Inorganica Chimica Acta, *168* (1990) 167–168

Inorganica Chimica Acta
LETTER

Multiline ESR From a Mn(III,III) Complex?

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(Received September 7, 1989; revised November 22, 1989)

Recently, Nishida reported the ESR spectrum of $MnL(CH_3COO)ClO_4$, where HL = 2-bis[(2-pyridylmethyl)aminomethyl]-4-nitrophenyl, in *N*,*N*-dimethylformamide at 77 K [1]. The 16-line spectrum was attributed to a dinuclear Mn(III,III) complex. The solid compound was weakly antiferromagnetic with $J = -0.88$ cm^{-1}. We consider the assignment of the frozen solution ESR spectrum to be in error for the following reason. Even if one ignores zero-field effects, a weakly coupled dinuclear system having equivalent centres with $S_1 = S_2 = 2$ and $I_1 = I_2 = 5/2$ will give rise to an 11-line pattern with intensity ratio 1:2:3:4:5:6:5:4:3:2:1. The hyperfine splitting will be equal to half that of the individual centres. The 16-line pattern with a spacing of ≈77 G is not compatible with this description. The 16-line spectrum, in all probability, arises from the doublet ground state of a strongly antiferromagnetically coupled Mn(III,IV) complex with $S_1 = 2$ and $S_2 = 3/2$. The likely source of this species is disproportionation of the original Mn(III) complex in DMF.

In another recent paper, Nishida *et al.* [2] discuss the similar multiline spectrum obtained for Mn(III) complexes of *N*-alkyl-*N*,*N*-bis(benzimidazol-2-ylmethyl)amine. The spectrum, together with their interpretation, is reproduced in Fig. 1. They suggest that the 77 K spectrum is a superposition of three 11-line spectra corresponding to three lower spin states (from among $S = 0, 1, 2, 3, 4$) resulting from magnetic coupling between two high-spin Mn(III) complex ions. The suggested components are indicated by C-1, C-2 and C-3 in Fig. 1. However, this assignment is inconsistent with the intensity pattern expected for equal hyperfine coupling with the two Mn nuclei. The four low-field lines of the C-1 set are free of overlap and should show a 1:2:3:4... pattern. However, the intensity distribution in these four lines is closer to the 1:1:2:2... pattern expected for unequal coupling with two Mn nuclei (with $A_1 \approx 2A_2$).

Our interpretation of the multiline spectrum and its temperature dependence is as follows. The Mn(III) complex disproportionates in solution and forms a Mn(III,IV) dinuclear complex. The solution therefore contains Mn(II), Mn(III) and Mn(III,IV) complex ions, all of which are paramagnetic. The major component appears to be the mixed-valence dimer which gives the usual 16-line pattern [3, 4], arising from its lowest spin state ($S = 1/2$, $A_1 \approx 2A_2$). The additional lines (marked with black dots) seen at 77 K arise most likely from the Mn(II) ions in the solution. The fact that these lines are almost invisible at 15 K is due to the relative increase in intensity of the $S = 1/2$

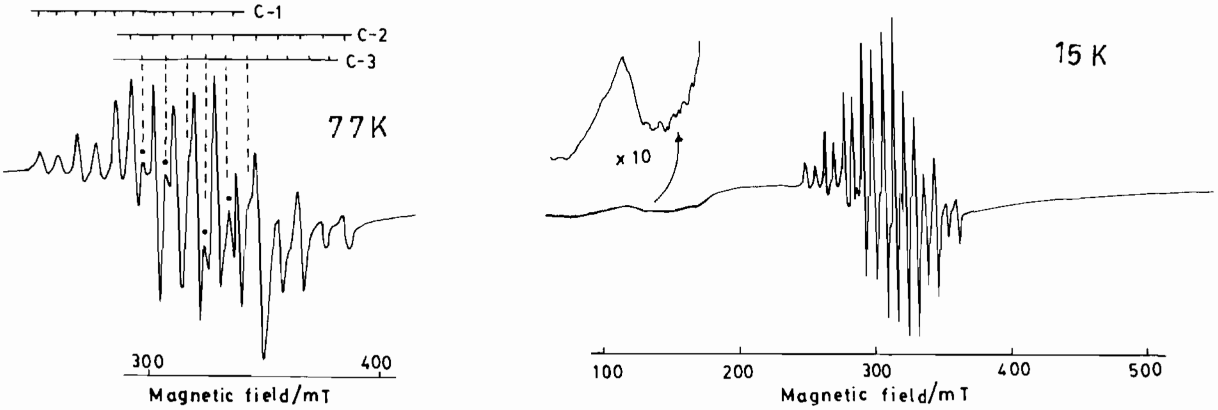

Fig. 1. X-band ESR spectra of $[Mn_2O(CH_3COO)_2L](ClO_4)_2$, L = *N*-n-propyl-*N*,*N*-bis(benzimidazol-2-ylmethyl)amine (reproduced from ref. 2).

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0020-1693/90/$3.50

signal from the Mn(III,IV) species due to depopulation of its higher excited states, while the Mn(II) intensity is practically unaffected by temperature change in the range 77–15 K. A modest $|J|$ of 30 cm^{-1} (the dioxo-bridged complexes have $|J| \gtrsim 100$ cm^{-1} [5]) will already lead to a change in the temperature factor between $S = 1/2$ and $S = 3/2$ states from 0.2 at 77 K to 0.2×10^{-3} at 15 K. The broad line having $g = 4$ seen at 15 K probably arises from the forbidden ($\Delta M_s = \pm 2$ or ± 4) transition in the free Mn(III) complex species. The Mn^{3+} ion normally has a negative D leading to the energy level ordering, $M_s = \pm 2 < \pm 1 < 0$ [6].

We have clearly not addressed the problem of identifying the actual mixed-valence species in solution. We have only presented arguments in favour of a Mn(III,IV) species as the source of the multiline spectrum. Isolation of the compound from solution and its structural characterisation will settle the issue.

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