σ-Bonded Organotransition-metal Ions. Part XIV.[1] Characterisation of Monomeric and Bridged Anionic Complexes of Organocobaloximes

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A number of alkyl-, alkenyl-, and alkynyl-bis(dioximato)cyanocobaltate(III) ions have been prepared and characterised as tetraphenylarsonium and tetra-alkylammonium salts. Corresponding dimeric bridged anionic complexes, in which two organocobalt groups are bonded to the same cyanide ligand, have been isolated and/or characterised in solution. The cyanide stretching frequency of the dimeric complexes is *ca.* 30—40 cm^{-1} greater than that of the monomeric complexes, and both increase with the electronegativity of the α-carbon of the organic group(s). Bridged cyanide complexes in which the two organocobalt components differ have been shown to rearrange and disproportionate by an intermolecular mechanism. A trimeric compound containing two cyanide bridges has also been isolated. Similar monomeric and dimeric azido- and thiocyanato-complexes have been isolated. Both *S*- and *N*-bonded thiocyanate complexes are believed to coexist and to exchange in solution, the latter being slightly favoured. Only monomeric cyanate complexes have been prepared, and may involve a rapidly established equilibrium between the *O*- and the *N*-bonded species in solution.

COBALT, in several oxidation states, forms a wide variety of complexes in which the metal is co-ordinated to from one to six cyanide ligands.[2] In these complexes each cyanide ion has a marked effect on the redox potentials of the metal and hence on its properties. Bridged cyanide complexes have also been postulated as intermediates [3,4] in some inner sphere electron transfer reactions of cyanocobalt compounds, and several such bridged complexes have been isolated.[5-8]

Our main interest in these complexes is in the manner in which the cyanide ligand influences the character of carbon–cobalt bonds. However, despite the fact that many organocyanocobalt(III) complexes have been detected in solution, very few, other than the organopentacyanocobaltate(III) salts, have been isolated.[9] Surprisingly, even though there are more than 400 known organocobaloximes,[9] none of the cyanide derivatives has been isolated. In this paper are described preliminary studies involving the preparation and characterisation of a range of salts of cyanide, azide, cyanate, and thiocyanate complexes of organocobaloximes, together with a number of bridged complexes containing cyanide, azide, and thiocyanate ion.

RESULTS

Isolation of Organocyanobis(dioximato)cobaltate(III) *Salts*.—The addition of an excess of cyanide ion to an aqueous solution of either organobis(dimethylglyoximato)-aquo- or -pyridine-cobalt(III) results in a change of colour from orange to yellow, the rate of which is limited, in the case of the pyridine complex, by the rate of dissolution of the pyridine complex. In those cases where the organic group is sensitive to cyanide ion, the complex could also be prepared by the addition of an aqueous solution containing one equivalent of cyanide ion to a methanolic solution containing the organobis(dioximato)pyridinecobalt(III) complex. On the addition of an appropriate salt of a heavy metal cation, such as the tetraphenylarsonium ion, to the solution, the salt of the corresponding monomeric organobis(dioximato)cyanocobaltate(III) ion usually precipitates. With other cations, such as tetra-alkylammonium ions, evaporation of the solution may be required before crystallisation occurs, although the salts may also be isolated following their extraction from the aqueous solution with chloroform.

$$\mathrm{RCo(dH)_2B} \underset{+\mathrm{B}}{\overset{-\mathrm{B}}{\rightleftharpoons}} \mathrm{RCo(dH)_2} \underset{-\mathrm{CN^-}}{\overset{+\mathrm{CN^-}}{\rightleftharpoons}} [\mathrm{RCo(dH)_2CN}]^- \quad (1)$$

dH = monoanion of an α,β-dioxime; B = H_2O(aq) or pyridine (py)

In one case, when the organobis(dimethylglyoximato)-aquocobalt(III) complex was treated with an excess of cyanide ion, the salt of the monomeric cyanide complex was not isolated. Instead, on slow evaporation of the aqueous solution the corresponding salt of the bridged dimeric species (I) was obtained.

$$[\mathrm{MeCo(dmgH)_2CN}]^- + \mathrm{MeCo(dmgH)_2aq} \rightleftharpoons [\mathrm{MeCo(dmgH)_2CNCo(dmgH)_2Me}]^- + \mathrm{H_2O} \quad (2)$$

(I)

dmgH = monoanion of dimethylglyoxime

Such dimeric salts were more conveniently obtained by treatment of a solution of the monomeric cyanocobaltate(III) complex salt in chloroform with the corresponding neutral, and relatively insoluble, aquocobalt(III) complex. Formation of the yellow bridged complex was accompanied by the gradual dissolution of the suspended aquo-species, until one equivalent had been consumed, after which the dimeric complex could be isolated from the filtrate.

The monomeric and dimeric cyanide organometallic complexes which have been isolated are shown in Table 1. A number of these are hydrates. A trimeric organometallic

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TABLE 1

Analytical data

Compound		% Found (Calc.) C	H	N
Ph_4As^+ MeCo(dmgH)$_2$CN$^-$,H$_2$O		55·4(55·8)	5·2(5·35)	9·55(9·55)
Ph_4As^+ MeCo(chgH)$_2$CN$^-$,H$_2$O		57·6(58·25)	5·3(5·55)	9·0(8·95)
Et_4N^+ MeCo(dmgH)$_2$CN$^-$,H$_2$O		44·7(45·2)	7·6(8·2)	17·6(17·55)
		45·6	7·85	17·75
Ph_4As^+ n-C$_8$H$_{17}$Co(dmgH)$_2$CN$^-$,H$_2$O		59·85(59·35)	6·2(6·45)	8·7(8·45)
Ph_4As^+ c-C$_6$H$_{11}$Co(dmgH)$_2$CN$^-$,H$_2$O		59·4(58·7)	5·85(5·9)	8·95(8·75)
Ph_4As^+ PhCH$_2$Co(dmgH)$_2$CN$^-$,H$_2$O		59·8(59·5)	5·1(5·35)	8·65(8·65)
Ph_4As^+ 3-MeOC$_6$H$_4$CH$_2$Co(dmgH)$_2$CN$^-$		59·95(60·1)	5·25(5·3)	8·35(8·55)
Ph_4As^+ CH$_2$=CHCo(dmgH)$_2$CN$^-$,H$_2$O	*a*	56·55(56·55 [b])	5·0(5·3 [b])	9·6(9·4 [b])
	c	56·4	5·0	9·65
	d	56·75	5·05	9·6
	e	56·3	4·9	9·4
Ph_4As^+ CH$_2$=CMeCo(dmgH)$_2$CN$^-$		58·1(58·45)	5·3(5·3)	9·7(9·45)
Ph_4As^+ CH$_2$=CPhCo(dmgH)$_2$CN$^-$		61·1(61·45)	5·25(5·15)	8·65(8·75)
Ph_4As^+ *trans*-PhCH=CHCo(dmgH)$_2$CN$^-$		60·1(61·45)	5·1(5·15)	8·7(8·75)
Ph_4As^+ *cis*-PhCH=CHCo(dmgH)$_2$CN$^-$,H$_2$O		59·85(60·1)	5·2(5·3)	8·6(8·55)
Ph_4As^+ PhC≡CCo(dmgH)$_2$CN$^-$,H$_2$O		59·2(60·25)	4·7(5·05)	8·4(8·55)
Bu_4N^+ MeCo(dmgH)$_2$CNCo(dmgH)$_2$Me$^-$,H$_2$O		47·25(47·0)	7·7(8·1)	15·8(15·65)
		47·2	7·85	15·8
Ph_4As^+ [MeCo(dmgH)$_2$NC]$_2$Co(dmgH)$_2$$^-$,H$_2$O		45·75(46·25)	5·05(5·25)	14·35(14·5)
Ph_4As^+ MeCo(dmgH)$_2$N$_3$$^-$		53·85(54·35)	5·2(5·1)	13·75(13·45)
Ph_4As^+ CH$_2$=CHCo(dmgH)$_2$N$_3$$^-$		54·5(55·05)	5·0(5·05)	13·4(13·2)
Ph_4As^+ MeCo(dmgH)$_2$N$_3$Co(dmgH)$_2$Me$^-$,CDCl$_3$		44·45(44·8)	4·75(4·8)	13·6(13·35)
Ph_4As^+ MeCo(dmgH)$_2$NCS$^-$		55·15(54·75)	4·9(5·0)	9·35(9·4)
Ph_4As^+ MeCo(dmgH)$_2$NCO$^-$		55·6(56·0)	4·85(5·1)	9·0(9·6)
Ph_4As^+ (NC)$_2$Co(dmgH)$_2$$^-$		55·75(56·35)	4·65(4·75)	11·2(11·6)
Ph_4As^+ (N$_3$)$_2$Co(dmgH)$_2$$^-$		50·85(50·8)	4·7(4·55)	19·65(18·5)
CH$_2$=CHCo(dmgH)$_2$OH$_2$		35·95(35·95)	5·65(5·75)	17·1(16·75)
MeCo(chgH)$_2$OH$_2$		41·2(41·7)	5·95(6·2)	15·1(14·95)

[a] By displacement of py. [b] Calc. without water of crystallisation, C, 57·95; H, 5·15; N, 9·65%. [c] After recrystallisation and drying. [d] After second recrystallisation from CHCl$_3$–petrol and drying over P$_2$O$_5$. [e] By displacement of water. chgH$_2$ = Cyclohexanedione dioxime.

complex was also obtained as the tetraphenylarsonium salt (Table 1) by addition of ether to the solution obtained by dissolving methylbis(dimethylglyoximato)aquocobalt(III) (2 mol) and the tetraphenylarsonium salt of dicyanobis(dimethylglyoximato)cobaltate(III) (1 mol) in chloroform.

$$2\mathrm{MeCo(dmgH)_2aq} + [\mathrm{NCCo(dmgH)_2CN}]^- \rightleftharpoons [\mathrm{MeCo(dmgH)_2NCCo(dmgH)_2CNCo(dmgH)_2Me}]^- + 2\mathrm{H_2O} \quad (3)$$

A few reactions were unsuccessful because of apparent displacement of the organic group by the cyanide ion. For example, only the dicyanobis(dimethylglyoximato)cobaltate(III) salt was obtained from the reactions of methanesulphonyl- and halomethyl-cobaloximes with an excess of cyanide ion in aqueous solution.

I.r. and ^{1}H *N.M.R. Spectra*.—The cyanide stretching frequencies of the monomeric and dimeric complexes in chloroform solution, and in some cases also in the solid state, were determined. Since the dimeric complexes were readily formed in solution, a number of i.r. measurements were also made on complexes which have not been separately isolated and characterised. The cyanide stretching frequencies are shown in Table 2. These values were not dependent upon dilution at the concentrations used.

The ^{1}H n.m.r. spectra (Table 3) of the same complexes, whether isolated or made only in solution, were measured in the same solvent as were used for the i.r. measurements. The effect of dilution was again negligible at the concentrations used, but some dependence on the nature of the cation was observed.

In the case of the 'symmetrical' bridged dimeric complexes such as (I) (equation 2), in which identical organic groups and identical dioximato-ligands are attached to each of the bridged cobalt atoms, two sets of resonances

TABLE 2

Cyanide stretching frequencies (cm^{-1}) of cyanocobaloximes (tetraphenylarsonium salts in chloroform) [a]

R	R(Co)CN$^-$ (±1 cm^{-1})	R(Co)CN(Co)Me$^-$ (±2 cm^{-1})	Increment/ cm^{-1}
n-C$_8$H$_{17}$	2109	2143	34
s-C$_8$H$_{17}$	2110	2144	34
Cyclohexyl	2109	2145	36
Me [b]		2143 [c]	
Me [d]	2112	2145	33
Me	2112 [e]	2148	36
PhCH$_2$	2112	2148	36
Me [g]	2113	2148	35
3-MeOC$_6$H$_4$CH$_2$	2114	2148	34
CH$_2$=CMe	2117	2151	34
CH$_2$=CH	2118	2153 [h]	35
trans-PhCH=CH	2119	2153	34
cis-PhCH=CH	2119	2154	35
CH$_2$=CPh	2120	2156	36
PhC≡C	2130 [i]	2167 [j]	37
NC	2130 [k]	2170 [l]	40
Me(Co)NC	2134 [l]	2171 [m]	37

[a] $Ph_4As^+CN^-$ Absorbs at 2125 cm^{-1}: (Co) represents Co(dmgH)$_2$. [b] Bu_4N^+ Cation. [c] Solid (Nujol mull) absorbs at 2159 cm^{-1}. [d] Et_4N^+ Cation. [e] Solid (Nujol mull) absorbs at 2121 cm^{-1}. [f] Me(Co)CN(Co)CH=CH$_2$$^-$ Absorbs at 2150 cm^{-1}. [g] MeCo(chgH)$_2$CN$^-$. [h] CH$_2$=CH(Co)CN(Co)CH=CH$_2$$^-$ Absorbs at 2154 cm^{-1}. [i] ±3 cm^{-1} Since it appears as a shoulder on ν(C≡C) 2119 cm^{-1}. [j] ν(C≡C) 2119 cm^{-1}. [k] ±3 cm^{-1} Since measurement, of necessity, on very dilute solution; solid (Nujol mull) absorbs at 2128 cm^{-1}. [l] The two cyanide absorptions of one compound. [m] Solid (Nujol mull) absorbs at 2168 cm^{-1}.

were observed for the organic groups and two sets of resonances were observed for the dioximato-ligands (Table 3). In the case of 'unsymmetrical' bridged complexes such as

$$\begin{array}{ccl} & & [\mathrm{MeCo(dmgH)_2NCCo(dmgH)_2CH{:}CH_2}]^- \\ [\mathrm{MeCo(dmgH)_2CNCo(dmgH)_2CH{:}CH_2}]^- & \rightleftharpoons & \qquad\qquad \mathrm{(III)} \\ \mathrm{(II)} & \rightleftharpoons & \mathrm{(I)} + [\mathrm{CH_2{:}CH{\cdot}Co(dmgH)_2CNCo(dmgH)_2CH{:}CH_2}]^- \\ & & \qquad\qquad \mathrm{(IV)} \end{array} \qquad (4)$$

(II) (equation 4), in which different organic groups are attached to the two cobalt atoms, one set of resonances were observed for each organic group and two sets of resonances were observed for the equatorial dioximato-ligands (Table 3). However, after several hours at room temperature, other sets of resonances corresponding to the alternative unsymmetrical bridged complex [*e.g.*, (III) (equation 4 and Table 3] and the two 'symmetrical' bridged complexes [*e.g.* (I) and (IV) equation 4 and Table 3] were also observed.

TABLE 3

^{1}H N.m.r. spectra [a] of anionic organocobalt(III) complexes

(*a*) Monomeric complexes $[\mathrm{RCo(dH)_2X}]^-\mathrm{Y}^+$

R	dH	X	Y	τR	τ(dH)
Me	dmgH [b]	CN	$\mathrm{Ph_4As}$	9·47	7·98 [c]
Me	dmgH	CN	$\mathrm{Et_4N}$	9·46	7·89
Me	chgH [d]	CN	$\mathrm{Ph_4As}$	9·46	7·26—7·66, 8·24—8·65 [e]
NC	dmgH	CN	$\mathrm{Ph_4As}$		7·81 [h]
Me	dmgH	$\mathrm{N_3}$	$\mathrm{Ph_4As}$	9·48	7·88
$\mathrm{N_3}$	dmgH	$\mathrm{N_3}$	$\mathrm{Ph_4As}$		7·66
Me	dmgH	NCS [f]	$\mathrm{Ph_4As}$	9·53	7·98
Me	dmgH	SCN [g]	$\mathrm{Ph_4As}$	9·19	7·87
Me	dmgH	NCO	$\mathrm{Ph_4As}$	9·57	7·95
Me	dmgH	aq(+)		9·27 [h]	7·78 [h]

(*b*) Dimeric and trimeric complexes $[\mathrm{R'Co(d'H)_2XCo(d''H)_2R''}]^-\mathrm{Y}^+$

R′	d′H	d″H	R″	X	Y	Text formula	τR′	τR″	τ(d′H)	τ(d″H)
Me	dmgH	dmgH	$\mathrm{CH{:}CH_2}$	CN	$\mathrm{Ph_4As}$	II	9·49	*i*	7·99	8·00
$\mathrm{CH_2{:}CH}$	dmgH	dmgH	Me	CN	$\mathrm{Ph_4As}$	III	*i*	9·58	7·97	8·01
$\mathrm{CH_2{:}CH}$	dmgH	dmgH	$\mathrm{CH{:}CH_2}$	CN	$\mathrm{Ph_4As}$	IV	*i*	*i*	7·98	8·00
Me	dmgH	dmgH	Me	CN	$\mathrm{Bu_4N}$	I	9·48	9·56	7·90	7·92
Me	chgH [d]	chgH	Me	CN	$\mathrm{Ph_4As}$	VIII	9·46	9·55	7·1—7·7,	8·1—8·7 [e]
$\mathrm{4\text{-}O_2NC_6H_4CH_2}$	dmgH	chgH	Me	CN	$\mathrm{Ph_4As}$	VI	7·65 [j]	9·55	8·10	7·1—7·8, 8·1—8·7 [e]
Me	chgH	dmgH	$\mathrm{4\text{-}O_2NC_6H_4CH_2}$	CN	$\mathrm{Ph_4As}$	V	9·47	7·69 [j]	7·1—7·7, 8·1—8·7 [e]	8·10
$\mathrm{4\text{-}O_2NC_6H_4CH_2}$	dmgH	dmgH	$\mathrm{4\text{-}O_2NC_6H_4CH_2}$	CN	$\mathrm{Et_4N}$	VII	7·62 [j]	7·65 [j]	8·05	8·01
Me	dmgH	dmgH	Me	$\mathrm{NCCo(dmgH)_2CN}$ [k]	$\mathrm{Ph_4As}$		9·57	9·57	7·95	7·95
Me	dmgH	dmgH	Me	$\mathrm{N_3}$	$\mathrm{Ph_4As}$		9·46	9·46	7·91	7·91
Me	dmgH	dmgH	Me	NCS	$\mathrm{Ph_4As}$		9·49	9·25	7·93	7·93

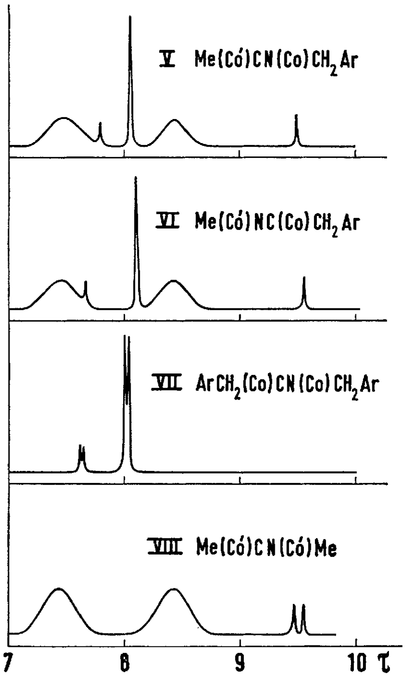
[a] τ ±0·02 p.p.m. [b] Monoanion of dimethylglyoxime. [c] Methyl resonances. [d] Monoanion of cyclohexanedione dioxime. [e] Broad multiplets. [f] *N*-Bonded $\mathrm{NCS^-}$. [g] *S*-Bonded $\mathrm{SCN^-}$ (see text). [h] Solvent contains a few % $\mathrm{CD_3OD}$. [i] Vinyl resonances (see below). [j] Benzyl methylene resonance (aryl resonances, see below). [k] dmgH Methyl resonance 7·87.

Other resonances: (a) *Vinyl*. II, α-H τ 3·61; β-(*trans*)H τ 5·45; β-(*cis*)H τ 5·37. III, α-H τ 3·32; β-(*trans*)H τ 5·17; β-(*cis*)H-τ 5·36. IV (R′) α-H τ 3·37; β-(*trans*)H τ 5·18; β-(*cis*)H τ 5·37. IV (R″) α-H τ 3·67; β-(*trans*)H τ 5·47; β-(*cis*)H τ 5·40. (b) *Phenyl* (2- and 6-hydrogens). V τ 3·17. VI τ 3·30. VII(R′) τ 3·27. VII(R″) τ 3·13.

Similar rearrangement and disproportionation were observed when an unsymmetrical bridged complex [*e.g.*, (V); Table 3 and the Figure] containing dissimilar organic groups and dissimilar dioximato-ligands was allowed to stand in solution at room temperature. *E.g.*,

$$\begin{array}{ccl} & & [\mathrm{MeCo(chgH)_2NCCo(dmgH)_2CH_2C_6H_4NO_2}]^- \\ [\mathrm{MeCo(chgH)_2CoCNCo(dmgH)_2CH_2C_6H_4NO_2}]^- & \rightleftharpoons & \qquad\qquad \mathrm{(VI)} \\ \mathrm{(V)} & \rightleftharpoons & [\mathrm{MeCo(chgH)_2CNCo(chgH)_2Me}]^- + \\ & & \qquad \mathrm{(VIII)} \\ & & [\mathrm{O_2NC_6H_4CH_2Co(dmgH)_2CNCo(dmgH)_2CH_2C_6H_4NO_2}]^- \\ & & \qquad\qquad \mathrm{(VII)} \end{array} \qquad (5)$$

Azide Complexes.—Salts of both monomeric and bridged dimeric azido-complexes were prepared in a similar manner from the aquocobalt complexes. Those complexes which were isolated and characterised are shown in Table 1. The i.r. spectra of these complexes in chloroform solution were measured. The azide stretching frequencies of the monomeric complexes (*ca.* 2030 cm^{-1}) are shown in Table 4, together with those (*ca.* 2049 cm^{-1}) for the bridged complex. Only single sets of resonances were observed for the organic groups and for the equatorial ligands in both monomeric and dimeric complexes (Table 3). The inorganic diazidobis(dimethylglyoximato)cobaltate(III) ion was the only product obtained from the reaction of the methanesulphonylbis(dimethylglyoximato)pyridinecobalt(III) species with an excess of azide ion.



^{1}H N.m.r. spectra of the four bridged cyanide complexes present during rearrangements corresponding to equation (5); complexes (V), (VI), and (VIII) are shown here as tetraphenylarsonium salts, (VII) is shown as the tetraethylammonium salt (cation spectra and fine structure of broad bands are omitted for clarity); Ar = 4-nitrophenyl; (Co) = Co(dmgH)$_2$; (Co′) = Co(chgH)$_2$; for assignment see Table 3

Cyanate Complexes.—A monomeric methylbis(dimethylglyoximato)cyanatocobaltate(III) salt was isolated. No bridged species could be detected. The i.r. spectrum of the monomeric complex in solution showed two strong bands at 2174 and 2212 cm^{-1} and in the solid state showed a strong band at 2227 cm^{-1} with a low frequency shoulder. However, the ^{1}H n.m.r. of the same solutions shows only one sharp methyl resonance and one sharp equatorial proton resonance.

Thiocyanate Complexes.—Both monomeric and bridged dimeric thiocyanate complexes were obtained in solution in the manner described above for the cyanide complexes, but only a monomeric complex, the methylbis(dimethylglyoximato)thiocyanatocobaltate(III) ion, was isolated as a salt (Table 1).

The i.r. spectrum of the solid monomeric salt shows a relatively broad ν(CN) band having an integrated intensity ratio [10] of 1·4 relative to the salicylic acid absorption at 1654 cm^{-1}. Solutions of the salt in chloroform show a fairly intense band at 2115 cm^{-1} with a shoulder at 2095 cm^{-1}, the integrated absorption intensity,[11] *A*, for the total peak being 6·3 × 10^4 l mol^{-1} cm^{-2}. In butan-2-one, the shoulder is not apparent, but *A* = 6·1 × 10^4 l mol^{-1} cm^{-2}.

The ^{1}H n.m.r. spectra of the monomeric complex in deuteriochloroform shows two distinct alkyl methyl resonances at τ 9·19 and 9·53, in the ratio 1 : 3, respectively. These do not change with time, are unaffected by the presence of bromotrichloromethane, which would remove any cobalt(II) species,[12] but are slightly sharpened on the addition of an excess of thiocyanate ion. There is evidence for some dissociation to free thiocyanate ion in solution, as shown by the presence of the appropriate band in the i.r. spectrum and the presence of a small amount of the resonances due to the methylaquo-complex in the ^{1}H n.m.r. spectrum.

TABLE 4

Infrared spectra (cm^{-1}) of anionic cobaloximes other than cyanides

Compound	Band	Solution (CHCl$_3$)	Solid (Nujol mull)
Ph_4As^+ $MeCo(dmgH)_2N_3^-$	ν(N$_3$)	2030 (±2)	2027 (±1) [a]
Ph_4As^+ $MeCo(dmgH)_2N_3Co(dmgH)_2Me^-$	ν(N$_3$)	2049 (±2) [b]	2041 (±1) [c]
Ph_4As^+ $N_3Co(dmgH)_2N_3^-$	ν(N$_3$)	2020 (±2) [d]	2014 (±1) [d]
Ph_4As^+ $CH_2{=}CHCo(dmgH)_2N_3^-$	ν(N$_3$)	2032 (±2)	2029, 2019 (±1)
Ph_4As^+ $MeCo(dmgH)_2NCS^-$ [e]	ν(CN)	2115 (±2) [f]	2114 (±1) [g]
	ν(CS)		799 (±1)
$MeCo(dmgH)_2SCN^-$ [e]	ν(CN)	2095(shoulder)	
Ph_4As^+ $MeCo(dmgH)_2NCSCo(dmgH)_2Me^-$	ν(CN)	2129 (±2)	
K^+ NCS^-	ν(CN)	2059 (±1) [h]	
Ph_4As^+ $MeCo(dmgH)_2NCO^-$	ν(CN)	2174, 2212 (±5) [i]	2227 (±1) [j]
Ph_4As^+ NCO^-	ν(CN)	2152 (±1)	

[a] Side peak at 2047 cm^{-1} and shoulder on low frequency side. [b] Side peak at 2023 cm^{-1}. [c] Shoulder to low frequency and side peak at 2005 cm^{-1}. [d] Solution has side peak at 2035 cm^{-1} initially appearing as a shoulder; solid has side peaks at 2034 and 1944 cm^{-1}. [e] Mixture of these two components. [f] Integrated absorption intensity of total absorption due to both components, *A* = 6·3 × 10^4 l mol^{-1} cm^{-2}; in methyl ethyl ketone, ν(CN) 2106 cm^{-1}, *A* = 6·1 × 10^4 l mol^{-1} cm^{-2}. [g] Integrated intensity ratio of total absorption due to both components, *R* = 1·4. [h] In methyl ethyl ketone (lit. 2060 cm^{-1}). [i] Overlapping bands of similar intensity; in CDCl$_3$ ν(CN) 2170, 2207 (±5) cm^{-1}. [j] Shoulder to low frequency.

The bridged complex is prepared fairly readily in solution, especially in the presence of an excess of the methylaquo-complex. As with the cyanide bridged complexes, the value for ν(CN) is slightly higher than for the monomeric species,

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[10] R. A. Bailey, T. W. Michelsen, and W. N. Mills, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3206.

[11] D. A. Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

[12] L. A. Epps and L. G. Marzilli, *J.C.S. Chem. Comm.*, 1972, 109.

and the ^{1}H n.m.r. spectrum shows two distinct organic resonances and two distinct equatorial ligand resonances.

DISCUSSION

Monomeric Complexes.—The formation constants for some monomeric cyanide, azide, and thiocyanate complexes in aqueous solution have been measured elsewhere.[13] They clearly indicate that such complexes should be formed by the addition of an equivalent of cyanide, azide, or thiocyanate ion to the methylbis-(dimethylglyoximato)aquocobalt(III) species in aqueous solution. For example, the formation constants (in aqueous solution at 10°) for the equation:

$$\mathrm{MeCo(dmgH)_2B} + \mathrm{X}^- \xrightleftharpoons{K_f} \underset{\text{(I)}}{[\mathrm{MeCo(dmgH)_2X}]^-} + \mathrm{B} \qquad (6)$$

are:

$$\mathrm{B} = \mathrm{H_2O},\ \mathrm{X} = \mathrm{CN};\ K_f = 10^6\ \mathrm{l\,mol^{-1}}$$
$$\mathrm{B} = \mathrm{H_2O},\ \mathrm{X} = \mathrm{SCN};\ K_f = 96\ \mathrm{l\,mol^{-1}}$$
$$\mathrm{B} = \mathrm{H_2O},\ \mathrm{X} = \mathrm{N_3};\ K_f = 200\ \mathrm{l\,mol^{-1}}$$
$$\mathrm{B} = \mathrm{py},\ \mathrm{X} = \mathrm{CN};\ K_f = 210$$

However, only in the case of the monomeric cyanide complex is the formation constant sufficiently large for the latter to be made from the anion and the methylbis-(dimethylglyoximato)pyridinecobalt(III) species. It would be expected from studies of inorganic cyanate complexes, that the formation of the cyanate complexes in this work would be somewhat less easy than the formation of the thiocyanate complexes.

It is usually assumed, as a result of structural studies on compounds[14] such as $\mathrm{Co(CN)_6}^{3-}$, that the *C*-bonded cyanide derivatives predominate. The observation, in the ^{1}H n.m.r. spectrum of the methylcyano-complex (I; X = CN), of only a single resonance for the axial methyl group and a single resonance for the equatorial methyl groups is consistent with the presence of a single component. Similarly, the i.r. spectra of compound (I) and of other organic derivatives of this complex in chloroform solution show only single cyanide stretching bands. The marked solubility of these salts in chloroform allows reliable measurements to be made of the variation of the cyanide stretching frequency with the axial organic ligand.

The value of ν(CN) increases progressively with increasing electronegativity of the α-carbon, *i.e.*,

$$\mathrm{PhC{\vdots}C}\ (2130\ \mathrm{cm^{-1}}) > \mathrm{PhCH{:}CH}\ (2119\ \mathrm{cm^{-1}}) > \mathrm{PhCH_2}\ (2112\ \mathrm{cm^{-1}})$$

Similar but less extensive variations were found in the spectra of solid organocyanocobalamins[15] and organopentacyanocobaltates.[16] The absence of significant steric effects of the organic ligand on the equatorial ligand, and hence on the axial cyanide, is apparent from the very similar values of ν(CN) observed for α- and β-styrylcobaloximes, for n-octyl- and s-octyl-cobaloximes, and for vinyl- and α-methylvinyl-cobaloximes.

The monomeric azido-complexes also showed single azide stretching bands in the i.r. spectra, though a number of bands were evident in the solid state. The frequency of this band in solution (*ca.* 2030 cm^{-1}) is very much less sensitive to the nature of the organic group than is the value of ν(CN) for the cyanide complexes.

The nature of the bonding in the complexes of thiocyanate ion is more difficult to ascertain. The two methyl proton resonances observed in the n.m.r. spectrum of methylbis(dimethylgloximato)thiocyanatocobaltate(III) ion, and the character of the cyanide band in the i.r. spectrum in solution, suggest a mixture of complexes which exchange fairly rapidly, though slowly with respect to the n.m.r. time scale. For example, the integrated absorption intensity of *ca.* $6{\cdot}2 \times 10^4$ l mol^{-1} cm^{-2} lies between that usually found for the *S*-bonded ($\leqslant 3 \times 10^4$) and for the *N*-bonded ($\geqslant 8 + 10^4$) thiocyanate ligand.[17] The slight sharpening of the two methyl proton resonances which is observed when an excess of thiocyanate ion is added to a solution containing the two complexes is probably, therefore, a result of a decrease in the rate of rapid exchange between these two complexes. Such exchange, if it occurred by reaction of the *S*- or *N*-bonded thiocyanate complex with some five-co-ordinate methylcobalt(III) complex (equation 8, X = S), would be suppressed by added thiocyanate ion which would greatly reduce the concentration of the latter.

$$\mathrm{Me(Co)aq} \rightleftharpoons \mathrm{Me(Co)} + \mathrm{aq} \qquad (7)$$

$$[\mathrm{Me(Co)XCN}]^- + \mathrm{Me(Co)} \rightleftharpoons [\mathrm{Me(Co)XCN(Co)Me}]^- \rightleftharpoons \mathrm{Me(Co)} + [\mathrm{XCN(Co)Me}]^- \qquad (8)$$

$$\mathrm{Me(Co)} + \mathrm{XCN}^- \rightleftharpoons [\mathrm{Me(Co)(XCN)}]^- \qquad (9)$$

$$(\mathrm{X} = \mathrm{O\ or\ S})$$

Indeed, in the solutions containing only one equivalent of methylcobalt(III), some free thiocyanate ion can be detected by its i.r. absorption.

It is interesting that, though traces of cobalt(II) species may be present in these solutions, they do not appear to catalyse these exchanges. The much slower exchanges between the corresponding inorganic cobalt(III) thiocyanate complexes are very susceptible to traces of cobalt(II) species which, by an inner-sphere electron transfer reaction, provide a mechanism for equilibration.[12]

The nature of the species which predominates in these solutions is not certain, but the assignment of spectra in the Tables has been made on the assumption that it is the *N*-bonded complex which is present in highest

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[13] A. L. Crumbliss and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1970, **92**, 2593.

[14] N. A. Curry and W. A. Runciman, *Acta Cryst.*, 1959, **12**, 674.

[15] R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *J. Chem. Soc.* (*A*), 1968, 2428.

[16] J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, 1965, **87**, 5361.

[17] C. Pecile, *Inorg. Chem.*, 1966, **5**, 210.

concentration. This assignment is partially based on previous assignments on the less labile inorganic complexes of the type (X-py)Co(dmgH)$_2$(SCN), where X = H [18] or 4-t-butyl,[12] in which the *S*-bonded complex has the lower ν(CN). It has also been suggested for methylcobaloximes that the higher degree of π-bonding (as in the *S*-bonded complex), the lower the τ-value for the axial methyl protons.[19]

In the solid state, the i.r. spectrum exhibits an integrated intensity ratio for the ν(CN) band of 1·4 [relative to the ν(CO) band of admixed salicylic acid] which once again lies well between the ratio expected for the *S*-bonded (0·3—1·0) and that for the *N*-bonded (1·6—5·4) thiocyanate ligand.[10] This suggests that similar proportions of the two species obtain in the crystals as in solution.

The azido-complex has the expected ν(N_3) stretch, and a ^{1}H n.m.r. spectrum characteristic of a single species. However, we have been unable fully to characterise the cyanato complex. The sharp singlet axial methyl and equatorial methyl resonances in the ^{1}H n.m.r. spectrum of the methylbis(dimethylglyoximato)cyanatocobaltate(III) ion (Table 3) suggest either a single species or a rapidly equilibrating mixture of species; the two strong ν(CN) bands in the i.r. spectrum of the same solution favour the latter interpretation. A rapid exchange between *O*- and *N*-bonded complexes seems possible, but this is mitigated by the fact that an exchange *via* equation (8; X = O) is unlikely in view of the absence of evidence for bridged cyanate complexes and the fact that, where bridged cyanate complexes are known, these usually have *both* metals *N*-bonded (*e.g.*, refs. 20 and 21).

Bridged Complexes.—Bridged cyanide complexes of cobalt(III) have been reported several times before, both as transient intermediates [3,4] and as isolable complexes.[5-8] For example, the reaction of the aquopenta-amminecobalt(III) ion with the hexacyanocobaltate(III) ion [6] (equation 9) and the reaction of the cyanopenta-amminecobalt(III) ion with the aquopentacyanocobaltate(III) ion [7] (equation 10) give two isolable isomers of a neutral penta-ammine-pentacyanodicobalt(III) complex containing a bridged cyanide ligand.

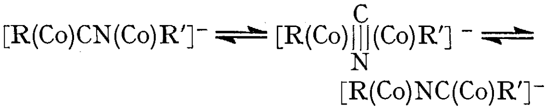
$$[(H_3N)_5Coaq]^{3+} + [NCCo(CN)_5]^{3-} \rightleftharpoons (H_3N)_5CoNCCo(CN)_5 \quad (9)$$

$$[(H_3N)_5CoCN]^{2+} + [aqCo(CN)_5]^{2-} \rightleftharpoons (H_3N)_5CoCNCo(CN)_5 \quad (10)$$

The formation of bridged cyanide complexes in this work is comparable with that described above. The two distinct axial methyl proton resonances and two distinct equatorial methyl resonances (Table 3) observed for the complex (I) formed from methylaquo- and methylcyano-bis(dimethylglyoximato)cobalt(III) species (equation 2) show clearly that the two cobalt atoms are *C*- and *N*-bonded, respectively. The unsymmetrical character of the bridged cyanide complexes is further confirmed by the observation of two distinct species (II and III, respectively) from the initial reactions of methylcyano- with vinylaquo-bis(dimethylglyoximato)cobalt(III) and methylaquo- with vinylcyano-bis-(dimethylglyoximato)cobalt(III), respectively.

However, the major difference between these organocobalt bridged cyanide complexes and the inorganic bridged cyanide complexes is that the former are much more labile. For example, both the methyl-vinyl and the vinyl-methyl bridged complexes (II) and (III), respectively, rearrange over a few hours (equation 4) to give the same equilibrium mixture of bridged complexes which includes (I) and (IV), and which contains approximately equal amounts of *C*- and *N*-bonded methyl cobalt moieties. Other mixed alkyl bridged complexes such as (V) rearrange in a comparable fashion (equation 5). These rearrangements were monitored by observation of the ^{1}H n.m.r. spectra (see the Figure); observation of the ^{19}F resonance of 4-fluorobenzylcobalt bridged species [22] was equally useful but did not provide more specific information about the constituents of the final mixtures.

The mechanism of this rearrangement might involve either an intramolecular rearrangement (equation 11) or an intermolecular rearrangement in which a prior dissociation occurs (equations 12—17). This latter mechanism may also involve isocyanide complexes as intermediates which requires a similar set of equations except that bond making and breaking occurs at the alternative end of the cyanide.



$$[R(Co)CN(Co)R']^- \rightleftharpoons [R(Co)\underset{\mathrm{N}}{\overset{\mathrm{C}}{|||}}(Co)R']^- \rightleftharpoons [R(Co)NC(Co)R']^- \quad (11)$$

$$[R(Co)CN(Co)R']^- \rightleftharpoons [R(Co)CN]^- + R'(Co) \quad (12)$$

$$[R(Co)CN]^- \rightleftharpoons R(Co) + CN^- \quad (13)$$

$$R'(Co) + CN^- \rightleftharpoons [R'(Co)CN]^- \quad (14)$$

$$[R'(Co)CN]^- + R'(Co) \rightleftharpoons [R'(Co)CN(Co)R']^- \quad (15)$$

$$[R'(Co)CN]^- + R(Co) \rightleftharpoons [R'(Co)CN(Co)R]^- \quad (16)$$

$$[R(Co)CN]^- + R(Co) \rightleftharpoons [R(Co)CN(Co)R]^- \quad (17)$$

Whilst it is possible that the intramolecular mechanism can take place, the fact that a mixture of the two symmetrical complexes, [4-O_2N-$C_6H_4CH_2$Co(dmgH)$_2$CNCo-(dmgH)$_2CH_2C_6H_4$-4-NO_2]$^-$ and [MeCo(chgH)$_2$CNCo-(chgH)$_2$Me]$^-$, rearranges (reverse, equation 5) to a mixture at least one third of which is the unsymmetrical complex [4-O_2N-$C_6H_4CH_2$Co(dmgH)$_2$CNCo(chgH)$_2$Me]$^-$, at a rate comparable with the rearrangements described above,

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[18] A. H. Norbury and A. I. P. Sinha, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 617.

[19] L. M. Ludwick and T. L. Brown, *J. Amer. Chem. Soc.*, 1969, **91**, 5188.

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[21] F. Stocco, G. C. Stocco, W. M. Scovell, and R. S. Tobias, *Inorg. Chem.*, 1971, **10**, 2639.

[22] D. Dodd, C. W. Fong, and M. D. Johnson, unpublished work.

shows clearly that the intermolecular mechanism predominates.

The formation of thiocyanate bridges has been observed less frequently (*e.g.*, refs. 23 and 24). The bridged complexes described here are formed less readily than the cyanide bridged complexes. The presence of two distinct axial methyl resonances and two distinct equatorial methyl resonances for the thiocyanate bridged complex shows clearly that the two cobalt atoms are bridged to nitrogen and sulphur, respectively, rather than to nitrogen alone. The very low solubility of the alkylaquocobalt(III) complexes in chloroform and the fact that such complexes dissolve in the presence of the monomeric thiocyanato-complex causing a shift in ν(CN), rules out the possibility that these proton resonances are due to the simple mixture of the thiocyanato- and aquo-complexes in solution. No attempt was made to isolate crystalline samples of these bridged complexes.

Bridged cyanate complexes in which the two metal atoms are bonded to nitrogen have been detected previously (*e.g.*, refs. 20 and 21). The inability to detect bridged cyanate complexes in this study may be a result of a general preference of cobalt(III) species to form terminal complexes in which the two metal atoms are bonded to the ends of the bidentate group.

The formation of azide bridged complexes is therefore of particular interest since azide bridges generally contain the two metal atoms attached to the same nitrogen atom rather than to the two terminal nitrogen atoms (*e.g.*, refs. 25—27). Of the latter type only a copper(I) complex is known and in a situation where bridging to the same nitrogen atom would cause considerable steric crowding.[28] The cobalt(III) complexes may be terminally bridged for the same reason. They are unusual in that they contain only one azide group while other known bridged azides are composed of polymeric units in which the metal atoms are bonded to more than one azide group. Confirmation of the structure awaits the results of *X*-ray structural studies.

The formation of bridged complexes has an effect on the i.r. absorption of the bridging ligand. The cyanide stretching vibrations increase by a fairly constant increment over that of the monomeric complexes, *i.e.*, $+35 \pm 2$ cm^{-1}, in agreement with the change predicted for bridge formation.[29] It is unnecessary to predict any change in bond order to account for this shift, which may also be affected if Co–C–N–Co is non-linear. The organometallic group bonded to the cyanide carbon has a much greater effect on the value of ν(CN) than does the organometallic group bonded to the cyanide nitrogen; this recalls previous observations that different groups bonded to the nitrogen end have little effect on the ligand field strength at the carbon end.[7,30] The changes in ν(CN) with different axial organic groups are insufficient to give a reliable measure of the changes occurring on rearrangement of these bridged complexes. The changes in ν(N_3) on formation of the bridged azide complexes are small but also to higher frequency (*ca.* +19 cm^{-1}) as is the change in ν(CN) on formation of the bridged thiocyanate complexes (*ca.* +14 cm^{-1} from *N*-bonded, +34 cm^{-1} from *S*-bonded). These changes, though of lower magnitude, are in the same direction as those previously observed for bridging azide (non-terminal) [25] and thiocyanate.[23,24]

EXPERIMENTAL

Organobis(dioximato)-aquo- and -pyridine-cobalt(III) *Compounds*.—These were all previously prepared complexes [9] except for the following. Orange crystals of methylbis(cyclohexanedione dioximato)aquocobalt(III) were prepared following the method of Yamazaki and Hohokabe [31] for methylaquocobaloxime (67% yield). Vinylbis(dimethylglyoximato)aquocobalt(III) was similarly produced as brown crystals (26% yield) from the comparable reaction of vinyl bromide at ambient temperature. These products crystallised out analytically pure from the respective reaction mixtures (Table 1).

Organobis(dioximato)cyanocobaltate(III) *Salts*.—A typical preparation is as follows.

Methylbis(cyclohexanedione dioximato)pyridinecobalt(III) (0·435 g, 1 mmol) was added to a solution of an excess (*ca.* 3 fold) of sodium cyanide in 0·5M aqueous sodium hydroxide (20 ml). On warming, the suspension dissolved to give an orange-yellow solution. A solution of tetraphenylarsonium chloride (Koch–Light) in 0·5M aqueous sodium hydroxide was added to the cooled solution until no further precipitate was obtained. The pale yellow crystals of *tetraphenylarsonium methylbis(cyclohexanedione dioximato)cyanocobaltate*(III) (0·650 g, 83%) were filtered off, washed with water, and dried before recrystallisation from methanol–ether.

The other salts (Table 1) were prepared in a similar manner with the following variations.

Aquo-complexes were used to prepare the benzylcyanocobaloxime salt and in some preparations of the methyl- and vinyl-cyanocobaloxime salts. These have the advantage of dissolving more readily in the aqueous alkaline cyanide solutions and warming is unnecessary for compounds with the smaller organic groups.

Pyridine complexes were used to prepare all the other cyanide salts and dissolution is very slow for the compounds with larger organic groups. Styrylpyridinecobaloximes required 2—3 h and phenylethynylpyridinecobaloxime some 4—5 h warming at *ca.* 90° before dissolution was

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[23] R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Co-ordination Chem. Rev.*, 1971, **6**, 407.

[24] R. C. Buckley and J. G. Wardeska, *Inorg. Chem.*, 1972, **11**, 1723.

[25] W. Beck, W. P. Fehlhammer, P. Pöllmann, and R. S. Tobias, *Inorg. Chim. Acta*, 1968, **2**, 467.

[26] W. P. Fehlhammer and L. F. Dahl, *J. Amer. Chem. Soc.*, 1972, **94**, 3377.

[27] R. Mason, G. A. Rusholme, W. Beck, H. Englemann, K. Joos, B. Lindenberg, and H. S. Smedal, *Chem. Comm.*, 1971, **496**.

[28] R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, 1971, **10**, 1289.

[29] D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nuclear Chem.*, 1961, **21**, 33.

[30] D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, 1965, **4**, 725.

[31] N. Yamazaki and Y. Hohokabe, *Bull. Chem. Soc. Japan*, 1971, **44**, 63.

complete. Yields of tetraphenylarsonium salts were however, practically quantitative.

Salts of the lower molecular weight organic cations are more soluble, particularly those of compounds having the smaller organic groups. Where such salts did not crystallise on evaporation of solvent water, they were obtained by extraction of the product with chloroform. The latter method was used for the preparation of tetraethylammonium methylcyanocobaloxime for which several extractions were required; it is generally desirable to use only one equivalent of the cation to minimise extraction of inorganic salts. The chloroform extracts were dried ($MgSO_4$) and partially evaporated. On addition of ether, the yellow crystalline salts precipitated. In some cases, the yellow-brown oils which first formed on addition of the cation were recrystallised from chloroform by the addition of ether.

For those organocobaloximes which were sensitive to cyanide ion and/or alkali, the latter was omitted and the stoicheiometric amount of alkali cyanide was added dropwise to a solution or suspension of the pyridine complex in methanol. The methanol was partially evaporated and the product precipitated. Such precautions were not observed in the preparation of the s-octylcyanocobaloxime salt, and the resulting product contained inorganic impurity. However, n.m.r. and i.r. spectra indicated the presence of the desired complex.

In the presence of local or overall excess of cyanide ion in alkaline solution, methanesulphonyl(pyridine)cobaloxime yielded yellow crystals of the dicyanocobaloxime salt, as did the mono- and di-bromomethyl(pyridine)cobaloximes. The sensitivity of the latter to nucleophilic attack at the organic group has already been observed.[32] Other salts of dicyanocobaloxime have been prepared previously.[8,33,34] Compared with the tetraphenylarsonium salt (mull, 2128 cm^{-1}), ν(CN) for the silver salt [34] may indicate some degree of bridging of the cyanide from Co to Ag^+, as observed for related cobalt(III) species,[35] perhaps also followed by flipping of the cyanide bridge.[36]

The colour of the organobis(dioximato)cyanocobalt(III) salts varied from pale yellow (phenylethynylcyanocobaloxime-salts) to dark orange-yellow (the *p*-nitrobenzylcyanocobaloxime salt).[22] The crystalline secondary-alkylcyanocobalt(III) salts are somewhat light sensitive.

Cyanide-bridged Organobis(dioximato)cobaltate(III) *Salts*.—The cyanide-bridged salts were readily prepared *in situ* for spectral measurements by the addition of 1 mol of the appropriate organobis(dioximato)aquocobalt(III) to a solution of the appropriate organobis(dioximato)cyanocobaltate(III) salt in chloroform. The aquo-complex dissolved as the bridged complex formed. On addition of ether to the solution, the crystalline bridged salt was precipitated. The bridged complex derived from methylaquocobaloxime (2 mol) and tetraphenylarsonium dicyanocobaloxime (1 mol) (Table 1) was prepared in this manner.

A solution of equimolar amounts of cyano- and pyridine-vinylcobaloxime was observed by n.m.r. and i.r. spectroscopy for several days. No bridge formation was observed. One bridged complex was isolated directly; when tetrabutylammonium chloride was added to an aqueous solution of methylpyridinecobaloxime and cyanide ion, a slow precipitation of yellow crystals of the bridged dimethyl complex took place over several days. On evaporation of the mother liquor a further crop of the same product was obtained. A closely related inorganic complex Ph_4As^+ $NCCo(dmgH)_2CNCo(dmgH)_2CN^-,H_2O$ has recently been described.[8]

The i.r. spectra of several of the cyanide salts indicated the presence of water of crystallisation. This was confirmed by the analyses, which were unchanged when the product was repeatedly recrystallised and dried *in vacuo* over phosphorus pentoxide.

Organobis(dimethylglyoximato)azidocobaltate(III) *Salts*.—These were prepared from organoaquocobaloximes in a similar manner to that described for the cyano-complexes.

Methylazidocobaloxime Tetraphenylarsonium Salt.—Methylaquocobaloxime (0·3 g) was dissolved at ambient temperature in a solution of sodium azide (0·5 g) in 0·2M aqueous sodium hydroxide. A solution of tetraphenylarsonium chloride in 0·2M aqueous sodium hydroxide was added with stirring until no further precipitate was formed. The orange crystals were filtered off, washed with water, and dried *in vacuo* (yield 0·31 g, 46%).

Orange crystals of the vinyl complex were prepared similarly (48%). Methanesulphonyl(pyridine)cobaloxime, in an alkaline solution containing tetraphenylarsonium chloride and a large excess of azide ion, deposited gold needles of tetraphenylarsonium diazidocobaloxime (Table 1).

Azide-bridged Methylcobaloxime Salt.—The azide bridged species are formed much less readily than the cyanide analogues. Thus a solution of tetraphenylarsonium methylazidocobaloxime in deuteriochloroform was equilibrated for several hours with an excess of methylaquocobaloxime. The mixture was filtered and the solution treated with ether to precipitate the bridged complex (Table 1), which was washed with ether and dried in air. I.r. spectra indicated the presence of $CDCl_3$ of crystallisation and this was confirmed by analysis. A chlorine analysis performed some weeks later (Found: 7·25%; Calc. for 1 mol $CDCl_3$: 9·20%) suggests that solvent may be lost on standing.

Tetraphenylarsonium Methylthiocyanatocobaloxime.—Methylaquocobaloxime (0·322 g, 1 mmol) was warmed to *ca.* 90° in a solution of sodium thiocyanate (0·081 g, 1 mmol) in 0·2M aqueous sodium hydroxide (5 ml). A little undissolved cobaloxime was filtered off and tetraphenylarsonium chloride in 0·2M aqueous sodium hydroxide was added dropwise with stirring until no further precipitate was obtained. The yellow crystals were filtered off, washed with a little water, and recrystallised from methanol–ether (0·38 g, 52%).

An aquo-complex is the required starter since the equilibrium constant is unfavourable with most other bases.[13]

Thiocyanate-bridged Organocobaloximes.—Thiocyanate bridges appear to form more readily than azide bridges but less readily than cyanide bridges. Only that formed from methylaquocobaloxime and the methylthiocyanatocobaloxime salt was prepared in chloroform solution. An excess of the aquocobaloxime aids the formation. No attempt was made to isolate a crystalline bridged complex.

Tetraphenylarsonium Methylcyanatocobaloxime.—This was prepared in a similar manner to the thiocyanate analogue except that an excess of potassium cyanate was utilised to provide the axial base. Yellow crystals of product were filtered off, washed with a little water, and dried *in vacuo* (0·336 g, 46%).

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[32] G. N. Schrauzer, A. Ribeiro, L. P. Lee, and R. K. Y. Ho, *Angew. Chem. Internat. Edn.*, 1971, **10**, 807.

[33] N. Maki, *Bull. Chem. Soc. Japan*, 1965, **38**, 2013.

[34] Cs. Várhelyi, I. Gănescu, and L. Szotyori, *Z. anorg. Chem.*, 1971, **386**, 232.

[35] H. Siebert, *Z. anorg. Chem.*, 1964, **327**, 63.

[36] J. P. Birk and J. H. Espenson, *Inorg. Chem.*, 1968, **7**, 991.

The formation constant is likely to be lower here than for the thiocyanate complex, thus an aquo-complex is again the preferred starter. A chloroform solution of the methylcyanatocobaloxime salt failed to dissolve any added methylaquocobaloxime so bridge formation is not evident.

I.r. Spectra.—I.r. spectra were recorded on the expanded scale of a Perkin-Elmer 257 spectrophotometer and were calibrated against atmospheric water vapour bands by switching to single beam operation during recording. The quoted wavenumbers represent averages of three or more scans. Samples were run as Nujol mulls or as chloroform solutions in a 0·5 mm cell.

Where cyanide bridged species were prepared by dissolution of an aquo-complex of one organocobalt moiety in a solution of a cyanide complex of another, spectra were run immediately after dissolution before any 'CN-flip' had taken place.

The absorption intensity of the ν(CN) band of the thiocyanate complex in solution was measured by the method of direct integration.[11] The ν(CN) band of potassium thiocyanate in butan-2-one, for which the extinction coefficient is known,[17] provided a check on cell width (0·5 mm).

The integrated intensity ratio of the ν(CN) band in the solid was measured relative to salicylic acid [ν(CO) 1654 cm^{-1}] in admixtures with the latter (Nujol mull) by the method previously described.[10] The ν(CN) band of $HgCo(NCS)_4$ (bridged thiocyanates, ratio = 1·3 [10]) was used as a check. These results are shown in Table 4.

^{1}H *N.M.R. Spectra.*—^{1}H N.m.r. spectra were recorded at 33° on a Perkin-Elmer R10 instrument; spectra of individual samples are shown in Table 3. Bridged species (*ca.* 0·1M) were prepared as previously from the respective anionic and aquo-complexes in $CDCl_3$. In cyanide bridge-flipping experiments, the solutions were kept at 33° and the spectra measured at intervals. The two bridged methylvinyl species came to equilibrium within *ca.* 10 h, around 10% flip having occurred within the first hour. Equilibrium in this case was a mixture having approximately equal amounts of *C*- and *N*-bonded Me(Co), and it was not possible to distinguish the bridged species involved since the spectrum also corresponded to that for an equimolar mixture of $Me(Co)CN(Co)Me^-$ and $CH_2{=}CH(Co)CN(Co)CH{=}CH_2^-$ (Table 3, but allow for different cations; see later). A freshly made solution of $MeCo(chgH)_2CNCo(dmgH)_2$-$CH_2C_6H_4$-4-NO_2^- took about a day to come to equilibrium though about 15% flip was already apparent after 2 h. Here the equilibrium lay on the side of *N*-bonded Me(Co) [and *C*-bonded $Co(dmgH)_2$ and *C*-bonded $(Co)CH_2C_6H_4$-4-NO_2; see Table 3] in the ratio 2 : 1 and thus at least a third of the mixture must be composed of the flipped species, $MeCo(chgH)_2NCCo(dmgH)_2CH_2C_6H_4$-4-$NO_2^-$. However the remaining two thirds could still be largely the 'symmetric' species since the ^{1}H n.m.r. spectra were again insufficiently distinguishable. But the presence of an intermolecular mechanism was shown by separately preparing the two 'symmetric' bridged species and following the changes in spectra of an equimolar mixture. After a day the ratio of *N*-bonded Me(Co) to *C*-bonded Me(Co) was approximately 2 : 1. This latter mixture contained both Ph_4As^+ and Et_4N^+ cations and some broadening was evident in the spectrum. Et_4N^+ Cl^- Added to the equilibrium mixture obtained from Ph_4As^+ $MeCo(chgH)_2CNCo$-$(dmgH)_2CH_2C_6H_4$-4-NO_2^- gave a similar broadening.

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