Tetrahedral chlorometal derivatives of redox-active cyanomanganese ligands: synthesis, structures and solvatochromic properties of a new class of cyanide-bridged complexes

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First row transition metal (M = Mn–Ni) dichlorides react with cyanomanganese(I) carbonyl ligands to give novel paramagnetic bi- and poly-nuclear cyanide-bridged complexes, X-ray structural studies on which are consistent with $Fe^{III}Mn^{I}$, $Fe^{III}Mn^{II}$ and $Mn^{II}Mn^{II}$ core oxidation states for $[Cl_3M(\mu\text{-NC})Mn(CO)(dppm)_2]^z$ (M = Fe, z = 0, 1; M = Mn, z = 0) respectively; $Fe^{III}Mn^{I}$ complexes show strong solvatochromism, consistent with low spin d^6 octahedral Mn^{I} to tetrahedral d^5 Fe^{III} charge transfer.

The archetypal mixed valence complex Prussian Blue, $Fe_4^{III}[Fe^{II}(CN)_6]_3$, has been known since the early 18th century,[1] yet the origin of its unusually intense colour was not understood until the 1960s.[2] Now it, analogues such as $Mn^{II}[Mn^{IV}(CN)_6]$, $CsM[Cr^{III}(CN)_6]$ (M = Mn^{II}, Ni^{II}) and $M_3[Fe^{III}(CN)_6]_2$ (M = Co^{II}, Ni^{II}),[3] and other novel cyanide-bridged complexes[4] are under intensive investigation as substances with novel electrochemical, opto-electronic and magnetic properties.

Our studies of cyanide-bridged[5] complexes are based on the systematic construction of bi- and poly-nuclear species by *N*-binding a second metal centre ML'_x to the redox-active, low spin Mn^{I} cyanomanganese carbonyl ligands *trans*-$[Mn(CN)(CO)(dppm)_2]$ and *cis*- and *trans*-$[Mn(CN)(CO)_2\{P(OR)_3\}(dppm)]$ (R = Et, Ph).[6] The resulting complexes are of interest not only in that one-electron oxidation of the Mn^{I} centre of $Mn(\mu\text{-CN})ML'_x$ may induce reactivity at M, but also in allowing studies of the interactions between two or more Mn^{I}–Mn^{II} redox centres within the cyanide-bridged cores $\{Mn(\mu\text{-CN})\}_nML'_x$ (n = 2–4, *etc.*). Our synthetic strategy may be viewed as complementary to that based on the use of $[M(CN)_6]^{z-}$ (M = Mn, Fe, Co, *etc.*) as building blocks where *N*-binding to other metal sites leads to three-dimensional solid-state arrays by a divergent pathway. The binding of two or more monocyanide donors, such as *trans*-$[Mn(CN)(CO)_2\{P(OEt)_3\}(dppm)]$ to M can be viewed as a convergent route to polynuclear molecular species.

Our previous studies have centred on systems where M is a low oxidation state metal centre such as Rh^{I},[7] Fe^{-I}[8] and Au^{I}.[9] Here, we describe simple species in which the cyanomanganese ligands bind to high spin, tetrahedral 3d metal centres in 'normal' oxidation states, and for which unusual electronic and magnetic properties may be anticipated.

Treatment of $MCl_2\cdot nH_2O$ (M = Mn, Co, Ni) with $[Mn(CN)L_x]$ [L_x = *cis*- or *trans*-$(CO)_2\{P(OR)_3\}(dppm)$; R = Et, Ph] gave $[Cl_2M\{(\mu\text{-NC})MnL_x\}_2]$ which show room temperature magnetic moments consistent with the presence of tetrahedral M. (Representative examples of the new complexes† are shown in Table 1.) These complexes are precursors to higher nuclearity species or can be oxidised to products in which low spin, paramagnetic Mn^{II} is bound to high spin tetrahedral centres. Thus, for example, treatment of $[Cl_2Co\{(\mu\text{-NC})MnL_x\}_2]$ [L_x = *trans*-$(CO)_2\{P(OEt)_3\}(dppm)$] **1** with 1 equiv. of $[Mn(CN)L_x]$ in the presence of $TlPF_6$ gives $[ClCo\{(\mu\text{-NC})MnL_x\}_3][PF_6]$ **2** [L_x = *trans*-$(CO)_2\{P(OEt)_3\}(dppm)$]; use of 2 equiv. gives $[Co\{(\mu\text{-NC})MnL_x\}_4][PF_6]_2$ **3**. Complexes **1–3** show room temperature magnetic moments in accord with the presence of tetrahedral, d^7 Co^{II}.[10] In CH_2Cl_2 the cyclic voltammograms of complexes **1** and **2** show two oxidation waves the separation of which (*ca.* 100 mV) is consistent with weak interactions between the manganese centres in the oxidation products. Chemical oxidation of **1** with $[N(C_6H_4Br\text{-}4)_3][SbCl_6]$ gives deep blue $[Cl_2Co\{(\mu\text{-NC})MnL_x\}_2][SbCl_6]_2$ [L_x = *trans*-$(CO)_2\{P(OEt)_3\}(dppm)$] $\mathbf{1}^{2+}$ the room temperature magnetic moment of which (μ_{eff} = 5.0 μ_B) indicates some spin pairing between the d^7 Co^{II} and two low spin d^5 Mn^{II} centres.

The reactions of $MCl_2\cdot nH_2O$ with the more electron-rich and sterically demanding ligand *trans*-$[Mn(CN)(CO)(dppm)_2]$ in thf give $[Cl_2(thf)M(\mu\text{-NC})Mn(CO)(dppm)_2]$ (M = Mn, Co, Ni)

Table 1 Representative IR spectroscopic data and room temperature magnetic moments

Complex	μ_{eff}/μ_B	Colour	Yield (%)	IR^a/cm^{-1} ν(CN)	IR^a/cm^{-1} ν(CO)^b
$[Cl_2Mn\{(\mu\text{-NC})Mn(CO)_2[P(OPh)_3](dppm)\text{-}cis\}_2]$	5.7	Cream	52	2105w	1973, 1919ms
$[Cl_2Co\{(\mu\text{-NC})Mn(CO)_2[P(OEt)_3](dppm)\text{-}trans\}_2]$ **1**	4.6	Green	63	2095mw	1924vs (2008)
$[Cl_2Co\{(\mu\text{-NC})Mn(CO)_2[P(OEt)_3](dppm)\text{-}trans\}_2][SbCl_6]_2$ $\mathbf{1}^{2+}$	5.0	Dark blue	79	2137vw	2003vs (2071)
$[ClCo\{(\mu\text{-NC})Mn(CO)_2[P(OEt)_3](dppm)\text{-}trans\}_3][PF_6]$ **2**	4.5	Green	82	2088m	1926s (2008)
$[Co\{\mu\text{-NC})Mn(CO)_2[P(OEt)_3](dppm)\text{-}trans\}_4][PF_6]_2$ **3**	4.6	Green	68	2075m	1925s (2008)
$[Cl_2Ni\{(\mu\text{-NC})Mn(CO)_2[P(OEt)_3](dppm)\text{-}cis\}_2]$	3.5	Blue	40	2123w	1960, 1903ms
$[Cl_3Fe(\mu\text{-NC})Mn(CO)(dppm)_2]$ **5**	5.6	Deep blue–green	55	2017mw	1889
$[Cl_3Fe(\mu\text{-NC})Mn(CO)(dppm)_2][BF_4]$ **7**	5.8	Deep purple	67	2085m	1961
$[PPN][Cl_3Mn(\mu\text{-NC})Mn(CO)(dppm)_2]$	6.0	Orange	81	2085mw	1871
$[Cl_3Mn(\mu\text{-NC})Mn(CO)(dppm)_2]$ **6**	5.8	Deep red	56	2117w	1944
$[Cl_2(thf)Ni(\mu\text{-NC})Mn(CO)(dppm)_2]$	3.3	Brown	56	2098w^c	1878^c

^{a} In CH_2Cl_2. Strong absorptions unless stated otherwise; vs = very strong, m = medium, w = weak, vw = very weak. ^{b} Very weak A-mode given in parentheses. ^{c} In thf.

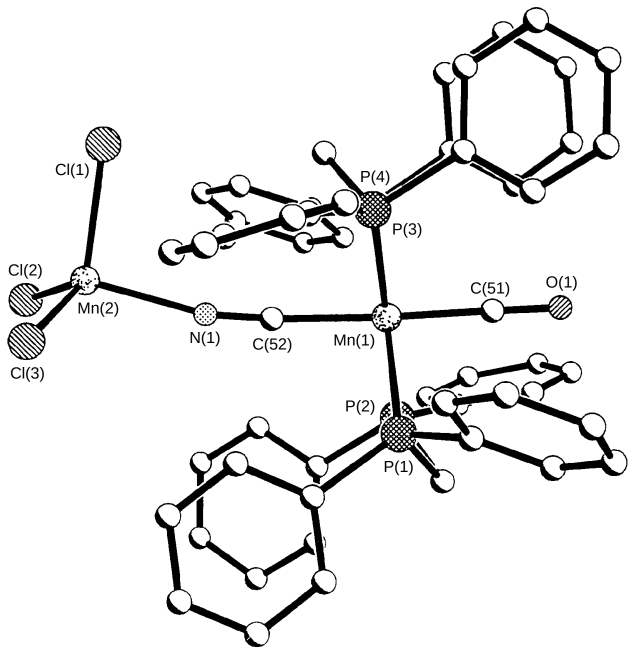

Fig. 1 Structure of **6** (hydrogen atoms and solvent molecule omitted for clarity); the molecular structures of **4** {as its $[FeCl_4]^-$ salt} and **5** are similar. Important bond lengths and angles: **4**, Fe–Cl 2.166, Mn–P 2.345; **5**, Fe–Cl 2.193, Mn–P 2.283; **6**, Mn–Cl 2.341, Mn–P 2.345. (Individual bond lengths have estimated standard uncertainties in the range 0.001–0.005 Å.)

which can be converted into $[PPN][Cl_3M^{II}(\mu\text{-NC})Mn^{I}(CO)(dppm)_2]$ {PPN = $[N(PPh_3)_2]^+$} and $[Cl_3M^{II}(\mu\text{-NC})Mn^{II}(CO)(dppm)_2]$ (M = Mn, Ni) by successive reactions with [PPN]Cl and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$.

Anhydrous $FeCl_2$ reacts with $[Mn(CN)L_x]$ [L_x = *cis*- or *trans*-$(CO)_2\{P(OR)_3\}$(dppm), R = Et, Ph] in air to give very different products from those of the other metals noted above, namely the intensely coloured (blue to purple) complexes $[Cl_3Fe^{III}(\mu\text{-NC})Mn^{I}L_x]$. The reaction of *trans*-$[Mn(CN)(CO)(dppm)_2]$ with $FeCl_2$ in air gives $[Cl_3Fe^{III}(\mu\text{-NC})Mn^{II}(CO)(dppm)_2][Fe^{III}Cl_4]$ which can be reduced by $[Fe(\eta\text{-}C_5Me_5)_2]$ to $[Cl_3Fe^{III}(\mu\text{-NC})Mn^{I}(CO)(dppm)_2]$. The presence of Mn^I and Fe^{III} in the neutral species is in marked contrast to the $M^{II}Mn^{II}$ cores of $[Cl_3M(\mu\text{-NC})Mn(CO)(dppm)_2]$ (M = Mn, Co, Ni).

The assignments of oxidation state, based on the IR carbonyl spectra, are supported by X-ray structural studies of $[Cl_3Fe(\mu\text{-NC})Mn(CO)(dppm)_2][FeCl_4]\cdot 2.5CHBr_3$ **4**, $[Cl_3Fe(\mu\text{-NC})Mn(CO)(dppm)_2]\cdot CH_2Cl_2$ **5** and $[Cl_3Mn(\mu\text{-NC})Mn(CO)(dppm)_2]\cdot CH_2Cl_2$ **6** (all three show similar structures[‡]). The structure of **6** is shown in Fig. 1, together with important bond lengths for **4**–**6**. As noted previously,[11] the Mn–P bond distances of the $(\mu\text{-NC})MN(CO)(dppm)_2$ fragment are diagnostic of the oxidation state of Mn. Thus, **4** and **6** contain Mn^{II} and **5** contains Mn^I.

The intense colours of $[Cl_3Fe(\mu\text{-NC})MnL_x]$ are in striking contrast to that of $[FeCl_4]^-$ (pale yellow) despite the presence of tetrahedral Fe^{III} in all cases. These intense colours arise from strong absorptions (ε_{max} *ca.* 3000 $dm^3\ mol^{-1}\ cm^{-1}$) in the visible spectrum which are highly solvatochromic (*e.g.* $[Cl_3Fe(\mu\text{-NC})MnL_x]$ [L_x = *cis*-$(CO)_2\{P(OPh)_3\}$(dppm) (λ_{max} = 508 nm in *n*-hexane; λ_{max} = 599 nm in 1,2-$C_2H_4Cl_2$), implying extensive intramolecular charge transfer.

Cyclic voltammetry provides some insight into the origin of the very different oxidation state distribution in the iron complexes compared with that in $[Cl_3M^{II}(\mu\text{-NC})Mn^{II}(CO)(dppm)_2]$ (M = Mn, Co, Ni). Thus, **5** shows one oxidation wave ($E^{0\prime}$ = 0.43 V) and one reduction wave ($E^{0\prime}$ = 0.02 V) associated with the Mn^I–Mn^{II} and Fe^{II}–Fe^{III} couples respectively; no equivalent wave for the M^{II}–M^{III} couple is observed for M = Mn, Co or Ni. These results also suggest that the colour and solvatochromism of the iron complexes result from Mn^I to Fe^{III} charge transfer through the cyanide bridge. {In this respect, it is noteworthy that $[Cl_3Fe^{III}(\mu\text{-NC})Mn^{II}(CO)(dppm)_2]^+$, where Mn^{II}-to-Fe^{III} charge transfer is impossible, is not solvatochromic.}

The magnetic behaviour of the iron complexes is also of interest. The magnetic moments of **4**, **5** and $[Cl_3Fe(\mu\text{-NC})Mn(CO)(dppm)_2][BF_4]$ **7** {prepared by $[Fe(\eta\text{-}C_5H_4COMe)Cp][BF_4]$ oxidation of **5**} are 8.2, 5.6 and 5.8 μ_B respectively at 295 K. Detailed studies of the magnetic and electronic properties of these complexes are in progress.

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Notes and References

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† All new complexes had satisfactory elemental analyses (C, H, N).

‡ Crystal structures were determined from data collected on a Siemens SMART diffractomer ($\bar{\lambda}$ = 0.71073 Å) at 173 K. The structures were solved by direct and Fourier methods and refined by least-squares against all F^2 data corrected for absorption. *Crystal data*: $[Cl_3Fe(\mu\text{-NC})Mn(CO)(dppm)_2][FeCl_4]\cdot 2.5CHBr_3$ **4**: $C_{52}H_{44}Cl_7Fe_2MnNOP_4\cdot C_{2.5}H_{2.5}Br_{7.5}$, M = 1869.451, monoclinic, space group $C2/c$ (no. 15), a = 46.157(3), b = 12.612(2), c = 24.455(4) Å, β = 104.721(14)°, U = 13769(3) $Å^3$, Z = 4, D_c = 1.658 Mg m^{-3}, μ = 5.351 mm^{-1}, 9577 unique data, $\theta \leqslant 23°$, R_1 = 0.0994; $[Cl_3Fe(\mu\text{-NC})Mn(CO)(dppm)_2]\cdot CH_2Cl_2$ **5**: $C_{52}H_{44}Cl_3FeMnNOP_4\cdot CH_2Cl_2$, M = 1124.898, triclinic, space group $P\bar{1}$ (no. 2), a = 14.092(3), b = 14.489(2), c = 14.791(3) Å, α = 89.111(17), β = 75.367(16), γ = 63.011(11)°, U = 2586.4(7) $Å^3$, Z = 2, D_c = 1.444 Mg m^{-3}, μ = 0.95 mm^{-1}, 8818 unique data, $\theta \leqslant 25°$, R_1 = 0.0479; $[Cl_3Mn(\mu\text{-NC})Mn(CO)(dppm)_2]\cdot CH_2Cl_2$ **6**: $C_{52}H_{44}Cl_3Mn_2NOP_4\cdot CH_2Cl_2$, M = 1123.989, monoclinic, space group $P2_1/n$ (no. 14), a = 12.629(3), b = 23.525(4), c = 18.306(4) Å, β = 104.306(17)°, U = 5270.0(2) $Å^3$, Z = 2, D_c = 1.417 Mg m^{-3}, μ = 0.89 mm^{-1}, 8253 unique data, $\theta \leqslant 24°$, R_1 = 0.0521. CCDC 182/730.

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