A Manganese(II) Complex in a Pure Spin Quartet State

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Summary Manganese(II) bis(diethyl dithiocarbamate) in a spin quartet ground state has been prepared and characterised.

MANGANESE(II) complexes of (*A*) $3d^5$ configuration, are known only in $^6A_1$ and $^2T_2$ ground states in weak or strong O_h fields, respectively. In intermediate symmetry of predominantly axial field, the state $^4T_1$ may cross the above two states and lie lowest.[1] Some ferric complexes are known in this ground state.[1] There is no mention in the literature of any Mn^{II} complex with $^4T_1$ ($^4A_2$ or ^4E in axial field) as the ground state.

We have prepared manganese(II) bis(diethyl dithiocarbamate) in alcoholic medium and characterised it through low-temperature magnetic susceptibility, e.s.r. *g*-values, powder *X*-ray pattern measurements, and elemental analysis.

The magnetic susceptibility of the compound has been measured at 298·5 K and at 98·5 K, and the values are 4·1 and 3·8 B.M., respectively. These values[1] are consistent with the pure spin quartet ground state and eliminate the possibility of any dominant antiferromagnetic type of exchange interaction either direct or superexchange. E.s.r. studies of the Mn^{II} complex in the powdered state at *X*-band using 100 kHz field modulation (Varian 4500 model) at room temperature give resonance signals from which the *g*-values [$g_{\|} = 1{\cdot}92$ and $g_{\perp} = 4{\cdot}11$] have been calculated. This order of *g*-value is expected[2] from transitions between the Kramer's doublet $Ms = \pm \frac{1}{2}$ which will be separated from the $Ms = \pm 3/2$ doublet by zero field splitting. Transitions between $Ms = \pm 3/2$ levels ($\Delta M = \pm 2$) are normally difficult to observe (with *g*-values of $g_{\|} = 6$ and $g_{\perp} = 0$ in the first order.[2]) The *X*-ray powder pattern of manganese(II) bis(diethyl dithiocarbamate) and of nickel(II) bis(diethyl dithiocarbamate) indicate clearly that these are isostructural, and hence planar, since the Ni^{II} complex is known to be planar from *X*-ray analysis.[3] The i.r. spectrum of the Mn^{II} complex in KBr shows bands characteristic of the dialkyl dithiocarbamates. The i.r. spectrum of manganese(II) bis(diethyl dithiocarbamate) differs from that of manganese(III) tris(diethyl dithiocarbamate) in the same way as observed by Nakamato *et al.*[4] for planar Ni^{II}, Pt^{II}, and Pd^{II} bis(dithiocarbamates) and Co^{III} or Cr^{III} tris(dithiocarbamates) (Figure).

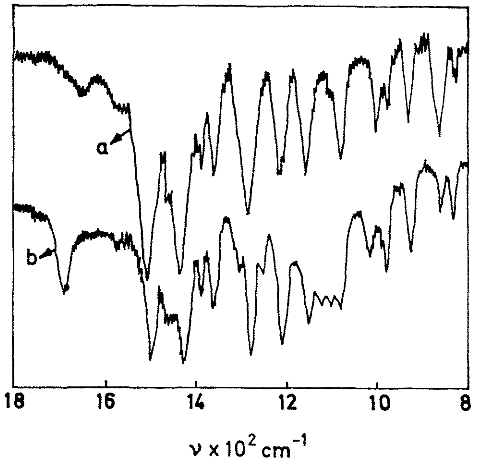

FIGURE. (a) *Manganese*(II) *bis*(*diethyl dithiocarbamate*); (b) *Manganese*(III) *tris*(*diethyl dithiocarbamate*).

Manganese(III) tris(diethyl dithiocarbamate), $Mn(C_5H_{10}NS_2)_3$, prepared in alcoholic medium, gave magnetic moment values of 4·4 B.M. at 298·5 K and 3·64 B.M. at 97 K. No e.s.r. could be observed at the *X*-band at room temperature.

The electronic spectra of both Mn^{II} and Mn^{III} complexes have been recorded in chloroform in the region 7000 to 27,000 Å. Since chloroform is not a good solvent in the near-i.r. region, and since the complexes are not very soluble in carbon tetrachloride, we intend to study the crystal spectra. We can, for the present, designate the broad bands at 8000—7700, 7200, and 6500 cm^{-1} (log ϵ 1·35) for the Mn^{II} complex as ligand-field bands, and likewise those for the Mn^{III} complex at 5900 cm^{-1} (log ϵ 1·55) and 4000 cm^{-1} (log $\epsilon = 1{\cdot}36$).

Similar results have been observed with other dialkyl dithiocarbamates. Full details of the ligand-field calculation to explain the temperature variation of magnetic susceptibility, g-values, and optical absorption will be reported in due course.

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Note added in proof: A single crystal of manganese(II) bis(diethyl dithiocarbamate) doped into the corresponding nickel(II) complex has been grown and e.s.r. studies of the polycrystalline doped material show an appreciable decrease (*ca.* 100 G) in peak to peak line width in the $g_{\parallel}$ transition with respect to the concentrated salt. Detailed studies are in progress.

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