Structures, Vibrational Spectra, and Ligand Behaviour of Tris(2-cyanoethyl)phosphine and its Oxide, Sulphide, and Selenide

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The crystal vibrational spectra of tris(2-cyanoethyl)phosphine, $P(CH_2CH_2CN)_3$, and its derivatives $P(CH_2CH_2CN)_3E$ (E = O, S, or Se) are discussed in the light of their known crystal structures. The CN stretching modes in $P(CH_2CH_2CN)_3$ are affected by intermolecular coupling effects but the spectra are otherwise interpreted in terms of the local molecular (site) symmetries. The difference between ν(PS) in $P(CH_2CH_2CN)_3S$ and ν(PSe) in $P(CH_2CH_2CN)_3Se$ is 161 cm^{-1}, much greater than the differences ν(PS) − ν(PSe) usually observed in related PR_3S and PR_3Se molecules. It is suggested that the PSe stretch may be severely affected by interaction with skeletal bending modes. The oxide, and more particularly, the sulphide and selenide, are much less effective ligands than the parent phosphine and the addition of an O, S, or Se atom to the phosphine molecule appears to have a pronounced deactivating effect on the donor abilities of the cyano-nitrogen atoms.

Tris(2-cyanoethyl)phosphine, $P(CH_2CH_2CN)_3$, and its oxide, sulphide, and selenide, $P(CH_2CH_2CN)_3E$ (E = O, S, or Se), are potentially multidentate ligands capable of co-ordinating through the cyano-groups as well as through the phosphorus or oxygen, sulphur, or selenium atoms. The versatility of the system is illustrated by the variety of structures identified in complexes of tris(2-cyanoethyl)phosphine,[1-5] which has attracted additional attention [6,7] because it is the least basic trialkylphosphine known.[8-11] There appears to be no published information on the ligand behaviour of the oxide, sulphide, or selenide molecules.

The crystal structures of tris(2-cyanoethyl)phosphine oxide, sulphide, and selenide have been determined by ourselves at levels sufficient to establish the molecular geometries; [12,13] more precise studies of the oxide have been reported by Foxman *et al.*[14] and by Cotton *et al.*,[6] and the latter authors have also determined the structure of the parent phosphine. In this paper we discuss the vibrational spectra of the four molecules in the light of the structural data, and report an initial study of their co-ordination chemistry.

Experimental

Tris(2-cyanoethyl)phosphine was obtained commercially; the oxide, sulphide, and selenide were prepared as described elsewhere.[15,16]

Preparation of Metal Complexes.—Typically, these were obtained from the reactions of equimolar quantities of ligand and metal salt in boiling acetone. Ethyl orthoformate was added, where necessary, as a dehydrating agent. The products separated on concentrating and cooling the reaction mixtures: addition of light petroleum (b.p. 40—60 °C)–diethyl ether (1 : 1) was necessary in some cases [$ZnCl_2{\cdot}P(CH_2CH_2CN)_3O$ and $HgCl_2{\cdot}2P(CH_2CH_2CN)_3S$] to induce precipitation.

Mercury complexes. The preparative reactions yielded 1 : 1 complexes $HgX_2{\cdot}L$ [X = Cl, L = $P(CH_2CH_2CN)_3$ or $P(CH_2CH_2CN)_3Se$; X = Br, L = $P(CH_2CH_2CN)_3S$ or $P(CH_2CH_2CN)_3Se$] except in the case of $HgCl_2{\cdot}2P(CH_2CH_2CN)_3S$ where the 1 : 2 complex was the only identifiable product.

Palladium and platinum thiocyanate complexes. These complexes precipitated on mixing warm ethanolic solutions of the $[M(SCN)_4]^{2-}$ salt and the ligand in 1 : 2 molar proportions.

$CuBr{\cdot}P(CH_2CH_2CN)_3$. The copper(I) bromide complex was obtained from the reaction of copper(II) bromide (0.001 mol) with tris(2-cyanoethyl)phosphine (0.002 mol) in acetone The initially green solution turned red, and white crystals of the complex separated. The oxidation product was not identified.

Physical Measurements.—Infrared spectra were recorded using a Perkin-Elmer 457 spectrophotometer and Raman spectra using a Cary 83 spectrophotometer with argon-ion (488.0 nm, *ca.* 50 mW) laser excitation.

Analytical data for hitherto unreported complexes are given in Table 1.

Results and Discussion

Structural Data.—The results of the *X*-ray crystal structure determinations for the four tris(2-cyanoethyl)phosphine compounds are summarised in Table 2. The atoms in the cyanoethyl groups are identified as PC(1)C(2)C(3)N and the conformations of the groups are indicated as *trans–trans*, *trans–gauche*, *etc.* to designate their internal orientations about P–C(1) [*i.e.* C(1)C(2) *trans* or *gauche* to P=E or to the phosphorus lone pair] and C(1)–C(2) [C(2)C(3) *trans* or *gauche* to PC(1)] respectively. In groups which do not lie on planes of symmetry [*e.g.* in $P(CH_2CH_2CN)_3O$] the crystallographically-determined dihedral angles may depart by 15—20° from the ideal *trans* (180°) or *gauche* (60°) values: to this extent, the descriptions are approximate. The molecular structures are illustrated in Figure 1. Tris(2-cyanoethyl)phosphine sulphide and tris(2-cyanoethyl)phosphine selenide are isomorphous and fully isostructural but apart from this there are no obvious correlations between the four compounds.

The cyano-groups in tris(2-cyanoethyl)phosphine occur in two inequivalent environments in the molecule and in the unit cell.[6] The two mirror-related cyanoethyl chains have the *gauche–gauche* conformation, with the terminal CCN groups lying close to, and antiparallel with, corresponding groups in adjoining molecules. The intermolecular contact distance is short enough to suggest an appreciable dipole–dipole interaction.[6] The unique cyanoethyl chain, lying in the mirror plane, is strictly *trans–trans*, with no significant intermolecular contacts.

In tris(2-cyanoethyl)phosphine oxide, with C_3 molecular symmetry, all three cyanoethyl groups are identical and make no intermolecular contacts comparable with those in the parent phosphine. The *gauche–trans* conformation of the cyanoethyl chains gives the $P(CH_2CH_2CN)_3$ grouping a rather flattened appearance with the phosphorus atom and all of the

Table 1. Analytical data for new complexes

	Found (calc.) (%)				
	C	H	N	Other	Colour
$CuBr·P(CH_2CH_2CN)_3$	31.6 (32.1)	3.6 (3.6)	—	23.2 (23.7) (Br)	
$PdBr_2·2P(CH_2CH_2CN)_3$	31.8 (33.1)	3.8 (3.7)	13.1 (12.9)	24.0 (24.5) (Br)	Pale green
$Pd(SCN)_2·2P(CH_2CH_2CN)_3$	39.2 (39.4)	3.9 (4.0)	18.1 (18.4)	10.3 (10.5) (S)	Yellow
$Pt(NCS)_2·2P(CH_2CH_2CN)_3$	34.0 (34.4)	3.4 (3.5)	14.7 (16.1)	8.9 (9.2) (S)	Orange
$HgCl_2·P(CH_2CH_2CN)_3$	23.0 (23.2)	2.7 (2.6)	9.2 (9.0)	15.0 (15.3) (Cl)	
$ZnCl_2·P(CH_2CH_2CN)_3O$	31.4 (31.3)	3.4 (3.5)	12.0 (12.2)	20.2 (20.5) (Cl)	
$2CoCl_2·P(CH_2CH_2CN)_3O·3H_2O$	20.5 (20.7)	3.6 (3.4)	8.4 (8.0)	26.8 (27.1) (Cl) 22.4 (22.5) (Co)	Blue
$HgCl_2·2P(CH_2CH_2CN)_3S$	29.8 (29.9)	3.9 (3.4)	11.8 (11.7)	8.6 (8.9) (S)	
$HgBr_2·P(CH_2CH_2CN)_3S$	18.3 (18.4)	2.4 (2.1)	6.8 (7.2)	5.4 (5.5) (S)	
$HgCl_2·P(CH_2CH_2CN)_3Se$	20.3 (19.9)	2.3 (2.2)	7.8 (7.7)	13.8 (14.5) (Se)	
$HgBr_2·P(CH_2CH_2CN)_2Se$	17.1 (17.1)	2.0 (1.9)	—	12.2 (12.5) (Se)	Pale yellow

Table 2. Structural data

	System	Space group	Z	Factor-group symmetry	Site symmetry	PCH_2CH_2CN Conformation	Ref.
$P(CH_2CH_2CN)_3$	Monoclinic	$P2_1/m$	2	C_{2h}	C_s	1 × *trans–trans* 2 × *gauche–gauche* [a]	6
$P(CH_2CH_2CN)_3O$	Trigonal	$R3c$	2 [b]	C_{3v}	C_3	3 × *gauche–trans* [a]	6, 12, 14
$P(CH_2CH_2CN)_3S$	Triclinic	$P\bar{1}$	2	C_i	C_1	2 × *gauche–trans* [a] 1 × *trans–trans* [a]	13, 16
$P(CH_2CH_2CN)_3Se$	Triclinic	$P\bar{1}$	2	C_i	C_1	2 × *gauche–trans* [a] 1 × *trans–trans* [a]	13, 16

[a] Approximate description (see text). [b] Rhombohedral cell.

carbon atoms lying within 1 Å of the plane defined by the three terminal nitrogen atoms (Figure 1). The phosphorus atom and the three C(2) carbon atoms are almost coplanar. Within the crystal, the molecules are arranged head-to-tail in chains along the *c* axis, with an intermolecular PO $\cdots$ P distance of 3.64 Å.[13]

Tris(2-cyanoethyl)phosphine sulphide and tris(2-cyanoethyl)phosphine selenide occupy sites of C_1 symmetry but have pseudo C_s structures in the sense that two of the cyanoethyl groups are mirror-related and the third is only slightly displaced from the imaginary mirror plane. The structure is nevertheless quite different from the C_s structure of the parent phosphine, as all three CN groups are (approximately) *trans* and there are no significant intermolecular contacts.

Vibrational Spectra.—Vibrational frequency data for the four crystalline tris(2-cyanoethyl)phosphine compounds in the region below 1 050 cm^{-1} are given in Tables 3—5. The CN and PO stretching vibrations, which occur above 1 050 cm^{-1}, are also included. All other vibrations in this high-frequency region arise from internal modes of the methylene groups and are not listed here.

Assignments for the internal skeletal modes of the cyanoethyl groups are made primarily by analogy with 3-halogenopropanenitriles [17,18] and alkyl halides.[19] Vibrations involving the phosphorus atom are related to those in triethylphosphine sulphide, triethylphosphine selenide [20] and numerous other phosphines and phosphine derivatives.[21-25]

The vibrations in the range 1 050—650 cm^{-1} in all four compounds fall consistently into two groups, 1 020—900 and ~ 820—650 cm^{-1}. In the absence of evidence to the contrary, we assign the higher-frequency groups to CCC stretching and the lower to PC_3 stretching and CH_2 rocking modes. These simple descriptions are undoubtedly inadequate in many cases, especially in *gauche* cyanoethyl groups where the C_1 local symmetry imposes no restrictions on vibrational interactions but the experimental data do not justify a more detailed vibrational assignment at this stage. Skeletal CCC and PCC bending modes occur between *ca.* 550 and 350 cm^{-1}; [18-20] to the extent that realistic distinctions can be made between them, the CCC vibrations are to be expected at somewhat higher frequencies (~ 550—450 cm^{-1}) than the PCC vibrations (~ 450—350 cm^{-1}). The vibrational data for 3-halogenopropanenitriles indicate that the skeletal bending frequencies are usually higher in *trans* than in *gauche* molecules.[18] The in-plane CCN bending modes occur close to 380 cm^{-1} in the 3-halogenopropanenitriles and corresponding bands appear at similar frequencies in all four tris(2-cyanoethyl)phosphine compounds.

The three cyanoethyl groups in tris(2-cyanoethyl)phosphine oxide are all equivalent, giving a relatively simple vibrational spectrum. The phosphine, phosphine sulphide, and phosphine selenide all contain conformationally inequivalent cyanoethyl groups, with noticeably more complicated spectra. Points of specific interest in the four compounds are discussed below.

Tris(2-cyanoethyl)phosphine. The CN stretching absorption appears as a well defined doublet at 2 254 and 2 242 cm^{-1} in the i.r. spectrum, but only one corresponding line (2 255 cm^{-1}) is detectable in the Raman (R). The intermolecular contacts involving the *gauche* CN groups, described in the preceding section, raise the possibility of significant vibrational coupling within the unit cell. The symmetrically- and antisymmetrically-coupled stretching modes of adjoining pairs of *gauche* CN groups span the irreducible representations A_g(R) and B_u(i.r.) of the C_{2h} factor group and hence are assigned at 2 255 (R) and 2 242 cm^{-1} (i.r.) respectively. The i.r. band at 2 254 cm^{-1} is assigned to the stretching vibration of the *trans* CN group: as these groups are effectively isolated in the unit cell, the

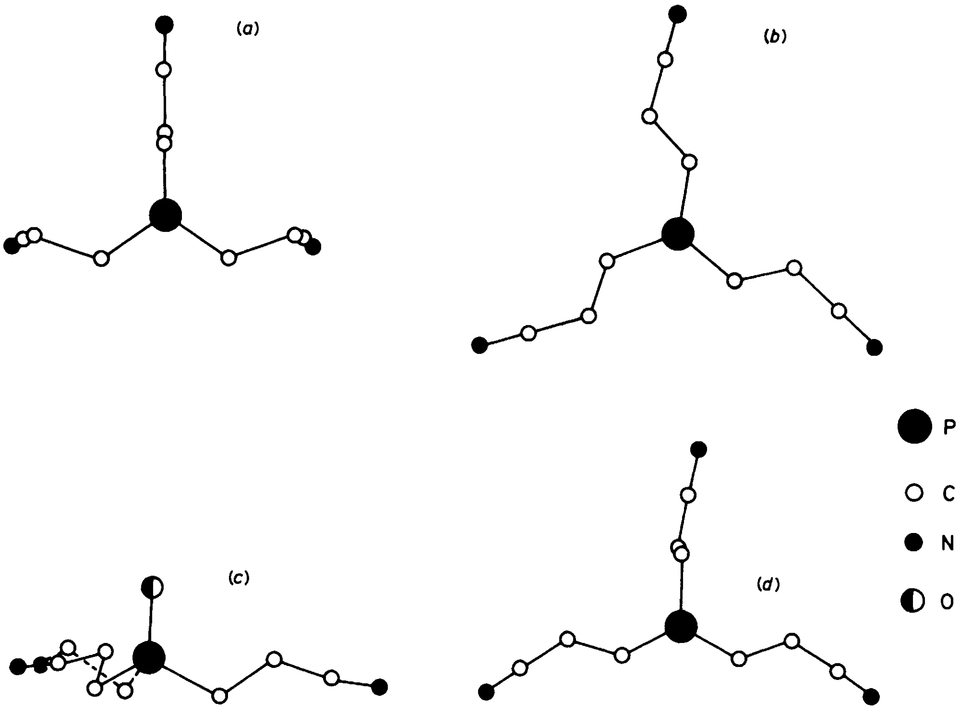

Figure 1. (*a*) $P(CH_2CH_2CN)_3$ viewed along phosphorus lone-pair axis; (*b*) $P(CH_2CH_2CN)_3O$ along PO axis; (*c*) $P(CH_2CH_2CN)_3O$ perpendicular to PO axis; (*d*) $P(CH_2CH_2CN)_3E$ (E = S or Se) along PS(Se) axes

Table 3. I.r. and Raman spectra of tris(2-cyanoethyl)phosphine

	I.r. [a]/cm^{-1}	Raman [b]/cm^{-1}
ν(CN) [c]	2 254s	2 255s
	2 242s (sh)	
	1 020w	
ν(CCC)	1 009m	1 011m
	1 001ms	1 000ms
	956ms	952w
	942ms	
		925w
	905ms	
		895w
ρ(CH_2)	799mw	802w
	772mw	
ν(PC_3), *A′* [d]	739s	739m
ρ(CH_2)	725 (sh)	
ν(PC_3), *A″* [d]	695ms	
ν(PC_3), *A′* [d]	654s	656vs
δ(CCC)	573m	572mw
δ(CCC)	494mw	494m
δ(CCN) (in plane)		387mw
	373w (sh)	377mw
δ(PCC)	363m	363w
δ(PCC)	334ms	332m
δ(PC_3)?	307vw	309m
	272ms	270mw

[a] Nujol mulls. [b] Powdered solids. [c] Assignments (A_g and B_u refer to the C_{2h} factor group): 2 254 (i.r.), ν(CN) *trans*; 2 255 (R), ν(CN) *trans* + ν(CN) *gauche* (A_g); 2 242 (i.r.), ν(CN) *gauche* (B_u). [d] C_s site group.

Table 4. I.r. and Raman spectra of tris(2-cyanoethyl)phosphine oxide

	I.r. [a]/cm^{-1}	Raman [b]/cm^{-1}
ν(CN)	2 244s	2 243s
ν(PO)	1 161vs	1 164m
ν(CCC)	1 018m	1 020m
	954s	955m
	923w	
		910m
ρ(CH_2)	796vs	801w
	748mw	752vw
ν(PC_3), *E*	720w	723mw
ν(PC_3), *A*		711mw
δ(CCC)	534s	
		510m
δ(PCC)	440ms	440m
δ(CCN) (in plane)	380w	380m
δ(PC_3)	307mw	309w

[a] Nujol mulls. [b] Powdered solids.

corresponding Raman line should occur at the same frequency and will coincide with the A_g mode of the *gauche* CN groups.

Three strong i.r. bands at 739, 695, and 654 cm^{-1} are assigned to PC_3 stretching modes. There is no evidence of factor-group coupling for these 'internal' skeletal modes and the assignment is more conveniently made in the C_s site group [ν(PC_3), $2A' + A''$]. The vibrations at 739 and 654 cm^{-1} are strongly active in the Raman effect and hence are identified as the two *A′* modes, leaving the vibration at 695 cm^{-1} which is undetectable in the Raman spectrum as the *A″* mode. A shoulder at 725 cm^{-1} on the 739 cm^{-1} i.r. band is assigned to an overlapping CH_2 rocking mode.

Tris(2-cyanoethyl)phosphine oxide. The CN stretching absorption has a single sharp maximum at 2 244 cm^{-1}, with some evidence of a very indistinct high-frequency shoulder which may arise from a weak intermolecular coupling effect. The PO stretch is assigned to a strong, rather broad i.r. band, at 1 161 cm^{-1}, with a strong Raman counterpart. The i.r. band has a well defined shoulder at 1 170 cm^{-1}, but this is not

Table 5. I.r. and Raman spectra of tris(2-cyanoethyl)phosphine sulphide and tris(2-cyanoethyl)phosphine selenide

	$P(CH_2CH_2CN)_3S$		$P(CH_2CH_2CN)_3Se$	
	I.r. [a]/cm^{-1}	Raman [b]/cm^{-1}	I.r. [a]/cm^{-1}	Raman [b]/cm^{-1}
ν(CN)	2 248s	2 245s	2 245s	2 244s
ν(CCC)		1 019ms		1 020w
	1 005s	1 009m	1 008ms	1 005m
	963s		960m, br	
	938m	941mw	939m	938w
	922w	924w	920w	921w
ρ(CH_2)	819ms	818mw	812m	809w
	762vs	764m	762mw	761w
			751s	
ν(PC_3)	731mw	734w	730m	732vvw?
	721s	723w	719m	721w
	699w	700vvw	698vw	700vvw?
ν(PS)	618s	618vs		
δ(CCC)/δ(PCC)			542s	538w
	517m, br	518w		
		484s		
ν(PSe)			456m	457vs
δ(PCC)/δ(CCC)	402mw	407w		
δ(CCN) (in-plane)			390w	390w (sh)
	384w	381m	380vw	379mw
δ(PCC)?	337mw	337m		
			290vw	290m
δ(PC_3)?	277mw	275m	270w	270w

[a] Nujol mulls. [b] Powdered solids.

shifted on complex formation (see below) and is therefore assigned to an internal methylene group vibration.

In the C_3 site group, the PC_3 stretching modes yield two vibrations ($A + E$) both of which should be i.r.- and Raman-active. Two relatively strong Raman lines appear at 723 and 711 cm^{-1}, but there is only one corresponding absorption, at 720 cm^{-1}, in the i.r. spectrum. Given the pseudo-planar distribution of the cyanoethyl groups around the phosphorus atom (described in the preceding structural section) it is possible to envisage a situation in which the symmetric PC_3 stretch, coupled to some extent with C–C stretching or skeletal bending motions, would produce little or no change in the overall molecular dipole. Accordingly, we assign the 711 cm^{-1} Raman line to the A species PC_3 stretch, and the 723 cm^{-1} line (i.r. 720 cm^{-1}) to the corresponding E species vibration. Additional evidence for the intramolecular coupling of the skeletal modes is provided by the appearance of three vibrational bands in the CCC stretching region (900—1 050 cm^{-1}) rather than the two which would be expected for an isolated CCCN grouping.

Tris(2-*cyanoethyl*)*phosphine sulphide and tris*(2-*cyanoethyl*)-*phosphine selenide*. The cyano-groups in these molecules, although not exactly equivalent, are all in the approximate *trans* conformation, and the CN stretching absorptions appear as single slightly broadened bands at 2 248 and 2 245 cm^{-1} (i.r.) respectively. The PC_3 stretches are assigned to a group of three closely-spaced bands at almost identical frequencies between 734 and 698 cm^{-1} in both molecules.

The PS and PSe stretching modes are identified at 618 and 457 cm^{-1}, respectively, by virtue of their very high Raman intensities. The frequency difference of 161 cm^{-1} between these vibrations is large compared with other pairs of PR_3S and PR_3Se molecules in which it is typically *ca.* 75—95 cm^{-1},[21] with a maximum of 129 cm^{-1} (PMe_3S and PMe_3Se [22]) and a minimum of 62 cm^{-1} (PEt_2PhS and PEt_2PhSe [21]). Phosphorus–sulphur stretching frequencies are reported between 627 cm^{-1} in PPh_3S [21] and 535 cm^{-1} in PEt_3S; [20] the corresponding range for ν(PSe) is from 560 cm^{-1} in PPh_3Se [21] to 421 cm^{-1} in PEt_3Se.[20] The PS and PSe frequencies in the tris(2-cyanoethyl)phosphine derivatives are thus close to the top and bottom, respectively, of their characteristic frequency ranges.

There is abundant evidence, from a variety of sources,[8–11,26] to demonstrate that the 2-cyanoethyl groups in tris(2-cyanoethyl)phosphine exert a strongly electron-withdrawing effect. On purely electronic grounds we would therefore expect to find the PS and PSe stretching vibrations in the sulphide and selenide at relatively high frequencies, broadly comparable with those in the corresponding triphenylphosphine derivatives. The PS stretching frequency of 618 cm^{-1} in tris(2-cyanoethyl)phosphine sulphide is consistent with this argument, but the PSe stretch in the selenide is unexpectedly low, and presumably is severely affected by vibrational interactions with other skeletal modes. Potential-energy calculations for PMe_3S and PMe_3Se,[24] which also display a wide ν(PS)–ν(PSe) separation, indicate that the PS and PSe stretching coordinates are distributed over several skeletal fundamentals, to the extent that the descriptions 'ν(PS)' and 'ν(PSe)' applied to individual vibrations are almost meaningless. A similar situation seems likely in the tris(2-cyanoethyl)phosphine compounds, and especially in the selenide. Coupling with the PC_3 stretching modes, which is a dominant effect in a number of other molecules,[20,24] does not appear to be significant here: the PC_3 stretching frequencies are virtually identical in the sulphide and selenide and would in any case tend to affect ν(PS) more than ν(PSe). However, the correlations between the spectra of the two compounds are noticeably poorer at frequencies below 550 cm^{-1} and suggest that the PSe vibration may interact significantly with the skeletal bending modes in the 550—300 cm^{-1} region.

Solution Spectra.—All of the tris(2-cyanoethyl)phosphine derivatives are insoluble, or very nearly so, in the more useful spectroscopic solvents, and we have been able to obtain only very limited i.r. and Raman data in acetonitrile or dimethyl sulphoxide solution. The PO stretch in tris(2-cyanoethyl)-phosphine oxide shifts from 1 161 cm^{-1} in the crystal to 1 185

Table 6. Skeletal infrared [a] stretching frequencies in $P(CH_2CH_2CN)_3$ and $P(CH_2CH_2CN)_3E$ (E = O, S, or Se) metal complexes

	ν(CN)	ν(PC)	νPO(S,Se)	ν(M–Cl) [b]
$HgCl_2{\cdot}P(CH_2CH_2CN)_3$	2 249s	727 (sh) 719s 666w(?)		
$CuBr{\cdot}P(CH_2CH_2CN)_3$	2 260 (sh) 2 245s	730s 720 (sh) 656w(?)		
$PdBr_2{\cdot}2P(CH_2CH_2CN)_3$	2 249s	719m 701s 660m		
$Pd(SCN)_2{\cdot}2P(CH_2CH_2CN)_3$ [c]	2 251s 2 242 (sh) 2 114vs [d]	731m 706m 702m 666m		
$Pt(NCS)_2{\cdot}2P(CH_2CH_2CN)_3$ [e]	2 260 (sh) 2 248s 2 130 (sh) [f] 2 100vs, br [f]	726m 716 (sh) 693mw		
$ZnCl_2{\cdot}P(CH_2CH_2CN)_3O$	2 301s 2 294 (sh) 2 255ms	730m 722s 669w	1 134vs	334m 292ms 282ms
$2CoCl_2{\cdot}P(CH_2CH_2CN)_3O{\cdot}3H_2O$	2 301s 2 295 (sh)	735w (sh) 722m	1 147s	334s 309s, br 277s
$3NiCl_2{\cdot}2P(CH_2CH_2CN)_3O{\cdot}xH_2O$	2 299s 2 281s	735 (sh) 721s, br 700w	1 137s	
$HgCl_2{\cdot}2P(CH_2CH_2CN)_3S$	2 259 (sh) 2 251s	732 (sh) 722s 699 (sh)	544ms [g]	260br(?)
$HgBr_2{\cdot}P(CH_2CH_2CN)_3S$	2 260 (sh) 2 248s	734 (sh) 720s, br 699 (sh)	543s [g]	
$HgCl_2{\cdot}P(CH_2CH_2CN)_3Se$	2 252m	714s 696m 688w	443m [g]	270s
$HgBr_2{\cdot}P(CH_2CH_2CN)_3Se$	2 260 (sh) 2 248s	715m 684s 666m	433m [g]	

[a] Nujol mulls; ν/cm^{-1}. [b] Possibly also ν(MO) in the oxide complexes. [c] One 'PC_3' band probably arises from thiocyanate ν(CS). [d] Thiocyanate ν(CN). [e] Thiocyanate ν(CS) at 854s cm^{-1}. [f] Thiocyanate ν(CN). [g] Strong corresponding Raman lines.

cm^{-1} in acetonitrile solution. Solutions of the sulphide in acetonitrile or dimethyl sulphoxide have two i.r. bands, with prominent Raman counterparts, in the PS stretching region near 600 cm^{-1}, possibly indicating the presence of two conformers of the molecule. No satisfactory spectra were obtained for solutions of the selenide.

Metal Complexes.—Tris(2-cyanoethyl)phosphine reacts with acceptors of strong class 'b'[27] character to yield relatively simple mononuclear complexes in which the ligand is bound through the phosphorus atom only, *e.g.* $Mo(CO)_5{\cdot}P(CH_2CH_2CN)_3$.[5] With acceptors of intermediate or class 'a' character, the nitrogen atoms also become involved in the metal–ligand interaction, forming complexes which may contain metal–nitrogen and metal–phosphorus bonds, *e.g.* $NiBr_2{\cdot}P(CH_2CH_2CN)_3$,[1,4] or metal–nitrogen bonds only, *e.g.* $3CoCl_2{\cdot}2P(CH_2CH_2CN)_3$.[1] The donor atom set may include one, two, or three nitrogen atoms per ligand molecule, making possible a wide range of monomeric, oligomeric, or polymeric structures. The situation is further complicated by the tendency of water or solvent molecules to become securely trapped in the 'cages' formed by the *N*-bonded cyanoethyl groups.[1] Co-ordination through the cyano-nitrogen atoms is indicated by an upward shift in the CN stretching frequency to the region 2 275—2 310 cm^{-1}. Vibrational data are listed in Table 6 for a number of complexes which to the best of our knowledge have not previously been reported elsewhere.

Tris(2-cyanoethyl)phosphine-metal complexes. The copper, mercury, platinum, and palladium complexes all have ν(CN) below 2 265 cm^{-1}, with the principal absorption near 2 250 cm^{-1} and clearly are 'simple' *P*-bonded species.

The palladium(II) and platinum(II) thiocyanate complexes contain, respectively, *S*-bonded and *N*-bonded thiocyanate, identified by the intensity of the thiocyanate CN stretching absorption and by the frequency of the CS stretching vibration.[28-30] The CN stretch in the platinum complex is very broad ($\nu_{\frac{1}{2}}$ = 50 cm^{-1}) and the CS stretch is assigned at 854s cm^{-1} (i.r.). These features are characteristic of the M–NCS linkage. In the palladium complex, in contrast, an M–SCN structure is indicated by the sharp CN stretching absorption ($\nu_{\frac{1}{2}}$ = 11 cm^{-1}) and by the absence of a CS stretching band near 850 cm^{-1}. Instead, an additional band appears in the 650—750 cm^{-1} region, overlapping with the PC_3 stretching modes (Table 6). The internal vibrations of the co-ordinated phosphine are noticeably dissimilar in the two complexes, suggesting that the conformations of the cyanoethyl groups are not the same in both cases. Thiocyanate co-ordination (*i.e.* linear M–NCS or bent M–SCN) is often very sensitive to the steric requirements of the other ligands in the metal co-ordination sphere[31-33] and the Pd–SCN and

Pt–NCS structures observed here may be dictated by relatively minor differences in the geometry of the co-ordinated tris(2-cyanoethyl)phosphine ligands. If so, it should be possible to prepare the corresponding Pd–NCS and Pt–SCN complexes under appropriate experimental conditions, but we have not yet succeeded in doing so.

Tris(2-cyanoethyl)phosphine oxide–metal complexes. The N_3O donor atoms in tris(2-cyanoethyl)phosphine oxide are all class 'a' in character and this ligand, unlike the parent phosphine, shows no tendency to react with heavy-metal acceptors. Attempts to prepare Hg^{II}, Pd^{II}, Pt^{II}, or Cu^{I} halide or Pd^{II} or Pt^{II} thiocyanate complexes yielded only the unchanged starting materials. Identifiable complexes were obtained only with acceptors having an element of class 'a' character (*i.e.* Zn^{II}, Cd^{II}, Co^{II}, or Ni^{II}).

The reaction of tris(2-cyanoethyl)phosphine oxide with zinc chloride under ambient conditions yielded the 1 : 1 complex $ZnCl_2{\cdot}P(CH_2CH_2CN)_3O$, containing no trapped water or solvent molecules. In the i.r. spectrum, strong CN stretching absorptions at 2 255 and 2 301 cm^{-1} (Figure 2) indicate the presence of free and co-ordinated cyanoethyl groups. The PO stretch is shifted to 1 134 cm^{-1}, 27 cm^{-1} lower than the free ligand crystal frequency, or 49 cm^{-1} lower than the frequency in MeCN solution. Downward shifts of this order in ν(PO) are usually typical of co-ordination through the phosphoryl oxygen atom.[34] The Zn–Cl stretches are assigned between 334 and 282 cm^{-1}, in the characteristic frequency region for tetrahedrally co-ordinated zinc.[35] Taken together, these observations point to a structure based on the $ZnCl_2ON$ unit, with each ligand co-ordinated through the oxygen and one nitrogen atom. Experiments with molecular models show that a mononuclear chelate structure, assuming a near linear Zn–N–C angle and a 'bent' Zn–O–P angle, could be achieved only at the expense of severe internal distortion of the ligand molecule. An extended structure, with bridging tris(2-cyanoethyl)phosphine oxide ligands, is more likely.

The reactions of $ZnBr_2$ and $CdCl_2$ with tris(2-cyanoethyl)phosphine oxide gave products analogous to $ZnCl_2{\cdot}P(CH_2CH_2CN)_3O$, but invariably containing unreacted ligand. Attempts to purify these products were uniformly unsuccessful, leading to further decomposition and the generation of more free ligand.

The addition of $P(CH_2CH_2CN)_3O$ to $CoCl_2$ in acetone, under ambient conditions, yielded the hydrated complex $2CoCl_2{\cdot}P(CH_2CH_2CN)_3O{\cdot}3H_2O$, even in the presence of ethyl orthoformate as a dehydrating agent. Under more strictly anhydrous conditions, the water molecules are replaced by acetone, identified by the appearance of a carbonyl stretching absorption at 1 720 cm^{-1}. The water- and acetone-containing compounds have identical blue colours and the vibrational frequencies of the co-ordinated ligand are the same in both cases. We conclude that the water and acetone molecules are trapped in the crystal rather than directly involved in the metal co-ordination sphere. The CN stretching vibrations are observed near 2 300 cm^{-1} (Figure 2) with no evidence of unco-ordinated cyanoethyl groups at lower frequencies, and the PO stretch is shifted to 1 147 cm^{-1}. A group of bands between 334 and 277 cm^{-1} are assigned to Co–Cl stretching vibrations, within the usual frequency range for the tetrahedrally co-ordinated metal ion.[35] The stoicheiometric and spectroscopic data are thus compatible with a structure in which the ligand molecules co-ordinate through all four potential donor atoms, implying the formation of equal numbers of $CoCl_2N_2$ and $CoCl_2NO$ chromophores. The extended network formed by the multiply co-ordinated ligand is ideally designed to trap solvent molecules, whereas the more open structure envisaged for $ZnCl_2{\cdot}P(CH_2CH_2CN)_3O$ is less likely to do so and yields solvent-free products. Attempts to remove the water or acetone from the cobalt complexes by gentle warming *in vacuo* were unsuccessful, but on more severe heating the solvent molecules were lost with the concomitant development of an unco-ordinated CN stretching absorption at 2 250 cm^{-1}, Figure 2(*d*).

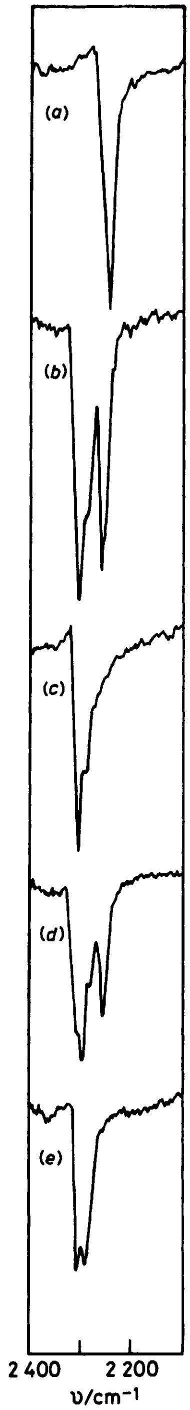

Figure 2. CN Stretching absorptions in (*a*) $P(CH_2CH_2CN)_3O$; (*b*) $ZnCl_2{\cdot}P(CH_2CH_2CN)_3O$; (*c*) $2CoCl_2{\cdot}P(CH_2CH_2CN)_3O{\cdot}3H_2O$; (*d*) cobalt complex in (*c*) after prolonged heating; and (*e*) $3NiCl_2{\cdot}2P(CH_2CH_2CN)_3O{\cdot}xH_2O$

Analogous reactions with nickel(II) chloride yielded rather ill defined products, but under ambient conditions with $NiCl_2{\cdot}6H_2O$ as the starting material, a pale green, heavily hydrated complex with approximately 3 : 2 metal : ligand stoicheiometry was isolated. The CN stretches appear at 2 299 and 2 281 cm^{-1} [Figure 2(*e*)] again with no evidence of unco-ordinated cyanoethyl groups, and the PO stretch falls to 1 137 cm^{-1}. The pale colour of the complex, and the absence of any identifiable Ni–Cl stretching absorptions above 250 cm^{-1}, suggest that the metal ion is octahedrally co-ordinated, presumably through the involvement of water molecules as well as the phosphine oxide in the co-ordination sphere. The OH stretching and H_2O bending absorptions each have two maxima, at 3 590 and 3 180 cm^{-1} [approximately, for ν(OH)] and 1 665 and 1 625 cm^{-1} [for δ(H_2O)], consistent with the presence of both co-ordinated and lattice water in the solid complex.

Tris(2-*cyanoethyl*)*phosphine sulphide- and tris*(2-*cyanoethyl*)-*phosphine selenide-metal complexes*. These phosphines yielded identifiable products only with the strongly class 'b' mercury(II) halides as acceptor compounds. Bonding is through the sulphur or selenium atoms, with ν(PS) and ν(PSe) shifted to lower frequencies [by ~ 70 cm^{-1} for ν(PS) and 10—20 cm^{-1} for ν(PSe)] and no CN stretching frequencies higher than 2 260 cm^{-1}. These results are consistent with the general pattern of ligand behaviour in PR_3S and PR_3Se molecules, which usually display marked donor properties only when the organic groups R are strongly electron-releasing.[36,37] Attempts to prepare complexes with Pd^{II}, Pt^{II}, Zn^{II}, Cd^{II}, Ni^{II}, or Co^{II} halides yielded only the unchanged starting materials. No evidence was found for the formation of *N*-bonded complexes analogous to $3CoCl_2 \cdot 2P(CH_2CH_2CN)_3$[1] or $2CoCl_2 \cdot P(CH_2CH_2CN)_3O \cdot 3H_2O$ (although the high frequency shoulders near 2 260 cm^{-1} on the CN stretching bands in some of the mercury complexes could conceivably arise from weak secondary CN $\cdots$ Hg interactions in the crystal).

The addition of a sulphur or selenium atom to the tris(2-cyanoethyl)phosphine molecule thus appears to have a pronounced deactivating effect on the donor abilities of the cyano-nitrogen atoms. This effect is less evident in the oxide, possibly because all four atoms in the donor set in this case have the same class 'a' character, but the relatively small number of oxide complexes identified, their tendency to decompose during recrystallisation, and the absence of any clear evidence for purely *N*-bonded structures, also suggest a weakening in the donor abilities of the nitrogen atoms compared with those in the parent phosphine. The experimental data thus seem to demonstrate an unexpectedly strong effect exerted by the P=E (E = O, S or Se) bond on the cyano-nitrogen electrons, although there is little tangible evidence of this in the ligand vibrational spectra. Further studies of these systems are obviously desirable.

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