Molecular Antiferromagnetism in a Novel Heterotrinuclear Complex of Copper(II) and Iron(III)

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Magnetic susceptibility, e.s.r., and Mössbauer data have been used to characterize the first $S = 3/2$ ground state, hetero-trinuclear cluster [{Cu(Mesalen)}$_2$Fe(acac)] [MesalenH$_2$ = *N,N'*-bis(7-methylsalicylidene)ethylenediamine; Hacac = acetylacetone] containing two copper(II) ions equally coupled antiferromagnetically to an iron(III) ion, but only weakly coupled to each other.

The synthetic model approach to the active site structure of cytochrome c oxidase has been of considerable recent interest. This structure is binuclear in copper and heme. Furthermore this binuclear centre in the resting state exhibits a strong antiferromagnetic coupling.[1] Several groups have concentrated on this aspect and models which are bimetallic Cu^{II}–Fe^{III} complexes have been proposed.[2—4] To date none of the models reproduces the magnetic properties of the coupled pair of the natural enzyme. With the intent of achieving a careful study of the interaction between the two metal ions, we report here the synthesis and magnetic properties of the first example of a hetero-trinuclear cluster containing two Cu^{II} ions and one Fe^{III} ion. The '2Cu–Fe' compound has not yet been isolated in crystalline form suitable for *X*-ray structure analysis. However, the combination of magnetic susceptibility, e.s.r., and Mössbauer spectroscopy shows the presence of magnetic coupling between the metal centres, reveals certain electronic properties of the molecule, and allows some predictions of structural features to be made. On the basis of these data, the molecular structure of this complex, [{Cu(Mesalen)}$_2$Fe(acac)] · (NO$_3$)$_2$ [MesalenH$_2$ = *N,N'*-bis(7-methylsalicylidene)ethylenediamine; Hacac = acetylacetone], may be described as a derivative of the Fe(acac)$_3$ complex in which two bidentate acac ligands have been replaced by two Cu(Mesalen) molecules acting as bridging bidentate ligands. The function of Cu(Mesalen) as a co-ordinating ligand to Fe^{3+} is analogous to Cu(Mesalen) adducts of certain divalent metal complexes reported previously by Sinn and co-workers.[5]

Cu(Mesalen) (3 mmol) was dissolved in CH_2Cl_2 (250 ml) and mixed with Fe(acac)$_3$ (0.5 mmol) and $Fe(NO_3)_3 \cdot 9H_2O$ (1 mmol) dissolved in methanol (50 ml). The resulting dark purple solution was then heated to 40 °C and stirred for 2 h. Upon cooling to room temperature, a brown-black precipitate was obtained after 2—3 h, which was filtered off, washed with CH_2Cl_2, and dried *in vacuo*; satisfactory elemental analyses were obtained for $C_{41}H_{43}N_6O_{12}Cu_2Fe \cdot \frac{1}{2}CH_2Cl_2 \cdot \frac{1}{2}H_2O$.

The magnetic moment of the sample was determined by the Faraday method (see Figure 1). E.s.r. spectra were obtained over a similar temperature range (3.8—300 K). Mössbauer spectra were recorded at 300, 77, 4.2, and 1.3 K.

Evidence for condensation of the monomeric complexes is provided by i.r. data for the Cu(Mesalen) and Fe(acac) groups. Two bands located at 1530 and 1550 cm^{-1} are observed instead of the characteristic ν_{CO} 1540 cm^{-1} band of the phenolic group of the salen, which has been shown to be shifted to higher energy when the oxygen atoms bridge two metal atoms.[6] These bands also happen to occur at the same positions as the ν_{CO} bands in Fe(acac)$_3$ where, however, they are much broader. An additional spectral feature of the cluster is a new band at 1480 cm^{-1} which cannot be assigned to either of the isolated complexes and is characteristic of trinuclear formation. Finally, the broad ν_{CO} 930 cm^{-1} band of Fe(acac)$_3$ is split into two well defined bands at 940 and and 920 cm^{-1}.

The magnetic moment data in Figure 1 may be interpreted as arising from antiferromagnetic coupling of two Cu^{II} ions with spin 1/2 to an Fe^{III} ion with spin 5/2. The minimum total spin state is 3/2, which is primarily populated at temperatures

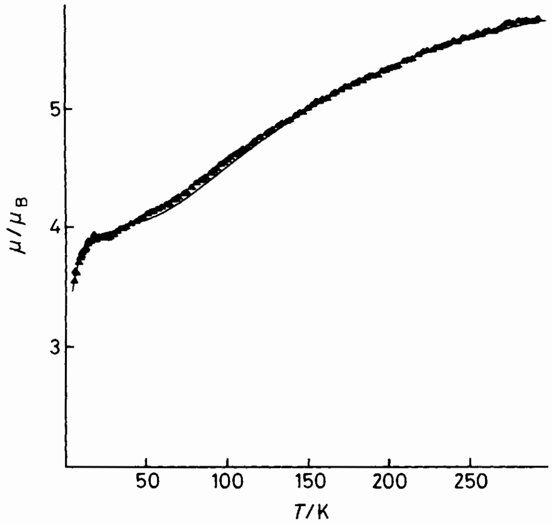

Figure 1. Magnetic moment data for the complex containing two Cu^{II} and one Fe^{III} ions.

below about 30 K. In this region, the effective moment of 3.92 μ_B is close to the value (3.88) expected for an $S = 3/2$ multiplet with $g = 2$. At higher temperatures, a larger effective moment is found owing to population of excited multiplets of higher spin multiplicities and larger moments. At lower temperatures, near 15 K, the moment decreases because kT is of the order of the zero-field-splitting. The upper of the two Kramers doublets is depopulated leaving a single doublet to contribute to the moment.

The e.s.r. data at 3.8 K show an effective spin $S = 1/2$ level with g values 4.68, 3.26, and 1.96, and an effective moment of 3.02 μ_B. This is in excellent agreement with a Kramers level from an $S = 3/2$ multiplet with rhombic zero-field splitting and a positive D parameter, and with the value expected for the magnetic moment when the magnetic susceptibility data are extrapolated to 0 K. At higher temperatures, additional resonances appear, none of which can be attributed (*via* the temperature variation of their intensity) to the upper Kramers level of the ground multiplet. This implies an upper Kramers level that is effectively nonresonant and hence must be highly anisotropic: $g_1 \gg g_2 \approx g_3 \approx 0$.

The Mössbauer spectra at 300, 77, and 4.2 K show broad patterns characteristic of paramagnetic hyperfine structure. However, between 4.2 and 1.3 K, the pattern sharpens considerably and at the lowest temperature a broad, asymmetric quadrupole pattern is found. Estimated parameters from the data at 1.3 K are $\delta E = 0.50$ mm/s (natural iron reference) and $\Delta E_Q = 0.90$ mm/s. The 'increase' of the effective electronic relaxation rate and sharpening of the pattern are connected with changes in population of the two Kramers levels, having markedly different magnetic anisotropies, from the $S = 3/2$ multiplet. An analysis for the corresponding case of Fe^{III} in an $S = 5/2$ manifold has been given by Blume.[7] We are not aware of a previous example of this type of relaxation effect involving a manifold with only two Kramers doublets. Model calculations of theoretical spectra are in progress.

It is possible to explain the foregoing in a quantitative fashion by constructing a cluster spin Hamiltonian involving exchange interactions between the copper and iron ions. We have found that a satisfactory initial fit to the magnetic data (T >30 K) is achieved with equal Cu^{II}–Fe^{III} exchange interactions ($J_{Cu-Fe} = -63$ cm^{-1}, $g = 2.08$) but negligible Cu^{II}–Cu^{II} exchange. All these results are consistent with the molecular trinuclear model noted above. Further analysis of the low-temperature magnetic data leads to a zero field splitting parameter D of 7.2 cm^{-1} (g is then equal to 2.05).

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