Manganese (IV) and Manganese (V) Complexes with *N*-(2-Hydroxyphenyl)-salicylamides†

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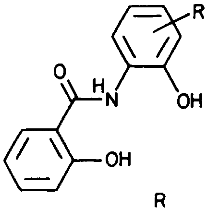
N-(2-Hydroxyphenyl)salicylamide (H_3L^1) and its homologues with a substituent on the 2-hydroxyphenyl moiety (5-Me, H_3L^2; 5-Cl, H_3L^3; 4-NO_2, H_3L^4; 5-NO_2, H_3L^5) form manganese(IV) complexes of general composition $K_2[MnL_2]$ (L = L^1—L^5) when treated with manganese(II) ion in methanolic KOH solution in air. They were characterized by their magnetic moments at room temperature ($\mu_{eff.}$ = 3.67—4.06), molar conductances in methanol (150—170 Ω^{-1} cm^2 mol^{-1}), and e.s.r. spectra. *X*-Band e.s.r. spectra of the complexes in frozen acetonitrile solution showed signals at *ca.* 2.0 and 4.0 which were assigned to the $g_{\parallel}$ and $g_{\perp}$ components, respectively, of Kramer's doublets ($M_s = +\frac{1}{2}$ and $-\frac{1}{2}$) derived from a d^3 electronic configuration. Intense absorptions in the region 16 000—20 000 cm^{-1} were attributed to ligand-to-metal charge-transfer bands. Cyclic voltammograms of the complexes determined in CH_2Cl_2 (solubilized with 1,4,7,10,13,16-hexaoxacyclo-octadecane) showed three irreversible couples which were assigned to Mn^{VI}/Mn^{V}, Mn^{V}/Mn^{IV}, and Mn^{IV}/Mn^{III} redox processes based on controlled-potential electrolyses. The redox potential of each process was significantly affected by the electronic nature of the substituents, and the higher oxidation states of manganese were stabilized when an electron-releasing group was attached to the ligand. Chemical oxidation of $K_2[MnL^2{}_2]$ with Ce^{IV} in acetonitrile led to the isolation of a novel manganese(V) complex of composition $K[MnL^2{}_2]$, which was characterized by its magnetic moment ($\mu_{eff.}$ = 2.83) corresponding to two unpaired electrons.

Manganese can adopt a wide variety of oxidation states and this ability is certainly related to the redox function of the metal ion in biological systems. However, the co-ordination chemistry of manganese is dominated by stable manganese(II) and manganese(III) ions, and the chemistry of the metal in higher oxidation states (Mn^{4+}—Mn^{7+}) is still little known.[1] Most manganese-(VII), -(VI), and -(V) complexes so far characterized are limited to those with inorganic ligands such as halide or oxide ions,[1] and only a few manganese(IV) complexes have been obtained with organic ligands.[2–8] Some oxo-bridged dimanganese(IV)[9–13] and dimanganese(III,IV)[12–15] complexes are known, where the Mn^{IV} state must be stabilized by the oxo co-ordination. In order to develop the co-ordination chemistry of manganese in high oxidation states, it is required to design new ligands which are resistant to the high oxidizing power of the central metal and are capable of forming strong σ- as well as π-co-ordination bonds so as to satisfy the high Lewis acidity of the metal.

It has been recognized that organic amide groups stabilize high oxidation states of metal ions when co-ordinated with the deprotonated nitrogen.[16–18] Phenolic oxygen is another potential donor group to stabilize high oxidation states.[4] Hence, quadridentate ligands involving both amide and phenolic hydroxy groups have been developed,[19,20] which are shown to form stable complexes with metal ions such as cobalt(IV) and osmium(VI). This paper deals with the synthesis and characterization of manganese(IV) and manganese(V) complexes of *N*-(2-hydroxyphenyl)salicylamides (H_3L), which function as trinegative tridentate chelating agents through the deprotonated amide nitrogen and phenolic oxygens.



	R
H_3L^1	H
H_3L^2	5-Me
H_3L^3	5-Cl
H_3L^4	4-NO_2
H_3L^5	5-NO_2

Experimental

Syntheses.—Ligands H_3L. The literature method[21] was modified for the preparation of the ligands. The synthesis of H_3L^1 is described as an example. To a solution of *o*-aminophenol (20 g) in dry dioxane (100 cm^3) was added dropwise a solution of 2-acetyloxybenzoyl chloride in dioxane (60 cm^3) with stirring. Soon yellow crystals of *o*-aminophenol hydrochloride separated out. Stirring was continued at this temperature for 1 h. When water (200 cm^3) was added to the reaction mixture, the hydrochloride disappeared and *N*-(2-hydroxyphenyl)-2-acetyloxybenzamide separated out as a pale pink mass.

The crude product (5 g) was dissolved in a mixture of dioxane (40 cm^3) and concentrated hydrochloric acid (35%, 40 cm^3), and the mixture was stirred for 24 h at ambient temperature. Almost colourless crystals thus formed were collected, washed with water, and recrystallized from methanol–water (80:20).

Non-S.I. unit employed: G = 10^{-4} T.

Melting points and elemental analyses of the ligands are given in Table 1.

Manganese(IV) *complexes*. The synthetic method is exemplified by that for the complex of H_3L^1. A solution of H_3L^1 (460 mg), KOH (300 mg), and manganese(II) acetate tetrahydrate (245 mg) in methanol (20 cm^3) was stirred overnight at room temperature, and the resulting dark green solution was kept in a refrigerator for 2 d. Dark green crystals thus formed were collected and recrystallized from methanol.

Manganese(V) *complex*, $K[MnL^2{}_2]$. To a solution of $K_2[MnL^2{}_2]\cdot 4.5H_2O$ (352 mg) in a mixture of methanol and *N*,*N*-dimethylformamide (1:1, 10 cm^3) a solution of $[NH_4]_2[Ce(NO_3)_6]$ (274 mg) was added, and the resulting purple solution was stirred overnight at room temperature. The reaction mixture was filtered once to separate inorganic materials. On adding water to the filtrate a purple crystalline precipitate was obtained, which was recrystallized from methanol to form purple crystals.

Elemental analyses of the manganese(IV) and manganese(V) complexes are given in Table 2.

Measurements.—Elemental analyses were obtained at the Elemental Analysis Service Center, Kyushu University. Thermogravimetric analysis (t.g.a.) was carried out on a Rigaku TG instrument. Infrared spectra were recorded on a JASCO IR spectrometer model 810 on KBr discs. Electronic spectra were recorded on a Shimadzu MPS-5000 multi-purpose spectrophotometer in *N*,*N*-dimethylformamide (dmf). Molar conductances were determined in methanol at 25 °C with a Yanagimoto MY-8 molar conductance outfit. Magnetic susceptibilities were determined by the Faraday method at room temperature, and the magnetic moments calculated using the equation $\mu_{eff.} = 2.828(\chi_A \cdot T)^{\frac{1}{2}}$, where χ_A is the susceptibility corrected for the diamagnetism of the constituent atoms by Pascal's constants. *X*-Band e.s.r. spectra were obtained in frozen acetonitrile solutions at liquid nitrogen temperature with a JES-ME-3 spectrometer. Direct current (d.c.) polarograms, cyclic voltammograms (c.v.s), and differential pulse polarograms (d.p.p.s) were obtained on a Yanagimoto P-1000 voltammetric analyzer, with a three-electrode cell equipped with a working electrode (glassy carbon for c.v. and d.p.p.), a platinum coil as the auxiliary electrode, and a saturated calomel electrode (s.c.e.) as reference.

Table 1. Melting points and elemental analysis of ligands

		Found (%)			Calculated (%)		
Ligand	M.p. (°C)	C	H	N	C	H	N
H_3L^1	165—166	68.0	4.85	6.00	68.1	4.85	6.10
H_3L^2	161—162	68.9	5.40	5.70	69.15	5.40	5.75
H_3L^3	189—191	59.15	3.85	5.15	59.2	3.80	5.30
H_3L^4	271—272	56.85	3.75	10.15	56.95	3.70	10.2
H_3L^5	238—239	56.75	3.70	10.05	56.95	3.70	10.2

Results and Discussion

Analytical results showed the general formula of the complexes obtained to be $K_2[MnL_2]\cdot nH_2O$ (n = 1—4.5). The presence of water was demonstrated by a broad i.r. band near 3 400 cm^{-1} (Nujol mull) and evaluated by t.g.a. (dehydrated at 120 °C). The results are given in Table 2. The free ligands show the amide vibrations at 1 620 and 1 560 cm^{-1}, while the corresponding vibrations in the complexes shift to 1 590 and 1 520 cm^{-1}, respectively. The ligands presumably act as trinegative tridentate chelating agents through the deprotonated amido nitrogen and phenolic oxygens. Molar conductivities for the complexes determined at a concentration of *ca.* 1 × 10^{-3} mol dm^{-3} in methanol fall in the range 150—170 Ω^{-1} cm^2 mol^{-1} (Table 3). The results clearly indicate that the complexes behave as 1:2 electrolytes in methanol,[22] consistent with the formula from elemental analyses.

The magnetic moments ($\mu_{eff.}$) of the complexes fall in the range 3.67—4.06 (Table 3), which are close to the spin-only value (3.87) for three unpaired electrons. Based on these observations we conclude that $K_2[MnL_2]$ are six-co-ordinate manganese(IV) complexes. All attempts to obtain single crystals suitable for *X*-ray analysis were unsuccessful.

Table 2. Elemental analysis of complexes

	Found (%)						Calculated (%)					
Complex	C	H	N	H_2O^a	Mn^b	K^b	C	H	N	H_2O	Mn	K
$K_2[MnL^1{}_2]\cdot 3.5H_2O$	47.6	3.00	4.35	10.3	8.7	13.0	48.15	3.45	4.30	11.0	8.5	12.1
$K_2[MnL^2{}_2]\cdot 4.5H_2O$	47.95	3.70	4.45	10.8	8.4	10.4	48.4	4.20	4.05	11.7	7.9	11.3
$K_2[MnL^3{}_2]\cdot 2H_2O$	44.75	2.45	4.05	6.2	7.5	11.0	45.25	2.65	4.05	5.2	8.0	11.3
$K_2[MnL^4{}_2]\cdot H_2O$	45.5	2.65	7.85	3.5	7.6	12.1	45.05	2.35	8.10	2.6	7.9	11.3
$K_2[MnL^5{}_2]\cdot 2H_2O$	43.95	2.80	7.75	4.8	8.1	10.5	43.9	2.55	7.85	5.1	7.7	11.0
$K[MnL^2{}_2]$	59.35	4.35	5.10		9.6	7.8	58.55	3.50	4.90		9.6	6.8

[a] Determined by t.g.a. [b] Determined by atomic absorption spectrometry.

Table 3. Molar conductance, magnetic moment, and electronic spectral data of complexes

Complex	Λ_M/Ω^{-1} cm^2 mol^{-1} [a]	$\mu_{eff.}$ [b]	$10^{-3}\lambda_{max.}/cm^{-1}$ (log ε/dm^3 mol^{-1} cm^{-1}) [c]			
$K_2[MnL^1{}_2]\cdot 3.5H_2O$	159	4.06	15.7 (sh)	20.0 (sh)		30.8 (4.33)
$K_2[MnL^2{}_2]\cdot 4.5H_2O$	167	3.76	16.4 (3.29)	21.0 (sh)		31.4 (4.62)
$K_2[MnL^3{}_2]\cdot 2H_2O$	151	3.67	15.9 (3.48)	20.0 (3.55)		30.3 (4.39)
$K_2[MnL^4{}_2]\cdot H_2O$	154	3.74	16.2 (sh)	19.7 (3.90)	23.5 (4.33)	32.7 (4.46)
$K_2[MnL^5{}_2]\cdot 2H_2O$	155	3.98	16.4 (sh)	19.5 (sh)	22.6 (4.28)	33.4 (4.35)
$K[MnL^2{}_2]$		2.83		19.8 (3.08)		31.5 (4.38)

[a] Determined at 25 °C in methanol. [b] At 295 K. [c] In dmf; sh = shoulder.

Table 4. Electrochemical data[a] of manganese(IV) complexes

	Mn^{VI}/Mn^{V} c.v.[b]		d.p.p.[c]	Mn^{V}/Mn^{IV} c.v.[b]		d.p.p.[c]	Mn^{IV}/Mn^{III} c.v.[b]		d.p.p.	
Complex	E_{pc}	E_{pa}	$E_{\frac{1}{2}}$	E_{pc}	E_{pa}	$E_{\frac{1}{2}}$	E_{pc}	E_{pa}	$E_{\frac{1}{2}}$[c]	$E_{\frac{1}{2}}$[d]
$K_2[MnL^1{}_2]\cdot3.5H_2O$	0.75	0.42	0.59	0.14	−0.07	0.09	−0.70	−1.08	−0.89	−0.89
$K_2[MnL^2{}_2]\cdot4.5H_2O$	0.76	0.50	0.65	0.38	0.14	0.27			−0.82	−0.83
$K_2[MnL^3{}_2]\cdot2H_2O$	1.08	0.64	0.79	0.75	0.24	0.46			−0.75	−0.77
$K_2[MnL^4{}_2]\cdot H_2O$	1.32		1.09	0.88		0.75	−0.36	−0.83	−0.65	−0.49
$K_2[MnL^5{}_2]\cdot2H_2O$	1.36	0.78	1.08	0.87	0.54	0.71	−0.48		−0.74	−0.63

[a] Values in V *vs.* s.c.e., scan rate 80 mV s^{-1} for c.v. and 10 mV s^{-1} for d.p.p. [b] Determined on a glassy carbon electrode in CH_2Cl_2. [c] On glassy carbon electrode in CH_2Cl_2. [d] Determined on dropping mercury electrode in dmf.

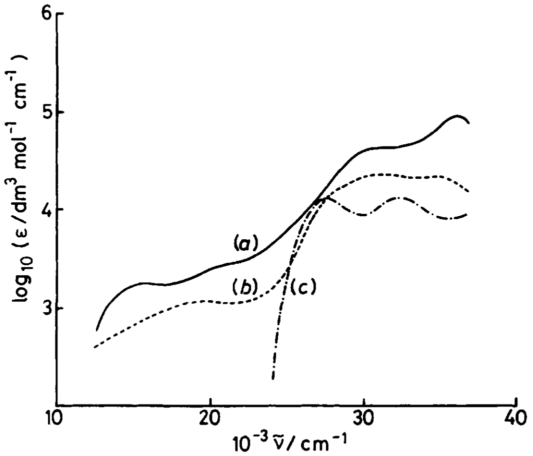


Figure 1. Electronic spectra of (*a*) $K_2[MnL^2{}_2]\cdot4.5H_2O$ and (*b*) $K[MnL^2{}_2]$ in dmf, and (*c*) H_3L^2 in dmf containing KOH (0.002 mol dm^{-3})

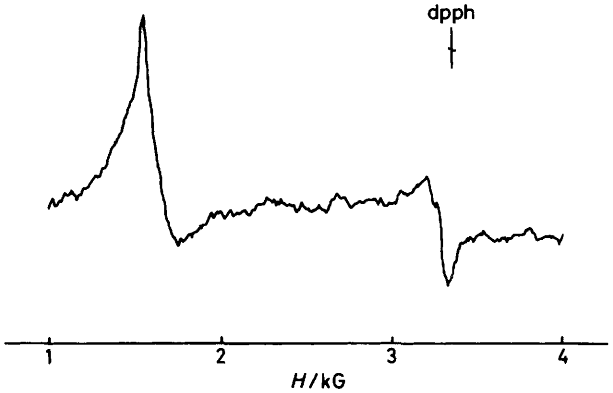


Figure 2. E.s.r. spectrum (*X*-band) of $K_2[MnL^3{}_2]\cdot2H_2O$ in CH_3CN at 77.3 K (dpph = diphenylpicrylhydrazyl)

Electronic spectra of the complexes in water obey Beer's law in the concentration range 1 × 10^{-3} to 1 × 10^{-4} mol dm^{-3}, and show two absorption bands in the region 16 000—20 000 cm^{-1} and some absorptions of higher intensity at higher frequency. However, the spectra gradually changed, the intensities of the bands at 16 000—20 000 cm^{-1} decreasing with time. This suggests that the complexes undergo dissociation or decomposition in water. On the other hand, the complexes are fairly stable in dmf, since no spectral change was observed in this solvent. A typical spectrum in dmf is shown in Figure 1, together with that of the corresponding free ligand measured in dmf solution containing KOH (0.002 mol dm^{-3}). Numerical data are given in Table 3. The spectra in dmf are essentially the same as those in fresh aqueous solutions. The very intense absorption near 32 000 cm^{-1} may be assigned to an intra-ligand transition. This band is shifted by 3 000 cm^{-1} to lower frequency compared with the corresponding band of the free ligand. For the complexes of H_3L^4 and H_3L^5, containing a nitro substituent, another intense absorption is seen near 23 000 cm^{-1}, which is also assigned to an intra-ligand transition. This absorption is also shifted by *ca.* 3 000 cm^{-1} to lower frequency on complexation. For octahedral manganese(IV) complexes three spin-allowed *d–d* transitions [$^4T_{2g}\leftarrow{}^4A_{2g}$, $^4T_{2g}(F)\leftarrow{}^4A_{2g}$, $^4T_{1g}\leftarrow{}^4A_{2g}$] are expected. The absorption bands found in the region 16 000—20 000 cm^{-1}, however, cannot be assigned to the spin-allowed *d–d* transitions, because (*i*) their absorption coefficients are very large ($\varepsilon >$ 1 × 10^3 dm^3 mol^{-1} cm^{-1}) and (*ii*) their frequencies are lower than expected from the crystal-field splitting of $[MnF_6]^{2-}$ (Δ 21 750 cm^{-1}).[23] These bands may be assigned to charge-transfer transitions, probably from the phenolic oxygen(s) to the *d* orbital of the manganese(IV) ion.[2]

Powder samples of the complexes showed no e.s.r. signals, either at room temperature or liquid nitrogen temperature. In frozen acetonitrile solution at 77.3 K, however, the complexes showed well resolved e.s.r. spectra composed of two signals at *g ca.* 4.0 and 2.0 (Figure 2). It is known that the nature and complexity of frozen-solution e.s.r. spectra of d^3 ions depend upon the zero-field splitting parameters,[24–26] and the spectra are simplified when the zero-field splitting parameter *D* takes the limiting form $2D \gg h\nu$ or $2D \ll h\nu$. In the former case two signals occur at *g ca.* 2.0 (weak) and *g ca.* 4.0 (strong),[3] whereas in the latter case the dominating signal is at *g ca.* 2.0 with one or more weak signals at lower field.[26,27] Therefore, the spectra observed for the present complexes correspond to the case of $2D \gg h\nu$, and the *g ca.* 4.0 and 2.0 signals can be assigned to the $g_{\perp}$ and $g_{\parallel}$ components, respectively, of the transitions between the Kramer's doublets $M_S = +\frac{1}{2}$ and $-\frac{1}{2}$. In general, octahedral complexes of d^3 ions show a small zero-field splitting,[28] and the manganese(IV) complexes with thiohydroxamates[3] and $[MnMe_3(dmpe)]$ [dmpe = 1,2-bis(dimethylphosphino)ethane][29] also showed e.s.r. spectra corresponding to $2D \ll h\nu$.

The polarograms of the complexes determined in dmf showed one reduction wave. Since free ligands do not show such a reduction wave down to −1.5 V, the wave observed is attributed to a redox process at the metal centre. Numerical data are given in Table 4. The number of electrons transferred in this process, however, could not be determined because of its irreversibility {the slope of the $E_{\frac{1}{2}} - E$ *vs.* log $[i/(i_d - i)]$ plot for the wave was >100 mV, where i_j is the diffusion current}.

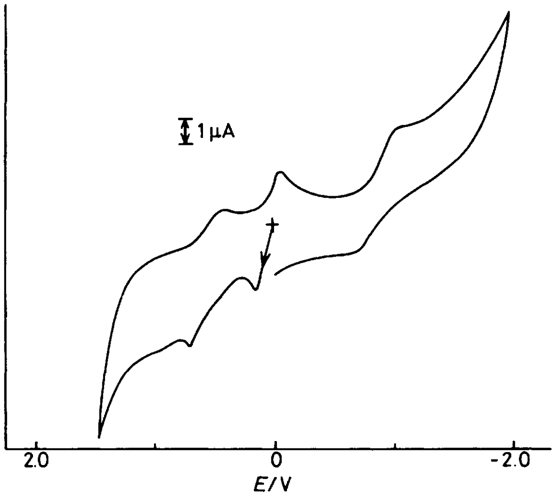


Figure 3. Cyclic voltammogram of $K_2[MnL^2_2]\cdot 4.5H_2O$ (10^{-4} mol dm^{-3}) in CH_2Cl_2 (0.1 mol dm^{-3} tbap) at a glassy carbon electrode: scan rate 80 mV s^{-1}

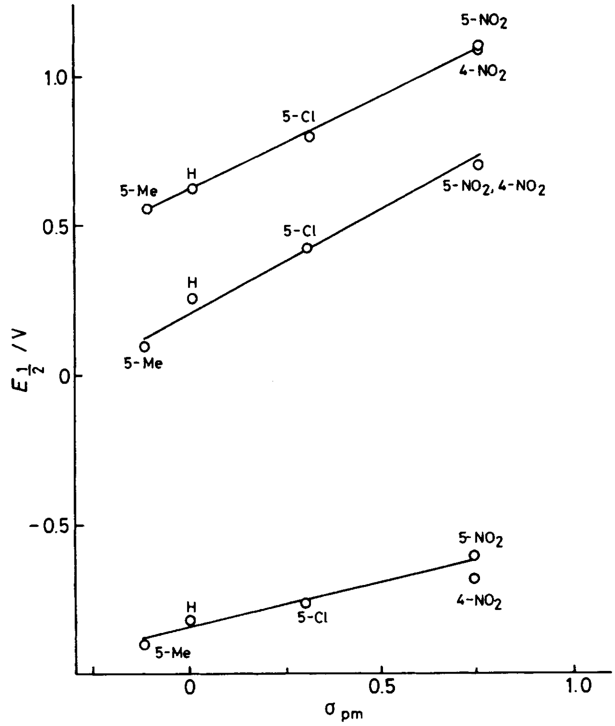


Figure 4. Correlation between the redox potentials $E_{\frac{1}{2}}$ and σ_{pm} values of the substituents R for the complexes

Our attempts to measure the oxidation wave on a solid working electrode (glassy carbon or platinum) in dmf were unsuccessful because of low stability of the complexes on these electrodes. In these measurements the colour of the solutions faded in a few seconds and uncharacterized compounds separated out.

Considerably well resolved cyclic voltammograms were obtained when the measurements were carried out in dichloromethane solution in which the complexes were solubilized using 1,4,7,10,13,16-hexaoxacyclo-octadecane. As seen in Figure 3, each complex shows three redox couples all of which are irreversible judging from the separation between the cathodic and anodic peaks. Numerical data are given in Table 4, together with the redox potential determined by differential pulse polarography. The redox potential of the third wave (lowest potential) is essentially the same as that determined by d.c. polarography in dmf. Controlled-potential electrolysis at −0.3 V did not cause any spectral change in the solution. Therefore, we may assign the three waves observed to the redox processes as shown below (from positive side).

$$[Mn^{VI}L_2]^0 \rightleftharpoons [Mn^{V}L_2]^- \rightleftharpoons [Mn^{IV}L_2]^{2-} \rightleftharpoons [Mn^{III}L_2]^{3-}$$

The Mn^{IV}/Mn^{III} redox potentials for the present complexes are *ca.* 0.5—0.6 V lower than the corresponding redox potential for manganese(IV) complexes with 2-(salicylideneimino)phenols.[2] Further, the Mn^{III}/Mn^{II} wave for the present complexes was not observed in the available potential range, while the latter complexes[2] showed the Mn^{III}/Mn^{II} wave at −1.05 to −0.75 V (*vs.* s.c.e.). Hence, it is obvious that the high oxidation state of manganese is significantly stabilized by the present ligands.

It is seen from Table 4 that the redox potentials depend upon the nature of the substituents on the ligands. The substituent on the 2-hydroxyphenyl moiety should exert an electronic effect both on the deprotonated phenolic oxygen and the deprotonated amide nitrogen. Thence, we adopt new parameters σ_{mp} for the substituent, defined by Hammett's substituent constants[30] as $\sigma_{mp} = \frac{1}{2}(\sigma_m + \sigma_p)$. When the redox potentials are plotted against the new substituent constants, good correlations are seen for all three processes (Figure 4). The results clearly indicate that the higher oxidation states of manganese are stabilized when an electron-releasing substituent is introduced into the ligand. A similar trend has been found for manganese(IV) complexes with 2-(salicylideneamino)phenols.[2]

It is to be noted that the Mn^{V}/Mn^{IV} potentials of the present complexes are very low, especially for the complexes with L^1 or L^2. This prompted us to obtain manganese(V) complexes by chemical oxidation of $K_2[MnL^2_2]$, which was achieved for the complex with L^2. Deep purple prismatic crystals of composition $K[MnL^2_2]$ were isolated when $K_2[MnL^2_2]$ was treated with Ce^{IV}. The product is stable in the solid state and shows a magnetic moment (2.83) corresponding to two unpaired electrons. Its absorption spectrum in dmf is shown in Figure 1. A very similar spectrum was obtained when one equivalent of Ce^{IV} was added to the dmf solution of $K_2[MnL^2_2]$. However, the manganese(V) complex must be decomposed or disproportionated to some extent in the solution because its frozen solution showed a six-line e.s.r. signal (*A ca.* 97 G) attributable to a manganese(II) species. To our knowledge manganese(V) complexes so far reported are limited to those of tetrahedral oxo, halogeno, or oxo–halogeno co-ordination, and $K[MnL^2_2]$ is the first example of a six-co-ordinate manganese(V) complex.

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