Oxidative Isomerisation as a Probe of Mixed Valency in Cyanide-bridged Dimanganese Carbonyl Phosphine Complexes

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The isomeric *trans,trans-* and *cis,trans-*$[Mn_2]^{2+}$-containing monocations (**3+**) and (**4+**) are oxidised to the trapped valence $[Mn_2]^{3+}$ dications (**3²⁺**) and (**4²⁺**); the oxidative isomerisation of (**5+**) to (**3²⁺**) results from intramolecular electron transfer within (**5²⁺**)

Cyclic voltammetry has proved an invaluable tool in the study of the oxidative isomerisation of metal carbonyl derivatives.[1] For example, *cis,cis-*$[MnL(CO)_2\{P(OPh)_3\}(dppm)]^{z+}$ [**1**; $z = 0$, L = CN; $z = 1$, L = CNMe or NCMe; dppm = bis(diphenylphosphino)methane] shows[2,3] an irreversible oxidation wave with a coupled, reversible product wave due to the formation of *trans-*$[MnL(CO)_2\{P(OPh)_3\}(dppm)]^{z+}$ (**2**; $z = 0$, L = CN; $z = 1$, L = CNMe or NCMe). We now show how cyclic voltammetric studies of the oxidative isomerisation of

the binuclear cyanide-bridged cations (**3+**)—(**6+**)† provide an insight into the mixed-valence properties of the $[Mn_2]^{3+}$-containing dications (**3²⁺**)—(**6²⁺**).

The cyclic voltammograms of (**3+**), (**4+**), and (**5+**) are shown in Figure 1; the *trans,trans-*isomer (**3+**) shows two

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† Complexes (**3+**) to (**6+**) have been characterised by elemental analysis, and their structures defined by i.r. and ³¹P n.m.r. spectroscopy.
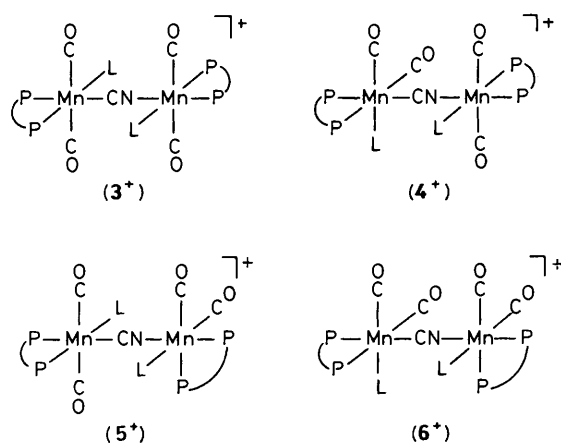
Table 1.

Complex	E_0^1/V^a	E_0^2/V
(3$^+$)	0.61	1.22
(4$^+$)	0.66	1.55^b
(5$^+$)	0.85	1.42^b
(6$^+$)	1.17^b	1.58^b

^{a} All electrochemical measurements were carried out in CH_2Cl_2, 0.1 mol dm^{-3} in [NBu$^n_4$][PF$_6$], as supporting electrolyte. Voltammetry employed a platinum bead electrode, controlled potential electrolysis a platinum basket. All potentials are quoted vs. the saturated calomel electrode; E^0 for the oxidation of ferrocene, added as an internal standard, was 0.47 V under the experimental conditions used. The one-electron oxidation processes are reversible unless stated otherwise. ^{b} Irreversible oxidation; value given is the oxidation peak potential, E_p(ox), at a scan rate of 200 mV s^{-1}.

Figure 1. The single scan cyclic voltammograms of (a) (3$^+$), (b) (4$^+$), and (c) (5$^+$), in CH_2Cl_2 at a platinum bead electrode.

reversible one-electron oxidation waves (see Table 1), but (4$^+$) and (5$^+$) each show one reversible oxidation wave and a second, irreversible oxidation wave at a more positive potential. For both (4$^+$) and (5$^+$) the second wave is coupled to two reversible product waves with exactly the potentials observed for the oxidations of (3$^+$).

These results can be simply rationalised if it is assumed, (i) that oxidation of the binuclear species occurs sequentially at two non-interacting manganese(ı) centres and, (ii) that, by comparison with the behaviour of the mononuclear complexes (1) and (2), oxidation at a *trans*-site is reversible but at a *cis*-site is irreversible and accompanied by isomerisation. Thus, for example, (3$^+$) is oxidised to (3^{2+}) and then to (3^{3+}) with retention of geometry throughout, whereas (4$^+$) is oxidised first at the *trans*-site, to give the *cis,trans*-dication (4^{2+}), and then at the *cis*-site to give (4^{3+}) which rapidly isomerises to (3^{3+}).‡

The chemical and electrochemical (controlled potential electrolysis) oxidation of (3$^+$)—(5$^+$), together with i.r. and e.s.r. spectroscopic studies on the products, provides strong evidence for the localised oxidation implied by cyclic voltammetry. For all of the complexes, reaction with excess [NO][PF$_6$] affords the *trans,trans*-trication (3^{3+}; $v_{(CO)}$ 2009 cm^{-1}). However, the mixed-valence dications, containing

‡ The cyclic voltammogram of the *cis,cis*-isomer (6$^+$) shows two irreversible oxidation waves (see Table 1). Isomerisation occurs after the first oxidation step to give (4^{2+}); the second irreversible peak for (6$^+$) occurs at the potential for the irreversible oxidation of (4^{2+}) to (4^{3+}).
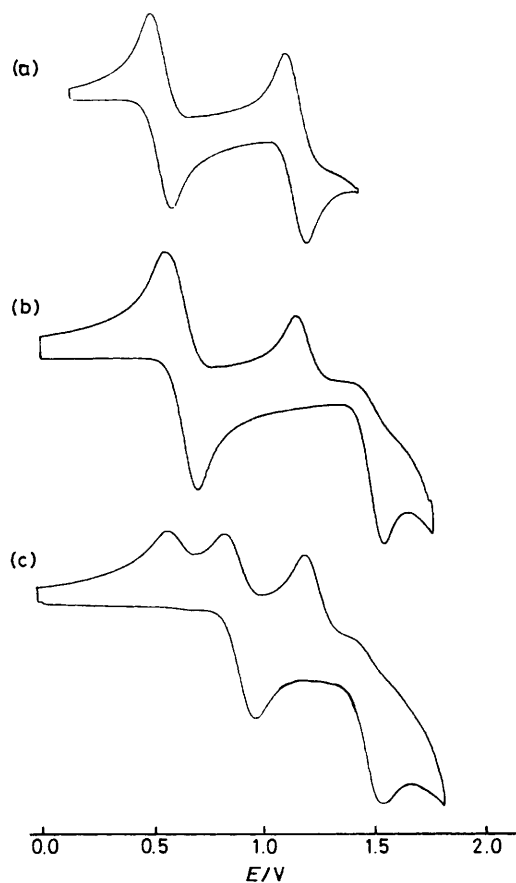
[Mn$_2$]$^{3+}$ cores, can be prepared by using stoicheiometric (1 : 1) quantities of [NO][PF$_6$] or by electrolysis at a potential ca. 0.2 V more positive than that of the first oxidation wave.

The addition of [NO][PF$_6$] to [3$^+$; $v_{(CO)}$ 1933 cm^{-1}] in CH_2Cl_2 gave a dark brown-purple solution from which the purple-black [PF$_6$]$^-$ salt of (3^{2+}) was isolated in excellent yield (90%). The dication shows two carbonyl bands in the i.r. spectrum [$v_{(CO)}$ 2000(s) and 1943(s) cm^{-1}], one similar in frequency to that of (3^{3+}) and the other only 10 cm^{-1} higher in frequency than that of (3$^+$). The implication of localised oxidation at one manganese site, and therefore of trapped valency for (3^{2+}), is strongly supported by the frozen solution e.s.r. spectrum (−120 °C; CH_2Cl_2-tetrahydrofuran, 1 : 2) which is similar to those of the mononuclear Mn^{II} derivatives [MnL(CO)$_2${P(OPh)$_3$}(dppm)]$^{z+}$ (z = 1, L = CN; z = 2, L = CNMe). The *cis,trans* dication (4^{2+}) is similarly isolable and shows i.r. carbonyl bands [2000(ms), 1972(s), and 1934(m) cm^{-1}] again consistent with localised oxidation at the *trans*-site [c.f. (4$^+$) : $v_{(CO)}$ 1971(m), 1928(s), and 1916(m, sh) cm^{-1}].

The oxidative behaviour of (5$^+$) is different from that of (3$^+$) and (4$^+$). On electrolytic oxidation at 0.90 V (20 min, n = 0.9) a dark brown-purple solution is formed, but cyclic voltammetry and voltammetry at a rotating platinum electrode reveal the quantitative formation of only the *trans,trans*-dication (3^{2+}) [i.e. the product solution shows reversible reduction (0.61 V) and oxidation (1.22 V) waves].

Monitoring the [NO][PF$_6$] oxidation of (5$^+$) shows that (3^{2+}) is formed after the initial generation of the *trans,cis*-dication [(5^{2+}): $v_{(CO)}$ 1997(s), 1966(ms), and 1921(m) cm^{-1}

c.f. (**5**$^+$): $\nu_{(CO)}$ 1968(m), 1931(s), and 1901(m) cm^{-1}] but without the formation of any trication [*i.e.* (**3**$^{3+}$)]. It appears, therefore, that *intra*molecular electron-transfer can occur in (**5**$^{2+}$) so that *cis*- to *trans*-isomerisation is induced in the [Mn$_2$]$^{3+}$ complex; the detection of (**5**$^{2+}$) as an intermediate in the formation of (**3**$^{2+}$) rules out fundamentally different oxidative behaviour for (**5**$^+$) (*i.e.* the electron is not removed from an orbital delocalised over the two metal centres).§

A comparison of ΔE [the difference between E^0 for the first, reversible, oxidation and E_p(ox) for the second, irreversible oxidation] for (**4**$^+$) and (**5**$^+$), 0.9 and 0.6 V, respectively, suggests an alternative reason for the increased stability of (**4**$^{2+}$) over (**5**$^{2+}$). For (**5**$^{2+}$), ΔE is small enough for partial oxidation to occur of the *cis*-Mn^{I} site by the *trans*-Mn^{II} centre; isomerisation then gives (**3**$^{2+}$) irreversibly, thus driving the intramolecular electron-transfer to completion. A similar

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§ An *inter*molecular electron-transfer reaction involving two dications (**5**$^{2+}$) cannot be ruled out; attempts to detect an intervalence band for (**5**$^{2+}$) have not yet been made.

process for (**4**$^{2+}$) is less favourable as ΔE is greater by *ca.* 0.3 V.

References

1 See, for example, R. N. Bagchi, A. M. Bond, G. Brain, R. Colton, T. L. E. Henderson, and J. R. Kevekordes, *Organometallics*, 1984, **3**, 4; A. M. Bond, S. W. Carr, and R. Colton, *ibid.*, 1984, **3**, 541; A. M. Bond, S. W. Carr, and R. Colton, *Inorg. Chem.*, 1984, **23**, 2343; N. G. Connelly and W. E. Geiger, *Adv. Organomet. Chem.*, 1984, **23**, 1, and references therein.
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