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# Manganese complexes of *bis*-benzimidazolyl ligand as novel quenchers of superoxide radical anion

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**Abstract**—A series of manganese$^{II}$/manganese$^{III}$ complexes have been synthesised utilising an exogenous anionic ligand OAc, SCN with tridentate *bis* (2-benzimidazolyl methyl) ether and tetradentate 1,2-*bis*(2-benzimidazolyloxamethyl) benzene ligands. The visible spectra of the $Mn^{III}$ compounds suggests pseudo $C_{4v}$ symmetry, and the EPR data on the manganese$^{II}$ complexes indicates a similar geometry. Cyclic-voltammetric studies reveal that the $E_{1/2}$ for the manganese$^{II}$/manganese$^{III}$ couple shifts to a positive value with acetate as an anionic ligand, implying that this anion stabilises the manganese$^{II}$ oxidation state while the $E_{1/2}$ data for SCN reveals that the anion stabilises the manganese$^{III}$ state. The reoxidation step of the superoxide formed in the cyclic-voltammetric experiments becomes irreversible in the presence of manganese complexes; suggesting that these complexes act as good quenchers for superoxide anion. © 1997 Elsevier Science Ltd

*Keywords*: Mn(III); bisbenzimidazoles; superoxide quencher.

Manganese in its +2/+3 oxidation states is the key catalytic site in a number of metallo enzymes that carry out redox reactions [1]. Among the best characterized manganese$^{III}$ containing proteins are the superoxide dismutase (MnSOD), catalases, pseudocatalases [2] the oxygen evolving complex (OEC) of Photosystem(II) [3] and possibly ribonucleotide reductase [4]. Superoxide, the one electron-reduction product of dioxygen has received much attention since it is supposed to be implicated as a cause of tissue inflammation following injury, symptoms of ageing, some cancers and the cellular degenerating process promoted by AIDS [5]. The effect could either arise from the reactivity of superoxide itself or from the hydroxyl radical intermediate derived from superoxide; the effects of superoxide are kept to minimum by the action of the superoxide dismustase (SOD) [6] family of enzymes. There is much interest in developing synthetic transition metal complexes which are able to mimic the effects of these enzymes as they would be expected to have considerable therapeutic potential [7]. Superoxide has been found to be an active intermediate in the autoxidation of heme proteins such as haemoglobin [8] and synthetic models [9].

In order to gain more insight into the reactivity of transition metal complexes with superoxides and in view of reported spectral evidence that the Mn-containing site in enzymes have N-based (histidine imidazole) terminal ligands [10], we have initiated a plan to investigate new Mn-coordination compounds with imidazole/benzimidazole based ligands, that could mimic the functional features of the active sites.

## EXPERIMENTAL

### *Materials and methods*

Solvents and reagents were of A.R. grade and used without purification. $Mn(C_2H_3O_2)_2$ was recrystallized from acetic acid and $Mn(C_2H_3O_2)_3 \cdot 2H_2O$ was prepared as previously described [11].

### *Synthesis of ligands*

*Bis*(2 benzimidazolyl methyl) ether (DGB), 1,2 *bis*(2 benzimidazolyl oxa methyl) benzene (BBB) were synthesised as follows.

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Diglycolic acid (12.1 gm, 90 mmol) for DGB and 1,2 phenylene dioxy diacetic acid (20.3 g, 90 mmol) for BBB were combined with O-phenylenediamine (19.5 g, 180 mmol) and powdered. The mixture was heated *ca* 3 h at a temperature of *ca* 150°C on an oil bath until all effervescence ceased. The resulting red–blue glass-like solid after cooling was powdered and was added to 4 M HCl (250 $cm^3$). Upon scratching the sides of the flask a grey white precipitate was obtained. This was filtered out and washed by slurrying in acetone several times. The above hydrochloride was dissolved in distilled water (200 $cm^3$) and the resulting filtrate was then neutralized with 1:1 ammonia until a white precipitate was formed this white precipitate was collected, washed with ether and recrystallized from acetone. The procedure is similar to that reported by Reed *et al.* [12]. The ligands were characterized by $^1H$ and $^{13}C$ NMR. $^1H$ NMR (DMSO-$d_6$) of $C_{16}H_{16}N_4O$(DGB): $\delta$7.7 (4H, m), 7.3 (4H, m), 4.95 (4H, S).

$^1H$ NMR (DMSO-$d_6$) of $C_{22}H_{18}N_4O_2$ (BBB): $\delta$12.6 (2H, S), $\delta$7.6 (4H, m), $\delta$7.2 (6H, m), $\delta$7.0 (2H, m), $\delta$5.3 (4H, S).

$^{13}C$ NMR (DMSO-$d_6$) of $C_{22}H_{18}N_4O_2$ (BBB): $\delta$147 ($C_2$), $\delta$138 ($C_8$, $C_9$), 122 ($C_5$, $C_6$), 115 ($C_4$, $C_7$), 64.7 (Aliphatic Carbon).

Elemental analysis and UV–vis of the ligands are reported in Tables 1 and 2.

*Synthesis of* $[Mn^{II}DGB\ X_2]\cdot nH_2O$. (X = $OAc^-$, $NCS^-$)

A solution of $Mn(CH_3COO)_2\cdot 4H_2O$ (245 mg; 1 mmol) in MeOH (5 $cm^3$) was added to the ligand (278 mg; 1 mmol) suspended in MeOH (20 $cm^3$) and a colourless solution was obtained. The solution was left for stirring for *ca* 1 h. The clear solution was then concentrated to a small volume on a rotary evaporator. The addition of ether to the clear solution precipitate's the crude product which was recrystallized from (1:2) $CH_3OCH_3$:MeOH mixture. The yield was 70%.

For the thiocyanato complex, to a solution of the $MnCl_2\cdot 2H_2O$ (1.2 mmol) in MeOH, a saturated solution of KSCN was added, until no further precipitation of KCl was obtained. This solution was centrifuged and filtrate was added to the ligand (1 mmol) suspended in 20 $cm^3$ of MeOH. The mixture was stirred for 2 h at room temperature. The clear solution was then reduced to small volume on a rotary evaporator and the product was precipitated by

Table 1. Microanalytical and magnetic moment data of $Mn^{II}/Mn^{III}$ compounds

| Compound | Formulae | C% found (calc.) | H% found (calc.) | N% found (calc.) | Mn% found (calc.) | $\mu_{eff}$ found |
|---|---|---|---|---|---|---|
| DGB | $C_{16}H_{14}N_4O$ | 68.6 (69.0) | 4.7 (5.0) | 20.5 (20.1) | — | — |
| $BBB\cdot H_2O$ | $C_{22}H_{18}N_4O_2\cdot H_2O$ | 68.9 (68.0) | 5.0 (5.1) | 14.3 (14.4) | — | — |
| $[Mn^{II}DGB(OAc)_2]\cdot 2H_2O$ | $MnC_{20}H_{20}N_4O_5\cdot 2H_2O$ | 49.3 (49.2) | 3.9 (4.9) | 12.0 (11.5) | 10.8 (11.3) | 6.02 |
| $[Mn^{II}DGB(NCS)_2]\cdot 1H_2O$ | $MnC_{18}H_{14}N_6OS_2\cdot 1H_2O$ | 47.2 (46.2) | 2.2 (3.4) | 17.8 (17.9) | 11.3 (11.7) | 6.04 |
| $[Mn^{III}DGB(NCS)_2]\cdot SCN$ | $MnC_{19}H_{14}N_7OS_3$ | 44.6 (44.9) | 2.1 (2.7) | 18.9 (19.3) | 10.2 (10.8) | 4.74 |
| $[Mn^{III}(BBB)_2OAc](ClO_4)_2\cdot H_2O$ | $MnC_{46}H_{39}N_8O_{14}Cl_2\cdot H_2O$ | 51.4 (51.5) | 3.4 (3.8) | 10.4 (10.4) | 4.7 (5.1) | 4.92 |
| $[Mn^{III}(BBB)_2NCS]\cdot(SCN)_2$ | $MnC_{47}H_{36}N_{11}O_4S_3$ | 59.0 (58.2) | 4.1 (3.7) | 15.7 (15.9) | 5.1 (5.6) | 4.89 |

Table 2. Observed optical bands (nm) and their molar extinction coefficients

| Compound | Solvent | $\lambda_{max}$ (nm) (Log $\varepsilon$, L $Mol^{-1}$ $cm^{-1}$) |
|---|---|---|
| DGB | MeOH | 252 (4.14), 272 (4.23), 282 (4.18) |
| $BBB\cdot H_2O$ | MeOH | 244 (4.13), 274 (4.29), 280 (4.21) |
| | DMSO | 250 (4.11), 278 (4.23), 282 (4.20) |
| $[Mn^{II}DGB(OAc)_2]\cdot 2H_2O$ | MeOH | 249 (4.32), 272 (4.19), 281 (4.38) |
| $[Mn^{II}DGB(NCS)_2]\cdot H_2O$ | MeOH | 250 (4.30), 271 (4.21), 280 (4.41) |
| $[Mn^{III}DGB(NCS)_2]\cdot SCN$ | DMSO | 250 (4.29), 270 (4.30), 280 (4.33), 335 (3.13), 720 (Sh) |
| $[Mn^{III}(BBB)_2OAc](ClO_4)_2\cdot H_2O$ | DMSO | 250 (4.16), 278 (4.51), 280 (4.49), 424 (2.67), 780 (2.06) |
| $[Mn^{III}(BBB)_2NCS]\cdot(SCN)_2$ | DMSO | 250 (4.21), 277 (4.50), 281 (4.51), 494 (2.46), 740 (2.14) |

addition of ether. The precipitate was recrystallized from (1:2) $CH_3OCH_3$:MeOH mixture and was air dried; yield ~ 80%.

*Synthesis of* $[Mn^{III}DGB(NCS)_2]$ SCN *and* $[Mn^{III}(BBB)_2NCS](SCN)_2$

$Mn(C_2H_3O_2)_2 \cdot 4H_2O$ (245 mg, 1 mmol) solution (5 $cm^3$) in MeOH was added to the ligand [278 mg (DGB), 370 mg (BBB); 1 mmol] dissolved in 20 $cm^3$ of MeOH. 39.5 mg (0.25 mmol) of $KMnO_4$ (which had been dissolved in 10 $cm^3$ of MeOH) was added in small portions to the above solution. After 30 min of stirring 582 mg (6 mmol) of KSCN was added to the solution followed by 1 h of stirring resulting in a brown precipitate. This was collected by filtration, washed with MeOH and was air dried.

*Synthesis of* $[Mn^{III}(BBB)_2OAc](ClO_4)_2 \cdot H_2O$

The ligand [370 mg, 1 mmol], 0.1 $cm^3$ of acetic acid and 306 mg of (2.25 mmol) $NaOAc \cdot 3H_2O$ were dissolved in 30 $cm^3$ of warm MeOH.$Mn(C_2H_3O_2)_3 \cdot 2H_2O$ (268 mg, 1 mmol) solution (5 $cm^3$) in MeOH was added to the above ligand solution and the mixture was left stirring for *ca* 1 h, after which time 1.12 g (8 mmol) of $NaClO_4 \cdot H_2O$ was added as a methanolic solution. The reaction mixture was further stirred for *ca* 2 h. The volume of the reddish/brown solution was reduced under vacuum. Upon overnight standing in the freezer a brown coloured precipitate formed. This was collected by filtration, washed with cold MeOH and was air dried.

*Physical measurements*

Elemental analyses were obtained from microanalytical laboratory of R.S.I.C. University of the Punjab, Chandigarh (India). Manganese was estimated spectrophotometrically. Electronic spectra were measured using a Beckman model DU-64 UV–vis spectrophotometer. $^1H$ and $^{13}C$ NMR were taken on Bruker 300 MHz FTNMR spectrometer at RSIC, Chandigarh (India). X-band EPR spectra were obtained on a VARIAN E-112 ESR spectrometer with a variable temperature liquid nitrogen cryostat at IIT Madras (India). IR spectra were recorded in the solid state as KBr pellets on a Perkin–Elmer model 1710 FTIR. The magnetic susceptibility was obtained in DMSO-$d_6$ with *t*-butylalcohol as an internal standard and was calculated by Evans' [13] method.

Cyclic-voltammetric measurements were carried out using a BAS, CV-50W electrochemical analysing system. A mixed solvent system DMSO:$CH_3CN$ (1:9) was employed for the CV studies with 0.1 M $NaClO_4$ as supporting electrolyte. A three electrode configuration was used, comprising of a platinum disk working electrode, platinum wire counter electrode and $Ag/AgNO_3$ reference electrode. Electrode performance was monitored by observing the ferrocenium/ferrocene ($Fc^+/Fc$) couple in the above solvent system. Experiments were carried out at room temperature (25°C) under dry nitrogen.

The cyclic voltammetric measurements of dissolved dioxygen, in DMSO:$CH_3CN$ (1:9) solvent system in the presence of manganese complexes were carried out containing 0.1 M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte, 0.001 M metal complex, at a glassy carbon electrode, with the potential referenced to $Ag/AgNO_3$ electrode. For the CV measurements under $O_2$ pressure, dry dioxygen gas was bubbled through the cell for 15 min before the measurements. The concentration of the dioxygen molecule in the reaction mixture was estimated to be at least 2 mM on the results reported by Sawyer *et al.* [14].

## RESULTS AND DISCUSSION

*Electrochemical data*

The manganese complexes used in this study did not give any oxidation and reduction peak in the CV diagram in the range of 0.0 to −1.5 V (*vs* $Ag/AgNO_3$) under dry nitrogen. The $[Mn^{II}DGB(OAc)_2]$ compound shows (Fig. 1(a)) a quasi-reversible redox wave in the region of +0.7 to 1.0 V with the $E_{1/2}$ of +0.84 V. This is ascribed to the $Mn^{II}/Mn^{III}$ oxidation couple. Similarly in the case of $[Mn^{II}DGB(NCS)_2]$ we tentatively assign (Fig. 1(b)) the $Mn^{II}/Mn^{III}$ couple in the range of +0.6 to +0.8 V with $E_{1/2}$ of +0.68 V and a subsequent couple due to $Mn^{III}/Mn^{IV}$ in the range of +1.1 to +0.92 V with an $E_{1/2}$ of +1.01 V.

Upon comparing the CV of above compound with the corresponding $[Mn^{III}DGB(NCS)_2]SCN$ it was interesting to note that the $Mn^{III}/Mn^{IV}$ couple is shifted cathodically with $E_{1/2}$ of 1.0 V. This difference possibly arises due to the presence of an additional thiocyanato ligand in the case of $[Mn^{III}DGB(NCS)_2]SCN$ that compensates for the charge difference in the above two cases.

The remaining new $[Mn^{III}(BBB)_2OAc](ClO_4)_2$ and $[Mn^{III}(BBB)_2(NCS)](SCN)_2$ compounds exhibits an irreversible oxidation wave at +0.85 and +0.95 V respectively (Table 3).

In general it appears that in comparison to the acetato complexes of the $Mn^{2+}$ ion, the thiocyanato complex is easier to oxidise, suggesting that the bivalent oxidation state is stabilised by the acetate anion but destabilised by the binding of the thiocyanate anion.

*Cyclic voltammetric measurements of dioxygen solution in the presence of manganese complexes*

Figure 2(a) depicts a reversible redox couple for dioxygen in the range of −1.0 to −1.2 V with $E_{1/2}$ of −1.11 V *vs* $Ag/AgNO_3$.

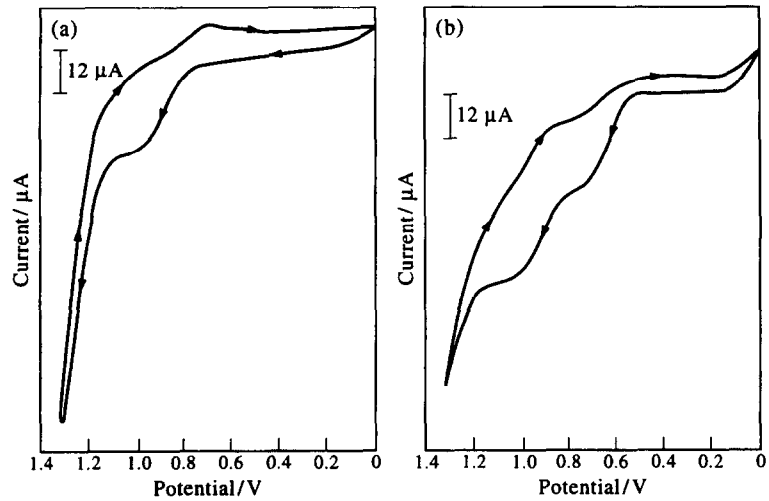


Fig. 1. (a) Cyclic-voltammogram of $[Mn^{II}DGB(OAc)_2]\cdot 2H_2O$ complex in DMSO : $CH_3CN$ (1:9) mixed solvent : scan rate 100 mV/s; (b) Cyclic-voltammogram of $[Mn^{II}DGB(NCS)_2]\cdot 1H_2O$ complex in DMSO : $CH_3CN$ (1:9) mixed solvent : scan rate 100 mV/s.

Since none of the above $Mn^{II}/Mn^{III}$ complexes show a redox wave in the region of 0.0 to $-1.5$ V, it is presumed that the changes in the redox couple of dioxygen in the presence of these compounds is indicative of the interaction of dioxygen with these manganese complexes.

Figure 2(b–f) shows that in the presence of manganese complexes with DGB as a ligand, the reversible dioxygen redox wave becomes totally irreversible with a cathodic potential which is slightly positive than that observed for the $O_2$–$O^{\cdot}_2^-$ (dioxygen to superoxide radical anion, Table 4). Such a phenomenon has been earlier ascribed to weak interaction of dioxygen to metal ion complex [15].

It is interesting to compare the results of dioxygen interaction to manganese complexes with DGB and BBB as ligand, it is found that for both $[Mn^{III}(BBB)_2OAc](ClO_4)_2$ and $[Mn^{III}(BBB)_2NCS](SCN)_2$ a prepeak at a fairly anodic potential (Table 4) is observed, this prepeak corresponds to the reduction of a species $[Mn^{III}\cdots O_2]$ where the dioxygen molecule is strongly interacting with the manganese complexes. The presence of a reduction wave beyond the potential of $O_2$–$O^{\cdot}_2^-$ in the case of $[Mn^{III}(BBB)_2OAc]^{2+}$ suggest that in this particular case the $[Mn^{III}\cdots O_2]$ species is capable of undergoing a two electron stepwise reduction to a species that may be assigned to a species $[Mn^{III}\cdots O_2^{2-}]$. This is probably amongst the few examples where both a pre- and a post peak has been observed [16,17]. Since in the presence of all the above complexes the reoxidation step of superoxide ion formed at $-1.21$ V (Table 4) becomes irreversible, this is consistent with the presumption that these complexes act as good quenchers for the superoxide anion radical.

*Electronic spectra, IR, EPR and magnetic susceptibility*

The ligands and their manganese complexes show UV spectra characteristic of the benzimidazolyl group, absorption bands and their extinction coefficients are given in Table 2. The UV bands are all blue shifted upon coordination and in general possess enhanced intensity, implying the binding of C=N to the metal centre [18].

Figure 3(a,b) shows the visible spectra of $[Mn^{III}DGB(NCS)_2]SCN$ and $[Mn^{III}(BBB)_2OAC](ClO_4)_2$ complexes in DMSO. The visible part of the spectrum show bands in the region of 335, 400–500 and 700–780 nm. The variation in $\lambda_{max}$ observed in the visible region indicates that the axial anion ($OAc^-SCN^-$)

Table 3. Cyclicvoltammetric data of $Mn^{II}/Mn^{III}$ complexes at 298 K

| Compound | $E_{Pa}$ (V) | $E_{Pc}$ (V) | $E_{1/2}$ (V) | $\Delta E$ (V) |
|---|---|---|---|---|
| $[Mn^{II}DGB(OAc)_2]\cdot 2H_2O$ | +0.98 | +0.70 | +0.84 | +0.28 |
| $[Mn^{II}DGB(NCS)_2]\cdot H_2O$ | +1.10 | +0.92 | +1.01 | +0.18 |
| | +0.80 | +0.57 | +0.68 | +0.23 |
| $[Mn^{III}DGB(NCS)_2]SCN$ | +1.10 | +0.88 | +0.99 | +0.22 |
| $[Mn^{III}(BBB)_2OAc](ClO_4)_2\cdot H_2O$ | +0.85 | — | — | — |
| $[Mn^{III}(BBB)_2NCS](SCN)_2$ | +0.93 | — | — | — |

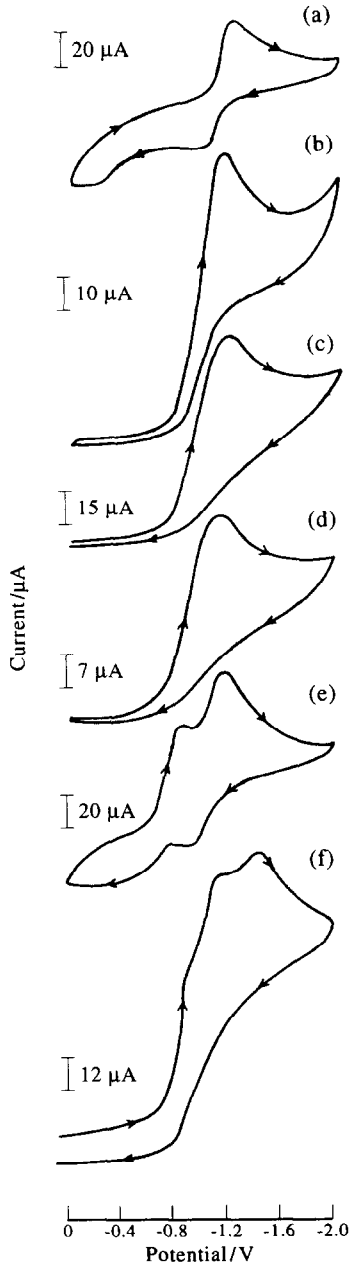


Fig. 2. Cyclic-voltammograms of DMSO:$CH_3CN$ (1:9) solution containing 0.1 M TBAP (a) saturated with dioxygen (~2.0 mM); (b) containing $[Mn^{II}DGB(OAc)_2]\cdot 2H_2O$; (c) containing $[Mn^{II}DGB(NCS)_2]\cdot H_2O$; (d) containing $[Mn^{II}{}^{I}DGB(NCS)_2]SCN\cdot H_2O$; (e) containing $[Mn^{III}(BBB)_2NCS(NCS)_2]$; (f) containing $[Mn^{III}(BBB)_2OAc](ClO_4)_2\cdot H_2O$. Scan rate 100 mV/s; temperature 25°C.

remains bound to $Mn^{III}$ centre in the solution and this is supported by our electrochemical studies.

The extinction coefficient of the bands in the near-UV region at 335 nm clearly indicate it to be charge transfer band, most likely assignable to $\sigma(N) \rightarrow Mn^{III}$ LMCT [19], while broad bands are observed at 424, 494 and 720–780 and have much lower extinction coefficients.

The broadening/splitting of the band is evidence for a Jahn–Teller distortion. This behavior is therefore best discussed in terms of pseudo $C_{4v}$ symmetry about the $Mn^{III}$ ion [20,21] in solution (Fig. 4). Under this symmetry the electronic energy level ordering $^5B_1 < {}^5B_2 < {}^5A_1 < {}^5E$ is employed in interpreting our data. The bands at 424 nm and 494 nm are assigned to $^5B_1 \rightarrow {}^5E$ while the broad band at 720 nm and 780 nm is assigned to the $^5B_1 \rightarrow {}^5B_2$ transition, respectively.

IR spectra were taken in KBr pellets. In free ligand, a strong band is found at *ca* 1460 $cm^{-1}$ with another weaker band at *ca* 1490 $cm^{-1}$. By analogy with the assigned bands for imidazole, the 1460 $cm^{-1}$ band is attributed to $\nu$(C=N—C=C—), while the other band is an overtone or combination [22].

In the present case, we find that the shift is of the order of 20 $cm^{-1}$ in the complex. This implies direct coordination of imine nitrogen atom to $Mn^{III}$. This is the preferred nitrogen atom for coordination as found in other complexes with benzimidazole [18,23]. In the acetate complex a strong band for perchlorate anion appears in the region of 1080–1110 $cm^{-1}$ suggesting the presence of ionic perchlorate and new bands at 1570 $cm^{-1}$ and 1320–1340 $cm^{-1}$ are assigned to a unidentate mode of binding of acetate group.

The thiocyanato complex has two bands in its infrared spectra characteristic of a coordinated NCS ligand [24,25], namely $\nu$(C—N) at 2080 $cm^{-1}$ and at 840–860 $cm^{-1}$. The $\nu$(C—S) stretching frequency is described as more useful in distinguishing the N and S coordinated thiocyanate. The $\nu$(C—S) at 840–860 $cm^{-1}$ falls in the region expected for an N bonded NCS group (780–860 $cm^{-1}$).

Figure 5(a,b) illustrates the X-band solid state EPR spectrum of the $[Mn^{II}DGB(OAc)_2]$ and $[Mn^{II}DGB(NCS)_2]$ complexes at 77 K. The spectrum of $Mn^{II}DGB(OAc)_2$ exhibits a strong signal in the $g \simeq 2.3$ region with a broad signal arising in the region of $g \simeq 4$. While the EPR spectra of $[Mn^{II}DGB(NCS)_2]$ complex shows a broad signal in the $g \simeq 3$ region. The EPR and analytical data suggest an axially distorted $Mn^{II}$ complex [26].

No well pronounced signal has been observed in the solid state EPR spectra at 77 K in any of the $Mn^{III}$ complexes. This indicates that the principal zero field splitting parameter D is greater than 0.33 $cm^{-1}$.

Magnetic susceptibility was determined by using Evans' method in DMSO-$d_6$. The magnetic moments were in the range 6.02–6.04 B.M. for the $Mn^{II}$ complexes and 4.74–4.90 B.M. for $Mn^{III}$ complexes. The error of ±0.2 B.M. is typical for Evans' method. These experimental $\mu_{eff}$ are in the range found for other $d^5$ $Mn^{II}$/$d^4$ $Mn^{III}$ complexes.

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Table 4. The reduction potential CV *vs* $Ag/AgNO_3$ of dioxygen molecule in (1:9) DMSO:$CH_3CN$ mixed solvent system, scan rate 100 mV/s in the absence and presence of $Mn^{II}/Mn^{III}$ complexes

| Dioxygen molecule in the absence and presence of $Mn^{II}/Mn^{III}$ compounds | $E_{Pa}$ (V) | $E_{Pc}$ (V) |
|---|---|---|
| Free dioxygen | −1.01 | −1.21 |
| $[Mn^{II}DGB(OAc)_2]\cdot 2H_2O$ | — | −1.15 |
| $[Mn^{II}DGB(NCS)_2]\cdot H_2O$ | — | −1.20 |
| $[Mn^{III}DGB(NCS)_2]SCN$ | — | −1.14 |
| $[Mn^{III}(BBB)_2OAc](ClO_4)_2\cdot H_2O$ | — | −1.02[a], −1.20, −1.56[b] |
| $[Mn^{III}(BBB)_2NCS](SCN)_2$ | −1.01, −0.46 | −0.98, −1.21 |

[a] Pre peak.
[b] Post peak.

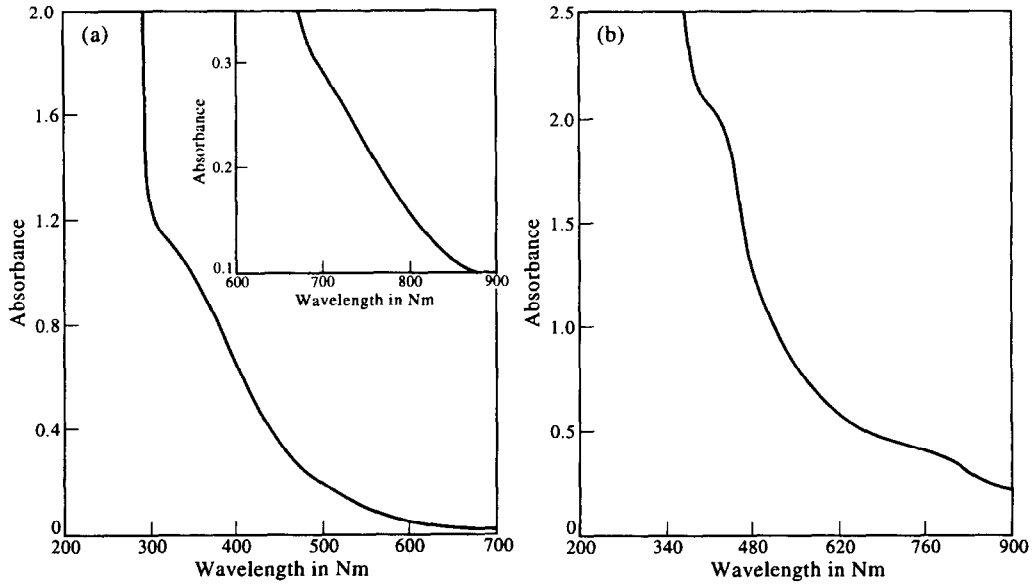
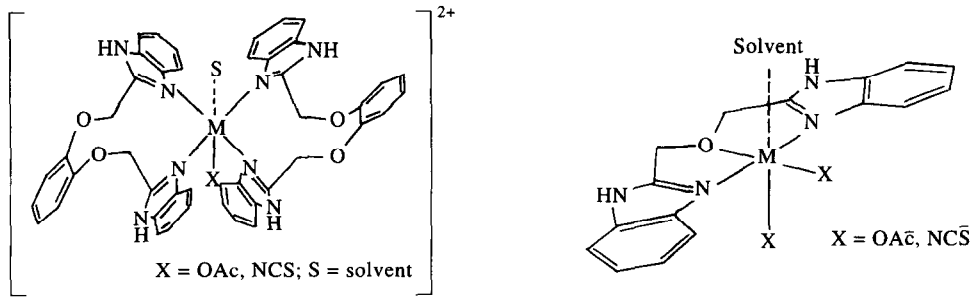



Fig. 3. (a) Visible spectra of $[Mn^{III}DGB(NCS)_2]SCN\cdot H_2O$ complexes in DMSO; (b) Visible spectra of $[Mn^{III}(BBB)_2OAc(ClO_4)_2$ complex in DMSO.




Proposed structure of [Mn( III) $(BBB)_2$ $X]^{2+}$ in solution  Proposed structure of [Mn( II)DGB $X_2$] in solution

Fig. 4. Proposed structure of $[Mn^{III}(BBB)_2X]^{2+}$ in solution. Proposed structure of $[Mn^{II}DGBX_2]$ in solution.

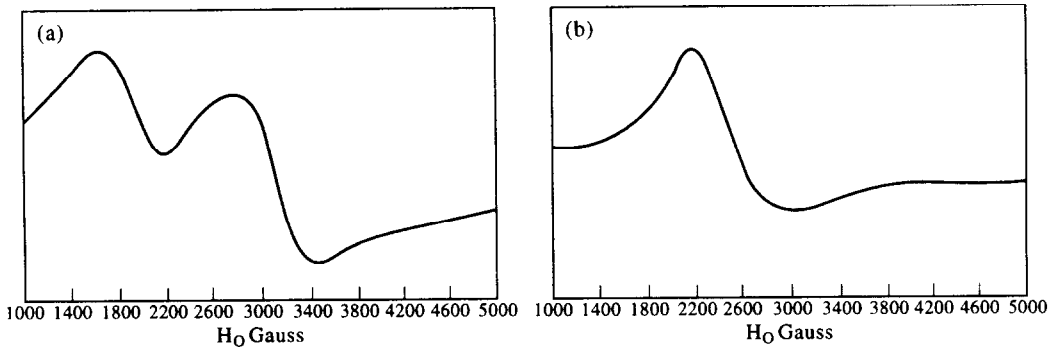



Fig. 5. (a) 4000 G scan of $[Mn^{II}DGB(OAc)_2]$ in solid state conditions: receiver gain = $10 \times 10^2$; microwave power 20 mW; microwave frequency 9.02 GHz; $T$ = 77 K at X-band, centred at 3000 G; (b) 4000 G scan of $[Mn^{II}DGB(NCS)_2]$ in solid state conditions: receiver gain = $2.0 \times 10^2$; microwave power 20 mW; microwave frequency 9.02 GHz; $T$ = 77 K at X-band, centred at 3000 G.

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