Notes

The Co-ordination of Small Molecules by Manganese(II) Phosphine Complexes. The Reaction of Some $[MnX_2L]$ (X = Cl, Br, or I; L = PPr^n_3, PMe_2Ph, or PPh_3) Complexes with Tetracyanoethylene

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When $[MnX_2L]$ (X = Cl, Br, or I; L = PPr^n_3, PMe_2Ph, or PPh_3) complexes react with tetracyanoethylene (tcne) in toluene slurries the 1 : 1 adducts [MnX_2L(tcne)] are formed. The magnetic moments of the adducts at room temperature, $\mu_{eff.}$ = 4.6—4.9, are consistent with a d^4 manganese(III) species, and i.r., visible, and e.s.r. spectroscopic data are also consistent with the transfer of an electron from manganese(II) to tcne on adduct formation resulting in a manganese(III)–tcne$^{\bullet -}$ species. The tcne co-ordinates *via* a nitrile nitrogen.

We have reported on the ability of simple manganese(II) phosphine complexes, $[MnX_2L]$ (L = tertiary phosphine) to bind reversibly dioxygen,[1] carbon monoxide,[2] and nitric oxide,[3] as well as to form irreversible adducts with carbon disulphide[4] and sulphur dioxide.[5] We have recently turned our attention to adducts formed between alkenes and these manganese complexes, and we wish to report here our studies of the reaction between $[MnX_2L]$ (X = Cl, Br, or I; L = PPr^n_3, PMe_2Ph, or PPh_3) and tetracyanoethylene (tcne).

Tetracyanoethylene has been found to react with a number of transition metal species to yield complexes in which it is bound to the metal centre either as a 'normal' alkene[6–9] or through one of the nitrile nitrogen atoms,[10–12] as shown in Figure 1. Reaction with $[Fe(\eta\text{-}C_5H_5)_2]$ leads to a complex in which the tcne ligand is found between the cyclopentadienyl rings of neighbouring ferrocene molecules;[13] charge-transfer complexes are also formed with $[Co(\eta\text{-}C_5H_5)_2]$ [14] and $[Cr(\eta\text{-}C_6H_6)_2]$.[15] Recently, cycloaddition reactions of tcne with the platinum complexes $[Pt(\sigma\text{-}C_3H_5)(PR_3)_2Cl]$ [16] and $[Pt(O_2)(PPh_3)_2]$,[17] to yield $[Pt\{\overline{CHCH_2C(CN)_2C(CN)_2CH_2}\}(PR_3)_2Cl]$ (R = Ph or Me) and $(Pt\{\overline{C(CN)_2C(CN)_2OO}\}(PPh_3)_2]$, respectively, have been reported.

In the π- and N-bonded complexes (Figure 1), electron transfer from the metal (M) to the tcne usually occurs giving rise to complexes containing the tcne$^{\bullet -}$ radical anion; the C≡N stretching region in the i.r. spectra of tetracyanoethylene complexes has been used to probe the nature of the tcne moiety present.[10] In alkali halide pellets tcne, tcne$^{\bullet -}$, and tcne^{2-} are all characterised by doublets in the 2 100—2 300 cm^{-1} region.[11] The number of i.r. stretches in the ν(CN) region can also give an indication of the bonding mode adopted by the tcne. Thus, in the π-bonded complexes only one band due to the ν(CN) is normally observed due to the effective (local) symmetry of the co-ordinated tcne.

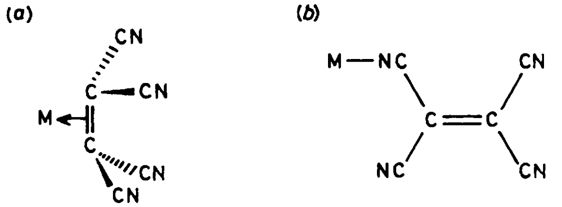

Figure 1. Bonding modes of tcne: (*a*) alkene π-bonded; (*b*) N-bonded

Results and Discussion

The $[MnX_2L]$ complexes (X = Cl, Br, or I; L = PPr^n_3, PMe_2Ph, or PPh_3) were reacted with an excess of tcne in toluene slurries. After stirring the reaction mixture for *ca.* 48 h the product was isolated by standard Schlenk techniques, washed with toluene, and dried *in vacuo*, yielding complexes of formula [MnX_2L(tcne)]. It was noticed that as the reaction proceeded the colour of the reaction mixture slowly changed from white (X = Cl or Br) or pink (X = I) to either green or brown. In the case of the reaction with $[MnCl_2(PPr^n_3)]$ a green complex was formed initially which rapidly decomposed to a dark brown viscous oil. All the other adducts were obtained as solids, Table 1. It can be seen that the complexes [$MnBr_2(PMe_2Ph)$(tcne)] and [$MnCl_2(PPh_3)$(tcne)] were obtained containing toluene of crystallisation, and elemental analyses suggest amounts of toluene present.

All of the complexes were found to be virtually insoluble in common aprotic solvents such as chloroform, diethyl ether, toluene *etc.* Because of this low solubility, attempts to grow crystals suitable for *X*-ray diffraction or to purify them completely were unsuccessful. The complexes do, however, dissolve readily in ethanol, but rapid decomposition was found to occur.

The i.r. spectra of the complexes showed bands assignable to the tcne ligand that are consistent with it being present as a monoanion. The positions of ν(CN) are shifted from those observed in free tcne and are similar to those observed for the tcne$^{\bullet -}$ anion in alkali halide pellets, Table 1. Also the position of ν(C=C) is shifted from the free-ligand position of 1 570 cm^{-1} to *ca.* 1 360 cm^{-1}, which is also similar to that found for tcne$^{\bullet -}$ (1 370 cm^{-1}). The fact that ν(CN) is not observed as a singlet suggests that the tcne is bound to the manganese through a nitrile nitrogen, and this is supported by the observation of bands in the far-i.r. spectra of the complexes that could be assigned to ν(Mn–N). The far-i.r. spectra of the complexes also showed bands assignable to ν(Mn–P) and bridging halide stretches ν(Mn–X–Mn), Table 2.

Further support that the complexes are manganese(III) species comes from the absence of any absorptions in the solid-state *X*-band e.s.r. spectra of the complexes at 0—10 000 G at −160 °C (G = 10^{-4} T). The lack of an e.s.r. signal from a manganese complex is often taken as strong circumstantial

Table 1. Physical properties, elemental analyses, and i.r. data for the [MnX_2L(tcne)] complexes

Complex	Colour	M.p.[a] (θ/°C)	$\mu_{eff.}$	Analysis[b] (%) C	H	N	P	ν(CN)/cm^{-1}	ν(C=C)/cm^{-1}
[$MnCl_2(PPr^n{}_3)$] + tcne	Dark brown	c		44.4 (43.5)	6.7 (5.1)	7.4 (13.5)	7.3 (7.5)	2 220s, 2 163vs	1 368m
[$MnBr_2(PPr^n{}_3)$(tcne)]	Brown	118	4.7	34.4 (35.8)	3.6 (4.2)	11.2 (11.1)	5.4 (6.2)	2 207s, 2 135vs	1 340m
[$MnI_2(PPr^n{}_3)$(tcne)]	Green		4.7	30.9 (30.2)	4.3 (3.5)	8.6 (9.4)	5.7 (5.2)	2 218vs, 2 208 (sh), 2 160s	1 367m
[$MnCl_2(PMe_2Ph)$(tcne)]	Brown	114	4.7	42.0 (42.9)	3.2 (2.8)	13.4 (14.3)		2 912 (sh), 2 199s, 2 152vs	1 342m
[$MnBr_2(PMe_2Ph)$(tcne)]·C_7H_8	Brown		4.9	43.0 (44.0)	4.0 (3.3)	8.9 (9.7)		2 200s, 2 143vs	1 356 (sh)
[$MnI_2(PMe_2Ph)$(tcne)]	Green	128	4.9	31.9 (29.2)	2.1 (1.9)	10.2 (9.7)	5.2 (5.4)	2 222 (sh), 2 216vs, 2 159s	1 364m
[$MnCl_2(PPh_3)$(tcne)]·0.5C_7H_8	Green	96	4.7	56.8 (57.6)	4.1 (3.4)	9.7 (10.0)	5.6 (5.5)	2 218s, 2 207s, 2 139s	1 366m
[$MnBr_2(PPh_3)$(tcne)]	Brown	139	4.6	48.7 (47.6)	3.0 (2.5)	9.0 (9.3)	5.0 (5.1)	2 219s, 2 210s, 2 182s, 2 140s	1 365m
[$MnI_2(PPh_3)$(tcne)]	Green	125	4.9	40.9 (41.2)	2.5 (2.2)	7.7 (8.0)	4.5 (4.4)	2 217 (sh), 2 200s, 2 158vs	1 362m
tcne								2 260s, 2 225s	1 570
tcne$^{\bullet -}$								2 200s, 2 175s	1 370
tcne^{2-}								2 160s, 2 095s	1 260

[a] All complexes decompose. [b] Calculated values in parentheses. [c] Oil.

Table 2. Far-i.r. (Nujol mulls) and diffuse reflectance data for some of the [MnX_2L(tcne)] complexes

Complex	ν(Mn–P)/cm^{-1}	ν(Mn–N)/cm^{-1}	ν(Mn–X–Mn)/cm^{-1}	$\lambda_{max.}$/nm						
[$MnCl_2(PPr^n{}_3)$] + tcne	402, 408, 414, 422	242, 272	200, 205, 209	365		385	400	420	475	500
[$MnBr_2(PPr^n{}_3)$(tcne)]	401, 407, 418	248, 255, 261	182, 188, 194	360		378	410	440	475	510
[$MnI_2(PPr^n{}_3)$(tcne)]	408, 416	242, 252, 258	102, 108, 111	360	370	385	400	440	480	510
[$MnCl_2(PMe_2Ph)$(tcne)]	400, 412, 417	245, 254, 260	193, 201, 207							
[$MnBr_2(PMe_2Ph)$(tcne)]	399, 410, 415	245, 260, 267	189, 196							
[$MnI_2(PMe_2Ph)$(tcne)]	402, 408	251, 260, 268	100, 106, 110	365	375	380	410	430	475	515
[$MnI_2(PPh_3)$(tcne)]				350	365	380	400	420	470	520

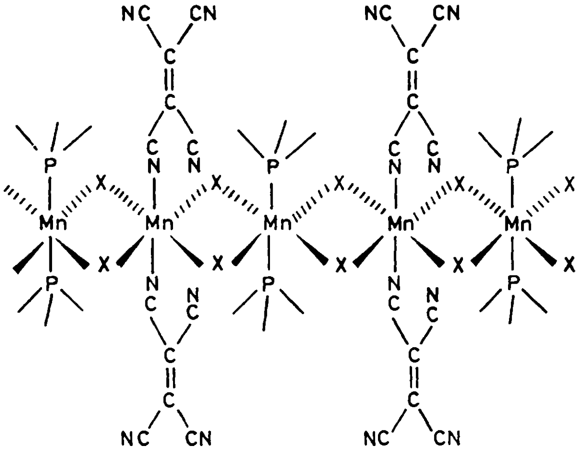

Figure 2. Proposed structure of the [MnX_2L(tcne)] complexes

evidence that the manganese is in the +3 oxidation state. However, it might be expected that a spectrum due to the tcne$^{\bullet -}$ radical would have been observed, but other complexes containing tcne$^{\bullet -}$ have been found to show no e.s.r. spectrum.[11]

The room-temperature magnetic moments ($\mu_{eff.}$) of the complexes were found to lie in the range 4.6—4.9 and this is close to the spin-only value of 4.9 expected for a high-spin d^4 species, *i.e.* manganese(III). The fact that some of the observed values are slightly lower than the spin-only value is probably due to some spin pairing through the halide bridges.

The diffuse reflectance spectra of the complexes were all very similar showing a broad absorption at *ca.* 330—600 nm with a number of vibrational maxima, Table 2. The visible absorption spectrum of tcne$^{\bullet -}$ in acetonitrile solution exhibits a broad absorption at 350—500 nm[18] and the similarity of the spectra of the complexes to this is further evidence that the tcne is present as tcne$^{\bullet -}$.

Because of the lack of crystals suitable for single-crystal *X*-ray diffraction, it is only possible to speculate on the structure of the complexes. The low solubility of the complexes together with the observation of bands assignable to ν(Mn–X–Mn) in the far-i.r. spectra of the complexes suggests that the complexes are probably polymeric in the solid state with the manganese atoms linked by halide bridges. Magnetic susceptibilities and e.s.r. spectra indicate that the complexes are manganese(III) species, and the i.r. and far-i.r. spectra of the complexes indicate that the tcne is bound *via* a nitrile nitrogen. Since King and co-workers[19] have shown that the complex [$MnI_2(PPhMe_2)$] consists of an infinite array of MnI_2 ribbon, with alternate manganese atoms having two co-ordinated phosphines, resulting in tetrahedral $-MnI_4-$ and pseudo-octahedral $-MnI_4P_2-$ sites, then it is not unreasonable to speculate that it is at the co-ordinatively unsaturated $-MnI_4-$ sites that the binding of such small molecules occurs; Figure 2 shows this and this is in keeping with the overall 1 : 1 Mn : tcne stoicheiometry observed.

Experimental

All manipulations involving air-sensitive materials were performed under a dry argon atmosphere. Solvents were dried by the published procedures and the [MnX_2L] complexes synthesised by published methods.[2,20] Tetracyanoethylene (Eastman Kodak) was vacuum-sublimed before use and stored under argon in a desiccator.

Reaction of [MnX_2L] *with Tetracyanoethylene.*—The [MnX_2L] complex (*ca.* 0.5 g) was placed in a pre-dried round-bottom flask (250 cm^3) equipped with side-arm and tap and the flask flushed several times with argon. Excess (1.5 mol per mol of

Mn complex) of tcne was added against a stream of argon and the flask again flushed several times with argon. Toluene (50 cm^3) was then added using a pre-dried syringe, and the mixture was stirred for 3 d. The product was isolated by standard Schlenk techniques, washed twice with toluene (25 cm^3), and dried *in vacuo*.

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