Synthesis & Characterization of a Neutral, Monomeric, Dinuclear Tetrahedral Manganese(II) Species

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A 2:3 manganese(II) bromide complex with 2-benzoylpyridine has been prepared and characterized from the results of molar conductance, molecular weight, room temperature magnetic moment, electronic and infrared spectral studies. The compound is monomeric and may have a dinuclear structure with a high-spin tetrahedral environment around each manganese(II) in the solid state.

Neutral, monomeric mononuclear manganese(II) complexes of the type \( \text{MnL}_2X_2 \), where \( L \) = a monodentate ligand and \( X = \text{Cl}, \text{Br}, \text{I} \) or NCS,\(^1-10\) are well known. However, no report has yet been made on monomeric dinuclear manganese(II) species exhibiting tetrahedral coordination around the metal ion. Herein we report the synthesis of a 2:3 manganese(II) bromide complex with 2-benzoylpyridine, a potentially bidentate ligand. The complex isolated has been shown, from molar conductance, molecular weight, room temperature magnetic moment, electronic and infrared spectral measurements (down to 200 cm\(^{-1}\)), to possess a neutral, monomeric dinuclear structure exhibiting high-spin tetrahedral environment around each manganese(II) in the solid state.

The manganese(II) bromide complex with 2-benzoylpyridine was prepared by mixing together hot solutions of the metal salt and excess of the ligand in ethanol. The complex, which crystallized out on cooling, was suction-filtered, washed with ethanol and dried at \( \sim 100^\circ\text{C} \) in an air oven. Mn\(_2\)(2-Benzoylpyridine)\(_3\)Br\(_4\), m.p. 157°C (Found: Mn 11.3, Br 33.0 Calc.: Mn 11.2; Br 32.7%).

Conductivity measurements were made on freshly prepared \( \sim M/1000 \) solutions in ethanol and DMF with a Philips conductivity bridge model PR 9500. Molecular weight measurements were carried out by Rast's method using camphor as the solvent. Electronic spectrum of the complex was recorded in nujol in the range 200-800 nm on a Hitachi UV/Visible spectrophotometer model 320 against nujol as a reference. Infrared spectra of the uncoordinated ligand and its manganese(II) complex were recorded in nujol on a Perkin-Elmer spectrophotometer model 783. Magnetic susceptibility was measured at room temperature by the Faraday's method with a Cahn R G Electrobalance Model 7550 using Hg[Co(NCS)]\(_4\) as the standard.

The manganese(II) bromide complex with 2-benzoylpyridine, isolated in the present study, is orange coloured and soluble in ethanol and DMF, in each of which solvents it behave as an electrolyte.\(^11\) No absorption bands were observed which could be attributed to water or ethanol in the infrared spectrum of the complex thus supporting it to be anhydrous and free from coordinated or lattice water/ethanol.

2-Benzoylpyridine possesses two potential donor sites: (i) pyridine ring nitrogen, and (ii) oxygen of the carbonyl group, and may coordinate through both or either of these sites. The infrared spectrum of the complex investigated herein shows absorption bands at 1650 and 1620 cm\(^{-1}\) due to vC=O indicating thereby the presence of two types of benzoylpyridine coordination\(^12\) (uncoordinated 2-benzoylpyridine shows vC=O at 1654 cm\(^{-1}\)). Moreover, pyridine ring vibrations at 990, 603 and 401 cm\(^{-1}\) undergo significant positive shifts\(^13\) and appear at 1012, 637 and 424 cm\(^{-1}\), respectively. The observed frequencies of vC=O and the pyridine ring vibrations strongly suggest the presence of two types of 2-benzoylpyridine molecules\(^13\) in the complex: (i) terminally pyridine ring nitrogen bonded, and (ii) pyridine ring nitrogen as well as oxygen (carbonyl) bonded bidentate ligand acting as a bridge between two manganese(II) ions.

The room temperature magnetic moment value (6.12 B.M.) of the present compound is consistent with the presence of high-spin manganese(II)\(^14\). Because of the additional stability of the half-filled d shell, manganese(II) generally forms high-spin complexes. Since the high-spin manganese(II) complexes have an orbitally non-degenerate \(^5S\) ground state term, the spin-only magnetic moment of \( \sim 5.92 \) B.M. is independent of temperature and stereochemistry. All the excited states of \( d^2 \) system have different spin multiplicities from
those of the ground state term and transitions to them are spin-forbidden. Because of the weak spin-orbit interactions, very weak absorption bands which are ~100 times weaker than the spin-allowed transitions are observed. Electronic spectra of tetrahedrally coordinated manganese(II) differ remarkably from the octahedral ones in (i) the number of bands, (ii) weakness of the bands, and (iii) variations in the widths of bands. Further, tetrahedral manganese(II) complexes are greenish-yellow or orange coloured whereas octahedral complexes are pale-pink or almost white. Moreover, the molar absorbance values for tetrahedral geometry are in the range 1.0 - 4.0 while those for octahedral ones are in the range 0.01 - 0.04. Energy level diagrams for tetrahedrally coordinated manganese(II) indicate that three sets of absorptions, each set comprising three closely-spaced bands occur in the ranges 20000-25000, 25000-28000 and 28000-50000 cm$^{-1}$ representing transitions to the excited states $^4G$, $^4D$ and $^4F$, respectively. Because of the low $\Delta$ values of tetrahedral complexes, resolution of the first two sets of closely-spaced peaks is not observed. The overlapping of bands in the third set is also severe which makes their Gaussian analysis rather difficult. Moreover, this third set of bands occurs in the region where solvent absorptions, absorptions due to the organic groups and the charge transfer bands become pertinent and tend to obscure the relatively weak $d \rightarrow d$ bands. Distinction between the ligand field and charge transfer bands cannot be made sharply if there is extensive mixing of the metal and ligand wave functions in the molecular orbitals of the complex. The observed bands in the electronic spectrum of the complex studied herein (20400, 28570 and 40000 cm$^{-1}$) are consistent with the three respective transitions, $^4G$, $^4D$ and $^4F$.

The frequencies of the observed absorption bands in the electronic spectrum and the orange colour of the complex are consistent with a tetrahedrally coordinated manganese(II), as octahedral manganese(II) complexes are either pale-pink or almost colourless and exhibit a strong absorption band at ~25000 cm$^{-1}$. In addition, the value of $10 Dq$ for tetrahedral manganese(II) complexes is much smaller than that for octahedral ones. The values for $10 Dq$ (5600 cm$^{-1}$) and $B$ (728 cm$^{-1}$) in the present study are consistent with tetrahedral environments around manganese(II).

The 650-200 cm$^{-1}$ region infrared spectrum of the present complex exhibits a strong band at 225 cm$^{-1}$ which is identified as vMn-Br mode consistent with terminally bonded metal-bromine bonds with tetrahedral environments around the metal(II) ions. The observed molecular weight (530, 528) as determined by the Rast's method suggests partial fragmentation of the dinuclear species (mol. wt. 970) into mononuclear one in molten camphor. Thus, the room temperature magnetic moment value, colour, molecular weight, electronic spectrum, ligand field parameters, presence of terminal as well as bridging 2-benzozylopyridine molecules and the vMn-Br mode of the present complex strongly suggest that it is a dinuclear tetrahedral manganese(II) species (structure I).

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References