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# SOME ASPECTS OF THE CHEMISTRY OF COBALT(I) CYANIDE AND RELATED COMPLEXES

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Low-spin coordination compounds of cobalt have been the objects of considerable recent attention and study, directed in part at the roles of such compounds in homogeneous catalysis[1] and as model systems for vitamin $B_{12}$ and its derivatives[2,3] The present article is concerned with some aspects of this subject, notably the chemistry of cobalt(I) cyanide and related complexes

## A LOW-SPIN COMPLEXES OF COBALT

The pattern of configurations characteristic of the low-spin complexes formed by cobalt is depicted in Table 1 This pattern is exemplified particularly by complexes containing

TABLE 1

Representative cyano- and related complexes of cobalt

| Compound | Oxidation state | No of *d* electrons | Total valence shell |
|---|---|---|---|
| *Hexacoordinate* | | | |
| $Co(CN)_6^{3-}$ | +3 | $d^6$ | 18 |
| $Co(CN)_5Cl^{3-}$ | +3 | $d^6$ | 18 |
| $Co(CN)_5H^{3-}$ | +3 | $d^6$ | 18 |
| *Pentacoordinate* | | | |
| $Co(CN)_5^{3-}$ | +2 | $d^7$ | 17 |
| $Co(CN)_2(PR_3)_3$ | +2 | $d^7$ | 17 |
| $Co(CNR)_5^{2+}$ | +2 | $d^7$ | 17 |
| $Co(CN)_5^{4-}$ | +1 | $d^8$ | 18 |
| $Co(CN)_3(CO)_2^{2-}$ | +1 | $d^8$ | 18 |
| $Co(CNR)_5^{+}$ | +1 | $d^8$ | 18 |
| $Co(CO)_4H$ | +1 | $d^8$ | 18 |
| *Tetracoordinate* | | | |
| $Co(DIPHOS)_2^{+}$ [a] | +1 | $d^8$ | 16 |
| $Co(DIPHOS)_2$ [a] | 0 | $d^9$ | 17 |
| $Co(CO)_4^{-}$ | −1 | $d^{10}$ | 18 |
| $Co(CO)_3(PR_3)^{-}$ | −1 | $d^{10}$ | 18 |

[a] DIPHOS = $Ph_2PCH_2CH_2PPh_2$

cyanide and related ligands (e g carbonyls, isonitriles and phosphines) but extends also more generally to other low-spin coordination compounds Attention is directed particularly to the following features and trends

(1) The inverse dependence of the preferred coordination number on the *d*-electron population, a trend which reflects the constraints of the "noble gas rule", whereby those configurations in which the total number of valence electrons approaches, *but does not exceed*, eighteen are favored.

(2) The tendency of strong $\sigma$-donor ligands such as $CN^-$ to stabilize the higher oxidation states (notably +3) of cobalt, whereas strong $\pi$-acceptor ligand such as CO stabilize the lowest oxidation states (−1 to +1).

(3) Whereas the wide range of oxidation states exhibited by cobalt is paralleled by certain other elements (e g $Pt^0$ to $Pt^{IV}$) the formation of stable mononuclear low-spin $d^7$ complexes is distinctive Thus, while complexes such as $Co(CN)_5{}^{3-}$ and $Co(CNR)_5{}^{2+}$ do exhibit some tendency to dimerize and/or disproportionate, this tendency is much less pronounced than for most other low-spin $d^7$ complexes such as $Mn^0$, $Rh^{II}$, $Ir^{II}$, $Pt^{III}$, etc

(4) Some of the characteristic reactions whereby the complexes conforming to the pattern depicted by Table 1 are interconverted are:

(i) simple electron transfer reactions in which the coordination number remains unchanged, e g

$$Co(CNR)_5{}^{2+} + e^- \rightarrow Co(CNR)_5{}^{+} \qquad (1)$$

(ii) "oxidative addition" reactions, in which oxidation is accompanied by an increase in the coordination number[4—6], e g

$$2\, Co^{II}(CN)_5{}^{3-} + CH_3I \rightarrow Co^{III}(CN)_5CH_3{}^{3-} + Co^{III}(CN)_5I^{3-} \qquad (2)$$

$$Co^{I}(dmg)_2(PR_3)^- + CH_3I \rightarrow Co^{III}(dmg)_2(PR_3)CH_3 + I^- \qquad (3)$$

(iii) acid–base reactions of hydrido-complexes which correspond, formally, to two-electron redox processes, e g

$$Co^{I}(CO)_4H \rightleftarrows Co^{-I}(CO)_4{}^{-1} + H^+ \qquad (4)$$

Oxidative addition reactions such as those depicted by eqns (2) and (3) are particularly significant as synthetic routes to organocobalt compounds, as steps in homogeneous catalytic processes and in the context of vitamin $B_{12}$ model system chemistry[4—6]

## B PENTACYANOCOBALTATE(I)

The pentacyanocobaltate(I) ion, $Co(CN)_5{}^{4-}$, previously postulated[7,8] as an intermediate in the chemical and electrochemical oxidations of $Co(CN)_5H^{3-}$, has recently been directly detected and spectrally characterized[9], following its formation by the reaction of hydrated electrons (generated by pulse radiolysis) with $Co(CN)_5{}^{3-}$ in aqueous solution according to eqn (5) The rate constant of this reaction, $k_5$, is $1\ 2 \times 10^{10}$ mole$^{-1}$ sec$^{-1}$ (ref. 9)

$$Co(CN)_5{}^{3-} + e_{aq}^{-} \xrightarrow{k_5} Co(CN)_5{}^{4-} \tag{5}$$

$Co(CN)_5{}^{4-}$ is highly unstable in aqueous solution and reacts[9] to form $Co(CN)_5H^{3-}$ according to reaction (6) with a half-life of ca $7 \times 10^{-6}$ sec ($k_6 = 1$ [illegible] $\times 10^5$ sec$^{-1}$).

$$Co(CN)_5{}^{4-} + H_2O \xrightarrow{k_6} Co(CN)_5H^{3-} + OH^- \tag{6}$$

$Co(CN)_5{}^{4-}$ can also be generated in aqueous solution by the reaction of $OH^-$ with $Co(CN)_5H^{3-}$. Whereas $Co(CN)_5H^{3-}$ is relatively reactive toward substrates such as free radicals and conjugated olefins to which it can transfer a hydrogen atom, it is intrinsically rather unreactive toward typical outer-sphere electron transfer oxidants such as $Fe(CN)_6{}^{3-}$ Reactions of the latter type are, however, promoted by $OH^-$, apparently through mechanisms such as that depicted in eqns (7)–(9), which is in accord with the observed rate law[10],

$$-d[Co(CN)_5H^{3-}]/dt = k_7[Co(CN)_5H^{3-}][OH^-]$$

where $k_7 = 0\ 1$ mole$^{-1}$ sec$^{-1}$

$$Co(CN)_5H^{3-} + OH^- \xrightarrow{k_7} Co(CN)_5{}^{4-} + H_2O \text{ (rate-determining)} \tag{7}$$

$$Co(CN)_5{}^{4-} + Fe(CN)_6{}^{3-} \xrightarrow{\text{fast}} Co(CN)_5{}^{3-} + Fe(CN)_6{}^{4-} \tag{8}$$

$$Co(CN)_5{}^{3-} + Fe(CN)_6{}^{3-} \xrightarrow{\text{fast}} [(CN)_5Fe\text{–}CN\text{–}Co(CN)_5]^{6-} \tag{9}$$

$$Co(CN)_5H^{3-} + 2\,Fe(CN)_6{}^{3-} + OH^- \rightarrow [(CN)_5Fe\text{–}CN\text{–}Co(CN)_5]^{6-} + Fe(CN)_6{}^{4-} + H_2O \tag{10}$$

The reaction of $Co(CN)_5H^{3-}$ with $Hg(CN)_2$ according to eqn (11) has recently been reported to exhibit similar kinetics, and has been interpreted in terms of an analogous mechanism in which reaction (7) also is the rate-determining step[11].

$$HCo(CN)_5{}^{3-} + Hg(CN)_2 + OH^- \rightarrow [NCHgCo(CN)_5]^{3-} + CN^- + H_2O \tag{11}$$

Combination of the above value of $k_7$ with the previously determined value of $k_6$ yields a value of $10^{-6}$ mole$^{-1}$ for the equilibrium constant ($K_{eq} = k_7/k_6$) of reaction (7) This corresponds to a p$K_a$ of ca 20 for $Co(CN)_5H^{3-}$, which is thus an extremely weak acid.

The trapping of $Co(CN)_5{}^{4-}$, following its generation by reaction (7), can also be effected by reaction with a ligand such as CO which is more effective than $CN^-$ at stabilizing cobalt(I) Thus, $OH^-$ was found[12] to promote the carbonylation of $Co(CN)_5H^{3-}$ with the formation of the mixed cyano–carbonyl complex, $Co(CN)_3(CO)_2{}^-$, according to eqn (12)

$$Co(CN)_5H^{3-} + 2\,CO + OH^- \rightarrow Co(CN)_3(CO)_2{}^{2-} + 2\,CN^- + H_2O \tag{12}$$

The form of the rate law for this reaction was found to be similar to that for reaction (10), i e.

$$-d[Co(CN)_5H^{3-}]/dt = k_{12}\,[Co(CN)_5H^{3-}]\,[OH^-]$$

but the value of $k_{12}$ ($6 \times 10^{-3}$ mole$^{-1}$ sec$^{-1}$) is only about 1/20 that of $k_7$. These observations have been interpreted in terms of the following mechanism, according to which $k_{12} = k_7k_{13}(k_6 + k_{13})$ and thus $k_{13} = 5 \times 10^3$ sec$^{-1}$

$$Co(CN)_5H^{3-} + OH^- \underset{k_6}{\overset{k_7}{\rightleftharpoons}} Co(CN)_5{}^{4-} + H_2O \tag{7}$$

$$Co(CN)_5{}^{4-} \xrightarrow{k_{13}} Co(CN)_4{}^{3-} + CN^- \tag{13}$$

$$Co(CN)_4{}^{3-} + CO \xrightarrow{\text{fast}} Co(CN)_4(CO)^{3-} \tag{14}$$

$$Co(CN)_4(CO)^{3-} + CO \xrightarrow{\text{fast}} Co(CN)_3(CO)_2{}^{2-} + CN^- \tag{15}$$

## C CARBONYLATION OF PENTACYANOCOBALTATE(II)

$Co(CN)_3(CO)_2{}^{2-}$ can also be generated[13] by the carbonylation of an aqueous solution of $Co(CN)_5{}^{3-}$ according to reaction (16)

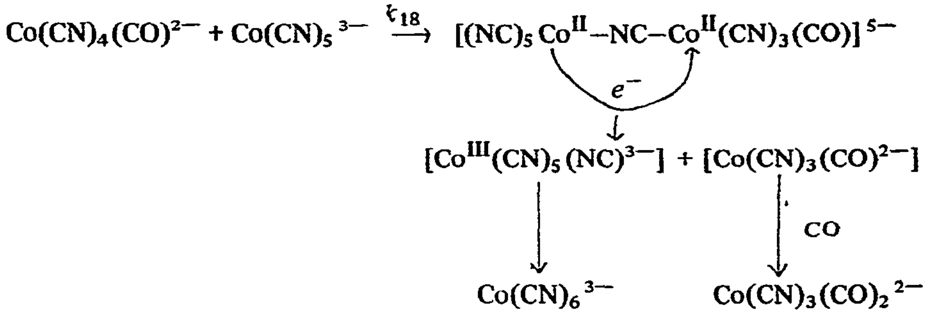
$$2\,Co(CN)_5{}^{3-} + 2\,CO \rightarrow Co(CN)_3(CO)_2{}^{2-} + Co(CN)_6{}^{3-} + CN^- \tag{16}$$

The rate law of this reaction, of the form

$$d[Co(CN)_3(CO)_2{}^{2-}]/dt = k_{16}\,[Co(CN)_5{}^{3-}]^2\,[CO]\,[CN^-]^{-1}$$

has been interpreted in terms of the mechanism depicted by eqns (17) and (18), according to which $k_{16} = K_{eq}k_{18}$

$$Co(CN)_5{}^{3-} + CO \overset{K_{eq}}{\rightleftharpoons} Co(CN)_4(CO)^{2-} + CN^- \text{ (pre-equilibrium)} \tag{17}$$



$$\begin{tikzcd}[column sep=small]
\mathrm{Co(CN)_4(CO)^{2-} + Co(CN)_5{}^{3-}} \arrow[r, "k_{18}"] & \mathrm{[(NC)_5Co^{II}{-}NC{-}Co^{II}(CN)_3(CO)]^{5-}} \arrow[d, "e^-"] & \\
& \mathrm{[Co^{III}(CN)_5(NC)^{3-}] + [Co(CN)_3(CO)^{2-}]} \arrow[dl] \arrow[d, "CO"] & \\
\mathrm{Co(CN)_6{}^{3-}} & \mathrm{Co(CN)_3(CO)_2{}^{2-}} &
\end{tikzcd}$$

(18)

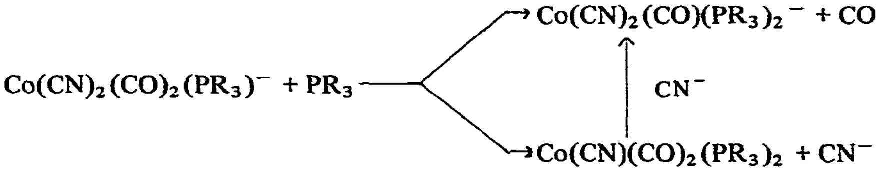
The disproportionation of cobalt(II), induced by the stabilization of cobalt(I) by CO, is illustrative of a general route for the formation of cobalt(I) complexes Another example of such a reaction, depicted by eqn (19), has recently been reported by Bressan et al [14].

$$2\,\mathrm{Co(CO)(PR_3)_2I_2} \xrightarrow{\mathrm{CO}} \mathrm{Co(CO)_2(PR_3)_2I} + \mathrm{Co^{III}} \qquad (19)$$

## D. COBALT(I) COMPLEXES DERIVED FROM THE REACTIONS OF PHOSPHINES WITH $Co(CN)_3(CO)_2{}^{2-}$

$Co(CN)_3(CO)_2{}^{2-}$ readily undergoes substitution reactions with phosphines[15] ($PR_3$) to yield a wide range of mixed phosphino–cyano–carbonyl cobalt(I) complexes of the types $Co(CN)_2(CO)_2(PR_3)^-$, $Co(CN)_2(CO)(PR_3)_2{}^-$ and $Co(CN)(CO)_2(PR_3)_2$, in accord with the scheme depicted by eqns. (20) and (21)

$$\mathrm{Co(CN)_3(CO)_2{}^{2-} + PR_3 \rightarrow Co(CN)_2(CO)_2(PR_3)^- + CN^-} \qquad (20)$$



$$\begin{tikzcd}
& \mathrm{Co(CN)_2(CO)(PR_3)_2{}^- + CO} \quad (21a) \\
\mathrm{Co(CN)_2(CO)_2(PR_3)^- + PR_3} \arrow[ur] \arrow[dr] & \\
& \mathrm{Co(CN)(CO)_2(PR_3)_2 + CN^-} \quad (21b) \arrow[uu, "CN^-"']
\end{tikzcd}$$

Some of the compounds that have been prepared by this procedure are described in Table 2 The synthesis of complexes of the type $Co(CN)(CO)_2(PR_3)_2$ by a different route has also been reported recently[14]

Initial examination of the chemistry of these complexes has revealed the following features

(1) Lowering the pH of an aqueous solution of $Co(CN)_2(CO)(PEt_3)_2{}^-$ from 11 to 4 results in a reversible spectral change and in the formation of a new species, presumably the hydrido-complex $HCo(CN)_2(CO)(PEt_3)_2$, formed in accord with reaction (22) and having a $pK_a$ of ca 5

$$\mathrm{Co(CN)_2(CO)(PEt_3)_2{}^- + H^+ \rightleftarrows HCo(CN)_2(CO)(PEt_3)_2} \qquad (22)$$

TABLE 2

Compounds derived from the reactions of phosphines with $Co(CN)_3(CO)_2{}^{2-}$

| Compound | $\nu_{CN}{}^a$ (Cm$^{-1}$) | $\nu_{CO}{}^a$ (cm$^{-1}$) |
|---|---|---|
| $Et_4N[Co(CN)_2(CO)_2(PCy_3)]\ H_2O$ [b] | 2105 m, 2085 ms | 1990 s, 1930 vs |
| $Et_4N[Co(CN)_2(CO)(PPh_3)_2]\ 2H_2O$ | 2081 m, 2065 ms | 1918 vs |
| $K[Co(CN)_2(CO)(PMePh_2)_2]\ 3H_2O$ | 2065 ms, 2050 m | 1890 vs |
| $K[Co(CN)_2(CO)(PMe_2Ph)_2]\ 3H_2O$ | 2070 m, 2060 s | 1875 vs |
| $K[Co(CN)_2(CO)(PEt_3)_2]\cdot CH_3COCH_3\ H_2O$ | 2062 m, 2045 ms | 1868 vs |
| $K[Co(CN)_2(CO)(Ph_2PCH_2CH_2PPh_2)]\ H_2O$ | 2085 m, 2080 ms | 1905 vs |
| $Co(CN)(CO)_2(PPh_3)_2$ | 2100 m | 1988 s, 1932 vs |
| $Co(CN)(CO)_2(PEt_3)_2$ | 2095 m | 1968 s, 1905 vs |
| $Co(CN)(CO)_2(PCy_3)_2$ [b] | 2092 m | 1967 s, 1908 vs |

[a] m = medium, s = strong, vs = very strong
[b] Cy = cyclohexyl

(2) In contrast to certain other cobalt(I) complexes, e g. $Co(dmg)_2(PR_3)^-$ (ref 6), these complexes exhibit only weak nucleophilicity toward organic halides, as reflected in the very slow reactions of $Co(CN)_2(CO)(PPh_3)_2{}^-$ with benzyl bromide in methanol to yield rather unstable products which have not yet been fully characterized The low nucleophilicities of these complexes, as well as their relatively low basicities toward protonation (eqn (22)), presumably reflect the strong tendency of the CO ligand to stabilize cobalt(I) against oxidation

(3) $Fe(CN)_6{}^{3-}$ reacts rapidly and quantitatively with $Co(CN)_2(CO)(PEt_3)_2{}^-$ in alkaline solutions in accord with the stoichiometry depicted by eqn (23) One of the products, tentatively identified as $[(CN)_5Fe{-}CN{-}Co(CN)_2(PEt_3)_2(OH_2)]^{3-}$, is the analog of the ion $[(CN)_5Fe{-}CN{-}Co(CN)_5]^{6-}$, which is the product of the corresponding oxidation of $Co(CN)_5{}^{4-}$ by $Fe(CN)_6{}^{3-}$ (eqns (7)–(10)) The facile oxidation of the CO ligand in this reaction is a feature of considerable novelty and interest

$$Co(CN)_2(CO)(PEt_3)_2{}^- + 4\ Fe(CN)_6{}^{3-} + 4\ OH^- \rightarrow 3\ Fe(CN)_6{}^{4-} + CO_3{}^{2-} + [(CN)_5Fe{-}CN{-}Co(CN)_2(PEt_3)_2(OH_2)]^{3-} + H_2O \qquad (23)$$

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## REFERENCES

1 J Kwiatek, *Catal Rev* , 1 (1967) 37
2 G N Schrauzer, *Accounts Chem Res.*, 1 (1968) 97.
3 A. Bigotto, G Costa, G Mestroni, G Pellizer, A Puxeddu, E Reisenhofer, L Stefani and G Tauzher, *Inorg Chim Acta*, 4 (1970) 41
4 P B Chock and J Halpern, *J Amer Chem Soc* , 91 (1969) 582
5 J Halpern and P F Phelan, *J Amer Chem Soc* , in press
6 G N Schrauzer and E Deutsch, *J. Amer Chem Soc* , 91 (1969) 3341
7 J Hanzlick and A A Vlček, *Inorg Chem.*, 8 (1969) 669.
8 J Hanzlick and A A Vlček, *Chem Commun* , (1969) 47
9 G D Venerable II and J Halpern, *J Amer Chem Soc* , 93 (1971) 2176
10 J Halpern and M Pribanić, *Inorg Chem.*, in press
11 H S Lim and F C Anson, *Inorg Chem* , 10 (1971) 103
12 G Guastalla, J Halpern and M Pribanić, *J. Amer Chem. Soc* , in press
13 J Halpern and M. Pribanić, *J Amer Chem Soc* , 93 (1971) 96
14 M Bressan, B Corrain, P Rigo and A Turco, *Inorg Chem.*, 9 (1970) 1733
15 J Bercaw, G Guastalla and J Halpern, *Chem Commun* , (1971) 1594