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Absorption Spectrum of Manganese(II) Diethylenetriamine Complexes

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The octahedral chromophore $Mn^{II}N_6$ is studied in the reflection spectrum of the solid perchlorate of the bis-diethylenetriamine cation and in aqueous solution of this complex as well as the tris-ethylenediamine analogue, in both cases protected against oxidation by hydrazine.

The absorption spectra of diethylenetriamine complexes have recently attracted considerable interest[1-4] and in many cases, quite normal octahedral complexes are formed with two molecules of the tridentate ligand, as also suggested by the formation constants.[5] Ligand field theory has successfully explained the alternating broad and narrow absorption bands of manganese(II) complexes having the ten excited quartet levels of $3d^5$ in octahedral symmetry.[6-8] However, it is an experimental difficulty to measure the very weak, spin-forbidden bands mostly having ε between 0.01 and 0.1, because the alkaline solutions produced by many ligands are extremely apt to oxidize to brown suspensions. Sometimes, traces of ascorbic acid[7] have been used to protect the solutions. It is now found that small amounts of hydrazine hydrate are even more effective to conserve limpid solutions under reasonably anaerobic conditions.

In Table I, the solution marked $Mn(den)_2^{2+}$ was made from 10 g $MnCl_2,4H_2O$ (0.05 mole) and 16 ml redistilled 6.5 molar diethylenetriamine diluted to 50 ml with water and added a few drops of hydrazine until a clear, pale violet solution was formed. This was measured in 5 cm cells on a Cary MS 14 recording spectrophotometer. A similar solution was made, 1 molar in $Mn(en)_3^{2+}$ and 1 molar in excess ethylenediamine. The essentially white crystals of $Mn(den)_2(ClO_4)_2$ were precipitated from the former solution with 5 *M* $NaClO_4$, but it was extremely difficult to keep them slightly wet with small amounts of N_2H_4. After several experiments, we succeeded in measuring the reflection spectrum with a Beckman DU spectrophotometer.

The results are in many ways an anticlimax. The solution spectra of $Mn^{II}N_6$ chromophores are quite characteristic and not at all reminiscent of the five-coordinated complexes formed by heavily alkyl-substituted diethylenetriamine.[9] The spectra obtained here are far better resolved than the previously reported[7] solution spectrum of $Mn(en)_3^{2+}$ (maxima at 15.9, 20.3, 23.7 and 26.9 kK) and in particular, the band group centered around 23.7 kK in this ion and around 23.5 kK in the slightly more covalent diethylenetriamine complex has several components. There has not been found definite evidence for co-excited vibrational lines close to 27 kK as may be the case for the hexa-aqua ion[8] at 26.54 kK (if it is not a doubly-spin-forbidden intra-sub-shell transition to a doublet level) and positively is the case[10] for $OsCl_6^{2-}$ in various solvents.

From a theoretical point of view, the most interesting conclusion is the nephelauxetic ratios $\beta_{35}=0.883$ and 0.875 for the two complexes derived by comparison of the first narrow band[11,12] with 26.85 kK for gaseous Mn^{2+}. The sub-shell energy difference Δ seems to be slightly smaller for $Mn(den)_2^{2+}$ than for $Mn(en)_3^{2+}$ in contrast to the usual position of the two amines in the spectrochemical series.[1] Thus, the second-order expression from the strong-field determinants are

$$[a^4T_{1g}] = [^4A_{1g}]-\Delta+4B-26B^2/\Delta \qquad (1)$$

assuming $C=4B$. In solution, the Δ values in kK are in this approximation

$$\begin{array}{ll} Mn(H_2O)_6^{2+} & 7.0 \\ Mn(en)_3^{2+} & 9.5 \\ Mn(den)_2^{2+} & 8.8 \end{array} \qquad (2)$$

but one should not ascribe too literal a significance to the absolute values. Recently, Foster and Gill[13] discussed the spectra of a variety of tetrahedral and octahedral manganese(II) complexes and concluded in $\Delta=7.6$ kK for the hexa-aqua ion and lower values for six halide ligands. However, the values (2) are somewhat below those for nickel(II) as one would

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Table I. Wavelengths λ, wavenumbers ν, molar extinction coefficients ε and half-widths toward smaller, δ(—), and larger, δ(+), wavenumbers. The excited levels are given in Mulliken notation.

	λ(mμ)	ν(kK)	ε	δ(—)(kK)
$Mn(den)_2(ClO_4)_2$				
a^4T_{1g}	~600	16.7	—	broad
a^4T_{2g}	495	20.2	—	broad
$^4A_{1g}$, a^4E_g	425	23.5	—	narrow
b^4T_{2g}	~385	26.0	—	shoulder
b^4E_g	360	27.8	—	narrow
$Mn(den)_2^{2+}$ aq.				
a^4T_{1g}	623	16.05	0.072	1.5
a^4T_{2g}	489	20.5	0.097	δ(+) 1.6
$^4A_{1g}$, a^4E_g	426.4	23.45	0.188	0.17
	(422.5)	23.67	0.125	—
	(419.9)	23.82	0.085	—
b^4T_{2g}	(383)	26.1	0.07	—
b^4E_g	357	28.0	(0.23)	0.7
$Mn(en)_3^{2+}$ aq.				
a^4T_{1g}	638	15.7	0.066	δ(+) 1.5
a^4T_{2g}	498	20.1	0.072	1.2
$^4A_{1g}$, a^4E_g	423.2	23.63	0.118	0.11
	421.5	23.72	0.116	—
	419.0	23.87	0.096	—
	(417.3)	23.96	0.082	—
b^4T_{2g}	375.5	26.63	0.12	0.75
	371.5	25.92	0.12	—
b^4E_g	(354.5)	28.2	(0.24)	—

expect. It may be noted that Watt and Manhas[14] prepared white $[Mn(den)_2]Br_2$. Quite recently, Larkworthy *et al.*[15] demonstrated that $\Delta = 15.0$ kK for $V(den)_2^{2+}$ is smaller than 15.6 kK for $V(en)_3^{2+}$. It may be that the central atoms V^{II} and Mn^{II} are too large to exploit the tridentate amine without steric stress.[16]

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