THE REACTIONS OF METAL HALIDES WITH ALKYL CYANIDES

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1. Introduction

Interest in the chemistry of the transition metals has resulted in the study of the complexes formed by transition metal halides with a large variety of donor molecules, *e.g.*, amines, phosphines, etc.[1] Alkyl cyanides (or nitriles) in particular form a large number of compounds with metal halides, and the recent interest in their preparation and structure has prompted this Review. The alkyl cyanides, particularly methyl cyanide, are also widely used as solvents in inorganic chemistry for preparative work and the measurement of the physical properties of compounds.

The aim of this Review is to show the versatility of the alkyl cyanides in inorganic chemistry. In addition to the above points which will be dealt with in detail, the complexes formed between metal carbonyls and alkyl cyanides and metal halides and phenyl cyanide are also discussed.

2. Properties and structure of alkyl cyanides

Before considering the complexes of alkyl cyanides with metal halides we will first discuss the properties and structure of the alkyl cyanides themselves. They are colourless, highly toxic liquids, which are generally stable in air, and although stable aromatic nitrile oxides $R-C\equiv N\rightarrow O$ are known,[2] where R is a bulky group, the corresponding aliphatic nitrile oxides are very unstable.

Methyl cyanide is a considerably stronger base than water,[3] and consequently a weaker acid. The physical constants[4] of the lower alkyl cyanides RCN, where R = Me, Et, or Pr, indicate their favourable solvent properties (see Section 6).

The infrared and Raman spectra of the lower alkyl cyanides have been investigated in great detail.[5] The spectral data for methyl cyanide is consistent with a pseudo-tetrahedral structure (C_{3v} symmetry)[5] and a *linear* $C—C\equiv N$ system. Ethyl cyanide as expected has a lower (C_S) symmetry.[6] The vibrations associated with the cyanide group are of particular interest. In liquid methyl cyanide the C–N stretching (ν_2) and C–C–N bending (ν_8)

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[1] See, *e.g.*, C. K. Jørgensen, "Inorganic Complexes", Academic Press, London and New York, 1963.

[2] C. Grundmann and J. M. Dean, *Angew. Chem.*, 1964, **76**, 682; Y. Iwakura, M. Akiyaman, and K. Nagakubo, *Bull. Chem. Soc. Japan*, 1964, **37**, 767.

[3] W. S. Muney, and J. F. Coetzee, *J. Phys. Chem.*, 1962, **66**, 89.

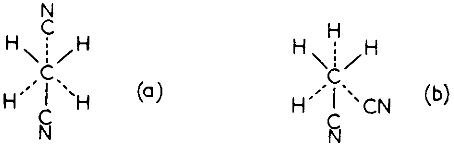
[4] A. Weissberger, "Technique in Organic Chemistry", vol. VII, Organic Solvents, Interscience Publ. Inc., New York, p. 224.

[5] See, *e.g.*, G. Herzberg, "Infrared and Raman Spectra", Van Nostrand, New York, 1945, p. 332.

[6] N. E. Duncan and G. J. Janz, *J. Chem. Phys.*, 1955, **23**, 434.

modes are observed at 2250 and 380 cm.$^{-1}$ respectively.[7] Similar bands are observed for the other alkyl cyanides. A band of medium intensity at 2290 cm.$^{-1}$ in methyl cyanide, very close to the C–N stretching vibration, is believed to arise from a combination of the symmetric CH_3 deformation and C–C stretching vibrations.[7]

Low-temperature spectroscopy of the aliphatic dinitriles[8] shows the presence of *trans* and *gauche* isomers; the amounts of each depend upon temperature.



Isomers of succinonitrile: (a) *trans*, (b) *gauche*.

Electron-diffraction investigations of methyl cyanide have been carried out by several workers,[9] and a C–N bond length of 1·155 ± 0·03 Å is close to the value expected for a C–N triple bond. The C–C bond length (1·465 Å)[9] and force constant[10] are consistent with *sp–sp*^{3} bond character.

It is clear that the Lewis base character of the alkyl cyanides can arise either by donation of the π electrons from the C–N triple bond, or from the "lone pair" localised on the nitrogen atom. In all the complexes of metal halides and alkyl cyanide so far isolated the bonding is believed to be of the latter type.

We shall now discuss these complexes, with emphasis on their structure and type of bonding involved.

3. Reactions of metal halides with unidentate alkyl cyanides

(a) Halides of Non-transition Metals.—The trihalides of boron and aluminium, and the tetrahalides of tin, form well characterised complexes with alkyl cyanides. These and other complexes of the non-transition metal halides are summarised in Table 1.[11–23]

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[7] P. Venkateswarlu, *J. Chem. Phys.*, 1951, **19**, 293; 1952, **20**, 923.

[8] See, *e.g.*, W. E. Fitzgerald and G. J. Janz, *J. Mol. Spectroscopy*, 1957, **1**, 49.

[9] L. Pauling, H. D. Springall, and K. J. Palmer, *J. Amer. Chem. Soc.*, 1939, **61**, 927; M. D. Danford and R. L. Livingston, *ibid.*, 1955, **77**, 2944.

[10] J. W. Linnett, *J. Chem. Phys.*, 1940, **8**, 91.

[11] R. Fricke and F. Ruschhaupt, *Z. anorg. Chem.*, 1925, **146**, 103.

[12] H. Bowlus and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1931, **53**, 3835.

[13] H. J. Coever and C. Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522.

[14] W. Gerrard, M. F. Lappert, and J. W. Wallis, *J.*, 1960, 2178.

[15] S. Geller and O. N. Salmon, *Acta Cryst.*, 1951, **4**, 379.

[16] E. L. Muetterties, *J. Inorg. Nuclear Chem.*, 1960, **15**, 182.

[17] A. K. Holliday, F. J. Marsden, and A. G. Massey, *J.*, 1961, 3348.

[18] C. D. Schmulbach, *J. Inorg. Nuclear Chem.*, 1964, **26**, 745, and references therein.

[19] A. I. Popov and F. B. Stute, *J. Amer. Chem. Soc.*, 1956, **78**, 5737.

[20] R. C. Aggarwal and M. Onyszchuk, *Proc. Chem. Soc.*, 1962, 20.

[21] A. A. Woolf, *J. Inorg. Nuclear Chem.*, 1956, **3**, 285.

[22] P. Pfeiffer and O. Halperin, *Z. anorg. Chem.*, 1914, **87**, 335.

[23] N. A. Pushin, M. Ristic, I. Parchomenko, and J. Ubovic, *Annalen*, 1942, **553**, 278.

TABLE 1. *Complexes of non-transition metal halides*

Halide	Alkyl cyanide R =	Halide/RCN mole ratio	Comments	Ref.
$BeCl_2$	Me, Et, Ph	1:2		11
BF_3	Me, Et, Pr	1:1	Dissociated in vapour phase	12, 13
BCl_3	Me, Et, Pr, Bu, Ph	1:1		13, 14
BBr_3	Me	1:1		15
BI_3	Me	1:2	Complex "impure"	16
B_2Cl_4	Me	1:2	Decomposes above 130° to BCl_3·MeCN	17
$AlCl_3$	Me	1:1, 2:3 and 1:2	Hygroscopic	18
$AlBr_3$	Me	1:2	Decomposes ~ 85°	19
GeF_4	Me	1:1 and 1:2	Thermally stable and non-volatile	20
SnF_4	Me	1:2	Sparingly soluble in excess MeCN	21
$SnCl_4$	Me, Et, Pr, Ph	1:2	In benzene dissociates to 1:1 adduct	13
$SnBr_4$	Me, Et, Ph	1:2		22, 23

The boron(III) iodide complex is of uncertain stoicheiometry as are several alkyl cyanide adducts of magnesium bromide which have been reported.[24] Silicon(IV) bromide has been described as forming a white 1:2 complex with methyl cyanide,[25] but recent work shows that no reaction occurs under anhydrous conditions.[26] Germanium(IV) chloride also fails to react with alkyl cyanides,[13,27] as do silicon(IV) chloride and tin(IV) iodide.[26] This behaviour is in keeping with the usual acceptor order of the tetrahalides of Group IVB,[26] *i.e.*, F>Cl>Br>I and Sn≫Ge>Si.

It is noteworthy that the phosphorus and antimony pentahalides dissolve in methyl cyanide. In the case of PCl_5, the usual ionic dissociation

$$PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$$

occurs,[28] and there is no evidence for the formation of solvated species of the type $[PCl_4(MeCN)_2]^+$. With $SbCl_5$ a solid solvate of composition $SbCl_5$,MeCN (m.p. 175°) has been isolated.[29] This was formulated as the heteropolar compound $[SbCl_4][SbCl_6]$,2MeCN,[29] but recent infrared spectra studies[28] on this system indicate that the octahedral species *trans*-$[SbCl_4(MeCN)_2]^+$ and $[SbCl_6]^-$ predominate.

Because the alkyl cyanide complexes of the boron, aluminium, and tin halides have been the most thoroughly investigated we will now consider them in more detail.

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[24] B. N. Menschutkin, *Z. anorg. Chem.*, 1909, **61**, 111.
[25] J. E. Reynolds, *J.*, 1909, 25, 512.
[26] I. R. Beattie, *Quart. Rev.*, 1963, **17**, 382.
[27] V. V. Udovenko and Yu. Ya Fialkov, *Zhur. neorg. Khim.*, 1957, **2**, 2126.
[28] I. R. Beattie and M. Webster, *J.*, 1963, 38.
[29] L. Kolditz and H. Preiss, *Z. anorg. Chem.*, 1961, **310**, 242.

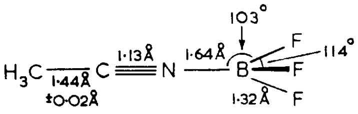
(i) *Boron*(III) *halides.* A wide variety of alkyl cyanides form 1:1 adducts with boron(III) halides and these are generally stable at room temperature in the absence of moisture.[14] They are readily hydrolysed by cold water, and ligand-exchange experiments of the type

$$BCl_3,MeCN + L \rightleftharpoons BCl_3,L + MeCN$$

have been carried out.[14] This gives the donor order: pyridine>tetrahydrofuran>Bu^n_2S>MeCN>acylic ethers, for BCl_3 as acceptor.

Vapour-pressure measurements[30] on BX_3,MeCN (X = F or Cl) show these complexes to be completely dissociated in the vapour phase, whereas in dilute benzene solutions no appreciable dissociation occurs.[13] This dissociation of the complexes in the vapour phase has been used as a method of purifying boron(III) fluoride *via* the complex BF_3,PhCN.[31]

The crystal structure of BF_3,MeCN has been determined[32] and the bond parameters are shown below. The most important conclusions from this structure determination is that the C–C–N–B system is linear. This is of particular significance since in all alkyl cyanide complexes of metal halides investigated the linearity of this system is apparently maintained,* and this is expected for donation from the lone-pair on the nitrogen atom. Both the C–C and C–N bond lengths in this complex are slightly shorter than in free methyl cyanide,[9] and this would imply a slight increase in the C–N bond order in the complex. The analogous chloride and bromide complexes are isomorphous but no structural details have been reported for these molecules.[15]



Bond parameters for BF_3,MeCN (C_{3v} symmetry).

In the series BF_3,L, where L = $MeNH_2$, MeCN, NH_3 and Me_3N, the methyl cyanide adduct has the longest and weakest B–N bond.[33] These structural data correlate well with the relative stabilities of these addition compounds. Thus BF_3,MeCN is completely dissociated in the vapour phase at 50°C whereas BF_3,$MeNH_2$ is stable.

The infrared active C–N stretching frequency increases by 70—110 cm.$^{-1}$ upon complex formation,[13,14] and this increase is diagnostic of complex formation *via* the lone-pair on the nitrogen atom. The intensity

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* There is some evidence for a bent C–N–Cu bond in $Cu_2Cl_4(MeCN)_2$ and $Cu_3Cl_6(MeCN)_2$ (see p. 136).

[30] A. W. Laubengayer and D. S. Sears, *J. Amer. Chem. Soc.*, 1945, **67**, 164.

[31] H. C. Brown and R. B. Johannesen, *J. Amer. Chem. Soc.*, 1950, **72**, 2934.

[32] J. L. Hoard, T. B. Owen, A. Buzzell, and O. N. Salmon, *Acta Cryst.*, 1950, **3**, 130.

[33] J. L. Hoard, S. Geller, and T. B. Owen, *Acta Cryst.*, 1951, **4**, 405.

of the C–N stretching vibration in the complexes is very much greater than in the free nitriles,[13,34] and this is attributed to an increase in the polarity of the C–N bond. Beattie and Gilson[35] have recently discussed the increase in the C–N stretching frequency in terms of (*a*) coupling of the C–N and B–N stretching frequencies, and (*b*) some increase in the C–N force constant. For BX_3,MeCN, the C–N stretching frequency is insensitive to variations of the mass of X and the B–N force constant. An alternative explanation of this frequency increase involves the postulation of structures with different bond multiplicities.[34] The infrared spectrum of these complexes is further dealt with in Section 5.

(ii) *Aluminium*(III) *halides.* A recent phase study[18] has confirmed the existence of $AlCl_3$,2MeCN[19,36] and $AlCl_3$,MeCN,[37] but earlier reports of $2AlCl_3$,MeCN[38] could not be substantiated. The complex $2AlCl_3$,3MeCN is also known,[18] and melting point data suggest it is more stable than $AlCl_3$,2MeCN. The above compounds and $AlBr_3$,2MeCN[19] are white, generally hygroscopic solids. The chloride complexes are believed to be of the type Al_2Cl_6,*n*MeCN, where $n = 2$, 3 or 4.

Molecular weight and Raman spectra studies have been used[18] to determine the nature of the solute species present in dilute solutions of aluminium(III) chloride in methyl cyanide. The cationic species $[Al_2Cl_5, n\text{MeCN}]^+$ have been proposed on the basis of the dissociation

$$2n\text{MeCN} + 3\text{Al}_2\text{Cl}_6 \rightarrow 2[\text{Al}_2\text{Cl}_5,n\text{MeCN}]^+ + 2\text{AlCl}_4^-$$

The presence of $AlCl_4^-$ in the system was shown by its characteristic Raman spectrum.

(iii) *Tin*(IV) *halides.* The 1:1 and 1:2 alkyl cyanide and phenyl cyanide adducts of tin(IV) chloride have been extensively investigated.[13,39,40] Dipole moment and molecular weight data show that in benzene solution $SnCl_4$,2RCN dissociate to form the corresponding 1:1 adducts.[39,41] Brown and Kubota[39] have also studied the dissociation of $SnCl_4$,2PhCN from infrared spectra studies. Using this, together with dielectric constants, they conclude that $SnCl_4$,PhCN has a dipole moment of 8·4D (*i.e.*, C_{3v} or C_{4v} symmetry possible).* Other workers however obtained no spectroscopic evidence for the presence of 1:1 adducts.[13] No reliable moment could be calculated for the 1:2 addition compound,[39] although earlier studies by Ulich and his co-workers[41] suggest that the moment for $SnCl_4$,2EtCN is high, thus favouring a *cis*-octahedral configuration.

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* In this and subsequent symmetry classifications we shall assume that R in RCN is a point.

[34] W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J.*, 1960, 2182.

[35] I. R. Beattie and T. Gilson, *J.*, 1964, 2292.

[36] W. L. Groeneveld and A. P. Zuur, *Rec. Trav. chim.*, 1957, **76**, 1005.

[37] G. Perrier, *Compt. rend.*, 1895, **120**, 1424.

[38] G. Perrier, *Bull. Soc. chim. France*, 1895, **13**, 1031.

[39] T. L. Brown and M. Kubota, *J. Amer. Chem. Soc.*, 1961, **83**, 331.

[40] T. L. Brown and M. Kubota, *J. Amer. Chem. Soc.*, 1961, **83**, 4175.

[41] H. Ulich, E. Hertel, and W. Nespital, *Z. phys. Chem.*, 1932, *B*, **17**, 21.

If dissociation does occur in solution it can give rise to the possibility of *cis–trans* isomerization

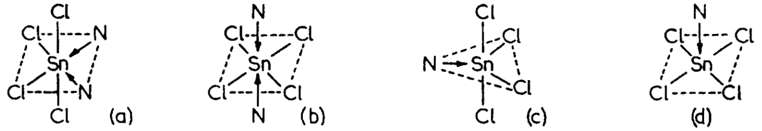
$$cis\text{-}SnCl_4,2MeCN \rightleftharpoons SnCl_4,MeCN + MeCN \rightleftharpoons trans\text{-}SnCl_4,2MeCN$$

and this must be generally true for soluble species of the type $MX_4,2L$.

Both the frequency and intensity of the C–N stretching vibration show characteristic increases in the complexes.[13,40,42] A simplified normal co-ordinate analysis for the methyl cyanide complex $SnCl_4,2MeCN$ indicates that a kinematic coupling should give rise to a small increase in frequency.[40]

The far infrared and Raman spectra of $SnCl_4,2RCN$ have been examined in the solid and solution.[40,43,44] The number of metal–halogen stretching vibrations in the infrared spectrum is consistent with a *cis*-configuration,[44] and bands previously assigned to Sn–N vibrations[40] have been shown to be associated with the Sn–Cl stretching vibrations.[44,45] Solution spectra below 400 cm.$^{-1}$ have confirmed the presence of the 1:1 adducts, $SnCl_4$, RCN.[44] Since the alkyl cyanides contain the linear C–C–N group, steric hindrance is unlikely to force a *trans*-configuration, as is found with other complexes of the type $SnCl_4,2L$,[45] where L is a fairly bulky ligand such as Et_2O or Me_3N.

For *cis*-$SnCl_4,2RCN$ a splitting of the C–N stretching frequency might be expected, as has been observed for *cis*-complexes containing co-ordinated phosphoryl molecules where the P=O stretching frequency is a doublet.[46] However, if the coupling through the central metal atom is weak, this splitting may not be observed.* Brune and Zeil[43] measured the Raman spectra of $SnCl_4,2RCN$ and suggested that these molecules possessed a *trans*-configuration. Their observation of a band at 340 cm.$^{-1}$, which is also observed in the infrared spectrum at 339 cm.$^{-1}$, is consistent with the *cis*-configuration, since molecules possessing a centre of symmetry (*i.e.*, *trans* D_{4h}) cannot have vibrations which are both infrared and Raman



Some possible stereochemistries for $SnCl_4,2RCN$: (a) *cis* (C_{2v}), (b) *trans* (D_{4h}), and $SnCl_4,RCN$: (c) trigonal bipyramid (C_{2v}), (d) square pyramid (C_{4v}).

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* The configuration of *cis*-$SnCl_4,2POCl_3$ has been confirmed by a crystal structure determination; see C. I. Branden, *Acta Chem. Scand.*, 1963, **17**, 759. The splitting of the P=O (or C≡N) stretching frequency could also arise from the presence of non-equivalent $POCl_3$ or RCN molecules, or from solid state effects.

[42] H. A. Brune and W. Zeil, *Z. Naturforsch.*, 1961, **16a**, 1251.

[43] H. A. Brune and W. Zeil, *Z. phys. Chem.* (*Frankfurt*), 1962, **32**, 384.

[44] I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J.*, 1963, 1514.

[45] I. R. Beattie and L. Rule, *J.*, 1964, 3267.

[46] J. C. Sheldon and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775.

active. This is a consequence of the well-known mutual-exclusion principle.[47]

A normal co-ordinate analysis of $SnCl_4$,MeCN[48] shows this molecule to have a trigonal-bipyramidal (C_{2v}) structure. This is only one of several possible structures for this molecule, two of which are shown above.

(b) Halides of Transition Metals.—Transition-metal halides have been by far the most extensively investigated and in some cases they form complexes in several metal oxidation states. Complexes of alkyl cyanides with transition-metal halides were first reported as long ago as 1858,[49] but few detailed studies have been carried out until recently.

We shall divide this section according to the solvolytic nature of the metal halides, *i.e.*, Group *A* being complexes formed by the scandium, titanium, vanadium, and chromium sub-groups, and Group *B* by the remaining transition metals.

(i) *Group A.* The crystalline complexes[50–66] formed by these metal halides are readily hydrolysed and consequently they can only be handled under rigorously anhydrous conditions. These experimental difficulties have until recently impeded the study of several of these complexes.

In several instances complexes of differing stoicheiometry and oxidation state can be obtained by altering the experimental conditions. Thus vanadium(IV) chloride reacts with alkyl cyanides to form complexes of the types VCl_4,2RCN or VCl_3,3RCN, depending upon the presence or absence of an inert solvent.[56]

In addition to the complexes shown in Table 2, several other systems have been investigated. The complexes $TiCl_4$,3RCN reported by Hertel and Demmer[53] could not be isolated by others,[23] and from the reactions of zirconium(IV) fluoride[52] and vanadium(II) chloride[67] with alkyl cyanides

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[47] See, *e.g.*, K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds", J. Wiley and Sons, Inc., New York, 1963, p. 24.

[48] W. Zeil and C. Dietrich, *Z. phys. Chem. (Frankfurt)*, 1963, **38**, 36.

[49] W. Henke, *Annalen*, 1858, **106**, 280.

[50] H. Funk and B. Koehler, *Z. anorg. Chem.*, 1963, **67**, 325.

[51] H. J. Emeléus and G. S. Rao, *J.*, 1958, 4245.

[52] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082.

[53] E. Hertel and A. Demmer, *Annalen*, 1932, **499**, 134.

[54] R. S. Kern, *J. Inorg. Nuclear Chem.*, 1963, **25**, 5.

[55] R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J.*, 1963, 379.

[56] M. W. Duckworth, G. W. A. Fowles, and R. A. Hoodless, *J.*, 1963, 5665.

[57] G. W. A. Fowles and R. A. Walton, *J.*, 1964, 4953.

[58] E. M. Larsen and L. E. Trevorron, *J. Inorg. Nuclear Chem.*, 1956, **2**, 254.

[59] H. Funk, G. Mohaupt, and A. Paul, *Z. anorg. Chem.*, 1959, **302**, 199.

[60] H. Funk, W. Weiss, and M. Zeising, *Z. anorg. Chem.*, 1958, **296**, 36.

[61] K. Feenan and G. W. A. Fowles, *J.*, 1964, 2842.

[61a] J. P. Fackler, personal communication.

[62] H. L. Krauss and W. Huber, *Ber.*, 1961, **94**, 2864.

[63] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J.*, 1964, 4531.

[64] D. A. Edwards, *J. Inorg. Nuclear Chem.*, 1965, **27**, 303.

[65] E. A. Allen, K. Feenan, and G. W. A. Fowles, *J.*, 1965, 1636.

[66] H. Funk and G. Mohaupt, *Z. anorg. Chem.*, 1962, **315**, 204; G. W. A. Fowles and J. Frost, unpublished observations.

[67] R. A. Walton, unpublished observations.

TABLE 2. *Complexes of Group A transition-metal halides*

Halide	Alkyl cyanide R =	Halide/RCN mole ratio	Comments	Ref.
$ScCl_3$	Me, Ph	1:3		50
TiF_4	Me, Et, Ph	1:1	Soluble in MeCN to give 1:2 adduct	51, 52
$TiCl_4$	Me, Et, Ph	1:1 and 1:2	Soluble in parent RCN	13, 51, 53
$TiBr_4$	Me, Et, Ph	1:2		51
TiI_4	Me	1:2		51
TiX_3	Me, Et, Pr	1:3	X=Cl and Br. Also prepared from $TiX_3,2NMe_3$	54—57
ZrX_4	Me, Et, Pr, Ph	1:2	X = Cl and Br. Soluble in parent RCN	51
$HfCl_4$	Me	1:2	Only investigated by phase study	58
VCl_4	Me, Et	1:2	Sublimes *in vacuo*; soluble in benzene	56, 59
VX_3	Me, Et	1:3 and 1:4	X = Cl and Br	55, 56
$VOCl_3$	Me, Ph	1:2	Prepared in "inert" solvent	60
NbX_5	Me, Et, Pr	1:1	X = Cl or Br. Soluble in excess RCN and in non-polar solvents	61
TaX_5	Me, Et, Pr	1:1		61
$CrCl_3$	Et	1:3	Purple-back solid	54
CrX_2	Me	1:2	X = Cl, Br or I. Complexes octahedral	61*a*
MoO_2Cl_2	Me, Ph	1:2		62
$MoCl_5$	Me, Et, Pr	1:2	$MoCl_4,2RCN$ isolated	63
$MoOCl_3$	Me, Et, Pr	1:2	Emerald-green crystalline solids	64
$MoBr_3$	Me, Et, Pr	1:3	$MoBr_3,3PrCN$ soluble in benzene	65
WCl_6	Me, Et, Pr	1:2	$WCl_4,2RCN$ isolated	63
WCl_5	Me	1:2	$WCl_4,2RCN$ isolated	63
WBr_5	Me, Et, Pr	1:2	$WBr_4,2RCN$ isolated	63
$WOCl_4$	Me, Et, Pr, Ph	1:1		66

no complex has been isolated. Also of some interest are several mixed-ligand complexes of the type $MX_3,nL,2RCN$, where $n = 1$ or 2, and L = 2,2′-bipyridyl, triphenylphosphine, or triphenylarsine. These are formed by the reaction of titanium(III) chloride[68] or molybdenum(III) bromide[65] with the donor ligand L in alkyl cyanide solutions.

We shall now discuss the stoicheiometry, properties, and stereochemistry of several of these complexes.

Stoicheiometry. Reaction of the halides with a large excess of alkyl cyanide invariably leads to the formation of complexes of empirical formula MX_5,RCN, MX_4,RCN, or $MX_3,3RCN$, depending upon the

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[68] G. W. A. Fowles, R. A. Hoodless, and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1965, **27**, 391.

halide used. The niobium(V) and tantalum(V) complexes are the only examples known of the first type, and they have been shown to be non-ionic six-co-ordinate monomers.[61]

In the case of MX_4,2RCN available evidence points to six co-ordinate species in the solid state, although in solution some are believed to dissociate to yield the 1:1 adducts. VCl_4,2RCN, for example,[56] dissociates in benzene solution but VCl_4,RCN has not been isolated from the solution. Titanium(IV) chloride forms both the 1:1 and 1:2 adducts,[23,53] whereas titanium(IV) fluoride forms only the 1:1 adduct,[51,52] and this is probably dimeric in the solid[52] and consequently six co-ordinate.

Only in case of $MoBr_3$,3PrCN has a complex of type MX_3,3RCN been shown to be monomeric in solution,[65] but those of titanium and vanadium(III) halides are non-ionic in the parent alkyl cyanide and almost certainly contain the discrete six-co-ordinate species [MX_3,3RCN].[55,56] The complexes of composition VX_3,4MeCN, probably contain one mol. of alkyl cyanide in the crystal lattice, since in the case of the chloride complex, washing with a non-polar solvent leaves only VCl_3,3MeCN.[56]

Reduction reactions. In several instances alkyl cyanides behave as strong reducing agents with transition-metal halides. Thus only complexes of quadrivalent molybdenum and tungsten can be isolated when alkyl cyanides react with the hexa- and penta-halides of these elements.[63] This is very similar to the behaviour of these halides with pyridine and other bases.[69,70] Vanadium(IV) chloride reacts with alkyl cyanides in carbon tetrachloride solution to give VCl_4,2RCN,[56,59] but direct reaction in the absence of a solvent results in reduction of vanadium to the tervalent state and formation of VCl_3,3RCN.[56] In no cases have oxidation products been isolated although HCl has been detected in some systems.[63]

With other halides (*e.g.*, $TiCl_4$,$NbCl_5$), no reduction occurs even under forcing conditions.

Solubility studies. All the cyanide complexes described in this section are soluble to some extent in the parent alkyl cyanide.

VCl_4,2RCN dissociates in benzene[56] and in this respect resembles the analogous tin(IV) chloride complexes. This is in contrast to the behaviour of the corresponding molybdenum and tungsten compounds which are monomeric in this solvent.[63] Ulich, Hertel, and Nespital[41] have reported a similar dissociation of $TiCl_4$,2EtCN in benzene, but other workers[67] find little evidence for this from molecular-weight studies. The above dissociations may well be dependent upon the experimental conditions and a trace of moisture in the system could lead to an apparent dissociation owing to a small amount of hydrolysis.

Feltz[71] has investigated the species present when $TiCl_4$,2MeCN is dissolved in "slightly moist" methyl cyanide, and isolated a crystalline

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[69] R. E. McCarley and T. M. Brown, *Inorg. Chem.*, 1964, **3**, 1232.

[70] G. W. A. Fowles, unpublished observations.

[71] A. Feltz, *Z. anorg. Chem.*, 1963, **323**, 35.

product of composition $Ti_2Cl_6O,4MeCN$. This again emphasises the need to work under rigorously anhydrous conditions when studying these complexes since hydrolysis often results in misleading analytical and structural data.

Magnetic and spectral properties. The magnetic moments of the paramagnetic complexes of the first-row transition-metal halides are, as expected, diagnostic of valency state and close to the "spin-only" moments.[54–56]

$TiCl_3,3MeCN$ is the only example where the variation of magnetic susceptibility with temperature has been investigated.[55] The magnetic data fit[72] a ground state distortion in which the $^2T_{2g}$ term is split by $\sim$ 600 cm.$^{-1}$.

In the case of $MoCl_4,2RCN$ ($\mu \sim 2{\cdot}5$ B.M.) and $WX_4,2RCN$ ($\mu \sim 1{\cdot}7$—$2{\cdot}0$ B.M.),[63] the low moments ($\mu_{\text{spin only}} = 2{\cdot}83$ B.M.) presumably arise from the larger values of the spin–orbit coupling constants found for second- the third-row transition elements.[73]

For $MoBr_3,3RCN$ the magnetic moments occur in the range 3·5—3·8 B.M.,[65] and these values are typical of octahedral molybdenum(III).

From a study of the spectral properties of a variety of complexes of titanium(III) chloride,[55,56] alkyl cyanides would appear to occupy a high position in the spectrochemical series. A comparison of *Dq* values leads to the order

$$RCN > H_2O > R_2CO > \text{dioxan} > \text{tetrahydrofuran} > Cl > Br.$$

With the complexes of molybdenum(IV) and tungsten(IV) halides,[63] the spectra are complicated by the presence of intense charge-transfer bands which obscure the weak spin-forbidden *d–d* transitions.

The ultraviolet spectra[74] of the titanium(IV) and zirconium(IV) d^0 complexes show intense bands which have been assigned to transitions of the types $RCN(\pi) \rightarrow d_\epsilon$ and halogen $(\pi) \rightarrow d_\epsilon$.

The infrared spectra of the complexes show the expected characteristic increase in the C–N stretching frequency. The complexity of the spectra of several complexes of the type $MX_4,2RCN$ (M = Ti or Zr and X = Cl or Br) favours a *cis*-configuration,[75] and the Raman spectrum[67] of $ZrCl_4,2RCN$ seems to confirm this. A previous assignment of the stereochemistry of the titanium and zirconium complexes from the splitting of the C–N stretching frequency[76] is questionable (see p. 131). Further evidence for the *cis*-configuration is provided by the ^{19}F magnetic resonance spectrum of $TiF_4,MeCN$ in methyl cyanide;[52] the *cis*-1:2 adduct is believed to be present in solution.

[72] B. N. Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198.

[73] See, *e.g.*, B. N. Figgis and J. Lewis, "Modern Co-ordination Chemistry," Interscience Publ. Inc., New York, 1960, p. 428.

[74] G. W. A. Fowles and R. A. Walton, *J.*, 1964, 2840.

[75] I. R. Beattie and M. Webster, *J.*, 1964, 3507.

[76] G. S. Rao, *Z. anorg. Chem.*, 1960, **304**, 351.

(ii) *Group B.* The diamagnetic colourless crystalline complexes $CuX,MeCN$, where $X = Cl$ or Br, and $CuNO_3,4MeCN$ were first reported by Morgan in 1923.[77] More recently, several complexes of the type $CuX,4RCN$, where $X = BF_4$, ClO_4 or NO_3, have been prepared by reduction of solutions of copper(II) salts in methyl cyanide,[78] or by the reaction of copper(I) oxide with a boron(III) fluoride–ether solution in the appropriate alkyl cyanide.[79] Conductivity data[78] in methyl cyanide show that these complexes behave as 1:1 electrolytes in this solvent. The corresponding silver and gold complexes $[M^I(RCN)_4]X$, where $X = BF_4$ or ClO_4 are also known,[79,80] and the stable zinc complex[81] has been isolated as its perchlorate and tetrafluoroborate salts.

Although the complex ions $[CuCl(MeCN)_3]^+$, $[CuCl_2(MeCN)_2]$, $[CuCl_3(MeCN)]^-$, and $[CuCl_4]^{2-}$ are believed to be present in a copper(II) chloride solution in methyl cyanide,[82] reduction occurs in the copper(II) bromide system[83] and bromine is liberated.

The orange-yellow gold(III) complexes $AuCl_3,RCN$ have been prepared,[49,84] and the chloride is also capable of aurating several aryl cyanides

$$AuCl_3 + (AH)\text{–}CN \rightarrow AuCl_2\text{–}A\text{–}CN + HCl$$

where (AH)–CN represents the original aryl cyanide.

Naumann[85] has described the preparation of the light blue and yellow-brown complexes $CuCl_2,2MeCN$ and $CuCl_2,MeCN$, respectively. Willett and Rundle[86] have recently prepared a third complex, $CuCl_2,\frac{2}{3}MeCN$, and determined the crystal structure of this complex and of $CuCl_2,MeCN$. These two complexes were shown to be a trimer and dimer, respectively, with an essentially planar arrangement of the ligands about the copper atoms and the alkyl cyanide molecules in terminal positions *trans* to one another. Although the methyl cyanide molecules were linear in the complexes, the Cu–N–C angle was significantly less than 180°. This is the first example known where the linearity of the M–N–C system in alkyl cyanide complexes is not maintained, and Willett and Rundle concluded[86] that the bonding nitrogen atom uses orbitals with partial sp^2 character. Whether this is unique will require a more exhaustive structural investigation of these and similar systems.

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[77] H. H. Morgan, *J.*, 1923, 2901.

[78] B. J. Hathaway, D. G. Holah, and J. D. Postlethwaite, *J.*, 1961, 3215.

[79] H. Meerwein, V. Hederich, and K. Wunderlich, *Arch. Pharm.*, 1958, **291**, 541 (*Chem. Abs.*, 1960, **54**, 5427).

[80] G. Bergerhoff, *Z. anorg. Chem.*, 1964, **327**, 139.

[81] B. J. Hathaway and A. E. Underhill, *J.*, 1960, 3705; B. J. Hathaway, D. G. Holah, and A. E. Underhill, *J.*, 1962, 2444.

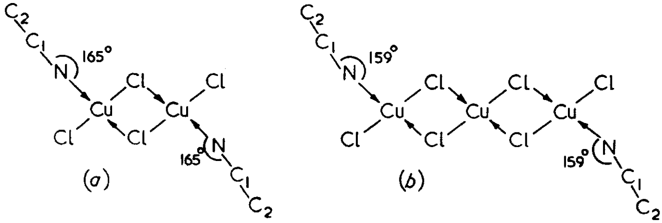
[82] C. Furlani, A. Sgamellanti, and G. Ciullo, *Ric. Sci.*, *Rend. Sez.*, 1964, *A*, **4**, 49.

[83] W. Schneider and A. V. Zelewsky, *Helv. Chim. Acta.*, 1963, **46**, 1848.

[84] M. S. Kharasch and T. M. Beck, *J. Amer. Chem. Soc.*, 1934, **56**, 2057.

[85] A. Naumann, *Ber.*, 1914, **47**, 247.

[86] R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, 1964, **40**, 838.



(a) $Cu_2Cl_4,2MeCN$
(b) $Cu_3Cl_6,2MeCN$

Chlorine-bridged methyl cyanide complexes of copper(II) chloride.

A single-crystal *X*-ray analysis of $ZnCl_2,2MeCN$[87] has confirmed a distorted tetrahedral arrangement of bonds about the zinc atom. The linearity of the C–C–N bond was again confirmed and the Zn–N bond length is 2·0 Å. This bond length is similar to that found for the copper(II) complexes described above, but is appreciably longer than the B–N bond in $BF_3,MeCN$.[32]

Until recently, few of the alkyl cyanide complexes of manganese, iron, cobalt, or nickel had been studied in any detail. The complexes CoX_2, nRCN, where $X = Cl$ or Br and $n = 2$ or 3, were isolated many years ago,[85,88] and solution studies on the CoX_2–MeCN system have received attention.[89] Spectral and conductivity data in methyl cyanide suggest that in solution a series of equilibria occur involving the tetrahedral species $[CoX_2(MeCN)_2]$, $[CoX_3(MeCN)]^-$, and $[CoX_4]^{2-}$ and the octahedral ion $[Co(MeCN)_6]^{2+}$. Janz and his co-workers[89] isolated the crystalline complexes $[CoX_2,3MeCN]_2$ from these systems which they formulated as ionic $[Co(MeCN)_6{}^{2+}][CoX_4{}^{2-}]$. Their conductivity data, however, were inconsistent with this ionic structure and later work[90] has shown the "complexes" $[CoX_2,3MeCN]_2$ to be tetrahedral $CoX_2,2MeCN$ with a further mol. of methyl cyanide held in the crystal lattice.

Hathaway and Holah[90] have recently investigated in great detail the methyl cyanide complexes of manganese, iron, cobalt, and nickel. The crystalline complexes were investigated by conductivity, spectral, and magnetic studies, and the presence of tetrahedral and/or octahedral species was established. Most complexes are of the general formula MX_2,nMeCN where $n = 2, 3, 4$ or 6 but the complexes $FeCl_3,2MeCN$ and $Fe_3X_8,6MeCN$ can also be isolated. The latter complex ($X = Cl$ or Br) is interesting since it was shown to be the mixed iron(II)–iron(III) complex $[Fe(MeCN)_6{}^{2+}]$ $[FeX_4{}^-]_2$, containing octahedral iron(II) and tetrahedral iron(III). It was

[87] I. V. Isakov, and Z. V. Zvonkova, *Doklady Akad. Nauk S.S.S.R.*, 1962, **145**, 801.

[88] A. Hantzsch, *Z. anorg. Chem.*, 1927, **159**, 273.

[89] W. Libus, *Roczniki Chem.*, 1962, **36**, 999; G. J. Janz, A. E. Marcinkowsky, and H. V. Venkatasetty, *Electrochim. Acta*, 1963, **8**, 867.

[90] B. J. Hathaway and D. G. Holah, *J.*, 1964, 2400, 2408.

suggested[90] that the formation of the chloride and bromide complexes was probably associated with the stability of the tetrachloro- and tetrabromoferrate(III) anions.

These workers[90] also concluded that the spectrochemical series

$$\mathrm{MeCN} > \mathrm{H_2O} > \text{Ethyl acetate} \approx \mathrm{MeNO_2}$$

holds, and we may compare this with the similar series derived for complexes of titanium(III) chloride (see p. 135).

The nickel(II) complexes $NiX_2,2RCN$ and $NiX_2,4RCN$, where R = Me, Et or Ph, have also been reported[91] by Russian workers. Few structural data are available although the structures which were suggested differ from those of Hathaway and Holah.[90] A series of aquocyanide and aminocyanide complexes of nickel can also be prepared.[91]

Of the platinum metals, only the complexes of platinum(II) with alkyl cyanides have been investigated in any detail. The rhodium(III) and iridium(III) complexes $(NH_4)_2(MCl_5,MeCN),H_2O$, are said to exist,[92] and a partial crystal structure of $PdCl_2,2PhCN$, shows[93] the molecule to have a *trans*-planar configuration.

In 1907 Hofmann and Bugge reported[94] the pale yellow complexes $PtCl_2,2RCN$, where R = Me or Ph, and on the basis of their chemical reactions Lebedinskii and his co-workers[95] assigned a *cis*-planar configuration to these complexes. The splitting of the C–N stretching vibration in $PtCl_2,2MeCN$ has been interpreted[96] as being consistent with this *cis*-configuration; this cannot however be regarded as unambiguous (see p. 131). Oxidation[97] of the bis(alkylcyanide) complexes yields derivatives of platinum(IV) of the types $PtX_4,2RCN$, where X = Cl or Br, or *trans*-$PtCl_2Br_2,2RCN$. The above platinum complexes were "normal", in that they show the characteristic increase in the C–N stretching frequency.

The so-called "anomalous" ammine–alkyl cyanide complexes[98] of platinum(II) form another class of complexes which have recently aroused interest.[99,100] They are of general formula $[Pt^{II}(RCN)_2(A)_n]X$, where $A = NH_3$ or a primary amine, $X = PtCl_4$ or Cl_2, and n = 1—4. In all cases the infrared spectrum shows absence of the C≡N frequency but

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[91] A. V. Babaeva and Kh. U. Ikramov, *Zhur. neorg. Khim.*, 1964, **9**, 591, 596.

[92] V. V. Lebedinskii and P. V. Simanovskii, *Izvest. Sekt. Platiny*, 1939, **16**, 53 (*Chem. Abs.*, 1940, **34**, 4685); V. V. Lebedinskii and I. A. Fedorov, *ibid.*, 1935, **12**, 87 (*Chem. Abs.*, 1935, **29**, 3254).

[93] J. R. Holden and N. C. Baenziger, *Acta Cryst.*, 1956, **9**, 194.

[94] K. A. Hofmann and G. Bugge, *Ber.*, 1907, **40**, 1772.

[95] V. V. Lebedinskii and V. A. Golovnya, *Izvest. Sekt. Platiny*, 1945, **18**, 38 (*Chem. Abs.*, 1947, **41**, 6187); 1948, **21**, 32 (*Chem. Abs.*, 1950, **44**, 10566).

[96] R. D. Gillard and G. Wilkinson, *J.*, 1964, 2835.

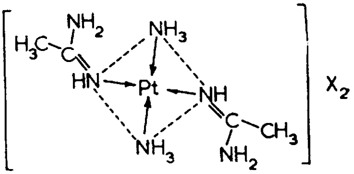
[97] V. A. Golovnya and Chia-Chien Ni, *Zhur. neorg. Khim.*, 1959, **3**, 1954.

[98] V. V. Lebendinskii and V. A. Golovnya, *Izvest. Sekt. Platiny*, 1939, **16**, 57 (*Chem. Abs.*, 1940, **34**, 4685).

[99] Yu. Ya Kharitonov, Chia-Chien Ni, and A. V. Babaeva, *Zhur. neorg. Khim.*, 1961, **6**, 131; 1962, **7**, 997; 1963, **8**, 34.

[100] Yu Ya Kharitonov, Chia-Chien Ni, and A. V. Babaeva, *Doklady Akad. Nauk S.S.S.R.*, 1961, **141**, 645.

presence of a C=N stretching frequency at ~ 1600 cm.$^{-1}$. It was concluded[99,100] that in the complexes the "free" alkyl cyanide was not co-ordinated, as in $[Pt(RCN)_2(R'NH_2)_4]X_2$, but that the complexes were in fact amidine derivatives $[Pt\{RC(NH)=NHR'\}_2(R'NH_2)_2]X_2$. Harris and Stephenson[101] had previously carried out an *X*-ray analysis on "$[Pt(MeCN)_2(NH_3)_4]Cl_2,H_2O$", and assigned a *trans*-octahedral configuration, in which the methyl cyanide molecules were bonded from the π electrons of the C–N triple bond. This they found was also consistent with the absence of the C=N stretching frequency. However, a recent redetermination of the crystal structure of this complex has confirmed[102] the amidine structure. The platinum is square planar with two ammonia molecules *trans* to one another.



Diammine bis(acetamidine) platinum(II) ion.

(iii) **Metal Carbonyls.**—Several metal carbonyls form complexes with alkyl cyanides. One, two, or three carbonyl groups are replaced in chromium, molybdenum, or tungsten hexacarbonyl, for example, to yield $(RCN)M(CO)_5$, $(RCN)_2M(CO)_4$, or $(RCN)_3M(CO)_3$. These complexes can be prepared photochemically[103,104] or by direct reaction.[105] The latter method gives $(RCN)_3M(CO)_3$ and these complexes are excellent intermediates in the formation of new compounds not available by other routes.[105]

Spectroscopic studies[106] have shown that complexes of the type $(MeCN)M(CO)_5$, $(MeCN)_2M(CO)_4$, and $(MeCN)_3M(CO)_3$, have C_{4v}, C_{2v}(*cis*), and C_{3v}(*cis*) symmetry, respectively. In all these complexes bonding is *via* the lone pair on the nitrogen atoms.[107]

4. Reactions of metal halides with bidentate alkyl cyanides

So far we have only considered complexes formed by the unidentate alkyl cyanides RCN. The bidentate cyanides $NC\cdot(CH_2)_2\cdot CN$ have also

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[101] C. M. Harris and N. C. Stephenson, *Chem. and Ind.*, 1957, 426.

[102] N. C. Stephenson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 801.

[103] W. Strohmeier and K. Gerlach, *Z. Naturforsch*, 1960, **15**, *b*, 622; W. Strohmeier and G. Schonauer, *Ber.*, 1961, **94**, 1346.

[104] G. R. Dobson, M. F. Amr El Sayed, I. W. Stolz, and R. K. Sheline, *Inorg. Chem.*, 1962, **1**, 526.

[105] D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.

[106] B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, 1963, **2**, 1023.

[107] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, 1963, **2**, 323.

been studied and in particular some interesting low-temperature spectroscopic studies carried out.

It has previously been shown that for BF_3,MeCN[32] and other complexes, donation from the lone pair on the nitrogen atom results in an essentially linear C–C≡N→M system. Thus formation of chelate complexes by bidentate cyanides will not be favoured for short chains, unless π bonding occurs from the C–N triple bond. Since no example of the latter type has been reported, the formation of chelates is unlikely. Although Morgan[77] suggested that $\{Cu^{I}[C_2H_4(CN)_2]_2\}NO_3$ contained chelating cyanide molecules, later work has shown this to be incorrect.

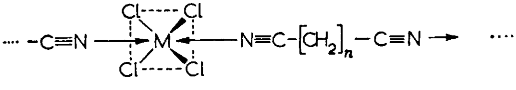
The vibrational spectrum[8,108] of liquid and solid succinonitrile $NC{\cdot}[CH_2]_2{\cdot}CN$ shows that the *trans*(C_2)–*gauche* (C_{2h}) ratio depends upon temperature, and that in the solid (—44°) the molecules exist in the pure *gauche* configuration. This *trans–gauche* isomerisation has proved invaluable in determining the configurations of the bidentate alkyl cyanides and their complexes with copper(I) nitrate.

The complex $\{Cu(NC{\cdot}[CH_2]_n{\cdot}CN)_2\}NO_3$ has been shown by *X*-ray analysis[109] and low-temperature spectroscopy[110] to consist of nitrate ions and polymeric chains with bridging alkyl cyanide molecules. The copper atoms are tetrahedrally surrounded by four nitrogen atoms with Cu–N distances of about 2·0 Å. The Cu–N–C–C grouping is essentially linear and the succinonitrile molecules take a *gauche* configuration.

Similar structural analyses have been carried out on glutaronitrile, adiponitrile, and their copper(I) nitrate complexes.[111]

Jain and Rivest[112] have found that the bidentate alkyl cyanides react with tin(IV), titanium(IV), and zirconium(IV) to give complexes of the type $2MX_4$,B, MX_4,B, or MX_4,2B, where B = $NC{\cdot}[CH_2]_n{\cdot}CN$, depending upon the experimental conditions and alkyl cyanide used. Few structural studies were carried out on these complexes although the 2:1 and 1:1 adducts were believed to be polymeric. The presence of free and co-ordinated cyanide groups was inferred from the infrared spectra of the 1:2 adducts. It was concluded that these complexes were six-co-ordinate addition compounds with only one CN group of each alkyl cyanide molecule co-ordinated.

Kubota and Schulze[113] have also prepared several of the 1:1 adducts with



[108] T. Fujiyama, K. Tokumaru, and T. Shimanouchi, *Spectrochim. Acta*, 1964, **20**, 415.

[109] Y. Kinoshita, I. Matsubara, and Y. Saito, *Bull. Chem. Soc. Japan*, 1959, **32**, 741.

[110] I. Matsubara, *Bull. Chem. Soc. Japan*, 1961, **34**, 1710.

[111] Y. Kinoshita, I. Matsubara, and Y. Saito, *Bull. Chem. Soc. Japan*, 1959, **32**, 1216; I. Matsubara, *ibid.*, 1961, **34**, 1719; 1962, **35**, 27.

[112] S. C. Jain and R. Rivest, *Canad. J. Chem.*, 1963, **41**, 2130.

[113] M. Kubota and S. R. Schulze, *Inorg. Chem.*, 1964, **3**, 853.

tin(IV) and titanium(IV) chloride, which they suggested were polymers with cyanide bridging.

Unlike the stable low-temperature conformer of succinonitrile, which is *gauche*,[8] this ligand assumes the *trans* form in these complexes.

The C–N stretching frequency increases by 30—60 cm.$^{-1}$ in the complexes, again ruling out π bonding from the C–N triple bond.

5. Infrared spectra of alkyl cyanide complexes

As emphasised in the preceding sections, alkyl cyanides co-ordinate to metal halides and carbonyls *via* the lone pair on the nitrogen atom. It seems to be worth correlating the C–N stretching frequency in the complexes with the bond type.

The shift of the C–N stretching frequency upon co-ordination is in the opposite sense to that observed with co-ordinated phosphine oxides, sulphoxides, ketones, and other donor groups, and clearly an explanation is required.

Two factors seem important in explaining this increase and both will now be discussed.

(a) Kinematic Coupling.—A simple valence-field calculation for the linear system R–C–N–M shows[40,114] that coupling of the C–N and M–N stretching vibrations should give rise to a small increase in the C–N stretching frequency, although the C–N force constant may be unchanged from that in the free ligand. The larger increase (70–110 cm.$^{-1}$) for the complexes BX_3,RCN arises from the higher frequency of the B–N stretching vibration than with other M–N vibrations.

It is of interest that a similar increase in frequency is observed for the nitrile oxides.[115]

(b) Ionic Contribution to the C–N Bond.—There appears to be some evidence for a slight increase in the C–N force constant[35] in BX_3,RCN, and this cannot be explained in terms of kinematic coupling.

It has recently been suggested[116] that the force constant of the C–H bond depends to a large extent on the ionic character of the bond. A small percentage of ionic character in the bond would increase its force constant, whereas larger amounts would decrease it.

Considering the C–N bond, then, a small increase in the polar nature of the bond may well give a shorter stronger bond. Evidence for this is provided by the intensity increase of the C–N stretching frequency on complex formation. This concept of ionic character has also been used to explain the C–N stretching frequencies of inorganic and organic cyanides.[117]

[114] E. R. Nightingale, Proc. 7th Internat. Conf. Co-ordination Chemistry, Stockholm, 1962, p. 217.

[115] S. Califano, R. Moccia, R. Scarpati, and G. Speroni, *J. Chem. Phys.*, 1957, **26**, 1770.

[116] R. G. Jones, J. A. Ladd, and W. J. Orville-Thomas, *Spectrochim. Acta*, 1964, **20**, 1697.

[117] M. F. Amr El-Sayed and R. K. Sheline, *J. Inorg. Nuclear Chem.*, 1958, **6**, 187.

It must be emphasised that the strength of the C–N bond may depend critically upon the percentage of ionic character and this in turn determines the sense of the frequency shift. Although kinematic coupling and ionic character of the C–N bond contribute to the frequency increase, neither is solely responsible for it.

6. Use of methyl cyanide as a solvent

The boiling point (81·6° at 760 mm.), freezing point (—45·7°), dielectric constant (37·5 at 20°), and other physical properties[4] of methyl cyanide make it a potentially useful solvent for inorganic chemists. It has consequently found wide application as a solvent for inorganic preparations and the measurement of physical properties of compounds.

These uses are now discussed and illustrated with suitable examples.

(a) Preparative Medium.—Addison and his co-workers[118] have found that the rates of reaction of copper, zinc, and uranium with dinitrogen tetroxide are greatly increased in the presence of methyl cyanide. Reactions of this type in methyl cyanide invariably lead to the formation of methyl cyanide complexes of the corresponding nitrate.[119] In several cases the co-ordinated methyl cyanide can be removed by pumping *in vacuo* or heating, and this may provide a route to the anhydrous nitrates. For example[120]

$$\mathrm{Ni} + \mathrm{N_2O_4} \xrightarrow{\mathrm{MeCN}} \mathrm{Ni(NO_3)_2,3MeCN} \xrightarrow[\textit{vacuo}]{\text{pump } \textit{in}} \mathrm{Ni(NO_3)_2,2MeCN}$$

$$\xrightarrow[\textit{in vacuo}]{170^\circ} \mathrm{Ni(NO_3)_2}.$$

Alkyl cyanide adducts are useful intermediates in the preparation of complex halides of transition metals. Nyholm and Schaife[121] have prepared the interesting tetrahedral species $[\mathrm{VX_4}]^-$, where X = Cl or Br, by reaction of vanadium(III) halides with RX, where R = $\mathrm{Et_4N}$ or $\mathrm{Ph_3MeAs}$, in methyl cyanide. The octahedral complex anions $[\mathrm{VX_4,2MeCN}]^-$ were first isolated and these when heated to 80° decomposed to give the tetrahedral halogeno-vanadate(III) anions.

Other complex halides of the type $[\mathrm{MX_6}]^{2-}$, where M = Ti, Zr, V, or Mo and X = Cl or Br, are formed[122] when the alkyl cyanide adducts $\mathrm{MX_4,2RCN}$ react with amine hydrohalide in chloroform.

Reaction of $\mathrm{MoCl_4,2RCN}$ and $\mathrm{MoBr_3,3RCN}$ with a variety of unidentate and bidentate ligands results in the replacement of co-ordinated alkyl cyanide and the formation of new complexes.[65] The 2,2′-bipyridyl and 1,10-phenanthroline adducts $\mathrm{MX_4,B}$, where M = Ti, Zr, Nb, or Ta

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[118] C. C. Addison, J. C. Sheldon, and N. Hodge, *J.*, 1956, 3906.

[119] C. C. Addison and N. Logan, "Preparative Inorganic Reactions", ed. W. L. Jolly, Vol. 1, p. 141.

[120] C. C. Addison and B. F. G. Johnson, unpublished observations.

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and X = Cl or Br, can be prepared[123] by reaction of the metal halide with the ligand in alkyl cyanide solution, the halide dissolving as its alkyl cyanide adduct.

Many other preparative uses of methyl cyanide are known in which complex formation with the solvent does not appear to occur. For example, it is a good solvent for the preparation of complex nitrates[124] of the type $[M(NO_3)_4]^{2-}$, where M = Mn^{II}, Co^{II}, Ni^{II}, or Cu^{II}.

(b) Solvent for Physical Measurements.—As a result of its appreciable dielectric constant many salts behave as strong electrolytes in methyl cyanide.[125] 1:1 and 1:2 electrolytes usually have molar conductivities in the ranges 120–160 and 220–280 $ohm^{-1}cm.^2$, respectively, for solutions containing about 10^{-3} mole of solute per litre.

Electrolytes generally have higher conductivities in methyl cyanide than in nitrobenzene or nitromethane and the former solvent is therefore to be preferred. All three solvents however suffer from the disadvantage that they may cause solvolysis which could lead to spurious conductivity data. For example, small conductivity values ($\Lambda_m \sim 30$ $ohm^{-1}cm.^2$) in methyl cyanide are usually indicative of an equilibrium of the type[123]

$$MX_n,L + MeCN \rightleftharpoons [MX_{n-1}\cdot L,MeCN]^+X^-$$

As a solvent for spectral measurements methyl cyanide again suffers from its tendency to cause solvolysis. The tetrahedral ions $[NiX_4]^{2-}$ and $[CuBr_4]^{2-}$, for example,[126] are very sensitive to solvolysis, but this can usually be reversed by addition of halide ions. The spectra of a variety of complex halides MX_6^{n-}, where M = U^{IV}, Np^{IV}, Pu^{IV}, W^{V} and X = Cl, Br, or I, have been measured[127] in methyl cyanide, and there is no evidence for reaction with the solvent.

Except for a band at 380 $cm.^{-1}$, which is infrared and Raman active, methyl cyanide is transparent below 400 $cm.^{-1}$ and is thus a particularly useful solvent for far infrared spectroscopy.[44]

In conclusion, it may be noted that the alkyl cyanides can be polymerised to the linear conjugated polymers $(-CR{=}N-)_n$ by heating many of the alkyl cyanide complexes of metal halides.[128]

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