)	126.8(0.4)	X	212

[a] E = Electron Diffraction; N = Neutron Diffraction; R = Rotational Raman Spectroscopy; X = X-ray Diffraction; XL = Low-temperature X-ray Diffraction.

phase structure, and that determined by X-ray diffraction lies in the C–H distance: as determined in the X-ray experiment, this is 0.998 Å, and is too short, as discussed above for $(HNCO)_3$. The rotational Raman spectrum affords moments of inertia, which are functions of nuclear position.

12. Discussion

Perhaps the most striking feature about the structures of the ionic pseudohalides of the metals of Groups I, IIA and III, is the common occurrence of structures closely related to those simple archetypes, the 6:6 NaCl and 8:8 CsCl structures. As a consequence of this, it may be supposed that these structures are almost wholly ionic in character and that a principal determinant of the detailed arrangement is geometrical packing, in such a way as to minimise the lattice energy.

Without doubt, the structures which provide the most accurate dimensions of an ionic pseudohalide are those of the azides[36, 37, 43, 45], of which the neutron study[45] of barium azide is the most thorough and accurate. This provides a mean N–N distance, uncorrected for libration, of 1.168(1) Å: corrected for libration[36], the "best" N–N distance is 1.174 Å.

There has unfortunately been no recent, high-accuracy study, of an ionic cyanide in which the cyanide groups are free from rotations, and a neutron diffraction study of the low temperature rhombohedral phase of caesium cyanide would consequently be welcome. The more recent studies of the alkali metal cyanides[30, 31] have been concerned more with molecular dynamics than with static geometry. No ionic cyanate has been the subject of an accurate structure determination, nor has an ionic thiocyanate been studied recently: in consequence, no really accurate values are known for the geometrical parameters of isolated NCO^- and NCS^- ions. The most accurate N–C distance in the linear, symmetrical cyanamide ion, NCN^{-2}, is that found[48] in the calcium salt, 1.224(16) Å: this value is uncorrected for libration.

In molecular pseudohalides, it has generally been assumed, in order to simplify a structure analysis by electron diffraction or microwave spectroscopy that fragments N–X–Y, (where X–Y = C–O, C–S, N–N or C–N) are linear, and also that fragments M–C–N in cyanides are linear. Any slight deviation from linearity in the solid state, as revealed by X-ray diffraction, which determines coordinates for each atom independent of all other atoms, has then been ascribed to the influence of intermolecular forces. However when this assumption has been relaxed, in microwave studies of NF_2CN[157], PF_2CN[156], ONCN[163], $S(CN)_2$[163], ClNCO[192] and ClN_3[193], the M–C–N or N–X–Y fragment has been found to be bent, with the distal end of the fragment in question tilted away from the rest of the molecule. It seems possible that many other molecular pseudohalides would turn out to have bent MCN or NXY fragments if the restriction of linearity were to be removed; although those which with linear MCN or NXY groups are symmetric tops may not undergo such bending. Often this relaxation would not be possible in a vapour phase structure determination, since the introduction of further geometrical parameters might complicate the analysis to the point of insolubility – after all, simplification of the problem to bring it within the bounds of tractability is usually the sole reason for applying constraints. However, such an assumption is quite likely to influence the values of the other geometrical parameters, as found for PF_2CN[155, 156]; comparison of structural parameters must therefore be made with caution, especially if comparing structures solved with and without an assumption of linearity. Almost certainly, the parameters for many compounds have associated with them standard deviations which are far too small to reflect the effects of a linearity assumption. There may be a number of such structures recorded in the literature whose parameters are of high precision, but low accuracy.

While structures are known of examples of all the pseudohalides of carbon and silicon, their neighbouring elements in the periodic table are represented only by an incomplete set of pseudohalide structures. Of boron, only isothiocyanates are structurally characterised; an isothiocyanate structure is lacking for germanium, both isocyanate and azide of tin, an azide for phosphorus, and an isothiocyanate structure for chlorine.

From this rather incomplete set of structures, what generalisations emerge? Firstly, so far as the structures are known, isocyanates and especially isothiocyanates of boron, silicon and tin appear to have ground vibrational states in which the minimum energy configuration has $<$(M–N–C) 180°; while these derivatives of hydrogen, carbon, germanium, phosphorus and chlorine appear to have distinctly bent ground states. Secondly, for all elements forming discrete monomeric derivatives except chlorine, the azides appear to have essentially the same $M–N_a–N_b$ angle, approximately 120°. Thirdly, in the solid state structures, there is an unmistakable tendency, observed in the derivatives of Groups III, IV, V and VII towards more ionic structures on passing from the lighter elements of the group to the heavier.

The isocyanates and isothiocyanates of silicon are linear at nitrogen in their vibrational ground states (*cf.* Table VIII). This has generally been attributed[213] to a $p_\pi–d_\pi$ interaction between the occupied π-orbitals of the pseudohalide and (vacant) $3d_\pi$ orbitals on silicon: photo-electron spectra have been interpreted[214] in terms of this view. This view seems however to be inadequate, as follows: (a) boron isothiocyanates are linear at nitrogen, in particular $NH_3 \cdot BH_2NCS$[77]: it

TABLE XIX. Some Non-bonded Distances in Azides and Isocyanates.

	R = H	CH_3	SiH_3	GeH_3	Cl
r(R···C) in RNCO (Å)	1.975[a]	2.464[c]	2.83[d]	2.858[e]	2.53[f]
r(R···N_b) in RN_3 (Å)	1.862[b]	2.290[c]	2.67[d]	2.684[e]	2.45[g]
Δ[h] (Å)	0.11_3	0.17_4	0.16	0.17_4	0.08

[a] Ref. 10. [b] Ref. 18. [c] Ref. 118. [d] Ref. 121. [e] Ref. 130. [f] Ref. 192. [g] Ref. 193. [h] Δ = {r(R···C)–r(R···N_b)}.

seems unlikely that $3d_\pi$, or $3p_\pi$ orbitals for that matter, of boron make any significant contribution to the bonding in this compound; (b) the isocyanate and isothiocyanate of the PF_2 group exhibit[164] angles at nitrogen little different from those in the CH_3 derivatives[117, 118], and markedly smaller than those in the SiH_3 compounds[119, 120]. Chlorine isocyanate[192] has an angle at nitrogen (119.4°) smaller even than in HNCO[10] or MeNCO[117, 118]. While it may be argued[164] that these results indicate merely a diminished d_π contribution, they are the exact opposite of what one might expect on the basis of orbital contraction[215]. On going from left to right across a row of the periodic table, the effective nuclear charge of the elements increases: the higher the effective nuclear charge, the more the higher unoccupied atomic orbitals (including 3d in the examples of phosphorus and chlorine) are contracted in size and lowered in energy, so becoming more likely to participate significantly in chemical bonding. Fluorination of phosphorus will only accentuate this; (c) the best available potential function for Si–N–C bending in SiH_3NCO indicates[121] that the energy required to change the Si–N–C angle between 180° and 140° is less than 1 kcal/mol. A similar result will be found for the bending potential of any of these pseudohalides in which there is a significant quartic term.

It is consistently found that azides RN_3 have a significantly smaller angle at N_a than do the isoelectronic isocyanates RNCO. Thus for R = H, the angles are 114.1°[18] and 128.1°[10]; R = CH_3, 116.8°[118] and 140.3°[118]; R = SiH_3, 123.8°[140] and 152.7°[121]; R = GeH_3, 119°[130] and 141.3°[130]; and R = Cl, 108.7°[193] and 119.4°[192]. This has been rationalised[118, 216, 217], in terms of structures for isocyanates of the form

$$\text{R}-\overset{+}{\text{N}}\equiv\text{C}-\overset{-}{\text{O}}$$

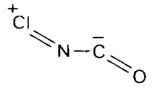
whose analogues for azide are less favourable, because of excessive charge separation. However, it should be noted that in terms of this rationalisation, angles at nitrogen are expected to be smaller in isothiocyanates as the form

$$\text{R}-\overset{+}{\text{N}}\equiv\text{C}-\overset{-}{\text{S}}$$

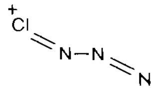
is less favoured in the presence of the less electronegative sulphur atom. The observed R–N–C angle is in fact greater in isothiocyanates than in isocyanates for R = H (isothiocyanate data first), 135.0°[11] and 128.1°[10]; R = CH_3, 141.6°[118] and 140.3°[118]; R = SiH_3, 163.8°[121] and 152.7°[121]; R = Me_3Si, 154°[124] and 150°[124]; and R = PF_2, 140.5°[164] and 130.6°[164].

An alternative interpretation has been suggested[140] for the differences between azides and isocyanates in terms of the steric interaction of non-bonded atoms[81]. This approach supposes that in those pseudohalides having angles at N_a appreciably greater than 120°, these angles are determined *primarily* by the steric properties of the immediate neighbours of N_a, that is to say by the non-bonded contact distances, in a hard-atom approximation, R···C in RNCO and R···N_b in RN_3. In Table XIX are set out some non-bonded distances in isocyanates and azides: for R = CH_3, SiH_3 and GeH_3, Δ = {r(R···C)–r(R···N_b)} is essentially identical, and may be identified with the difference in non-bonded radii of carbon and central nitrogen in these pseudohalogens. That the hydrogen and chlorine species give different Δ values is probably only a reflection of the fact that in both HN_3[18] and ClN_3[193], the angle at N_a is less than 120° and may not therefore be primarily determined by steric phenomena.

This approach, simple as it is, casts little light on the consistent differences in skeletal angle R–N–C between isocyanates and isothiocyanates. Although the bending at the central atom in Cl·NCO[192] and ClN_3[193] can be simply rationalised in terms of valence bond structures



and



which presumably implicate π orbitals on chlorine, contrary to the suppositions earlier made about the angles at N_a in chlorine pseudohalides, no such simple rationalisation can be put forward for the bending at carbon in NF_2CN[157], PF_2CN[156], ONCN[163] and $S(CN)_2$[169]. In an attempt to gain a better understanding of the bond angles in molecular pseudohalides, a study of the bending potential functions in these molecules has been initiated in this laboratory[218].

It is almost a truism that on going from the lighter to the heavier members of p-block group, the solid phase structures tend to become more ionic in character: part, at least, of the cause for this may be traced to the reduced polarisation power of the larger, heavy

TABLE XX. Comparison of $M–N_a$ Distances in Some Molecular Pseudohalides.

M	r(M–NCO)Å	r(M–NCS)Å	r(M–NNN)Å	r(M–NCNM)Å	Ref.
H	0.987(10)	0.989(3)	0.975(15)	–	10, 11, 18
CH_3	1.450(4)	1.479(8)	1.468(5)	–	118
SiH_3	1.703(4)	1.704(6)	1.719(8).	1.696(4)	121, 140
$SiMe_3$	1.76(2)	1.78(2)	–	–	124
GeH_3	1.831(4)	–	1.845(6)	1.813(5)	130
PF_2	1.683(6)	1.686(7)	–	1.680(6)	164, 165
Cl	1.703(11)	–	1.745(5)	–	192, 193
CN	1.283	–	1.312(20)	–	198, 199

cations. Such a variation is noticeable among the cyanides of Groups IV, V and VI, and to a lesser extent, among the isothiocyanates azides and carbodiimides of Group IV also.

While rather few structures are known of the pseudohalides of zinc and cadmium, it is mercury of all the Group IIB elements which presents such a bewildering variety of structures in its pseudohalides. Perhaps, with the benefit of hindsight, this should not be so surprising: the structural chemistry of mercury is among the most rich and diverse of any element's[219]. The general features of the mercury pseudohalide structures, however, are those found in the derivatives of other larger, heavier cations: cyanide and thiocyanate are bidentate, azide is at least bidentate and perhaps polydentate, and the coordination number of the cation is increased from four to six and beyond. Although no analogues of the cation[60] $Zn(OH_2)_4(NCHgCN)_2^{+2}$ are known for other molecular cyanides, this may well have the same rationalisation as many other curiosities in science; namely that the experiment using $Hg(CN)_2$ as a ligand to zinc(II) has been tried and the product characterised, while the experiments with say Me_2AsCN or Me_3SiCN remain as yet unattempted. Since a number of molecular cyanides are known to be capable of functioning as donors towards boron trihalides[94,95,220], there seems little reason why certain of them should not act as donors to p-block metals.

For only two pseudohalides of lead(II), the azide[144] and the cyanamide[149], are structures known: no structures appear to be known for pseudohalides of thallium(III) or bismuth. In view of the structural diversity displayed by the known pseudohalides of mercury and lead, further investigation of bismuth, lead and thallium (of the type $RTlX_2$ and R_2TlX) derivatives would surely be rewarding.

Turning now from the gross features of molecular geometry to the fine detail, namely bond distances, it is of interest to compare $M–N_a$ distances in some N-bonded molecular pseudohalides; these, for convenience, are collected in Table XX. With the exception of M = H, some clear patterns emerge. The $M–N_a$ distance is always longer in an azide than in an isocyanate, where in turn it is longer than in a carbodiimide: $r(M–N_a)$ seems also to be longer in isothiocyanates than in isocyanates. While for certain individual pairs of molecules, the differences in $r(M–N_a)$ are barely significant, overall the pattern is consistent and must be regarded as real. For the hydrogen pseudohalides, there is no significant difference between any pair of $H–N_a$ distances.

It should be emphasised that none of the bonded distances of Table XX, can be used for comparison with some 'ideal' distance derived from addition of bonded atomic radii. Bonded atomic radii are by no means an additive molecular property, nor does the commonly used electronegativity correction effect a great improvement[82]. Hence, no deduction can be made from an isolated distance of the type $M–N_a$ about the occurrence or otherwise of any π interaction between M and N_a. In general, *qualitative* attempts to describe the fine detail of the electron distribution within a polyatomic molecule from a knowledge only of the relative nuclear positions, should be treated with great reserve. At present, however, no simple rationalisation of the trends shown up in Table XX is possible: confirmation of these trends by elimination of some of the gaps in the table would indeed be welcome.

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