Manganese(III) Complexes of 1,2-Bis(2-pyridinecarboxamido)benzene: Synthesis, Spectra, and Electrochemistry

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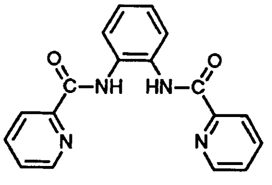
The synthesis and solution properties of the high-spin ($\mu_{eff.}$ = 4.78—4.86 at 298 K) manganese(III) complexes [Mn(bpb)X] [X = Cl^-, N_3^-, or SCN^-; H_2bpb = 1,2-bis(2-pyridinecarboxamido)benzene], are described. The brown crystalline complexes display ligand-to-metal charge-transfer transitions at *ca.* 430 nm, while in the near-infrared region crystal-field transitions are observed. In *N,N*-dimethylformamide solution the complexes exhibit a quasi-reversible Mn^{III}–Mn^{II} couple [$E_{298}°$ −0.03 to + 0.03 V *vs.* saturated calomel electrode (s.c.e.)]. The complexes [Mn(bpb)Cl] and [Mn(bpb)(N_3)] display an additional quasi-reversible Mn^{IV}–Mn^{III} couple [$E_{298}°$ +0.87 (Cl^-); +0.49 V (N_3^-) *vs.* s.c.e.].

High-valent oxoiron–porphyrin species have been proposed as active intermediates in the catalytic cycle of catalases,[1–3] peroxidases,[1–3] cytochrome P-450,[2–4] and cytochrome c oxidase.[2,5] While oxoiron(IV)–porphyrin complexes have been studied extensively[6] as simple active-site models for these biological systems, those of chromium[7] and manganese[8] have proven fruitful in terms of redox and/or oxygen-atom transfer[9] chemistry. The present work stems from our interest in the development of non-porphyrin synthetic oxidation catalysts.[10]

It has been recognized that organic amide groups stabilize high oxidation states of metal ions when co-ordinated with the deprotonated nitrogen.[11] The bis(picolinamide) ligand 1,2-bis(2-pyridinecarboxamido)benzene (H_2bpb) is known[12,13] to co-ordinate to a central metal atom in both the protonated and deprotonated amide forms. The dianionic form (bpb) has been used in the generation[14,15] of highly oxidizing metal complexes. Che and Cheng[15] demonstrated the epoxidation of cyclohexene, styrene, and toluene in acetonitrile using the manganese(III) complexes [Mn(bpb)X] (X = Cl^- or N_3^-) in the presence of iodosylbenzene. They proposed[15] the involvement of a high-valent oxomanganese intermediate in the epoxidation of these organic substrates, without throwing any light on the solution properties (u.v.–visible spectra, electrochemistry *etc.*) of these complexes. It is noteworthy that only a small number of rather scattered reports of non-porphyrin manganese(III) complexes of tetradentate N_4 ligands have appeared in the literature.[16] We have therefore undertaken a systematic study of manganese(III)–bpb complexes to gain further information on their syntheses and detailed characterization. In this investigation we have tried to probe the generality of the synthetic procedure and, more importantly, to unravel the solution properties of the manganese(III) complexes [Mn(bpb)X] (X = Cl^-, N_3^-, or SCN^-) by use of i.r. and u.v.–visible spectroscopy, solution electrical conductivity, and measurements of effective magnetic moment in solution. Their redox behaviour has also been examined using electrochemical techniques.

Experimental

Chemicals and Starting Materials.—Solvents and reagents were obtained from commercial sources and used without further purification unless otherwise stated. Methanol was distilled from magnesium methoxide. *N,N*-Dimethylformamide (dmf) was purified first by azeotropic distillation with benzene followed by shaking with alumina (neutral) and vacuum distillation. Pyridine was dried by distilling over sodium hydroxide pellets. Tetrabutylammonium perchlorate was prepared from tetrabutylammonium bromide (Aldrich Chemical Co.) and 70% aqueous perchloric acid. This was recrystallized from ethanol and dried *in vacuo*. The ligand H_2bpb[17] and $Mn(O_2CMe)_3 \cdot 2H_2O$[18] were prepared as previously described. The quaternary ammonium salts $[NBu^n_4]N_3$ and $[NBu^n_4]SCN$ were prepared by metathesis of NaN_3 and KSCN with $[NBu^n_4]Cl$ in acetone.



H_2bpb

Measurements.—Spectroscopic data were obtained by using the following instruments: electronic spectra, Perkin-Elmer Lambda-2 spectrophotometer; i.r. spectra (KBr disc, 4 000—200 cm^{-1}), Perkin-Elmer M-580 IR spectrophotometer; ^1H n.m.r. spectra, PMX-60 JEOL (60 MHz) or Brüker WP-80 spectrometer. Solution electrical conductivity was measured with an Elico conductivity bridge (Hyderabad, India) type CM-82 T with solute concentrations of *ca.* 10^{-3} mol dm^{-3}. Cyclic voltammetric measurements were performed by using a PAR model 370-4 electrochemistry system: 174A, polarographic analyzer; 175, universal programmer; and RE 0074, *x*—*y* recorder. Potentials are reported at 298 K relative to a saturated calomel reference electrode (s.c.e.) and are uncorrected for junction potentials. A sealed all-glass cell was used; measurements were made under an atmosphere of dinitrogen. The auxiliary electrode, which consisted of a platinum flag sealed in soft glass, and the reference electrode were separated from the working solution by means of a fritted bridge filled with the same solvent and supporting electrolyte. Uncompensated solution resistance in the cell configuration was minimized by placing the tip of the reference electrode as close to the working electrode as possible and using an approximately constant ratio of $[NBu^n_4]ClO_4$ supporting electrolyte and solute concentration (≈100:1). A PAR G0021 glassy carbon electrode was used as the working electrode. The system was calibrated against ferrocene, $[Fe(\eta\text{-}C_5H_5)_2]$,[19a] and tris(2,2′-

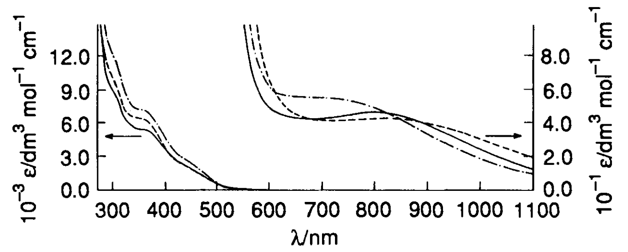


Figure 1. Electronic spectra of [Mn(bpb)Cl] (——), [Mn(bpb)(N_3)] (– – –), and [Mn(bpb)(NCS)] (– . – . –) in dmf solution

bipyridine)iron(II) perchlorate, $[Fe(bipy)_3][ClO_4]_2$.[19b] With the same electrode assembly in dmf solution and at a scan rate of 50 mV s^{-1} the values for $E_{298}°$ and the peak-to-peak separation (ΔE_p) for $[Fe(bipy)_3]^{2+}$ were 1.11 V and 100 mV respectively. The magnetic susceptibility measurements in solution were made by the method of Evans[20] and made use of the paramagnetic shift of the methyl protons of dmf and the $SiMe_4$ reference as the measured n.m.r. parameter; the susceptibility of dmf[21a] and diamagnetic corrections[21b] were taken from the literature.

Syntheses of [Mn(bpb)X] (X = Cl^-, N_3^-, *or* SCN^-).—The compounds were prepared by using similar procedures as outlined in the literature.[15]

[Mn(bpb)Cl]. To a mixture of H_2bpb (160 mg, 0.5 mmol) and $Mn(O_2CMe)_3{\cdot}2H_2O$ (130 mg, 0.5 mmol) in methanol (15 cm^3) was added solid LiCl (300 mg, 5 mmol). The mixture was stirred at 298 K for 15 min and then heated to reflux for 1 h. It was then cooled and the precipitated brown microcrystalline complex was filtered off, washed with a small amount of methanol and dried *in vacuo* (yield *ca.* 70%). This simple procedure afforded the complex in good yield and purity (Found: C, 53.50; H, 3.15; N, 13.70. Calc. for $C_{18}H_{12}ClMnN_4O_2$: C, 53.15; H, 2.95; N, 13.80%).

[Mn(bpb)(N_3)]. A solution of NaN_3 (40 mg, 0.61 mmol) in methanol (15 cm^3) was treated with H_2bpb (160 mg, 0.5 mmol) and $Mn(O_2CMe)_3{\cdot}2H_2O$ (130 mg, 0.5 mmol) and the mixture was stirred at 298 K for 15 min and then heated to reflux for 1 h. After cooling, the brown microcrystalline solid which had formed was filtered off, washed with a small amount of methanol, and dried *in vacuo* (yield *ca.* 65%) (Found: C, 52.50; H, 3.05; N, 24.10. Calc. for $C_{18}H_{12}MnN_7O_2$: C, 52.30; H, 2.90; N, 23.75%). **CAUTION**: This complex should be treated as being potentially liable to detonate.

[Mn(bpb)(NCS)]. A mixture of H_2bpb (160 mg, 0.5 mmol) and $Mn(O_2CMe)_3{\cdot}2H_2O$ (130 mg, 0.5 mmol) was prepared in methanol (15 cm^3). To this was added solid KSCN (215 mg, 2.21 mmol) and the mixture stirred at 298 K for 15 min and then refluxed for 1 h. After cooling, the brown microcrystalline solid which had precipitated was filtered off, washed with a small amount of methanol, and dried *in vacuo* (yield *ca.* 60%) (Found: C, 52.75; H, 3.10; N, 16.45. Calc. for $C_{19}H_{12}MnN_5O_2S$; C, 53.15; H, 2.80; N, 16.30%).

Results and Discussion

Syntheses, Spectra, and Structures.—The complexes [Mn(bpb)X] (X = Cl^-, N_3^-, or SCN^-) are prepared readily using $Mn(O_2CMe)_3{\cdot}2H_2O$ and Li^+, Na^+, or K^+ salts of the appropriate anions in methanol. The manganese(III) complexes are isolated as brown crystalline solids. The syntheses and i.r. spectra of the Cl^- and N_3^- complexes have been reported previously.[15] The SCN^- complex was synthesized following a similar procedure and shows an intense ν(CN) absorption at 2 050 cm^{-1}. However, the ν(CS) stretching mode of SCN^- is apparently obscured by the ligand absorptions. The ν(CS) absorption has been shown to be diagnostic[22] of N- or S-bonded SCN^- and, less critically, the presence of ν(CN) below 2 100 cm^{-1} indicates[22] (bpb)Mn-NCS bonding. The complexes are soluble in reasonable concentrations only in dmf and dimethyl sulphoxide, and the solution studies were performed in dmf. Conductivity measurements show the Cl^- and N_3^- compounds to be predominantly non-conducting and the SCN^- derivative to behave as a 1:1 electrolyte[23] (Table). Measurements of the magnetic moments in dmf solution give values of $\mu_{eff.}$ in the range 4.78—4.86 (Table), consistent with the presence of monomeric high-spin d^4(S = 2) manganese(III) and in excellent agreement with the solid-state values of 4.7—4.9 reported previously.[15]

The absorption spectra of the complexes in dmf solution were measured in the region 270—1 100 nm. Typical spectra are shown in Figure 1 and the data are listed in the Table. The u.v.–visible spectra contain intense bands and shoulders in the u.v. and a moderately intense shoulder at *ca.* 430 nm. The intense brown colour of the manganese(III) complexes in solution is attributable to the ligand-to-metal charge-transfer transitions at *ca.* 430 nm. In the near-infrared region weak, broad absorptions are observed. The high-spin manganese(III) complexes are expected to experience strong Jahn–Teller distortions. Assuming a square-pyramidal structure for these five-co-ordinate complexes, and that the bpb ligand donor atoms are approximately equivalent, the ligand field about the metal would approximate to C_{4v} symmetry. Under this symmetry, three *d*–*d* transitions are expected: $d_{z^2} \longrightarrow d_{x^2-y^2}$ (I), $d_{xy} \longrightarrow d_{x^2-y^2}$ (II), and $d_{xz}, d_{yz} \longrightarrow d_{x^2-y^2}$ (III) (from lower to higher energy).[24] The low-energy bands observed for the Cl^- and N_3^- complexes can be assigned to transition (I) rather than (II), since the energy of this band is found to be sensitive to the nature of the axial anion (Table). As the SCN^- complex dissociates completely in solution, the absorbing species present in solution is presumably the tetragonal six-co-ordinate complex $[Mn(bpb)(dmf)_2]^+$. The higher energy observed in this instance is consistent with the decreased ligand-field strength of the axial dmf and consequent stabilization of the d_{z^2} orbital.

The spectral features of these complexes are very similar to those reported for Mn^{III}–Schiff base[24] and Mn^{III}–N_4 macrocyclic ligand[16b–d,f] complexes.

The structure of the complexes in the solid state is presumably five-co-ordinate with bpb functioning as a dianionic tetradentate N_4 ligand and the fifth co-ordination site occupied by an anion (Cl^-, N_3^-, or SCN^-). This structural pattern has been authenticated in the complexes [Mn(acen)Cl] [acen = *N,N'*-ethylenebis(acetylacetoneiminate) dianion] and [Mn(tpp)X] (X = Cl^- or N_3^-, H_2tpp = 5,10,15,20-tetraphenylporphyrin.[16a]

Electron-transfer Properties.—The purpose of the electrochemical measurements was to investigate the suitability of the bpb ligand to stabilize the manganese(III) state towards reduction, and in addition to determine whether or not an oxidative response corresponding to the accessibility of higher oxidation states could be achieved.

Manganese(III)–*manganese*(II) *couple.* All three complexes display a cyclic response with characteristic anodic (E_{pa}) and cathodic (E_{pc}) peak potentials and with $E_{298}°$ values in the range −0.03 V to +0.03 V *vs.* s.c.e. (Figure 2) due to the Mn^{III}–Mn^{II} couple. The one-electron nature of this redox response has been confirmed by comparison of current height with the redox response of a sample of $[Fe(bipy)_3]^{2+}$ under the same experimental conditions. The $E_{298}°$ values calculated from the average of the peak potentials for the oxidation and reduction waves are recorded in the Table.

Table. Molar conductances, magnetic moments, electronic spectra, and cyclic voltametric[a] data [Mn(bpb)X](X = Cl^-, N_3^-, or SCN^-) in dmf at 298 K

				Mn^{III}–Mn^{II} couple		Mn^{IV}–Mn^{III} couple	
Complex	Λ_M[b]/ Ω^{-1} cm^2 mol^{-1}	$\mu_{eff.}$[c]	λ/nm (ε/dm^3 mol^{-1} cm^{-1})	E_{298}°/V	ΔE_p/mV	E_{298}°/V	ΔE_p/mV
[Mn(bpb)Cl]	13	4.86	791(46), 435(sh)[d] (2 500), 367(sh) (5 400), 300(9 100)	0.00	140	0.87	100
[Mn(bpb)(N_3)]	16	4.78	816(43), 435(sh) (2 400), 367(sh) (6 300), 300(sh) (10 100)	−0.03	150	0.48	90
[Mn(bpb)(NCS)]	60	4.86	673(56), 435(sh) (3 100), 367(sh) (7 050), 300(sh) (12 100)	0.03	140	—	—

[a] Supporting electrolyte [NBu^n_4]ClO_4 (0.1 mol dm^{-3}); all potentials are referenced to s.c.e.; $E_{298}° = 0.5(E_{pc} + E_{pa})$; E_{pc} and E_{pa} are the cathodic and anodic peak potentials respectively; scan rate, 50 mV s^{-1} at a glassy carbon electrode. [b] Expected 1:1 electrolyte range: 65—90 Ω^{-1} cm^2 mol^{-1}. [c] Measured in solution using Evans' method.[20] [d] sh = Shoulder.

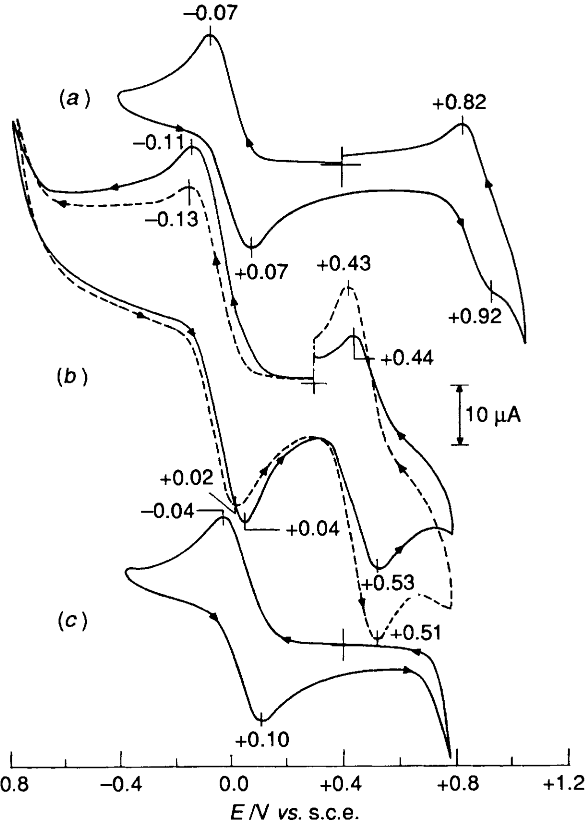


Figure 2. Cyclic voltammograms of (*a*) [Mn(bpb)Cl] (0.98 × 10^{-3} mol dm^{-3}); (*b*) [Mn(bpb)(N_3)] (1.58 × 10^{-3} mol dm^{-3}) (——) and after the addition of one equivalent of [NBu^n_4]N_3 (– – –); and (*c*) [Mn(bpb)(NCS)] (1.28 × 10^{-3} mol dm^{-3}) in dmf (0.1 mol dm^{-3} [NBu^n_4]ClO_4) at a glassy carbon electrode: scan rate 50 mV s^{-1}

The peak-to-peak separations (ΔE_p) are *ca.* 150 mV at a scan rate of 50 mV s^{-1} with anodic and cathodic peak heights being equal. The Mn^{III}–Mn^{II} couple is evidently quasi-reversible in nature. Accordingly, we assume that the lack of reversibility observed (Figure 2) is most likely due to the loss of axial ligands from the manganese(II) complex followed by solvation [equation (1)]. This behaviour has been noted

$$[Mn^{III}(bpp)X] + e^- \longrightarrow [Mn^{II}(bpb)X]^- \xrightarrow{dmf} [Mn^{II}(bpb)(dmf)_2] + X^- \quad (1)$$

previously for manganese(III) macrocyclic complexes.[25] The potentials are comparable to those for Mn^{III}–Schiff base[26] and Mn^{III}–porphyrin[27] complexes. The Mn^{III}–Mn^{II} formal potentials have a measurable dependence on the nature of the axial ligands, with the E_{298}° value for N_3^- being more negative than that for Cl^- (Figure 2, Table). The SCN^- complex cannot be considered here since it is dissociated completely in dmf solution. Among the Cl^- and N_3^- complexes the shift in the potentials and the ordering are in excellent agreement with Mn^{III}–porphyrin systems.[27]

Manganese (IV)–*manganese*(III) *couple.* An interesting feature of the [Mn(bpb)Cl] and [Mn(bpb)(N_3)] complexes is the appearance of a quasi-reversible oxidative wave at *ca.* +0.9 and +0.5 V respectively (Figure 2, Table). In an effort to determine whether the oxidation is metal- or ligand-centred, the following controlled experiments were performed. First the cyclic voltammetric behaviour of the complexes [Ni(bpb)] and [Cu(bpb)][12] in dmf was examined. Only ill defined irreversible oxidative responses at *ca.* + 1.0 V were observed, most probably as a result of oxidation of the bound ligand. Secondly the redox behaviour of [NBu^n_4]N_3 and [NBu^n_4]SCN was examined in dmf solution. Again only irreversible oxidative responses of the anions were observed and the E_{298}° values were +0.8 and + 0.96 V respectively. Thus the oxidative responses observed for [Mn(bpb)X] (X = Cl^- or N_3^-) could be due to a manganese(III) ⟶ manganese(IV) oxidation. This seems quite reasonable since the accessibility of higher oxidation states of metal ions using bpb as ligand is well documented for an electrochemically generated osmium(IV) complex[14a] and a nitridochromium(V) complex.[14b] Our results clearly demonstrate the accessibility of a formally manganese(IV) state using bpb as a ligand, thus confirming the prediction by Che and Cheng.[15]

When the axial ligand is bound to the metal centre there is a possibility of achieving the manganese(IV) state. As the SCN^- complex is almost completely dissociated in dmf solution, we do not observe a Mn^{IV}–Mn^{III} couple (Figure 2, Table). In this instance the sharp rise in the anodic current (at *ca.* +0.8 V) could be due to the oxidation of SCN^-. The current height of the oxidative response for the N_3^- complex is slightly less than the reductive response (Figure 2) possibly as a result of partial dissociation of the axial ligand. When the voltammetric experiment was performed in the presence of [NBu^n_4]N_3 enhancement of the current height was clearly observed, strengthening our hypothesis. For [Mn(bpb)Cl] there is also a decrease in the current height of the oxidative response compared to the reductive one but it is less discernible here because the wave is near the solvent cut-off limit (Figure 2).

Conclusion

Our goal of exploring the solution properties of [Mn(bpb)X] (X = Cl^-, N_3^-, or SCN^-) has been achieved. The complexes display a Mn^{III}–Mn^{II} couple subject to a shift of formal potentials under the influence of axial ligands. The accessibility of an additional Mn^{IV}–Mn^{III} couple for the Cl^- and N_3^- complexes reveals that the bpb ligand is ideally suited for stabilizing manganese in a higher oxidation state as was proposed by Che and Cheng.[15] Future work will explore the versatility of these manganese(III) complexes as potential inorganic oxidizing agents as has been done[28] with related Schiff base complexes. We have also been able to develop a rich iron chemistry using H_2bpb and bpb ligands and this will be reported elsewhere.

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