Oxidation of Compounds Containing the π-Cyclopentadienylnitrosylmanganese Group

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The syntheses and characterisation of the thioxanthate complexes, $[(\pi\text{-}C_5H_5)Mn(NO)\{S_2CSR\}]$ (R = Bu^t, Bu^s, Bu^n, Pr^i, or Pr^n), and of the binuclear mercaptide complexes, $[(\pi\text{-}C_5H_5)Mn(NO)SR]_2^z$ (z = 0 or +1; R = Bu^t, Bu^s, or Pr^i), are described. The former group are shown, by voltammetry, to undergo a reversible one-electron oxidation, and the latter group can be oxidised in two one-electron steps. The Lewis base complexes, $[(\pi\text{-}C_5H_5)Mn(NO)LL']^+$ [L = L' = CO, P(OPh)$_3$, PPh$_3$, PMe$_2$Ph, 4-methylpyridine, bipyridyl, *etc.*], also undergo a one-electron voltammetric oxidation process. These new voltammetric data are compared with those previously obtained from related 1,2-dithiolene, 1,1-dithiolene, and dithiocarbamate complexes, and it is shown that the $E_{\frac{1}{2}}$ values can be correlated with the charge on the complex, and with the N–O stretching frequency. The data indicate that the $\{(\pi\text{-}C_5H_5)Mn(NO)\}$ group is significantly responsible for the redox behaviour of the complexes.

IN a previous series of papers, we have described how 1,2- and 1,1-dithiolato-complexes of π-cyclopentadienylnitrosylmanganese, $[(\pi\text{-}C_5H_5)Mn(NO)(S\text{–}S)]^z$ (z = 0 or −1 [S–S here represents ligands derived from *cis*-1,2-disubstituted ethylene dithiolates, benzene-1,2-dithiols, $S_2C{:}X$, where $X = C(CN)_2$, $C(CN)(CO_2Et)$, N(CN), NMe$_2$, or NEt$_2$] readily underwent reversible oxidation and/or reduction reactions leading to the generation of a three-membered electron-transfer series, *viz.* $[(\pi\text{-}C_5H_5)Mn(NO)(S\text{–}S)]^+ \rightleftharpoons [(\pi\text{-}C_5H_5)Mn(NO)(S\text{–}S)]^0 \rightleftharpoons [(\pi\text{-}C_5H_5)Mn(NO)(S\text{–}S)]^{-}$ [1,2]. However, in the molybdenum series,[3] $[(\pi\text{-}C_5H_5)Mo(NO)(I)(S\text{–}S)]^-$, only an ill-defined one-electron oxidation step was detected. Considering these facts, it occurred to us that in the manganese system, the $\{(\pi\text{-}C_5H_5)Mn(NO)\}$ group might be responsible for the extensive redox behaviour of the complexes, rather than the 1,2- or 1,1-dithiolato-ligand systems. We were reinforced in this view when we recalled that the $\{(\pi\text{-}C_5H_5)Mn(NO)\}$ group is isoelectronic with the $\{(\pi\text{-}C_5H_5)Fe(CO)\}$ group, and, since the compounds $[(\pi\text{-}C_5H_5)Fe(CO)\{S_2CNMe_2\}]$,[4] $[(\pi\text{-}C_5H_5)Fe(CO)PPh_2]_2$,[3] and $[(\pi\text{-}C_5H_5)Fe(CO)SMe]_2$ [5,6] exhibited redox behaviour, we might expect manganese compounds of an analogous type to behave similarly. In this paper, we describe some experiments designed to test this.

EXPERIMENTAL

Conductivity measurements were made at room temperature (20°) using a Phillips conductivity meter. ¹H N.m.r. spectra were recorded for carbon disulphide solutions using a Varian HA 100 spectrometer, and e.s.r. spectra were recorded in dichloromethane solutions at room temperature using a Varian E3 spectrometer. I.r. spectra were obtained using an Infracord 457 instrument and mass spectra were recorded with an A.E.I. MS 12 spectrometer.

Voltammetric data were obtained using a Beckmann Electroscan 30 Polarograph (dichloromethane as solvent). All results were standardised against an aqueous saturated calomel electrode, 1M in LiCl, and the results were corrected for *iR* drop. Cyclic voltammetric data were obtained using a stationary platinum electrode.

Microanalyses were performed by the Microanalytical Laboratory of this Department. Molecular weight data were obtained by vapour phase osmometry and mass spectrometry.[6] Yields are calculated relative to $[(\pi\text{-}C_5H_5)Mn(NO)(CO)_2][PF_6]$, which was prepared by a literature method.[7]

$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\cdot S\cdot CMe_3\}]$.—To sodium hydride (0·72 g; 50% dispersion) in dry tetrahydrofuran (THF) (10 ml) at 0° was added 1,1-dimethylethanethiol (1·35 g) in dry THF (10 ml). A white suspension of Na$^+\{SCMe_3\}^-$ formed; after 30 min carbon disulphide (2·25 ml) in dry THF (10 ml) was added dropwise with stirring. The mixture was then maintained at 0° until a clear yellow solution had formed (*ca.* 30 min).

To the yellow solution (10 ml) was added slowly, and with stirring, $[(\pi\text{-}C_5H_5)Mn(NO)(CO)_2][PF_6]$ (0·95 g) dissolved in degassed (N$_2$) acetone (50 ml). The solution, which was initially dark brown but changed to bright green, was gently warmed on a steam-bath for 10 min then evaporated *in vacuo*. The remaining solid was redissolved in acetone and chromatographed on alumina using acetone as eluant. The single green band was eluted from the column, the eluate was evaporated *in vacuo*, and residue afforded dark green crystals (0·80 g, 94%), m.p. 107—108° (from propan-2-ol). The complex was soluble in organic solvents giving green solutions; $\nu_{max.}$ (KBr) 2967m, 2920w, 1710vs, 1450m, 1423m, 1369m, 1357m, 1219w, 1162m, 1143w, 1014w, 1001w, 988s, 920s, 841m, and 813s; $\nu_{max.}$ (CH$_2$Cl$_2$) 2970w, 2962w, 2900w, 2870w, 1720s, 1370m, 1167m, 983s, 930s, 837m, and 820m cm^{-1}; τ (CS$_2$) 5·15 (5H, s, π-C$_5$H$_5$) and 8·40 (9H, s, CH$_3$); m/e 315 (M^+) and 285 ($[M - NO]^+$).

$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\cdot S\cdot CH_2\cdot CHMe_2\}]$.—This complex was prepared in the same way as its t-butyl analogue, from 3-methylpropanethiol (1·35 g), and was obtained as purple crystals (0·5 g, 59%), m.p. 70°. The complex dissolved in organic solvents giving purple solutions; $\nu_{max.}$ (KBr) 2960w, 2925w, 2870w, 1724vs, 1460w, 1423w, 1400w, 1383w, 1364w, 1248w, 990s, 958s, 840m, and 812m; $\nu_{max.}$ (CH$_2$Cl$_2$) 2965m, 2935w, 2875w, 1725vs, 1468w, 1387w, 1370w, 988s, 958s, 838m, and 820m cm^{-1}; τ (CS$_2$)

[1] J. A. McCleverty, T. A. James, and E. J. Wharton, *Inorg. Chem.*, 1969, **8**, 1340.
[2] J. A. McCleverty and D. G. Orchard, *J. Chem. Soc. (A)*, 1970, 3315.
[3] T. A. James and J. A. McCleverty, *J. Chem. Soc. (A)*, 1971, 3308.
[4] R. E. Dessy, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, 1966, **88**, 5112.
[5] R. E. Dessy, R. Kornmann, C. Smith, and R. Haytor, *J. Amer. Chem. Soc.*, 1968, **90**, 2001.
[6] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1967, **6**, 469.
[7] R. B. King, *Organometallic Synth.*, 1965, **1**, 163.

5·15 (5H, s, π-C_5H_5), 7·00 (2H, d, $-CH_2-$), 8·00 (1H, $-CH-$), and 8·95 (6H, d, CH_3), m/e 315 (M^+) and 285 ([$M - NO$]$^+$).

[(π-C_5H_5)Mn(NO){$S_2C·S·CHMe_2$}].—This complex was prepared in the same way as its t-butyl analogue, from 1-methylethanethiol (1·14 g), and was obtained as dark green crystals (0·7 g, 86%), m.p. 66°. The complex dissolved in organic solvents giving green solutions; $\nu_{max.}$ (KBr) 3110w, 2967w, 2960m, 2925m, 1860w, 1710vs, 1697s, 1455w, 1433w, 1368w, 1158w, 1061m, 978s, 950s, 833m, and 822s; $\nu_{max.}$ (CH$_2$Cl$_2$) 3030w, 2970w, 2930w, 1725vs, 1600w, 1495w, 1450w, 1060w, 980m, 952m, 838w, and 820w cm^{-1}; τ (CS$_2$) 5·15 (5H, s, π-C_5H_5), $ca.$ 6·2 (weak, $-CH-$), and 8·60 (6H, d, CH_3), m/e 301 (M^+), 271 ([$M - NO$]$^+$), 196 ([$M - NO - SCHMe_2$]$^+$), and 195 ([$M - NO - CS_2$]$^+$).

[(π-C_5H_5)Mn(NO){$S_2C·S·CH_2·CH_2Me$}].—This complex was prepared in the same way as its t-butyl analogue, but could only be isolated as a green oil; $\nu_{max.}$ (KBr) 2960s, 2930s, 2860m, 1770sh, 1720vs, 1518m, 1460m, 980s, 950s, 836w, and 815w; $\nu_{max.}$ (CH$_2$Cl$_2$) 2970m, 2935m, 2880m, 1725vs, 1610w, 1460w, 1380w, 1365w, 1060w, 983s, 957s, 838m, and 820m cm^{-1}; τ (CS$_2$) 5·16 (5H, s, π-C_5H_5), 6·91 (2H, t, $-CH_2-$), 8·30 (2H, m, $-CH_2-$), and 8·99 (3H, t, CH_3).

[(π-C_5H_5)Mn(NO){SCMe$_3$}]$_2$.—A suspension of Na$^+$-{SCMe$_3$}$^-$ in THF was prepared as previously described, and to this was added, at 0° with stirring, [(π-C_5H_5Mn(NO)-(CO)$_2$][PF$_6$] (0·95 g) in degassed acetone (50 ml). The resulting red-brown solution was stirred for 30 min at room temperature, partially evaporated in $vacuo$, and chromatographed on alumina using acetone as eluant. Two bands, one red-brown (eluted first) and the other green, separated on the column. Evaporation of the red-brown fraction afforded red-brown crystals of the complex, (0·55 g, 85%). The complex dissolved in organic solvents under N$_2$ giving red-brown solutions; $\nu_{max.}$ (KBr) 2950w, 1750m, 1720s, 1630w, 1475w, 1455w, 1445w, 1386w, 1275w, 1160m, 1018w, 1005w, 843w, 835w, and 810s; $\nu_{max.}$ (CH$_2$Cl$_2$) 2960w, 2940w, 2020w, 2900w, 1720vs, 1690sh, 1630w, 1475w, 1455w, 1380w, 1363w, 1160m, 1010w, 835w, and 815m cm^{-1}; τ [(CD$_3$)$_2$CO; 60 MHz] 5·22br (5H, s, π-C_5H_5) and 8·96br (9H, s, CH_3), m/e 478 (M^+), 448 ([$M - NO$]$^+$), 418 ($M - 2NO$]$^+$), 362 ([$M - 2NO - C_4H_8$]$^+$), 305 ([$M - NO - C_8H_{17}$]$^+$), 239 ([$M/2$]$^+$), 209 ([$M/2 - NO$]$^+$), and 179 ([$M/2 - NO - C_2H_6$]$^+$).

[(π-C_5H_5)Mn(NO){S_2CMe_3}]$_2$[PF$_6$].—The complex was obtained by evaporation of the second (green) band obtained by chromatographing the red-brown mixture described above, and was isolated, in low yields, as green crystals; yields could be increased by prior treatment of the red-brown mixture with iodine; $\nu_{max.}$ (KBr) 2930w, 1760vs, 1730vs, 1460w, 1430w, 1390w, 1365w, 1275w, 1155m, 1017w, 845s, and 560s; $\nu_{max.}$ (CH$_2$Cl$_2$) 2985w, 1770vs, 1735vs, 1475w, 1455w, 1395w, 1365m, 1150m, 850vs, and 560w cm^{-1}.

[(π-C_5H_5)Mn(NO){$S·CH_2·CHMe_2$}]$_2$ and [(π-C_5H_5)Mn(NO)-{$S·CH_2·CHMe_2$}]$_2$[PF$_6$].—These complexes were prepared in the same way as their t-butyl analogues, and were obtained as brown (0·2 g, 31%) and green (0·35 g, 54%) crystals, respectively. The brown, neutral, species dissolved, under nitrogen, in organic solvents giving brown solutions; $\nu_{max.}$ (KBr) 2960m, 2925m, 2860m, 1752vs,

1733s, 1718s, 1703s, 1660s, 1627s, 1455m, 1363m, 1270m, 1155w, 1020w, 850w, and 817w; $\nu_{max.}$ (CH$_2$Cl$_2$) 2965w, 2930w, 2860w, 1768sh, 1733m, 1675w, 1630w, 1365w, 1160w, 845w, and 815w cm^{-1}. The green species dissolved in polar organic solvents giving green solutions; $\nu_{max.}$ (KBr) 2960m, 2930w, 2880w, 1770vs, 1740vs, 1468m, 1430m, 1390m, 1360m, 1242w, 1170w, 1020w, 1010w, 850vs, and 560s; $\nu_{max.}$ (CH$_2$Cl$_2$) 2970w, 2960w, 2900w, 2880w, 1780vs, 1748vs, 1465w, 1425w, 1388w, 1370m, 1238w, 1170w, and 850vs cm^{-1}.

[(π-C_5H_5)Mn(NO){$S·CHMe_2$}]$_2$ and [(π-C_5H_5)Mn(NO)-{$S·CHMe_2$}]$_2$[PF$_6$].—These complexes were prepared in the same way as their t-butyl analogues, and were isolated as brown (0·40 g, 66%) and green (0·1 g, 13%) solids, respectively. The neutral brown species dissolved under N$_2$ in organic solvents giving red-brown solutions; $\nu_{max.}$ (KBr) 2980w, 2960m, 2920w, 2860w, 1758m, 1718vs, 1680m, 1660w, 1625w, 1450m, 1365w, 1228w, 1158w, 1042m, 1010w, 840sh, 833m, 805s, 585w, and 550w; $\nu_{max.}$ (CH$_2$Cl$_2$) 2960w, 2930w, 2860w, 1770sh, 1720vs, 1690sh, 1630w, 1378w, 1360w, 1233w, 1150w, 1047w, 1005w, 835w, and 815m cm^{-1}; τ [(CD$_3$)$_2$CO; 60 MHz] 5·20br (5H, s, π-C_5H_5) and 9·25br (6H, s, CH_3); m/e 450 (M^+), 420 ([$M - NO$]$^+$), 390 ([$M - 2NO$]$^+$), 347 ([$M - 2NO - C_3H_7$]$^+$), 385 ([$M - C_5H_5$]$^+$), 355 ([$M - NO - C_5H_5$]$^+$), 325 ([$M - 2NO - C_5H_5$]$^+$), 225 ([$M/2$]$^+$), and 195 ([$M/2 - NO$]$^+$).

RESULTS AND DISCUSSION

The new complexes are [(π-C_5H_5)Mn(NO){$S_2C·SR$}], (R = Bu^t, Bu^s, Pr^i, Pr^n, or Bu^n) and [(π-C_5H_5)Mn(NO)-SR]$_2^z$ ($z = 0$, or +1; R = Bu^t, Bu^s, or Pr^i). Many of the complexes were obtained as crystalline solids and, for the most part, were satisfactorily characterised by elemental analyses, conductivity measurements, molecular weight data (Table 1), and spectral studies. The Lewis base adducts, [(π-C_5H_5)Mn(NO)LL′][PF$_6$] (L = L′ = tertiary phosphines or phoshite, pyridines, $etc.$) have been previously described.[8]

$Synthetic$ $Studies.$—The thioxanthate complexes, [(π-C_5H_5)Mn(NO){$S_2C·SR$}], were obtained by addition of Na$^+${$S_2C·SR$}$^-$ to [(π-C_5H_5)Mn(NO)(CO)$_2$][PF$_6$] in acetone–THF. The compounds were stable in solvents in the cold, but decomposed on boiling, or on exposure to u.v. light (the nature of these decomposition products will be discussed elsewhere). Attempts to isolate thioxanthate complexes where R = Me, Et, CH$_2$Ph, or Ph were unsuccessful.

The neutral binuclear species, [(π-C_5H_5)Mn(NO)SR]$_2$, were obtained by reaction of NaSR with [(π-C_5H_5)Mn-(NO)(CO)$_2$][PF$_6$] in THF. These compounds were brown or purple, and their dimeric nature was established by osmometry, mass spectrometry and, indirectly, by voltammetry (see below). These neutral compounds were readily oxidised by air or iodine to the corresponding monocations, [(π-C_5H_5)Mn(NO)SR]$_2^+$, which were isolated directly from the reaction mixtures designed to produce the neutral compounds, as the [PF$_6$]$^-$ salts. Mixtures of the neutral and charged species could be separated conveniently by chromatography.

$Spectral$ $Studies.$—The N–O stretching frequencies

[8] T. A. James and J. A. McCleverty, $J.$ $Chem.$ $Soc.$ (A), 1970, 850.

of the new complexes are typical of terminal metal-bonded NO, and are listed together with those of analogous, previously described, sulphur complexes in Table 2.

Within the thioxanthate series, ν_{NO} occurred at *ca.* 1725 cm^{-1}, showing little variation with R, and was 15 cm^{-1} higher than the N–O stretching frequencies in the isoelectronic dithiocarbamate compounds. The

five possible isomers for these compounds, which are defined by the relative positions of the π-C$_5$H$_5$ and NO ligands with respect to the Mn(SR)$_2$Mn group (*cis* and *trans*), and by the relative orientations of the substituents R within the Mn(SR)$_2$Mn group (*syn* and *anti*). Such a problem has already been encountered in the isoelectronic [(π-C$_5$H$_5$)Fe(CO)SR]$_2^z$ ($z = 0$ or $+1$)[6,9] where the two C–O stretching frequencies

TABLE 1

Analytical and conductivity data obtained from nitrosylmanganese complexes

	Analyses (%)								
	Calc.				Found				
Complex	C	H	N	S	C	H	N	S	Λ [a]
[(π-C$_5$H$_5$)Mn(NO){S$_2$C·S·CMe$_3$}]	38·1	4·4	4·4	30·5	37·8	4·5	4·5	30·6	b
[(π-C$_5$H$_5$)Mn(NO){S$_2$C·S·CH$_2$·CHMe$_2$}]	38·1	4·4	4·4	30·5	37·8	4·4	4·3	30·1	b
[(π-C$_5$H$_5$)Mn(NO){S$_2$C·S·CHMe$_2$}]	35·9	4·0	4·6	31·9	36·1	4·0	4·6	31·2	b
[(π-C$_5$H$_5$)Mn(NO){S·CMe$_3$}]$_2$	45·2	5·9	5·9	13·4	45·2	5·6	5·9	12·3	b
[(π-C$_5$H$_5$)Mn(NO){S·CMe$_3$}]$_2$[PF$_6$]	34·7	4·5	4·5	10·3	34·2	3·8	4·6	10·2	160
[(π-C$_5$H$_5$)Mn(NO){S·CH$_2$·CHMe$_2$}]$_2$	45·2	5·9	5·9	13·4	39·6	5·5	4·9	8·7	b
[(π-C$_5$H$_5$)Mn(NO){S·CH$_2$·CHMe$_2$}]$_2$[PF$_6$]	34·7	4·5	4·5	10·3	35·3	4·5	4·9	10·9	172
[(π-C$_5$H$_5$)Mn(NO){S·CHMe$_2$}]$_2$	42·7	5·3	6·2	14·2	42·2	5·3	6·2	13·7	b
[(π-C$_5$H$_5$)Mn(NO){S·CHMe$_2$}]$_2$[PF$_6$]	32·3	4·0	4·7	10·8	32·2	3·5	4·2	10·8	176

[a] Conductivity in cm^2 mol^{-1} ohm^{-1}, in 10^{-4}M acetone solution.   [b] Non-conductor.

TABLE 2

N–O Stretching frequencies and e.s.r. spectral data obtained from some π-cyclopentadienylnitrosylmanganese sulphur complexes

	ν_{NO} (cm^{-1})			
Complex	KBr	CH$_2$Cl$_2$	$\langle g \rangle$ [a]	$\langle a \rangle_{Mn}$
[(π-C$_5$H$_5$)Mn(NO){S$_2$C·S·CMe$_3$}]	1710	1720		
[(π-C$_5$H$_5$)Mn(NO){S$_2$C·S·CH$_2$·CHMe$_2$}]	1724	1723		
[(π-C$_5$H$_5$)Mn(NO){S$_2$C·S·CHMe$_2$}]	1710, 1697	1725		
[(π-C$_5$H$_5$)Mn(NO){S$_2$C·S·CH$_2$·CH$_2$·CH$_2$Me}] [c]		1725		
[(π-C$_5$H$_5$)Mn(NO){S$_2$C·S·CH$_2$·CH$_2$Me}] [c]	1720	1725		
[(π-C$_5$H$_5$)Mn(NO){S·CMe$_3$}]$_2$		1720		
[(π-C$_5$H$_5$)Mn(NO){S·CMe$_3$}]$_2^+$ [d]		1771, 1736	2·012	36·8
[(π-C$_5$H$_5$)Mn(NO){S·CH$_2$·CHMe$_2$}]$_2$		1722		
[(π-C$_5$H$_5$)Mn(NO){S·CH$_2$·CHMe$_2$}]$_2^+$		1780, 1748	2·009	37·0
[(π-C$_5$H$_5$)Mn(NO){S·CHMe$_2$}]$_2$		1722		
[(π-C$_5$H$_5$)Mn(NO){S·CHMe$_2$}]$_2^+$		1779, 1742	2·011	36·6
[(π-C$_5$H$_5$)Mn(NO){S$_2$C:C(CN)$_2$}]$^-$		1698	2·024 [e]	67·7
[(π-C$_5$H$_5$)Mn(NO){S$_2$C:C(CN)(CO$_2$Et)}]$^-$		1710	20·24 [e]	67·9
[(π-C$_5$H$_5$)Mn(NO){S$_2$C:N(CN)}]$^-$		1690	2·016 [e]	65·8
[(π-C$_5$H$_5$)Mn(NO){S$_2$C·NMe$_2$}]		1710	2·025 [e]	67·5
[(π-C$_5$H$_5$)Mn(NO){S$_2$C·NEt$_2$}]		1710	2·025 [e]	67·5
[(π-C$_5$H$_5$)Mn(NO){S$_3$CS}]			2·013 [f]	71·2
[(π-C$_5$H$_5$)Mn(NO){S$_2$C$_2$(CN)$_2$}]$^-$		1700	2·015 [e]	56·9
[(π-C$_5$H$_5$)Mn(NO){S$_2$C$_6$Cl$_4$}]$^-$		1670	2·016 [e]	58·5
[(π-C$_5$H$_5$)Mn(NO){S$_2$C$_6$H$_3$Me}]$^-$		1670	2·016 [e]	59·0

[a] In CH$_2$Cl$_2$ at room temperature.   [b] In gauss, ^{55}Mn, $I = 5/2$, 100% abundant.   [c] Not isolated.   [d] As [PF$_6$]$^-$ salts.   [e] Data obtained from oxidised species, *e.g.* [(π-C$_5$H$_5$)Mn(NO){S$_2$C:C(CN)$_2$}]^0, *etc.*, ref. 4, 5.   [f] Species prepared in solution, ref. 5.

latter effect would be expected in view of the relatively better π-acceptor properties of S$_2$C·SR when compared with S$_2$C·NR$_2$.

The neutral dimeric species, [(π-C$_5$H$_5$)Mn(NO)SR]$_2$, exhibited a single N–O stretching frequency, again insensitive to R. However, the related monocationic species exhibited two N–O stretching frequencies in solution ($\Delta\nu$ *ca.* 35 cm^{-1}) which occurred, as expected, at higher values than those of the corresponding neutral compounds. The occurrence of only one band in the neutral complexes, and two in the monocations, is puzzling, but it must be recognised that there exist

observed were assigned to two of the possible five isomers. Definite structural assignments cannot be made, even with the help of ^{1}H n.m.r. spectra. We must conclude that in the manganese system, the neutral species are obtained isomerically pure, or that a number of isomers have coincident ν_{NO}, whereas the monocations are obtained as two isomeric forms.

The mass spectra of the thioxanthate complexes exhibited parent ions, [M]$^+$, and peaks corresponding to [M − NO]$^+$ and, in one case (R = Pr^i) [M − NO −

[9] M. Ahmad, R. Bruce, and G. R. Knox, *J. Organometallic Chem.*, 1966, **6**, 1.

$CS_2]^+$. The mass spectra of the neutral dimeric species exhibited the expected parent ions, and fragmentation patterns containing ions corresponding to $[M - NO]^+$, $[M - 2NO]^+$, $[M/2]^+$, $[M/2 - NO]^+$, and $[M - NO - R]^+$.

The thioxanthate complexes and neutral dimers were diamagnetic and exhibited ^{1}H n.m.r. spectra in accord with their structures. The spectra of the neutral dimers were, however, slightly broadened, probably because of the presence of traces of the paramagnetic methane, and the results, together with comparable information obtained from related sulphur complexes, are summarised in Table 3. Voltammetric data and N–O stretching frequencies obtained from the Lewis base adducts, $[(\pi\text{-}C_5H_5)Mn(NO)LL']^+$, are given in Table 4.

The thioxanthate complexes underwent a reversible one-electron transfer reaction corresponding to the generation of $[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\cdot SR\}]^+$; no other waves were detected in the voltammograms of these

TABLE 3

Voltammetric data obtained from some π-cyclopentadienylnitrosylmanganese sulphur complexes

Complex	$E_{\frac{1}{2}}$ [a]	R [b]	CV [c]	i_d/c [d]	Couple
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\cdot S\cdot CMe_3\}]$	+0·53	57	170	7·0	$0 \longrightarrow +1$
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\cdot S\cdot CH_2\cdot CHMe_2\}]$	+0·54	56	170	7·2	$0 \longrightarrow +1$
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\cdot S\cdot CHMe_2\}]$	+0·53	51	170	6·9	$0 \longrightarrow +1$
$[(\pi\text{-}C_5H_5)Mn(NO)\{S\cdot CMe_3\}]_2$	−0·18	53	160	7·1	$0 \longrightarrow +1$
	+0·55	52	e		$+1 \longrightarrow +2$
$[(\pi\text{-}C_5H_5)Mn(NO)\{S\cdot CH_2\cdot CHMe_2\}]_2$	−0·18	69	150	7·1	$0 \longrightarrow +1$
	+0·54	59	180	7·0	$+1 \longrightarrow +2$
$[(\pi\text{-}C_5H_5)Mn(NO)\{S\cdot CHMe_2\}]_2$	−0·33	60	170	7·2	$0 \longrightarrow +1$
	+0·43	50	h	7·1	$+1 \longrightarrow +2$
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\colon C(CN)_2\}]^-$	+0·20				$-1 \longrightarrow 0$ [f]
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\colon C(CN)(CO_2Et)\}]^-$	+0·09				$-1 \longrightarrow 0$ [f]
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\colon N(CN)\}]^{-2}$	+0·17				$-1 \longrightarrow 0$ [f]
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\cdot NMe_2\}]$	+0·42				$0 \longrightarrow +1$ [f]
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C\cdot NEt_2\}]$	+0·41				$0 \longrightarrow +1$ [f]
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C_2(CN)_2\}]^-$	+0·10				$-1 \longrightarrow 0$ [g]
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C_6Cl_4\}]^0$	−0·34				$0 \longrightarrow -1$ [g]
	+0·90				$0 \longrightarrow +1$ [g]
$[(\pi\text{-}C_5H_5)Mn(NO)\{S_2C_6H_3Me\}]^0$	−0·51				$0 \longrightarrow -1$ [g]
	+0·56				$0 \longrightarrow +1$ [g]

[a] In V, in CH_2Cl_2 vs. SCE, using rotating Pt electrode (620 r.p.m.); complex 10^{-3}M, base electrolyte $[Et_4N][ClO_4]$ (0·5M), at 20°; results corrected for iR drop, and error ± 10 mV   [b] $R = E_{\frac{3}{4}} - E_{\frac{1}{4}}$, in mV; for reversible one electron transfer reaction, viz. $[Ni\{S_2C_2(CN)_2\}_2]^- + e^- \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^{2-}$, $R = 56$.   [c] Cyclic voltammetry using stationary Pt wire and scan speeds of v/sec; for a reversible couple, $CV = 160 \pm 10$ mV.   [d] In μA mmol^{-1}; for nickel dithiolene couple, $i_d/c = 7·0$.   [e] Electrode coated. Data from ref. 5.   [g] Data from ref. 4.   [h] Coupled chemical reaction, no reduction peak.

TABLE 4

N–O Stretching frequencies and voltammetric data obtained from π-cyclopentadienylnitrosylmanganese Lewis base complexes

Complex	ν_{NO} [a]	$E_{\frac{1}{2}}$ [b]	R [c]	i_d/c [d]	CV [e]
$[(\pi\text{-}C_5H_4Me)Mn(NO)(o\text{-phen})]^+$	1749	+0·89	50	7·3	
$[(\pi\text{-}C_5H_4Me)Mn(NO)(bipyr)]^+$	1748	+0·90	56	7·3	
$[(\pi\text{-}C_5H_4Me)Mn(NO)(C_{13}H_{12}N_2)]^+$	1745	+0·92	50	6·8	170
$[(\pi\text{-}C_5H_5)Mn(NO)(CO)(PPh_3)]^+$	1794	+1·62	54	7·1	
$[(\pi\text{-}C_5H_5)Mn(NO)(CO)(PMe_2Ph)]^+$	1790	+1·6 [f]			
$[(\pi\text{-}C_5H_5)Mn(NO)(PMe_2Ph)_2]^+$	1742	+0·90	50	7·1	
$[(\pi\text{-}C_5H_5)Mn(NO)\{P(OPh)_3\}_2]^+$	1797	+1·6 [f]			
$[(\pi\text{-}C_5H_5)Mn(NO)\{P(OPh)_3\}(4\text{-Mepyr})]^+$ [h]	1769	+1·16	50	7·1	
$[(\pi\text{-}C_5H_5)Mn(NO)(PPh_3)(4\text{-Mepyr})]^+$ [h]	1740	+0·84	56	7·0	170

[a] In cm^{-1}, in CH_2Cl_2.   [b] In V, for the couple $[\text{complex}]^+ \rightleftharpoons [\text{complex}]^{2+} + e^-$, data as in Table 3.   [c] Reversibility criterion, as in Table 3, in mV.   [d] In μA mmol^{-1}; for couple $[Ni\{S_2C_2(CN)_2\}_2]^- + e^- \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^{2-}$, $i_d/c = 7·0$.   [e] Cyclic voltammetry, as in Table 3.   [f] Wave height diminished because of electrode coating.   [g] Ligand $C_{13}H_{12}N_2 = N$-(2-pyridylmethylene)-p-toluidine.   [h] Ligand 4-Mepyr = 4-methylpyridine.

monocations. The oxidised species, $[(\pi\text{-}C_5H_5)Mn(NO)SR]_2^+$, were paramagnetic ($S = 1/2$) and exhibited characteristic e.s.r. spectra in solution at room temperature (Table 2). The spectra consisted of 11 equally spaced lines and confirmed the presence of two equivalent Mn atoms (^{53}Mn, $I = 5/2$); the Mn hyperfine splittings were considerably different from those of other related manganese sulphur complexes.

Voltammetric Studies.—The new complexes were investigated by voltammetric techniques in dichloro-compounds. The half-wave potentials for this one-electron oxidation process were apparently insensitive to R, but occurred at values ca. 100 mV more positive than the corresponding dithiocarbamates. The latter is reasonable in view of the greater electron-attracting abilities of $S_2C\cdot SR$ in comparison to $S_2C\cdot NR_2$. The numerical values of $E_{\frac{1}{2}}$ indicate that synthesis of the monocations, using conventional oxidising agents, is not possible.

The binuclear complexes, $[(\pi\text{-}C_5H_5)Mn(NO)SR]_2$,

underwent two one-electron oxidation processes, corresponding to the generation of a mono- and a di-cation; no reduction waves were detected in their voltammograms. The relatively low first-oxidation potential can be correlated with the easy synthesis and stability of the monocationic species, but attempts to prepare the dication by conventional chemical methods were unsuccessful. The $E_{\frac{1}{2}}$ values for both oxidation waves in the complexes with R = Bu^t or Bu^s were almost
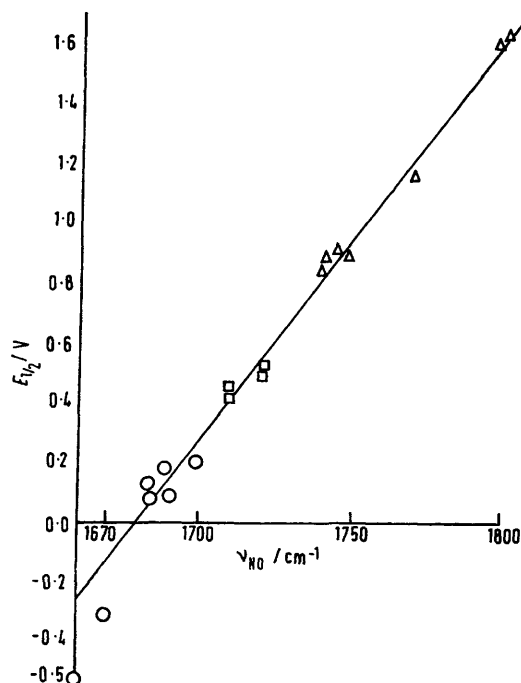
Plot of $E_{\frac{1}{2}}$ vs. ν_{NO} in CH$_2$Cl$_2$ solution for, triangles, cationic species [(π-C$_5$H$_5$)Mn(NO)LL']$^+$ (L = L' = Lewis base ligand) and [(π-C$_5$H$_5$)Mn(NO)(bidentate sulphur ligand)]^z, squares, neutral species $z = 0$; circles, anionic species $z = -1$

identical, but, surprisingly, were significantly different to those of the compound with R = Pr^i.

The Lewis base compounds, [(π-C$_5$H$_5$)Mn(NO)LL']$^+$, each exhibited one one-electron oxidation wave, whose $E_{\frac{1}{2}}$ values were highly dependent on the nature of L and L', and were relatively very positive ($\geqslant +0.84$ V). Thus, the half-wave potential values reflect very closely the π-acceptor properties of the Lewis base ligands, those compounds containing CO, P(OPh)$_3$, or PPh$_3$ in the presence of other good π-acceptors having $E_{\frac{1}{2}}$ at, or greater than, $+1.16$ V. Interestingly, the complex containing 4-methylpyridine and PPh$_3$ had a lower

$E_{\frac{1}{2}}$ value than those containing bidentate aromatic heterocycles.

Comparison of these new electrochemical results with those obtained earlier from other π-cyclopentadienyl nitrosyl manganese sulphur complexes reveals that there is a crude relationship between $E_{\frac{1}{2}}$ values for the first oxidation wave, involving isoelectronic species, e.g. [(π-C$_5$H$_5$)Mn(NO)S$_2$CX]$^-$, X = CR'R'', [(π-C$_5$H$_5$)Mn(NO)(S–S)]$^-$, (S–S) = 1,2-dithiolato-ligand, [(π-C$_5$H$_5$)Mn(NO)S$_2$CY], Y = SR or NR$_2$, and [(π-C$_5$H$_5$)Mn(NO)LL']$^+$, and the charge on the species involved. Thus, the monocationic Lewis base complexes have potentials for the couple [compound]$^+$ $\rightleftharpoons$ [compound]$^{2+}$ + e$^-$ in the range $+0.84$ to $+1.60$ V (that is, up to the breakdown of the base electrolyte-solvent system), the neutral species [(π-C$_5$H$_5$)Mn(NO)-S$_2$CY] have $E_{\frac{1}{2}}$ values in the range $+0.41$ to $+0.54$ V, and the anionic species, the largest class so far investigated, have potentials in the range -0.51 to $+0.20$ V. A further correlation can be made between $E_{\frac{1}{2}}$ values and ν_{NO} and, although this may be fortuitous and of little real physical significance, it must be recognised that ν_{NO} also depends on the charge on a series of isoelectronic complexes and on the electronic demands of the attached ligands. The only major deviants from the apparently good linear relationship between $E_{\frac{1}{2}}$ and ν_{NO} (Figure) are the 1,2-dithiolene complexes.

We consider that these results indicate that the {(π-C$_5$H$_5$)Mn(NO)} group is significantly 'redox-active' since reversible electron-transfer reactions occur in systems whose attached ligands themselves exhibit no redox activity within the voltage range investigated (-1.8 to $+1.6$ V). It has been observed by Vlcek [10] that the effects exerted by given ligands on the oxidation or reduction potentials of metal complexes containing these ligands are usually parallel but not necessarily proportional to the oxidation or reduction potentials of the free ligands. It is possible that in the Lewis base complexes, the effect of the {(π-C$_5$H$_5$)Mn(NO)} group is to lower the oxidation potentials of the Lewis bases to such an extent as to be 'visible' within the voltage scan. Even if this is so, we still believe that the metal group plays a very significant role in the total redox behaviour of the complexes.

[10] A. A. Vlcek, Progr. Inorg. Chem., 1963, **5**, 211.