35. *Dimethylaluminium Cyanide and its Gallium, Indium, and Thallium Analogues; Beryllium and Methylberyllium Cyanide.*

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The cyanides $Me_2M\cdot CN$ (M = Al, Ga, In, or Tl) have been prepared from the trimethylmetal and hydrogen cyanide. In contrast to the polymeric boron cyanides, $R_2B\cdot CN$, the aluminium, gallium, and indium compounds are tetrameric in benzene, and dimethylthallium cyanide is a salt in aqueous solution. Reactions between dimethylberyllium (and its trimethylamine complex) and hydrogen cyanide are also described.

COMPOUNDS in which an element of Group III is bound to an element of donor character, commonly nitrogen or oxygen, are often associated in order that both elements can become co-ordinatively saturated. Well-known examples are the aminoboron halides, *e.g.*, $(Cl_2B\cdot NMe_2)_2$, and the aluminium alkoxides. Boron cyanides are interesting in this connection since the linear $B-C\equiv N\rightarrow$ group would not allow the formation of the four- and six-membered rings so frequently found among boron compounds. Boron cyanide is a polymeric solid[1] $[B(CN)_3]_x$, and di-n-butylcyanoborane[2] is an involatile viscous liquid for which cryoscopic measurements in benzene indicate a degree of association of about twenty. Some diarylcyanoboranes have also been found to be polymeric, and both these[3] and $(Bu^n{}_2B\cdot CN)_x$ are depolymerized by bases such as ammonia or pyridine.

The formation of dimethylaluminium cyanide (m. p. 88°) from trimethylaluminium and hydrogen cyanide has been mentioned briefly,[4] but without indication of its molecular complexity. We find that this compound is tetrameric in benzene solution, and that so are the corresponding gallium and indium compounds (prepared from hydrogen cyanide

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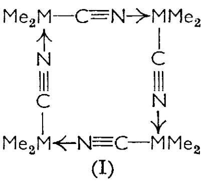
[1] Chaigneau, *Compt. rend.*, 1954, **239**, 1220; Guy and Chaigneau, *Bull. Soc. chim. France*, 1956, 257.

[2] Evers, Freitag, Kriner, and MacDiarmid, *J. Amer. Chem. Soc.*, 1959, **81**, 5106.

[3] Lappert, Prokai, and Pyszora, unpublished work.

[4] Wilberg and Stecher, FIAT Review of German Science (1939—46), Inorganic Chemistry, Part II, 1948, p. 162.

and trimethyl-gallium and -indium). Aluminium,[5] gallium,[6] indium, and thallium[7] all form compounds, *e.g.*, $(Me_2M{\cdot}NMe_2)_2$, M = Al, Ga, In, or Tl, in which the metal is bound to four ligands and is also part of a four-membered ring, implying easy distortion of the valency angle from 109° to about 90°. Gillespie[8] has shown that distortions from the tetrahedral angle occur much more readily for elements of the second or higher period than for elements of the first period. Thus structure (I; M = Al, Ga, or In) is reasonable, even if we assume the $M{-}C{\equiv}N{\rightarrow}M$ group to remain linear.


(I)

We examined the reactions of the cyanides with trimethylamine, rather than with ammonia or pyridine (whose reactions with $R_2B{\cdot}CN$ have been studied), because there are data on similar reactions between trimethylamine and $(Me_2M{\cdot}SMe)_2$ (M = Al[5] or Ga[6]), in which $Me_2M(SMe),NMe_3$ is formed. The tetramers (I) absorb four mol. of trimethylamine, which doubtless competes with cyanide groups in co-ordination with the metal, forming solid adducts whose dissociation pressures are given by the equations:

$$(Me_2AlCN)_4 + NMe_3\colon\ \log_{10} p_{\text{mm.}} = 5{\cdot}288 - 1140/T\ (T \text{ in } {}^{\circ}\text{K})$$

$$(Me_2GaCN)_4 + NMe_3\colon\ \log_{10} p_{\text{mm.}} = 11{\cdot}297 - 3330/T$$

At 25° the dissociation pressures are 29 (Al) and 1·3 mm. (Ga), and the above equations correspond to heat content changes of 5·2 and 15·2 kcal. mole^{-1} (of trimethylamine). Thus, relative to trimethylamine, the co-ordination affinity of the cyanide group is greater to gallium than to aluminium, though this conclusion would be invalidated in the event of large disparities between the sublimation energies of the aluminium adduct and tetramer and those of the gallium analogue.

The aluminium compound (I; M = Al) is very sensitive to air and sometimes inflames in the air when touched with a drop of water. The gallium compound slowly liquefies when exposed to the air, smells strongly of hydrogen cyanide, and gradually deposits crystals of the hydroxydimethylgallium tetramer[9] $(Me_2Ga{\cdot}OH)_4$. The air-sensitivity of the indium compound is very similar to that of $(Me_2Ga{\cdot}CN)_4$, and is much less than that of $(Me_2Al{\cdot}CN)_4$.

Reaction between trimethylaluminium and more than one mol. of hydrogen cyanide results in the displacement of more than one methyl group from each aluminium atom, but the products appear to catalyse the polymerization of hydrogen cyanide and we have not succeeded in isolating a pure product. An excess of hydrogen cyanide may be used in the preparation of dimethyl-gallium and -indium cyanide, without the loss of further methyl groups (reactions under pressure at high temperature were not attempted). Dimethylindium cyanide, however, reacts very slowly with an excess of hydrogen cyanide at room temperature.

Dimethylthallium cyanide was prepared both from trimethylthallium and hydrogen cyanide and from dimethylthallium fluoride and potassium cyanide in aqueous solution. Diphenylthallium cyanide[10] is a high-melting solid [m. p. 318° (decomp.)], which is sparingly soluble in water, with slight hydrolysis. The dimethyl compound is soluble in water (2·7 g. in 100 g. of water at 25°), in which it behaves as a 1 : 1 strong electrolyte, $[Me_2Tl]^+CN^-$. Its conductance at 25° is given approximately by the equation $\Lambda_c = 99 - 50c^{\frac{1}{2}}$ ($c = 0{\cdot}004$—$0{\cdot}02$ mole l.$^{-1}$). It is insoluble in ether and in benzene.

We have made a brief study of the reaction between dimethylberyllium and hydrogen

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[5] Davidson and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 316.

[6] Coates, *J.*, 1951, 2003; Coates and Hayter *J.*, 1953, 2519.

[7] Coates and Whitcombe, *J.*, 1956, 3351.

[8] Gillespie, *J. Amer. Chem. Soc.*, 1960, **82**, 5978.

[9] Kenney and Laubengayer, *J. Amer. Chem. Soc.*, 1954, **76**, 4839; Smith and Hoard, *ibid.*, 1959, **81**, 3907.

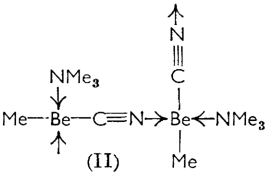
[10] Challenger and Richards, *J.*, 1934, 405.

cyanide. Beryllium cyanide does not appear to have been described previously, but it seems to be present in the product of the reaction between beryllium iodide and cyanogen at about 500°: this substance dissolves in water to a viscous solution which shows reactions characteristic of aqueous cyanide solutions.[11] Beryllium cyanide is precipitated at once when dimethylberyllium is added to an excess of hydrogen cyanide in an inert solvent. It is insoluble in solvents other than those which cause hydrolysis, does not absorb trimethylamine at room temperature or at 70°, and no doubt has a cross-linked polymeric constitution as would be expected if each beryllium atom had a co-ordination number of four.

If dimethylberyllium and hydrogen cyanide are added simultaneously to ether, some insoluble matter is precipitated but the filtrate evidently contains methylberyllium cyanide. Solutions so obtained are mobile and are unlikely to contain highly polymeric material. The beryllium is co-ordinated to ether, which may be removed by pumping at 70°, but the residue does not redissolve in ether. We were not able to devise a method for purifying methylberyllium cyanide, but our product had a Be : CH_3 ratio of 1·00 : 1, though the analysis indicated a purity of only 97—98%.

Addition of 2,2′-bipyridyl to an ether solution of methylberyllium cyanide gave an orange-yellow solution. Coloured bipyridyl complexes of organoberyllium compounds have been described elsewhere.[12]

We investigated the reaction between hydrogen cyanide and one of the dimethylberyllium–trimethylamine complexes (Me_2Be,NMe_3), because the beryllium atom in the hypothetical primary reaction product, $(Me_3N)MeBe{\cdot}CN$, would have only one vacant co-ordination position, unlike that in $MeBe{\cdot}CN$ which has two vacant co-ordination positions. The reaction (in benzene solution) resulted in the deposition of a little insoluble matter, but most of the product remained in solution. Removal of benzene gave an apparently amorphous product, very sparingly soluble in benzene and involatile at 200°/0·01 mm., which evidently is a polymer. Thus *trans*-association (II) is favoured by both the beryllium and the boron cyanides rather than the *cis*-association displayed in the tetramers (I).


(II)

Infrared Spectra.—The spectra of the cyanides each had a single sharp band in the 2100—2200 cm.$^{-1}$ region, clearly due to ν(C⋮N) (see Table). The stretching frequencies of the cyanide group in many metal complexes have been discussed with particular regard to the distinction between terminal and bridging cyanide groups,[13] the former having the lower ν(C⋮N). In compounds of six elements containing bridging cyanide groups, ν(C⋮N) was in the range 2164—2239 cm.$^{-1}$, and in the tetramers described here ν(C⋮N) falls within that range. In agreement with the formulation of dimethylthallium cyanide as a salt, ν(C⋮N) is quite near the values observed for sodium and potassium cyanide[14] (2085, 2076, respectively, both measured for Nujol mulls).

Cyanide stretching frequencies, ν(C⋮N) (cm.$^{-1}$) in $R_2M{\cdot}CN$.

Compound	ν(C⋮N)	Compound	ν(C⋮N)	Compound	ν(C⋮N)
$(Bu^n{}_2B{\cdot}CN)^2{}_n$	2280 *	$(Me_2In{\cdot}CN)_4$	2178 *	$(MeBe{\cdot}CN)_n$	2222 ‡
$(Me_2Al{\cdot}CN)_4$	2213,* 2224 †	$Me_2Tl{\cdot}CN$	2101 ‡	$[(Me_3N)MeBe{\cdot}CN]_n$	2200 ‡
$(Me_2Ga{\cdot}CN)_4$	2202,* 2216 ‡				

* In CCl_4. † Hexachlorobutadiene mull. ‡ Nujol mull.

Examination of the spectrum of the aluminium tetramer at lower frequencies was restricted by the difficulty of finding suitable solvents. The tetramer reacts with, for

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[11] Lebeau, *Compt. rend.*, 1898, **126**, 1274; *Ann. Chim. Phys.*, 1899, **16**, 491.

[12] Coates and Green, *Proc. Chem. Soc.*, 1961, 376; *J.*, 1962, 3340.

[13] Dows, Haim, and Wilmarth, *J. Inorg. Nuclear Chem.*, 1962, **21**, 33.

[14] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1255; see also El Sayed and Sheline, *J. Inorg. Nuclear Chem.*, 1958, **6**, 187.

example, carbon disulphide, forming a yellow substance. Features noted in the spectrum of $(Me_2Al{\cdot}CN)_4$ in carbon tetrachloride include a prominent band at 1195 $cm.^{-1}$ due to CH_3 symmetric deformation (compare [15] 1201 $cm.^{-1}$ for Me_6Al_2 and 1205 $cm.^{-1}$ for $Me_4Al_2Cl_2$), and a single strong band at 1047 $cm.^{-1}$ probably due to a methyl rocking vibration. The sharp absorption at 1207 $cm.^{-1}$ in the spectrum of $(Me_2Ga{\cdot}CN)_4$ must be δ(Me)(sym); other features of this spectrum will be described elsewhere in connection with other dimethylgallium complexes.

EXPERIMENTAL

Infrared spectra were recorded with a Grubb–Parsons GS2A prism-grating spectrometer. Nearly all the compounds described are air-sensitive and were handled in a vacuum or in nitrogen. Analyses for hydrolysable methyl groups, and measurements of dissociation pressures of trimethylamine adducts, were carried out in a vacuum apparatus suitable for the quantitative handling of gases.

Dimethylaluminium Cyanide Tetramer, $[Me_2Al{\cdot}CN]_4$.—Hydrogen cyanide (42·9 c.c. at S.T.P., 0·0019 mole) was condensed on trimethylaluminium (0·1439 g., 0·0020 mole) and the mixture allowed to warm to room temperature in a sealed tube. After reaction, removal of material volatile at room temperature gave methane (42·5 c.c. at S.T.P.) and the tetramer, m. p. 90°.

On a larger scale, hydrogen cyanide (3 g.) in benzene (35 c.c.), and a solution of trimethylaluminium (8 g.) in benzene (40 c.c.), were simultaneously added to benzene (10 c.c.) which was stirred. Benzene was pumped (at room temperature) from the resulting pale brown solution, and the solid product purified by sublimation at 100°/*ca.* 10^{-2} mm. The *tetramer*, m. p. 89° (60%), condensed as colourless crystals, leaving some involatile brown residue (Found: Al, 32·2; hydrolysable Me, 35·8%; *M*, cryoscopically in 0·69, 1·16, 1·31 wt. % benzene solution, 330, 331·5, 326. $C_{12}H_{24}Al_4N_4$ requires Al, 32·5; hydrolysable Me, 36·2%; *M*, 332).

The tetramer reacts very slowly with liquid hydrogen cyanide at room temperature, with formation of methane. No reaction appears to take place between the tetramer and gaseous hydrogen cyanide at room temperature, but at 100° a deep brown product is formed from which unchanged tetramer has been isolated by sublimation. No other product could be isolated from this reaction or from the insoluble involatile brown substance resulting from reaction between trimethylaluminium and an excess of hydrogen cyanide in benzene.

Dimethylgallium Cyanide Tetramer, $[Me_2Ga{\cdot}CN]_4$.—Prepared from trimethylgallium and hydrogen cyanide in benzene solution, this was separated, after removal of solvent, by sublimation at 90°/$\sim 10^{-2}$ mm. (sublimation began at 60°). The *tetramer* (73%) had m. p. 79°. It was also prepared by the quantitative reaction between trimethylgallium and hydrogen cyanide carried out in a vacuum apparatus (Found: Ga, 55·0%; *M*, cryoscopically in 0·38, 1·12, 1·68 wt.% benzene solution, 536, 541, 496. $C_{12}H_{24}Ga_4N_4$ requires Ga, 55·3%; *M*, 503).

Dimethylindium Cyanide Tetramer, $[Me_2In{\cdot}CN]_4$.—This was prepared from trimethylindium and hydrogen cyanide in ether; it was separated, after removal of ether, on sublimation at 120—140°/0·05 mm. and had m. p. 147° (Found: In, 67·1; hydrolysable Me 4·3%; *M*, cryoscopically in 0·28, 0·43 wt.-% benzene solution, 663, 688. $C_{12}H_{24}In_4N_4$ requires In, 67·2; hydrolysable Me, 4·4%; *M*, 683). The indium *tetramer* is less soluble in benzene than the aluminium and the gallium tetramer. It dissolves in 2-methoxyethanol without gas evolution; addition of 2N-sulphuric acid causes slow evolution of methane at room temperature, and for measurement of methyl content the reaction mixture had to be heated to 60°. In contrast, the aluminium tetramer reacts quantitatively with 2-methoxyethanol and dilute sulphuric acid at room temperature, and evolution of methane from the gallium compound was too slow for this to be a useful analytical method (this is true for most compounds containing the Me_2Ga group).

Dimethylthallium Cyanide.—Hydrogen cyanide (0·5 g.) in excess in benzene (10 c.c.) was added to trimethylthallium (3·2 g.) in ether (40 c.c.), giving methane and an immediate quantitative precipitate of *dimethylthallium cyanide*, which was washed with ether and pumped dry; it decomposed to a black mass at 275° (Found: C, 13·8; H, 2·4; CN, 10·0. C_3H_6NTl requires C, 13·8; H, 2·3; CN, 10·0%). The same compound was also prepared by adding potassium cyanide (0·5 g.) in water (10 c.c.) to dimethylthallium fluoride (2·0 g.) in water (20 c.c.); the resulting crystalline precipitate was washed with a little cold water and pumped dry.

Reaction between Dimethylberyllium and Hydrogen Cyanide.—Dimethylberyllium (0·014

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[15] Hoffmann, *Z. Elektrochem.*, 1960, **64**, 616.

mole in 5 c.c. of ether) and hydrogen cyanide (0·016 mole in 5 c.c. of benzene) were simultaneously added, drop by drop and with stirring, to ether (4 c.c.). After the reaction, in which gas was evolved, ether (10 c.c.) was added, and white insoluble matter separated by filtration through a sintered disc under nitrogen. Evaporation of the colourless filtrate gave a solid product which lost ether slowly when pumped at room temperature. The solid lost more ether when pumped at 70°, and a very small amount of colourless material sublimed. The white, involatile, and insoluble residue appeared to have been impure polymeric methylberyllium cyanide (Found: Be, 17·5; hydrolysable Me, 29·2. Calc. for C_2H_3BeN: Be, 18·0; hydrolysable Me, 30·0%).

Dimethylberyllium (0·014 mole in 5 c.c. of ether) was added dropwise to an excess of hydrogen cyanide (0·066 mole in 8 c.c. of benzene). Methane was evolved and the white precipitate of beryllium cyanide was collected and pumped dry (Found: Be, 15·0; CN, 84·1. Calc. for C_2BeN_2: Be, 14·75; CN, 85·2%). No residue remained when the filtrate was evaporated. No methane was detected when the beryllium cyanide was hydrolysed with dilute sulphuric acid.

Cyanomethyl(trimethylamine)beryllium, $[(Me_3N)MeBe{\cdot}CN]_n$.—Dimethyl(trimethylamine)-beryllium, $Me_2(Me_3N)Be$ (2·7 g.), in benzene (25 c.c.), and hydrogen cyanide (0·8 g.) in benzene (15 c.c.), were slowly and simultaneously added to stirred benzene (10 c.c.). Gas was evolved and after the reaction the clear supernatant liquid was decanted from a small amount of white insoluble matter, and solvent was removed by pumping first at room temperature and then for 15 min. at 80°. The colourless involatile amorphous *product* did not melt or decompose below 300° (Found: CN, 23·7; hydrolysable Me, 13·3. $C_5H_{12}BeN_2$ requires CN, 23·85; hydrolysable Me, 13·8%). It was sensitive to air.

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