Reductive Nitrosylation of Tetraoxometalates. Part 15.[1] Generation of $Mn(NO)^{3+}$, $Mn(NO)^{2+}$, and $Mn(NO)_2{}^{2+}$ Moieties Directly from MnO_4^-. Synthesis, Characterization, and Electrochemistry of Cyanonitrosyl Derivatives of Manganese†

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In an aqueous–alkaline medium MnO_4^- undergoes an apparently single-step nitrosylation reaction, in the presence of an excess of $NH_2OH{\cdot}HCl$ and CN^-, to afford complexes containing $Mn(NO)^{2+}$, $Mn(NO)_2{}^{2+}$ (hitherto unknown), or $Mn(NO)^{3+}$ moieties. This is evident from the products $K_3[Mn(NO)(CN)_5]{\cdot}2H_2O$ (**1**), $[PPh_4]_2[Mn(NO)_2(CN)_4]{\cdot}H_2O$ (**2**), $[NMe_4]_2[Mn(NO)(CN)_4]{\cdot}2H_2O$ (**3**), and isomeric $[Mn(NO)(CN)_3(L\text{–}L)]$ [(**4a**), (**10a**), for L–L = 2,2′-bipyridine; (**4b**), (**10b**), for L–L = 1,10-phenanthroline]. The last compounds contain formally Mn^{II} in a spin-quartet ground state, as confirmed by their variable-temperature magnetic susceptibility and e.s.r. data. The reductive nitrosylation also generates $Mn_2(NO)_2{}^{4+}$ present in $Mn^{II}{}_3\,[Mn_2(NO)_2(CN)_{10}]$ (**5**) or $[PPh_4]Mn_2[Mn_2(NO)_2(CN)_9]$ (**9**) and $Mn_2(NO)_2{}^{5+}$ in $[PPh_4]_3[Mn_2(NO)_2(CN)_8]$ (**6a**). Complex (**6a**) is an one-electron paramagnet, shows an highly featured e.s.r. spectrum, and exhibits a rather irreversible cyclic voltammetric oxidative response at an apparent E^0_{298} of 0.98 V *vs.* saturated calomel electrode (s.c.e.) corresponding to the process $Mn_2(NO)_2{}^{5+} \rightleftharpoons Mn_2(NO)_2{}^{6+}$. The reaction when conducted in a near neutral medium, produces besides (**10a**), (**10b**), and (**5**), another product of possible composition $R_3[Mn_2(NO)_2(CN)_8]{\cdot}3H_2O$ [R = PPh_4 (**6b**), NMe_4 (**7**), or Cs (**8**)] obviously containing a $Mn_2(NO)_2{}^{5+}$ core. The product (**6b**) is an isomer of (**6a**) and shows an e.s.r. spectrum having even more features than that of (**6a**). Compound (**6b**), however, shows a reversible cyclic reponse [E^0_{298} = 0.85 V *vs.* s.c.e. (0.47 V *vs.* ferrocene–ferrocenium] assigned to the electrode process shown for (**6a**).

Reductive nitrosylation of tetraoxometalates, *viz.* $MoO_4{}^{2-}$, $CrO_4{}^{2-}$, and $VO_4{}^{3-}$, using $NH_2OH{\cdot}HCl$ in the presence of CN^- in an aqueous–alkaline medium and syntheses of the corresponding pentacyanonitrosylmetalates were reported some time ago.[2–5] A related reaction of ReO_4^- has also been reported recently.[6,7] However, reductive nitrosylation of MnO_4^- using any of the known nitroysylating agents[8] has not been reported so far. Pentacyanonitrosylmanganate, $[Mn(NO)(CN)_5]^{3-}$, containing the $Mn(NO)^{2+}$ core was reported[9] to be synthesized from $K_3[Mn(CN)_6]$ using $NH_2OH{\cdot}HCl$, and shown to undergo oxidation by chemical (HNO_3[9]) or electrochemical means,[10] forming $[Mn(NO)(CN)_5]^{2-}$ contaning the $Mn(NO)^{3+}$ moiety.

In the present paper we report, for the first time, that MnO_4^- undergoes a single-step facile conversion into $Mn(NO)_2{}^{2+}$, hitherto unknown, as well as to $Mn(NO)^{2+}$ and $Mn(NO)^{3+}$ species, on reaction with an excess of $NH_2OH{\cdot}HCl$ and CN^- in an aqueous alkaline medium. The isolated complex anions have the compositions $[Mn(NO)_2(CN)_4]^{2-}$, $[Mn(NO)(CN)_5]^{3-}$, $[Mn(NO)(CN)_4]^{2-}$, and $[Mn(NO)(CN)_5]^{2-}$, precipitable with suitable counter ions. Three other anionic species isolated have the probable compositions $[Mn_2(NO)_2(CN)_8]^{3-}$ and $[Mn_2(NO)_2(CN)_9]^{5-}$ {besides $[Mn_2(NO)_2(CN)_{10}]^{6-}$}, which apparently contain $Mn_2(NO)_2{}^{5+}$ and $Mn_2(NO)_2{}^{4+}$ (also for the 6 – complex) cores respectively, being generated possibly *via* the conglomeration of the monomeric units $Mn(NO)^{3+}$ and $Mn(NO)^{2+}$ in the case of the former and two $Mn(NO)^{2+}$ units in the case of the latter. Also reported is the single-step synthesis of the hitherto unknown isomeric $[Mn(NO)(CN)_3(L\text{–}L)]$ complexes [L–L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)] directly from MnO_4^-, which are, to our knowledge, the first examples[10] of manganese(II) complexes, albeit in the formal sense, conclusively shown to exist in a spin-quartet ground state.

Results and Discussion

(*a*) Overall Reaction Pattern.—A hot aqueous solution of MnO_4^- when treated with an excess of $NH_2OH{\cdot}HCl$ and KCN and the reaction medium rendered highly alkaline (pH ≈ 11) gave a red-violet solution (A) which upon addition of ethanol afforded $K_3[Mn(NO)(CN)_5]{\cdot}2H_2O$ (**1**). Solution A retains its colour when the pH is reduced to ≈6 (A′), and addition of PPh_4Cl, NMe_4Cl, or L–L to the above solution (A′) yields $[PPh_4]_2[Mn(NO)_2(CN)_4]{\cdot}H_2O$ (**2**), $[NMe_4]_2[Mn(NO)(CN)_4]{\cdot}2H_2O$ (**3**), or $[Mn(NO)(CN)_3(L\text{–}L)]$ [L–L = bipy (**4a**) or phen (**4b**)] respectively. Complexes (**2**)—(**4**) were previously unknown, and (**1**), otherwise known,[9] was prepared for the first time directly from MnO_4^- *via* reductive nitrosylation. However, when the MnO_4^- solution, $NH_2OH{\cdot}HCl$, and KCN are kept at pH ≈ 7 and gently heated, a vigorous reaction occurs yielding a rose product having the probable composition $Mn_3[Mn(NO)(CN)_5]_2$ (**5**), obtained otherwise by Cotton *et al.*,[9] leaving a dark green solution (B). Addition of counter ions as chloride salt, RCl, to solution B did not give any discrete monomeric species; in each case the precipitated green compounds closely correspond to the formula $R_3[Mn_2(NO)_2(CN)_8]{\cdot}3H_2O$ [R = PPh_4 (**6b**), NMe_4 (**7**), or Cs (**8**)]. Another compound (**6a**),

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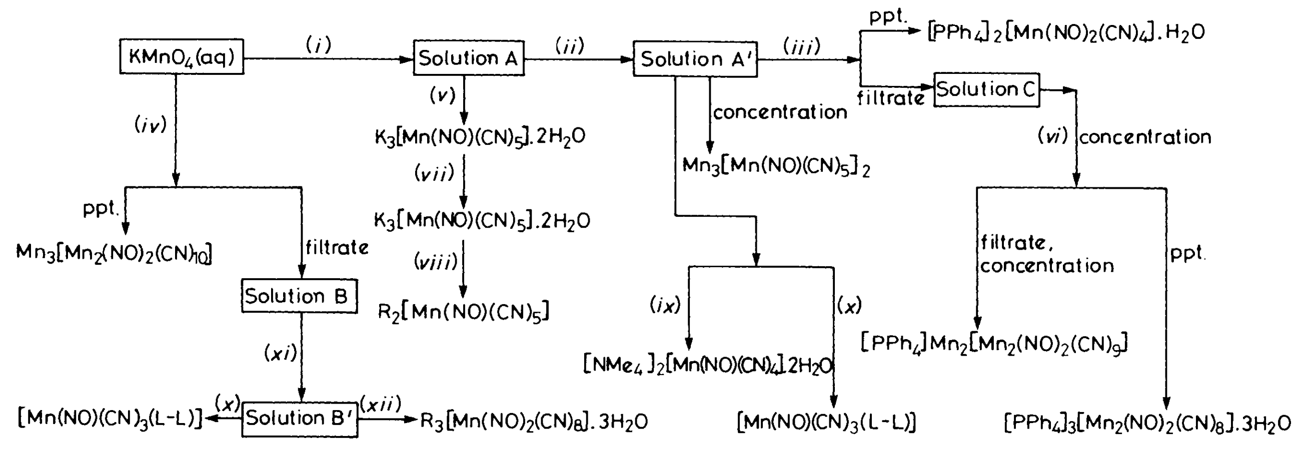
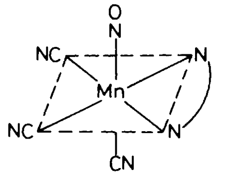
† *Supplementary data available* (No. SUP 56760, 5 pp.): e.s.r. and i.r. spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

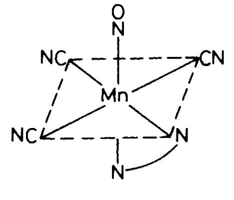
Non-S.I. units employed: eV ≈ 1.60 × 10^{-19} J, G = 10^{-4} T.



Scheme. L–L = bipy or phen; R = Cs, NMe_4, or PPh_4. (*i*) KCN, $[NH_3OH]Cl$, OH^- (pH ≈ 11); (*ii*) 6 mol dm^{-3} HCl (pH ≈ 5); (*iii*) PPh_4Cl; (*iv*) KCN, $[NH_3OH]Cl$ (pH ≈ 7); (*v*) EtOH; (*vi*) three or four drops of HCl; (*vii*) water–ethanol; (*viii*) 6 mol dm^{-3} HNO_3 + RCl; (*ix*) NMe_4Cl; (*x*) L–L; (*xi*) 6 mol dm^{-3} HCl (pH ≈ 3); (*xii*) RCl



(I)



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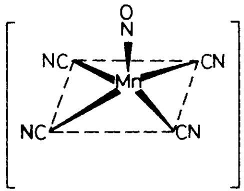

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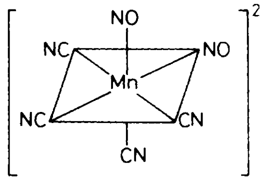

(IV)

isomeric* to (**6b**), can be obtained from solution A′ after filtering out (**2**) and acidifying the filtrate followed by concentration of the solution. Also, after (**6a**) is filtered out and the solution further concentrated, a mauve microcrystalline solid, probably $[PPh_4]Mn_2[Mn_2(NO)_2(CN)_9]$ (**9**), is obtained (Scheme). However, when solution B is treated with L–L the corresponding green isomers (**10a**) and (**10b**), of (**4a**) and (**4b**), are obtained. Compound (**1**) affords a yellow solution when dissolved in 6 mol dm^{-3} HNO_3 at room temperature from which $R_2[Mn(NO)(CN)_5]$ [R = Cs (**11**) or NMe_4 (**12**)], obviously containing the $Mn(NO)^{3+}$ moiety, can be precipitated by adding suitable counter ions RCl. As mentioned earlier, the potassium salt of the anion was also obtained by Cotton *et al.*[9] using a method which is grossly similar to that reported here.

(*b*) *Characterization of the Isolated Products*.—(*i*) *Monomeric compounds*. Compound (**1**) behaves as a 3:1, (**3**), (**11**), and (**12**) as 2:1, electrolytes in water,[11] as expected from their molecular formulae. Also, as expected, (**2**) behaves as a 2:1 electrolyte in acetonitrile[12] (Table 1). The neutral and isomeric L–L compounds (**4a**), (**4b**), and (**10a**), (**10b**) are practically non-electrolytes in dimethyl sulphoxide (dmso), showing only marginal dissociation.

The dinitrosyl compound (**2**), shows two ν(NO) bands, as expected for a *cis*-dinitrosyl moiety, while all the other mononitrosyls show a single band (Table 1). The anionic and monomeric mononitrosyl products possessing a $Mn(NO)^{2+}$ core show ν(NO) vibrations at 1 720 cm^{-1} while those containing a $Mn(NO)^{3+}$ core absorb at 1 900 cm^{-1}. (For the potassium salt the previous workers[9] obtained a band at 1 885 ± 5 cm^{-1}.) In the former cases, where the formal oxidation state of Mn is +1, a better Mn $3d\pi \longrightarrow \pi^*$ NO back donation is achieved than that in the latter, where Mn is formally in a +2 state, which is reflected in their ν(NO) vibrations. However, the brown neutral complexes (**4a**) and (**4b**) containing the same $Mn(NO)^{3+}$ moiety display ν(NO) around 1 760 cm^{-1} (a higher region than that of the corresponding anionic complexes is ascribable to the slightly lower amount of back donation in the neutral complexes than that achieved in the anionic ones) as against 1 775 cm^{-1} for the corresponding green isomers (**10a**) and (**10b**). This indicates that the position *trans* to the axial NO^+ of the green isomers is occupied by a stronger π acid than that in the brown varieties. So, presumably, (**4a**) and (**4b**) may be represented by structure (**I**) (**10a**) and (**10b**) by structure (**II**) insofar as the π acidity of L–L ligands is expected to be higher and the σ basicity lower than those of CN^-. Unfortunately, even after repeated reprecipitation from dmso–water, the crystallinity of both the brown and green varieties was poor and their *X*-ray powder diffractograms show broad envelopes rather than the well defined *d*-spacing lines obtained in all the other cases (see Experimental section). However, the magnetic properties of compounds (**4a**), (**4b**), (**10a**), and (**10b**) are interesting. The $\mu_{eff.}$ value in all the cases is 3.9 and this is independent of temperature in the region 300—4.8 K, indicating an orbitally non-degenerate spin-quartet ground state configuration in all the four cases. This is expected insofar as the molecular symmetry species in both (**I**) and (**II**) will not be greater then C_s and hence their expected m.o. diagram[13] with the valence electron occupancy is as shown in Figure 1. Further experimental evidence corresponding to a spin-quartet ground term has been obtained from the e.s.r. spectra of the compounds at 298, 80, and 4.8 K in the polycrystalline state (SUP 56760). The $\langle g \rangle_\perp$ (≈4—4.5) line is weak but is observable at all temperatures, apart from the a very prominent and structureless $\langle g \rangle_\parallel$ (= 2.10) line. Assuming the NO^+ formalism,[13] the formal oxidation state of the Mn in all the four isomeric L–L derivatives is +2. The N_{1s} binding energy of a representative compound (**4b**) has been measured using *X*-ray photoelectron spectroscopy (x.p.s.) to be 403 eV, further evidence in favour of co-ordination of NO as NO^+.[14] Hence,

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* The isomers have identical elemental analysis data but differ in i.r. and u.v.–visible spectra as well as their *X*-ray powder diffraction patterns (see Experimental section).

Table 1. Analytical[a] and physical data for the complexes

Compound	Analysis (%)				Selected i.r. data (cm^{-1})					
	C	H	N	Mn	ν(CN)	ν(NO)	ν[MnN-(NO)]	ν(MnC)	λ/Ω^{-1} cm^2 mol^{-1}	$\mu_{eff.}$
(**1**) $K_3[Mn(NO)(CN)_5]\cdot 2H_2O$	16.8	0.9	23.0	14.6	2 120 (sh)	1 720s	660w	560w	360	Dia-
	(16.3)	(1.1)	(22.8)	(14.9)	2 080s					magnetic
(**2**) $[PPh_4]_2[Mn(NO)_2(CN)_4]\cdot H_2O$[b]	67.9	4.7	8.9	5.8	2 124 (sh)	1 700s	610w	340w	235[c]	1.9
	(68.2)	(4.6)	(9.2)	(6.0)	2 115s	1 640s				
(**3**) $[NMe_4]_2[Mn(NO)(CN)_4]\cdot 2H_2O$	38.4	7.2	26.2	14.5	2 125 (sh)[c]	1 720s	650w	310w	236[d]	Dia-
	(38.6)	(7.5)	(26.3)	(14.7)	2 095s[e]					magnetic
(**4a**) $[Mn(NO)(CN)_3(bipy)]$[f]	48.6	2.2	26.1	17.1	2 140 (sh)	1 755s	620w	320w	*g*	3.9
	(48.9)	(2.5)	(26.3)	(17.2)	2 100m					
(**4b**) $[Mn(NO)(CN)_3(phen)]$[f]	52.2	2.0	24.3	15.2	2 140 (sh)	1 750s	630w	315w	*g*	3.9
	(52.5)	(2.3)	(24.5)	(16.0)	2 100m					
(**5**) $Mn_3[Mn_2(NO)_2(CN)_{10}]$	21.0		28.0	45.9	2 165 (sh)	1 830s	655w	320w	360[d]	7.7
	(21.2)		(28.3)	(46.2)	2 110s					
(**6a**) $[PPh_4]_3[Mn_2(NO)_2(CN)_8]\cdot 3H_2O$[b]	66.0	4.3	9.5	7.4	2 140 (sh)	1 775s	610w	315w	354[c]	1.9
	(66.3)	(4.5)	(9.7)	(7.6)	2 110s					
(**6b**) $[PPh_4]_3[Mn_2(NO)_2(CN)_8]\cdot 3H_2O$[b]	66.1	4.2	9.5	7.4	2 160s	1 777s	620w	320w	354[c]	1.9
					2 130s					
(**7**) $[NMe_4]_3[Mn_2(NO)_2(CN)_8]\cdot 3H_2O$	36.5	6.2	27.6	16.5	2 185 (sh)	1 775s	610w	320w	*g*	1.9
	(36.7)	(6.4)	(27.8)	(16.8)	2 145s					
(**8**) $Cs_3[Mn_2(NO)_2(CN)_8]\cdot 3H_2O$	11.3	0.6	16.6	13.1	2 160 (sh)	1 770s	610w	320w	*g*	1.9
	(11.5)	(0.7)	(16.8)	(13.2)	2 125s					
(**9**) $[PPh_4]Mn_2[Mn_2(NO)_2(CN)_9]$[b]	45.2	2.3	17.5	25.2	2 170 (sh)	1 760s	655w	320w	*g*	7.6
	(45.5)	(2.3)	(17.7)	(25.3)	2 120s					
(**10a**) $[Mn(NO)(CN)_3(bipy)]$[f]	48.7	2.3	26.0	17.0	2 140 (sh)	1 775s	630w	320w	*g*	3.9
	(48.9)	(2.5)	(26.3)	(17.2)	2 100m					
(**10b**) $[Mn(NO)(CN)_3(phen)]$[f]	57.3	2.2	24.2	15.9	2 140m	1 775s	630w	320w	*g*	3.9
	(52.5)	(2.3)	(24.5)	(16.0)	2 100 (sh)					
(**11**) $Cs_2[Mn(NO)(CN)_5]$	12.3		17.1	11.1	2 160 (sh)	1 900s	660w	340w	230[d]	1.8
	(12.5)		(17.5)	(11.3)	2 120s					
(**12**) $[NMe_4]_2[Mn(NO)(CN)_5]$	42.7	6.4	30.6	14.9	2 140m	1 900s	620w	340w	232[d]	1.8
	(43.0)	(6.6)	(30.8)	(15.1)						

[a] Calculated values are shown in parentheses. [b] P 6.7 (6.8); 6.2 (6.4), and 3.4 (3.6) % respectively for (**2**), (**6a** and **b**), and (**9**) respectively. [c] In acetonitrile. [d] In water. [e] At 2 150w and 2 080s cm^{-1} in aqueous solution. [f] ν(Mn–N) (L–L) 390 cm^{-1} in all cases. [g] Insoluble or sparingly soluble.

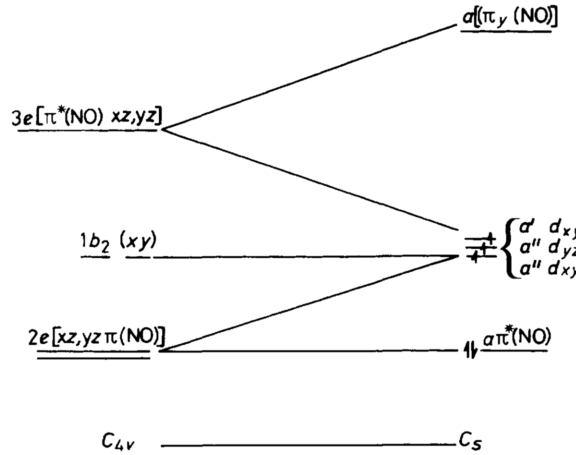


Figure 1. Expected m.o. diagram for $[Mn(NO)(CN)_3(L\text{–}L)]$ compounds in C_s symmetry

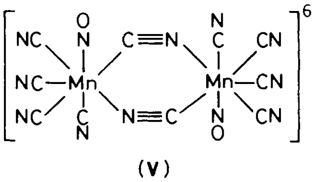
the present work demonstrates for the first time manganese(II) compounds where the metal ion almost certainly posseses a spin-quartet ground state. The earlier claim of a rather poorly established $4T_1$ ground term for the apparently polymeric compound $[Mn(dtc)_2]$[15] (dtc = diethyldithiocarbamate) containing a MnS_6 chromophore was subsequently contradicted by others.[16]

The ν(CN) vibrations of this class of compounds are interesting. Considering L–L = phen as a typical example, it is apparent that two ν(CN) bands, of relative intensities 1:2, are obtained. Interestingly, the low-intensity band for (**I**) appears in a higher spectral region (2 140 cm^{-1}), where the higher-intensity band of (**II**) lies and *vice versa* (SUP 56760). This observation very nicely supports the suggested structure. In structure (**I**), two equatorial CN^- ligands have identical environments, both being situated *trans* to the phen nitrogens. The third cyanide, however, is situated *trans* to the strongest π acid, the NO^+ ligand, and hence in the latter case the Mn $3d_\pi \longrightarrow CN^-$ π* back donation will be rather poor, resulting in the low-intensity band [due to 1 ν(CN)] appearing at a higher wavenumber than that of the high-intensity band [due to 2 ν(CN)]. This, is fortuitously the wavenumber where two *trans* equatorial CN^- groups, in structure (**II**), absorb (and hence should be of higher intensity), and which compete for the same Mn $3d_\pi$ orbitals. The CN^- in (**II**) *trans* to one of the phen nitrogens will be able to back accept Mn $3d_\pi$ electron density, since the metal ion has already chanelled some electron density to phen, however small, at the cost of the π cloud being received by the π* NO orbital (see above), and thus explaining the position of the weaker intensity band at the lower wavenumber. The ν(CN) bands are actually split even for monomeric cyanonitrosyl complexes (Table 1) including the anion $[Mn(NO)(CN)_4]^{2-}$ of (**3**). So far as the known structural aspects of five-co-ordinate tetracyanonitrosylmetalates[17] or of complexes of the type $M(NO)L_4$ (neutral, anionic, or cationic) are concerned, a square-pyramidal geometry [and not trigonal bipyramidal, which otherwise would have been the conclusion based on the double ν(CN) absorption] with axial NO is realistic for the anion of (**3**), the splitting of ν(CN) band (observable even in aqueous

Table 2. Electronic spectral data

Complex	$\lambda_{max.}$/(ε/dm^3 mol^{-1} cm^{-1})	Assignments
(1)^a	540 (20), 364 (52), 228 (4 630)	$b_2 \longrightarrow e, b_1, a_1$
(2)^b	571 (15), 400 (1 640), 320 (588)	$1b_1 \longrightarrow 2a', 3a', 2a''$
(3)^{a,c}	540 (45), 361 (105), 254 (3 655)	$b_2 \longrightarrow e, b_1, a_1$
(4a)^c	621, 471, 300	$a' \longrightarrow a'(x^2 - y^2), a'(z^2), a''$
(4b)^c	606, 472, 296	$a'' \longrightarrow a'(x^2 - y^2), a' \longrightarrow a'(z^2), a' \longrightarrow a''$
(5)^a	576 (20), 350 (65), 227 (5 075)	
(6a)^b	653 (255), 452 (145), 352 (5 090)	
(6b)	632 (450), 444 (420), 356 (13 470)	
(7)^c	641, 442, 350	
(8)^c	633, 478, 350	
(9)^c	562, 376	
(10a)^c	671, 472, 373	$a' \longrightarrow a'(x^2 - y^2), a'(z^2), a''$
(10b)^c	675, 475, 370	$a' \longrightarrow a'(x^2 - y^2), a'(z^2), a_1''$
(11)^a	392 (30), 316 (200)	$b_2 \longrightarrow e, b_1$
(12)^a	394 (80), 315 (725)	$b_2 \longrightarrow e, b_1$

^{a} In water. ^{b} In acetonitrile. ^{c} Mull spectra of solid. Intraligand transitions are not listed.



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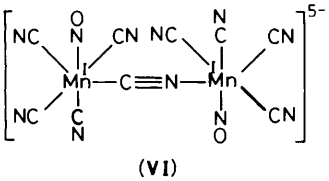

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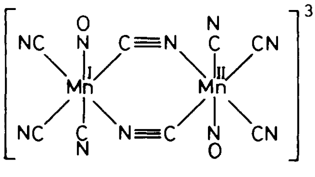

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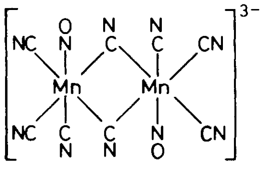

(VIII)

solutions) implying that the metal ion is slightly lifted from the equatorial plane occupied by four CN$^-$ ligands, towards the NO ligand, as depicted in **(III)**.

Compound **(2)**, possessing a $\{Mn(NO)_2\}^{7,*}$ valence electron configuration, should have[13] a ground-state m.o. configuration $(1a'')^2(1a')^2(1a')^2(1b_1)^1$ in C_s symmetry [2 NO in a–e (axial–equatorial) configuration, structure(**IV**)]. Another possibility is the configuration $(1a_2)^2(1a_2)^2(1b_2)^2(1b_1)^1$ in C_{2v} symmetry [e–e (equatorial–equatorial)]. However, in both cases, normally a spin-only single-electron magnetic moment is expected and the observed value of 1.9 (Table 1) is due to the negative value of the spin–orbit coupling constant in the present case. This is also reflected in the $\langle g \rangle_{av.}$ value obtained from the e.s.r. spectrum at ambient temperature as well as at 77 K (SUP 56760). The hyperfine sextet in both cases ($\langle A \rangle$ ^{55}Mn $\approx$ 140 G) seems to arise from coupling of the unpaired electron to ^{55}Mn ($I = \frac{5}{2}$). The further splitting of the two low-field lines to triplets may be due to ligand hyperfine interaction of the electron with ^{14}N (I = 1) of NO ($\langle A \rangle$ ^{14}N $\approx$ 10 G).

The $Mn(NO)^{3+}$ species **(11)** and **(12)** should possess C_{4v} molecular symmetry and hence $e^4b_2^1$ ground-state configurations. Their magnetic moments are slightly higher than the single-electron spin-only value (Table 1) and in the polycrystalline state they both show a broad structureless isotropic e.s.r. signal with g_s = 2.02, at ambient temperature as well as at 77 K. Unfortunately, the PPh_4 salt of the complex anion existing in **(11)** and **(12)** could not be isolated pure so that it is not possible to know whether the cation has any effect in forcing the resolution of the structures corresponding to the g and A tensors (see below).

Differential thermal analysis (d.t.a.) and thermal gravimetric analysis (t.g.a.) studies show that compounds **(1)**—**(3)** lose water molecules at or below 100 °C implying that the latter are only held in the lattice. The d.t.a. curve for **(3)** is interesting, showing a stepwise loss of the water molecules below 100 °C, endothermically, the t.g.a. is grossly comparable to this, showing that the compound starts to lose water molecules from 50 °C and the weight-loss data (found 9.6, calc. 9.7%) corresponding to the stable horizontal region between 130 and 200 °C (where obviously the anhydrous compound exists) show the loss of two water molecules. The compound is, therefore, five-co-ordinate. However, its electronic spectrum in aqueous solution as well as the mull spectrum in dry Nujol are essentially identical (Table 2) showing that no aquation has probably taken place, and that five-co-ordination in the $Mn(NO)^{2+}$ complexes is not an unstable arrangement. Also, the other complexes containing discrete $Mn(NO)^{n+}$ (n = 2 or 3) cores show appropriate electronic spectral bands as expected from their predicted molecular symmetry. The possible origins of the bands are indicated in Table 2.

(*ii*) *Supposed dimeric compounds.* A reaction mixture containing MnO_4^- CN^-, and NH_2OH or their reaction products in alkaline solution when acidified and worked up (Scheme) has a pronounced tendency to afford oligonuclear aggregates presumably *via* cyanide bridging. The bridging possibly takes place in the M–C≡N–M′ mode since for complexes **(5)**—**(9)** the vibrations in the ν(CN) region are markedly different from those of the monomeric species **(1)**—**(3)** (Table 1); the former complexes show a medium-intensity band close to 2 200 cm^{-1} [18] and a shoulder at *ca.* 2 100 cm^{-1}, while for the latter bands are found only in the viscinity of 2 100 cm^{-1} and none in the neighbourhood of 2 200 cm^{-1} [19] (SUP 56760). Clearly three distinct classes of compounds exist, $[Mn^I_2(NO)_2(CN)_{10}]^{6-}$, $[Mn^I_2(NO)_2(CN)_9]^{5-}$, and $[Mn^IMn^{II}(NO)_2(CN)_8]^{3-}$ in the anions of **(5)**, **(9)**, and **(6)**—**(8)** respectively and since all show only a single ν(NO) vibration in the i.r. region, their structures are predicted to be **(V)**—**(VII)**. The cations associated with the silky pink complex **(5)** **(V)** are $3Mn^{2+}$, with the mauve complex **(9)** **(VI)** are $PPh_4^+ + 2Mn^{2+}$, and with the green complexes **(6b)**, **(7)**, and **(8)**, *i.e.* **(VII)**, are $3PPh_4^+$, $3NMe_4^+$, or $3Cs^+$. Besides the dimeric nature of the complex anions in **(V)** and **(VI)** (some of the cations in the respective complexes also comprise a transition-metal ion, here Mn^{2+}. Hence, the latter will also enter into a second-order interaction with the co-ordinated cyanide ligands. Almost diagnostically in the above situations, the band at *ca.* 430 cm^{-1} [ν(MC) or δ(M–C≡N–M)] unusually becomes prominent, *e.g.* for **(5)** and **(9)**, but not for **(6b)**, **(7)**, and **(8)**. Of the oligomeric compounds **(6)**—**(9)**, only **(6)** is soluble in aceonitrile [**(7)** and **(8)** weakly so in water] to a significant extent and its molar conductance (*ca.* 10^{-3} mol dm^{-3} solution) shows that it behaves as a 3:1 electrolyte in this solvent.[12] The structure type **(VII)**, suggested for it, contains one Mn^I and one Mn^{II}. The bulk magnetic moment of 1.9 is as expected for a magnetically isolated strong-field manganese(II) complex; the manganese(I) centre [$\{Mn(NO)\}^6$] is diamagnetic.

The e.s.r. spectrum of microcrystalline sample of compound **(6b)** at 298 K (Figure 2) is quite interesting. Besides the $\langle g \rangle$ ($g_\perp \approx 2.06, g_\parallel \approx 1.96, g_{av.} \approx 2.03$) and $\langle A \rangle$ (^{55}Mn) ($A_\parallel \approx$ 150,

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[*] The numerical superscript indicates the total number of valence electrons in the orbitals of Mn and NO.

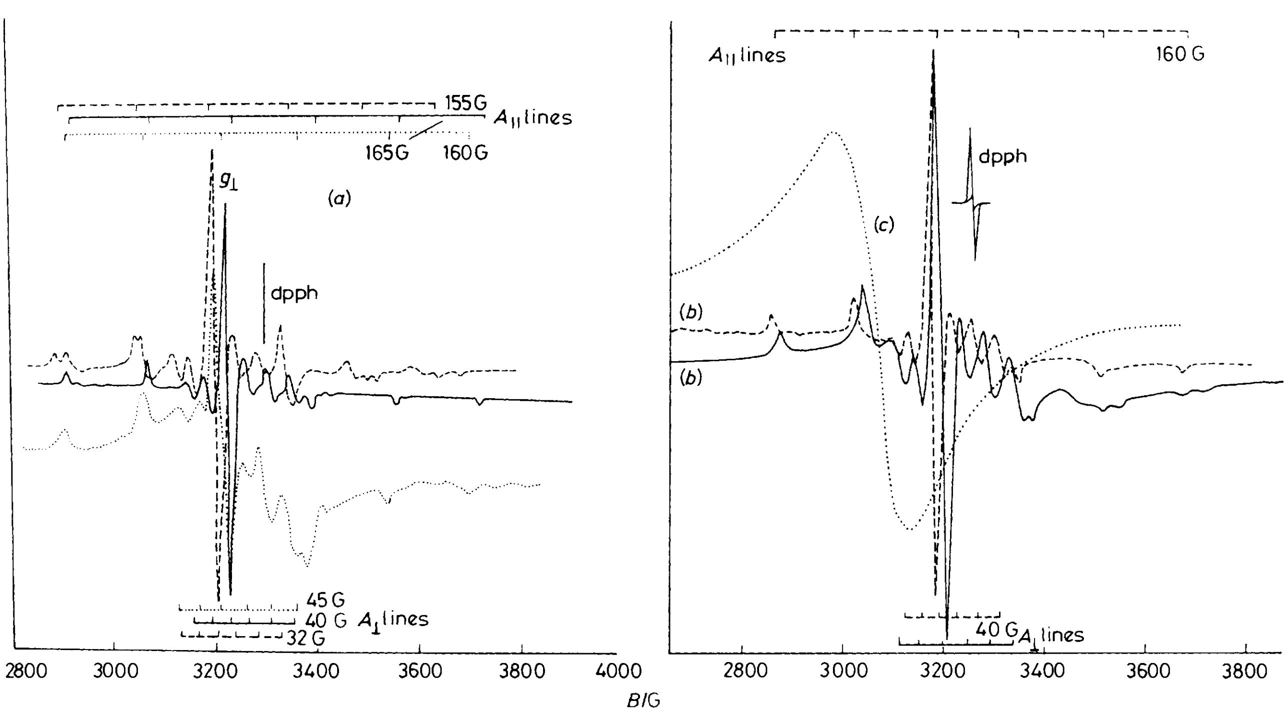

Figure 2. E.s.r. spectra of (*a*) $[PPh_4]_3[Mn_2(NO)_2(CN)_8]\cdot3H_2O$ (**6b**), polycrystalline, 298 K (– – – –), in frozen CH_3CN (——), and in frozen CH_3CN after coulometry (· · · ·), (*b*) $[PPh_4]_3[Mn_2(NO)_2(CN)_8]\cdot3H_2O$ (**6a**), polycrystalline, 298 K (——), in frozen CH_3CN after coulometry (– – – –), and (*c*) $[NMe_4]_3[Mn_2(NO)_2(CN)_8]\cdot3H_2O$ (**7**), polycrystalline, 298 K (· · · ·)

$A_{\perp} \approx 32$, $A_{iso} \approx 71$ G) tensor anisotropy, the spectrum also shows field dependent s.h.f. interaction of the unpaired electron [localized on a predominantly metal-based m.o. (d_{xy})[13] which is non-bonding with respect to the NO group] with both the ^{13}C ($A \approx 25$ G) and ^{14}N ($A \approx 20$—32 G) of the CN^- ligand. This is quite feasible, so far as the predicted structure (**VII**) of compound (**6**) is concerned. The s.h.f. interaction due to the ^{14}N of NO is less probable, since in that case a configurational interaction *via* spin polarization of the *e* orbital which has a pronounced NO π and π^* character[13,20,21] has to be assumed. Interestingly, the NMe_4^+ and Cs^+ salts of the above oligomeric anion [*i.e.* complexes (**7**) and (**8**)] show rather broad and featureless e.s.r. spectra [those of (**7**) and (**8**) are identical; for (**7**), see Figure 2) with $g_s = 2.03$. The cation PPh_4^+ being highly polarizable as well as containing four phenyl groups giving rise to large total ring currents may induce an effect leading to resolution of the e.s.r. spectrum. In frozen acetonitrile solution also, most of the features ($\langle g \rangle$ and $\langle A \rangle$ tensor anisotropy) are retained but the s.h.f. due to the possible interaction of the unpaired electron with ^{13}C and ^{14}N collapses (Figure 2). However, like complex (**6b**), (**7**) and (**8**) also have normal room-temperature magnetic moments. Also the isomer of (**6b**), (**6a**), exhibits a $\mu_{eff.}$ value of 1.9 and shows an e.s.r. spectrum (Figure 2) grossly comparable ($g_{\perp}, g_{\parallel}, g_{av.}, A_{\parallel}, A_{\perp}$, and A_{iso}) to the former but differing in the finer details. For instance, here the s.h.f. due to the interaction of the unpaired electron with ^{13}C remains but is shifted predominantly to the high-field parallel region, but no signal corresponding to interaction with ^{14}N of CN^- is present. These observations are in accord with structure (**VIII**) for (**6a**). The i.r. spectrum (SUP 56760) is also consistent with the proposed structure since there does not appear to be any ν(CN) band close to 2 200 cm^{-1} typical of M–C≡N–M interaction as is observed for (**6b**) and similar compounds [(**5a**), (**7**)—(**9**)].

Finally, it may be mentioned that it is, at present, very difficult to apportion the total magnetic moment (Table 1) between the individual Mn atoms in the polynuclear compounds (**5**) and (**9**), since their structural features are not yet known.

All these binuclear (or polynuclear) complexes show three electronic absorption bands in the solution or solid phase (Nujol mull spectra) (see Table 2), except for (**9**) for which only two bands are observed. Since multiple metal centres exist in the complexes the origin of the bands cannot be ascertained.

(*c*) *Electrochemistry of the Compounds containing* $Mn(NO)_2{}^{2+}$, $Mn(NO)^{2+}$, *and* $Mn_2(NO)_2{}^{5+}$ *Cores.*—Voltammetry of the compounds (**2**), (**6a**), and (**6b**) was carried out in acetonitrile and that of (**1**) containing a $Mn(NO)^{2+}$ core, in aqueous solutions, at a platinum working electrode. All potentials are referred to the saturated calomel electrode (s.c.e.) and the following notations were used $E_{p.c.}$-cathodic peak potential; $E_{p.a.}$-anodic peak potential; $\Delta E_p = E_{p.c.} - E_{p.a.}$; $i_{p.c.}$-cathodic peak current; $i_{p.a.}$-anodic peak current. The formal potential, E^0_{298}, is taken as the average of $E_{p.a.}$ and $E_{p.c.}$. Tetraethylammonium perchlorate was used as an inert electrolyte in each case. The formal potentials are also expressed (in parentheses in Table 3) relative to E^0_{298} for ferrocene–ferrocenium *vs.* s.c.e., measured separately under identical conditions, solvents, and inert electrolytes as used for measurements of the sample solutions.

The dinitrosyl compound (**2**) containing a $Mn(NO)_2{}^{2+}$ moiety shows two irreversible oxidation peaks at +0.45 and at +0.70 V in acetonitrile solution (the latter peak becomes more well defined at a faster scan rate; see Figure 3) *vs.* s.c.e. (−0.03 and +0.22 V *vs.* ferrocene–ferrocenium). These two irreversible oxidation waves may represent the electrochemical oxidations in equation (1), since exhaustive electrolysis (coulometry) well

$$\underset{\{Mn(NO)_2\}^7}{[Mn(NO)_2(CN)_4]^{2-}} \xrightarrow{-e^-} \underset{\{Mn(NO)_2\}^6}{[Mn(NO)_2(CN)_4]^{-}} \xrightarrow{-e^-} \underset{\{Mn(NO)_2\}^5}{[Mn(NO)_2(CN)_4]} \quad (1)$$

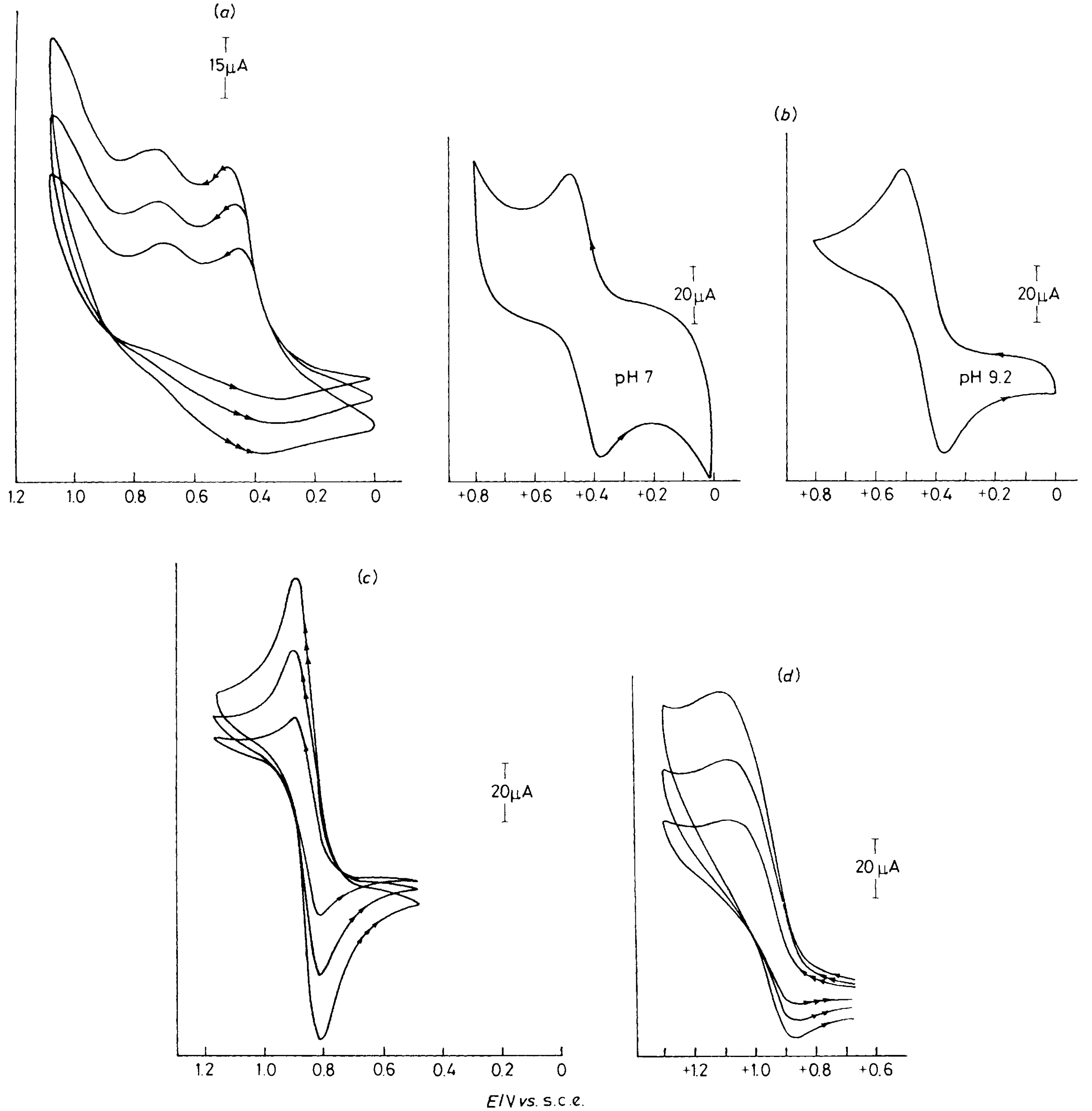

Figure 3. Segmented cyclic voltammograms of (*a*) $[PPh_4]_3[Mn(NO)_2(CN)_4]\cdot H_2O$, (*b*) $K_3[Mn(NO)CN)_5]\cdot 2H_2O$, (*c*) $[PPh_4]_3[Mn_2(NO)_2(CN)_8]\cdot 3H_2O$ (**6b**), and (*d*) $[PPh_4]_3[Mn_2(NO)_2(CN)_8]\cdot 3H_2O$ (**6a**)

past the second peak (B) results in a prominent colour change (yellow to brown) and the species obtained is again e.s.r. sensitive $\{Mn(NO)_2\}^5$ (SUP 56760) as is the starting compound (**2**). However, the diamagnetism of the intermediate corresponding to peak (A), $\{Mn(NO)_2\}$,[6] could not be tested due to the closeness of the reduction waves (A) and (B) and the concomitant difficulty in carrying out a coulometric oxidation to prepare (A) free of (B). However an indication that (A) is e.s.r. silent has been obtained during coulometry. At a stage corresponding to a one-electron change the e.s.r. spectrum shows a very weak derivative curve, but when the electrolysis was continued to a two-electron change where a steady state was shown a reasonably good e.s.r. spectrum was obtained [SUP 56750; $\langle g\rangle_{\perp}$ 2.05, $\langle g\rangle_{\parallel}$ 2.03 $\langle g\rangle_{av.}$ 2.047, hyperfine sextet due to ^{55}Mn ($I = \frac{5}{2}$), though not very prominent].

It is known that $[Mn(NO)(CN)_5]^{2-}$ can be prepared by electrochemical oxidation of $[Mn(NO)(CN)_5]^{3-}$ (**1**).[10] However, complex (**1**) on dissolution in water shows a pH of 8.5 but the solution does not seem to be stable towards electrochemical oxidation even in the presence of sufficient NEt_4ClO_4 since the voltammogram shows that the oxidation peak shifts position continuously towards higher peak potentials in successive scans and the reversibility is also pretty weak. Also the pH of the solution changes significantly with time as the scanning proceeds.* However in buffered mediums, either alkaline

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* The undisturbed aqueous solution also changes pH but the rate of change is very slow.

Table 3. Cyclic voltammetric data at 298 K for the complex $K_3[Mn(NO)(CN)_5]\cdot 2H_2O$ (**1**) in water and for $[PPh_4]_3[Mn_2(NO)_2(CN)_8]\cdot 3H_2O$ (**6b**) in acetonitrile, *vs.* s.c.e. [for (**6b**) values *vs.* ferrocene–ferrocenium are shown in parentheses]

Compd.		Scan rate (mV s^{-1})	$E_{p.c.}$/V	$E_{p.a.}$/V	E^0_{298}/V	E_p/ mV	$i_{p.a.}/i_{p.c.}$
(**1**)	pH 7.0	50	0.47	0.38	0.43	90	0.99
	pH 9.3	50	0.48	0.37	0.43	100	1.00
(**6b**)		20	0.90	0.82	0.86	80	1.02
			(0.52)	(0.44)	(0.48)		
		50	0.90	0.82	0.86	80	1.03
			(0.52)	(0.44)	(0.48)		
		100	0.90	0.82	0.86	80	1.06
			(0.52)	(0.44)	(0.48)		

(pH ≈ 9.3) or neutral (pH ≈ 7), a good and stable cyclic response has been found (Figure 3). The corresponding voltammetric parameters are shown in Table 3; the reversibility in the neutral medium is slightly better than that in the alkaline one, and strictly speaking the redox couple is pseudo-reversible. This electrochemical response is due to the redox process shown in equation (2) since, on exhaustive electrolysis at a more positive

$$\begin{array}{ccc} [Mn(NO)(CN)_5]^{3-} & \xrightarrow{-e^-} & [Mn(NO)(CN)_5]^{2-} \\ \text{pink} & & \text{yellow} \\ Mn(NO)^{2+} & & Mn(NO)^{3+} \end{array} \qquad (2)$$

potential, the pink colour changes to yellow corresponding to the dianionic species. The electronic spectrum of the yellow solution is also identical with that of all aqueous solution of the authentic compound (**11**) (see also ref. 9).

Compound (**6b**) containing formally manganese-(I) and (II) centres displays a reversible cyclic response (Figure 3) at a potential around 0.85 V (0.47 V *vs.* ferrocene–ferrocenium) assigned to the electrode process shown in equation (3). This indicates the oxidation of formally Mn^I to Mn^{II}. The voltammetric parameters are in Table 3. Exhaustive electrolysis well past the oxidation peak gives a coulomb count corresponding to a one-electron change. The colour of the solution changes from deep green to yellow after oxidation and since the product

$$[Mn_2(NO)_2]^{5+} \rightleftharpoons [Mn_2(NO)_2]^{6+} + e^- \qquad (3)$$

[equation (3)] is supposed to be made up of the conglomeration of two $Mn(NO)^{3+}$ [*i.e.* $\{Mn(NO)\}^5$] cores the solution produced by coulommetric oxidation should be e.s.r. sensitive if the two $\{Mn(NO)\}^5$ moieties do not interact with each other *via* direct or superexchange. Actually, the yellow solution frozen at 77 K displays an e.s.r. spectrum comparable (Figure 2) in many respects.* to that of the species existing before electrochemical oxidation [*i.e.* to (**6b**)], when measured in frozen acetonitrile (Figure 2). The compound (**6b**) in acetonitrile solution does not show any s.h.f. splitting due to ^{14}N or ^{13}C (of CN^- in both cases, see above) as found for the polycrystalline solid, but shows $\langle g \rangle$ and $\langle A \rangle$ tensor anisotropy ($\langle g \rangle_\perp \approx 2.04$, $\langle g \rangle_\parallel \approx 2.03$, $\langle g \rangle_{av.} \approx 2.03$, $\langle A \rangle_\parallel \approx 165$, $\langle A \rangle_\perp \approx 40$, and $\langle A \rangle_{iso} \approx 123$ G).

However, the isomeric species (**6a**) shows a rather irreversible (Figure 3) response with an apparent E^0_{298} value for the couple in equation (1) of 0.98 V the cathodic current being much lesser than the anodic one with ΔE_p quite high. Interestingly, coulometric reduction of (**6a**) at a potential well past the E^0 gave a yellow solution whose e.s.r. spectrum in frozen solution (Figure 2) is almost identical with that of a frozen acetonitrile solution of (**6a**) ($\langle g \rangle_\perp \approx 2.05$, $\langle g \rangle_\parallel \approx 2.04$, $\langle g \rangle_{av.} \approx 2.05$, $\langle A \rangle_\parallel \approx 160$, $\langle A \rangle_\perp \approx 40$, and $\langle A \rangle_{iso} \approx 120$ G; no ligand hyperfines).

Conclusions

Reductive nitrosylation of MnO_4^- using NH_2OH in the presence of CN^- gives cyanonitrosyl derivatives of manganese, but the nature of the products depends on the alkalinity of the reaction medium. While mainly a $Mn(NO)^{2+}$ core is generated at high alkalinity (pH ⩾ 9), with minimum amounts of $Mn(NO)_2^{2+}$ and $Mn(NO)^{3+}$, when the alkalinity is low (pH 8) mainly $Mn(NO)^{3+}$ is generated along with a limited amount of $Mn(NO)^{2+}$, both being conglomerated to $Mn_2(NO)_2^{5+}$ species but no $Mn(NO)_2^{2+}$ core is generated. The said conglomerate present in the isolated complex $R_3[Mn_2(NO)_2(CN)_8]\cdot 3H_2O$ is also generated in highly alkaline medium and this with R = PPh_4 forms an isomer of the compound obtained *via* the low alkaline pathway. The manganese(II) centre in the above isomeric complexes is magnetically dilute and shows interesting e.s.r. properties and electrochemistry.

Apart from the discrete monomeric units, $[Mn(NO)_2(CN)_4]^{2-}$, $[Mn(NO)(CN)_5]^{n-}$ (*n* = 3 or 2), $[Mn(NO)(CN)_4]^{2-}$, and $[Mn(NO)(CN)_3(L\text{–}L)]$ (possessing spin-quartet ground states) and the above mentioned conglomerate, also two $Mn(NO)^{2+}$ moieties interact forming $Mn_2(NO)_2^{4+}$ cores in several of the di- or oligo-meric species isolated.

The monomeric products have been adequately characterized and their structures predicted with reasonable certainly. For the oligomeric species, structures have been proposed from analytical and spectroscopic data, but because of the complex nature of these molecules a three-dimensional *X*-ray diffractomeric study is necessary. It is to this end that the present investigations are continuing.

Experimental

Materials and Methods.—The starting material, $KMnO_4$, was of G.R. grade. All reagents required for compound preparation were of analytical grade. The analytical grade solvents used for physiocochemical studies were further purified by a literature method[22] before use. Water of high purity was obtained by distillation of deionized water from $KMnO_4$. Sodium perchlorate for electrochemical work was recrystallized from water and the supporting electrolyte, tetraethylammonium perchlorate, was prepared using the literature method.[23] Dinitrogen for electrochemical and thermoanalytical work was purified by passage through an alkaline dithionite reducing solution. Chemically pure grade ferrocene from Sigma Chemical Company was used directly.

Infrared spectra for KBr pellets (4 000—200 cm^{-1}) were recorded on a Perkin-Elmer model 597 spectrophotometer. For the measurements in aqueous solution (4 000—700 cm^{-1}), an Intran 2 demountable cell with poly(tetrafluoroethylene) spacers were used. Electronic spectra were recorded on a Philips Scientific SP8-150 UV-VIS or Hitachi 330 UV-VIS-NIR spectrophotometer. All the pH measurements were made with an E.C. (India) digital pH meter (model 5651). The solution conductances were measured with a Wayne Kerr B 331 Autobalance Precision Bridge. The magnetic susceptibilities were obtained by the Gouy method with the help of a PAR model 155 vibrating sample magnetometer. *X*-Band e.s.r. spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at low temperatures. The spectra were calibrated with diphenylpicrylhydrazyl (dpph) (*g* = 2.0037). Thermoanalyses were made on a Shimadzu

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* $\langle g \rangle$ and $\langle A \rangle^{Mn^{II}}$ tensor anisotropy but no s.h.f. splitting [$\langle g \rangle_\perp \approx 2.06$, $\langle g \rangle_\parallel \approx 2.01$, $\langle g \rangle_{av.} \approx 2.04$, $\langle A \rangle_\parallel \approx 160$, $\langle A \rangle_\perp \approx 45$, and $\langle A \rangle_{iso} \approx 122$ G (Figure 2)].

thermoanalyser DT 30. Voltammetric measurements were done with the use of a PAR model 370-4 electrochemistry system: model 174A polarographic analyzer, model 175 univeral programmer, model RE 0074 XY recorder, model 173 potentiostat, model 179 digital coulometer, and model 377A cell system. All experiments were made at 298 K under a dinitrogen atmosphere in a three-electrode configuration using a planar Beckman model 39273 platinum-inlay working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (s.c.e.). For coulometry a platinum wire-gauze working electrode was used. The potentials reported are uncorrected for the junction contribution. Elemental analyses were performed using a Perkin-Elmer 240C elemental analyser. *X*-Ray photoelectron spectra were recorded using ESCA-3 spectrometer (Vacuum Generators) with the Al-K_α line (1 486.6 eV) as the excitation source. The spectra were calibrated with the help of the $C_{1s\ 1/2}$ binding energy at 285.0 eV of the coordinated organic ligand[24] (here bipy). A Phillips XRD system model PW 1730/1710 and Cu-K_α radiation was used for measuring *d* spacings.

All the compounds prepared were dried at reduced pressure (0.1 mmHg *ca.* 13.3 Pa) over fused $CaCl_2$.

Preparation of the Complexes.—*Solution* (A). In a saturated solution of KOH (2 g, in 20 cm^3 water), $KMnO_4$ (0.5 g, 3.2 mmol) was dissolved. The resulting solution was heated at *ca.* 80 °C with stirring and to the stirred solution KCN (3.1 g, 48 mmol) was added. Heating and stirring was continued for another few minutes and then $NH_2OH{\cdot}HCl$ (3.3 g, 48 mmol) was added portionwise. The mixture was again heated with stirring for *ca.* 30 min, when its colour became red-purple and the pH was *ca.* 10.5. This is a solution (A). Subsequently this solution was treated dropwise with dilute (1:4) HCl solution until pH *ca.* 5. This is solution A′.

Tripotassium pentacyanonitrosylmanganate dihydrate (**1**). Solution A was cooled below 10 °C and added to cold (15 °C) ethanol (90%, 100 cm^3), dropwise, without stirring. A red-purple precipitate slowly appeared. After completion of the addition, the resulting solution was kept cold (15 °C) for 20 min to allow the precipitate to settle. The supernatant was then carefully decanted to remove some of the white, flocculent mass. The red-purple solid was then filtered off, washed with ethanol, and dried. The crude product was then dissolved in water (80 cm^3) and poured over ethanol (chilled) (100 cm^3) when a red-purple product separated. The process was twice repeated, yielding shiny red-purple microcrystals. These were then washed with cold ethanol, then diethyl ether, and finally dried. Yield: 0.5 g (42%); *d* 6.42s, 4.42m, 4.09m, 3.90w, 3.65m, 3.33w, 3.21w, 3.14m, 2.90s, 2.83w,, 2.76s, 2.66w, 2.61m, 2.52w, 2.17m, 2.12w, 1.95w, and 1.85w Å.

Bis(tetraphenylphosphonium) tetracyanodinitrosylmanganate monohydrate (**2**). An aqueous (10 cm^3) solution of PPh_4Cl 2.96 g (7.9 mmol) was added to solution A′, with stirring, and the precipitated yellow solid was filtered off, washed thoroughly with water, and dried over fused $CaCl_2$ *in vacuo.* This yellow product was further crystallized from acetonitrile–diethyl ether (5:10) and finally dried. Yield: 0.8 g (30%); *d* 9.26w, 8.34w, 7.97m, 7.19m, 6.70w, 6.22m, 5.83m, 5.45w, 5.17m, 4.88w, 4.62s, 4.49m, 4.37w, 4.23m, 4.11m, 3.96w, 3.86m, and 3.66w Å.

Bis(tetramethylammonium)tetracyanonitrosylmanganatedihydrate (**3**). The above procedure was applied but with NMe_4Cl (0.86 g, 7.9 mmol) instead of PPh_4Cl. The violet compound precipitated was filtered off, washed with ethanol and finally with ether. The product was crystallized from water–ethanol (5:15). The crystalline substance was filtered off, washed with ether, and vacuum-dried. Yield 0.7 g, (75%); *d* 7.19s, 6.28w, 4.42s, 3.80w, 3.70w, 3.60m, 3.16s, 3.06m, 2.83m, 2.76m, 2.43w, and 2.20w Å.

$[Mn(NO)(CN)_3(L\text{-}L)]$ [L–L = bipy (**4a**) *or* phen (**4b**)]. The above procedure was applied but employing a hot aqueous solution (25 cm^3) of L–L [bipy (1.23 g, 7.9 mmol) or phen (1.56 g, 7.9 mmol)] instead of the counter ions. The yellowish brown precipitate was filtered off and washed with water, ethanol, and finally ether. The yellow-brown solid was then extracted with dmso and from the extract the pure solid was separated by adding water. The substance was filtered off, washed as above, and dried as usual. Yields: (**4a**) 0.75 g (75%); (**4b**) 0.8 g (80%).

Trimanganese(II) *di-μ-cyano-octacyanodinitrosyldimanganate* (**5**).—Solution A′ was concentrated on a water-bath to 10 cm^3, resulting in the separation of a silky pink compound. This was filtered off, washed quickly with water, ethanol, and ether, and dried over fused $CaCl_2$ *in vacuo.* Yield: 1.5 g (80%); *d* 10.28w, 5.20s, 4.20m, 3.80w, 3.30w, 3.20w, 2.60m, 2.50s, 2.35w, 2.20w, 2.10w, 2.00w, 1.80w, and 1.70w Å.

Tris(tetraphenylphosphonium) di-μ-cyano-hexacyanodinitrosyldimanganate trihydrate (**6a**). The filtrate obtained after the separation of the yellow compound (**2**) (see also the Scheme) was heated on a water-bath after addition of five or six drops of 6 mol dm^{-3} HCl. It was then allowed to cool to room temperature and stand overnight when green needle-shaped crystals were obtained. These were filtered off, thoroughly washed with water, and vacuum dried. The crude product was crystallized from acetone–light petroleum (b.p. 60—80 °C) (10:15). Yield: 1.1 g (25%); *d* 5.90m, 5.01w, 4.70m, 4.48m, 4.23m, 4.07m, 3.95m, 3.63w, 3.46w, and 3.23w Å.

Solution B. Potassium permanganate (0.5 g, 3.2 mmol) was dissolved in water (25 cm^3) and the solution heated at *ca.* 80 °C with stirring. Then KCN (3.1 g, 48 mmol) and $NH_2OH{\cdot}HCl$ (4.4 g, 64 mmol) were added portionwise alternatively to the above solution. A vigorous reaction occurred and ultimately a dark green solution was obtained. Reaction was continued for another 1 h and then the solution was cooled to room temperature and filtered. A clear dark green solution was obtained. The pH was adjusted from 7 to *ca.* 3.5. This is solution B.

Tris(tetraphenylphosphonium) di-μ-cyano-hexacyanodinitrosyldimanganate trihydrate (**6b**). An aqueous solution (10 cm^3) of PPh_4Cl (2.69 g, 7.9 mmol) was added to solution B, with stirring. A deep green solid then precipitated. It was filtered off, washed thoroughly with water, and dried over fused $CaCl_2$ under vacuum. The product was finally crystallized from acetone–light petroleum (b.p. 60—80 °C). Yield: 1.4 g (30%); *d* 8.67w, 7.90m, 7.23s, 6.33s, 5.90m, 5.63w, 5.22s, 4.79s, 4.69s, 4.42s, 4.20s, 4.00s, 3.60m, 3.56m, 3.52m, 3.23w, 3.13w, and 3.02w Å.

Tris(tetramethylammonium) di-μ-cyano-hexacyanodinitrosyldimanganate trihydrate (**7**). The above procedure was applied but employing NMe_4Cl (0.86 g, 7.9 mmol). A deep green solid was precipitated on concentration. It was filtered off, washed quickly with water, ethanol, and ether and then dried over fused $CaCl_2$ under vacuum. It was finally crystallized from methanol–ether (5:10), then dried under vacuum over fused $CaCl_2$. Yield: 0.6 g (30%); *d* 9.30m, 6.37s, 5.51m, 4.79w, 4.42m, 3.86m, 3.67s, 3.44w, 3.27w, 3.16w, 2.96w, and 2.62w Å.

Tricaesium di-μ-cyanohexacyanodinitrosyldimanganate trihydrate (**8**). The above procedure was applied but employing CsCl insteaed of PPh_4Cl. The deep green precipitate was filtered off and washed with ethanol and ether. It was crystallised from methanol–ether (5:10). Yield: 0.9 g (35%); *d* 9.20w, 6.86s, 5.57s, 4.98m, 4.50m, 4.09m, 3.74s, 3.18w, 3.04w, 2.64m, and 2.25w Å.

Manganese(II) *tetraphenylphosphonium μ-cyano-octacyanodinitrosyldimanganate* (**9**). The filtrate obtained after separation of the green compound (**6a**) was concentrated, whereupon a mauve silky crystalline compound graudally separated. This was filtered off, washed thoroughly with water, ethanol, and ether, and finally dried over fused $CaCl_2$ *in vacuo.* Yield: 1.2 g (45%); *d* 8.67s, 5.79m, 5.20w, 4.79s, 4.25m, 4.15w, 3.70w, 3.62m, 2.84s, 2.62m, 2.50m, 2.46w, and 2.36w Å.

[Mn(NO)(CN)$_3$(L–L)] [L–L = bipy (**10a**) *or* phen (**10b**)]. A hot aqueous solution of bipy or phen (1.2 g, 7.9 mmol; 1.56 g, 7.9 mmol) was added with stirring to solution **B** when a dark green precipitate separated. This was filtered off, washed with water, ethanol, and ether, and finally dried over fused CaCl$_2$ under vacuum. The crude compound was further crystallized from dmso–water and the pure product was finally dried over fused CaCl$_2$ under vacuum. Yields: (**10a**) 0.4 g (40%); (**10b**), 0.45 g (45%).

Dicaesium pentacyanonitrosylmanganate (**11**). The purple salt (**1**) (0.5 g) was stirred at room temperature with 6 mol dm^{-3} HNO$_3$, the resulting yellow solution was filtered and to the filtrate was added CsCl (1.47 g, 3.4 mmol). The yellow precipitate which formed was filtered off, washed quickly with ethanol, then ether, and finally dried over fused CaCl$_2$ *in vacuo*. Yield: 0.4 g (25%); *d* 5.25m, 4.44w, 4.21w, 4.11w, 3.94w, 3.74s, 3.29w, 3.12s, 3.04w, 2.75m, 2.64w, 2.55w, 2.47w, 2.22m, 2.16w, 1.98w, 1.95w, 1.86w, 1.81w, and 1.67w Å.

Bis(tetramethylammonium) pentacyanonitrosylmanganate (**12**). The same procedure as for compound (**11**) was used, but employing NMe$_4$Cl (0.86 g, 3.4 mmol) instead of CsCl. Yield: 0.3 g (25%).

Acknowledgements

This work was supported by the University Grants Commission and the Council of Scientific and Industrial Research, New Delhi. We thank the Alexander von Humboldt Foundation (West Germany) for the donation of the i.r. spectrophotometer (PE 597) used, Professor A. Chakravorty (Indian Association for the Cultivation of Science, Calcutta) for the electrochemistry and e.s.r. spectra, Professor N. Ray Chaudhuri of the same Institute for the thermoanalytical work, and Professor A. Müller (Bielefeld, West Germany) for the *X*-ray photoelectron spectrum. The *X*-ray powder diffractograms have been obtained by courtesy of the Department of Geology, of this University.

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Received 15*th February* 1989; *Paper* 9/01977D