

# Polynuclear Hydroxy-Bridged Structure in Metallo- $\beta$ -Cyclodextrin Complexes: A Study of Magnetic Susceptibility versus Temperature

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**Abstract.** Data of the variation of magnetic susceptibility with temperature were obtained by the Gouy balance method for a series of metallo- $\beta$ -CD complexes. The results support the proposal for the presence of polynuclear hydroxy-bridged structures with interacting paramagnetic centres giving rise to an antiferromagnetic character for these complexes. In the case of the Cu(II) complex estimates of the Cu—Cu distance and the Cu—O—Cu bond angle were obtained from the data.

**Key words.**  $\beta$ -Cyclodextrin, metallo-complex, binuclear, magnetic.

## 1. Introduction

A series of metallo- $\beta$ -cyclodextrin complexes have been prepared and formulated [1–4] as  $[(M(III)(OH))_2\beta\text{-CD}] \cdot 2\text{H}_2\text{O}$  for Mn(III) and Cr(III) and as  $[(M(II)(OH))_2\beta\text{-CD}]X_2 \cdot 2\text{H}_2\text{O}$  for Co(II), Ni(II) and Cu(II) where  $X^+$  is the counter cation.

An iron(III) complex has also been prepared and formulated as  $[(Fe(III)(OH))_4\beta\text{-CD}] \cdot 3\text{H}_2\text{O}$  [5]. FT-IR and Raman spectra have been reported [3, 4] together with vis/UV and solution-phase magnetic susceptibility studies, all of which lend support to the proposal [2] of binuclear hydroxy-bridged structures, except in the case of the Fe(III) complex, where a tetranuclear hydroxy-bridged structure is proposed [5] (Figure 1).

The solution-phase magnetic susceptibility studies [4] show room temperature magnetic moments well below the spin-only values, indicating the presence of magnetic coupling between the metal ion centres which gives rise to an antiferromagnetic character. Here a study of magnetic susceptibility versus temperature is described which lends further support to these conclusions.

## 2. Experimental

The methods of preparation and the analytical results for these metallo- $\beta$ -CD complexes, with the exception of the Fe(III) complex, have been reported previously [3, 4]. The Fe(III) complex was prepared using the non-aqueous procedure of Nair and Dismukes [1] with minor alterations, such as the vacuum drying of the

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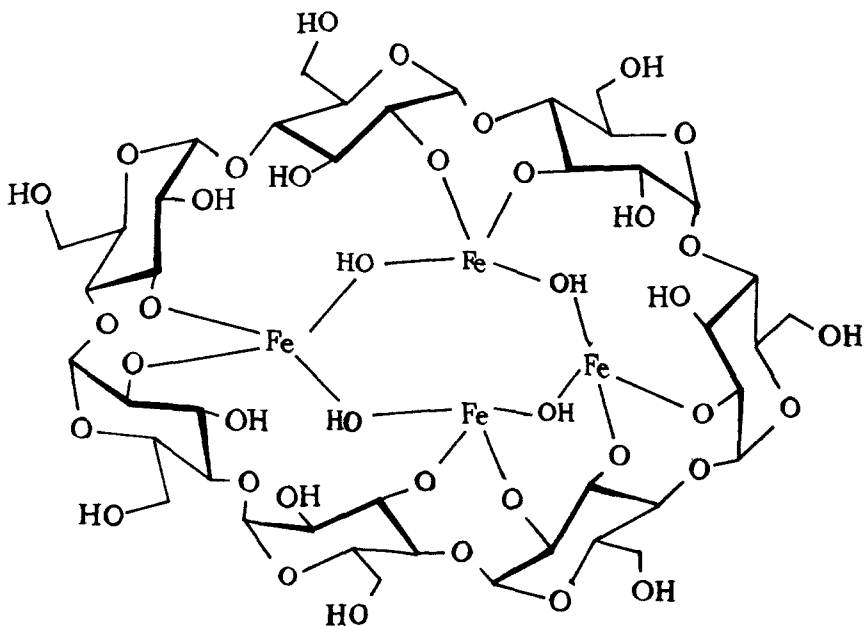


Fig. 1. Proposed tetranuclear structure for the Fe(III)- $\beta$ -CD complex.

product at 60°C. The final product, similar to those of the other metallo- $\beta$ -CD complexes, was isolated as a pale orange-coloured powder. All attempts to obtain crystalline products of these materials have so far failed. The metal analysis was carried out using a Shimadzu atomic absorption spectrophotometer (Model AA 670). The  $\beta$ -CD content was determined by fully dissociating the complex in acid solution and determining the optical rotation using a Bellingham and Stanley digital polarimeter (Model P10).

For both the metal and  $\beta$ -CD determinations, standard addition and normal calibration methods were employed. *Anal. Found:* Fe 15.25%,  $\beta$ -CD 76.54%. *Calcd.* for  $(\text{FeOH})_4 \cdot \beta\text{-CD} \cdot 3 \text{H}_2\text{O}$ : Fe 15.17%,  $\beta$ -CD 76.54%.

Magnetic susceptibilities of powdered samples of the complexes were determined using the Staunton Gouy Balance [6]. The balance was calibrated using tetracyanocobaltate mercury(II) as calibrant (molar susceptibility =  $16.44 \times 10^{-6}$  at 20°C). Diamagnetic corrections were evaluated using Pascal's constants.

### 3. Results

Molar susceptibilities were determined over a range of temperatures (80–290 K) for each of the complexes. These data were substituted into the set of Bleaney–Bowers equations [7] shown in Table I and fitted to best-fit curves (Figures 2–7) using a Simplex program [8] which optimised the values of  $g$  and  $J$  for each complex (Table II).  $J$  values were accepted only on the basis that the corresponding value for  $g$  was in the range,  $1.8 < g < 2.05$ . In the case of the Fe(III) complex the system was initially regarded as containing two non-interacting hydroxy-bridged Fe(III) dimers each having  $S_1 = S_2 = 5/2$ . This approach gave rise to an unacceptable value for  $g$ .

Table I. Magnetic susceptibility equations for polynuclear complexes with various spin quantum numbers under the effects of Heisenberg magnetic exchange

$S_1 = 1/2$	$\chi = C \frac{2e^{2x}}{1 + 3e^{2x}}$
$S_2 = 1/2$	
$S_1 = 1$	$\chi = C \frac{2e^{2x} + 10e^{6x}}{1 + 3e^{2x} + 5e^{6x}}$
$S_2 = 1$	
$S_1 = 3/2$	$\chi = C \frac{2e^{2x} + 10e^{6x} + 28e^{12x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x}}$
$S_2 = 3/2$	
$S_1 = 2$	$\chi = C \frac{2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{20x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x}}$
$S_2 = 2$	
$S_1 = S_2 = S_3 = S_4 = 5/2$	$\chi = C \frac{[15e^{2x} + 105e^{6x} + 336e^{12x} + 720e^{20x} + 1155e^{30x} + 1365e^{42x} + 1400e^{56x} + 1224e^{72x} + 855e^{90x} + 385e^{110x}]}{[2 + 15e^{2x} + 35e^{6x} + 56e^{12x} + 72e^{20x} + 77e^{30x} + 65e^{42x} + 50e^{56x} + 34e^{72x} + 19e^{90x} + 7e^{110x}]}$

$$x = hcJ/kT \quad C = Ng^2\beta^2/kT$$

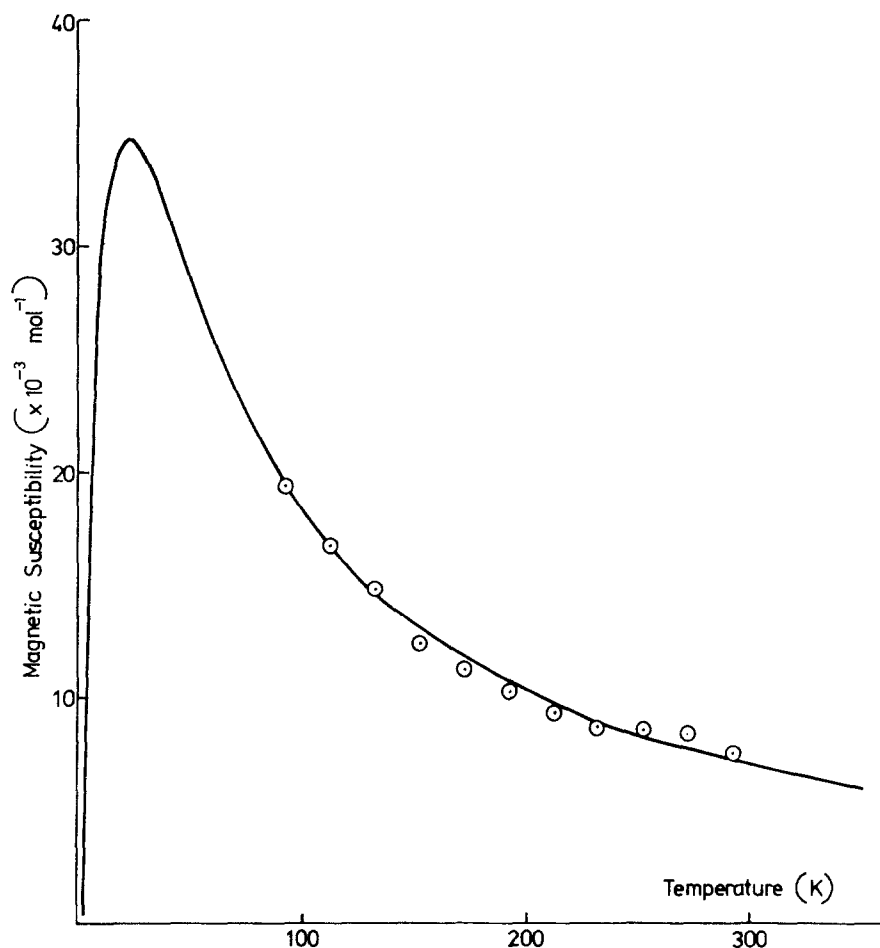
Fig. 2. Magnetic susceptibility data ( $\circ$ ) for Cr(III)- $\beta$ -CD. Solid line was calculated with  $g = 1.81$  and  $J = -5.21 \text{ cm}^{-1}$ .

Table II. Values for  $J$  and  $g$  for the metallo- $\beta$ -CD complexes

M	$J$ ( $\text{cm}^{-1}$ )	$g$	$T_n$ (Néel Point) (K)
Cr(III)	-5.21	1.81	23
Mn(III)	-5.43	1.82	34
Fe(III)	-3.24	1.79	13
Co(II)	-2.03	1.80	9
Ni(II)	-4.89	1.94	14
Cu(II)	-8.59	1.98	15

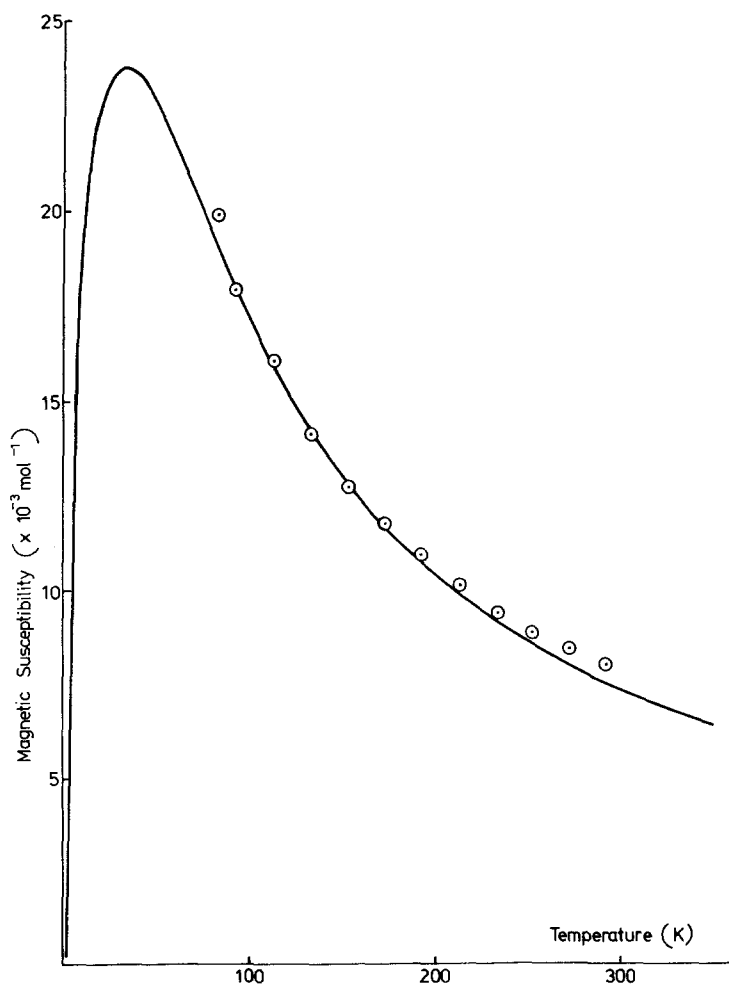


Fig. 3. Magnetic susceptibility data ( $\circ$ ) for Mn(III)- $\beta$ -CD. Solid line was calculated with  $g = 1.82$  and  $J = -5.43 \text{ cm}^{-1}$ .

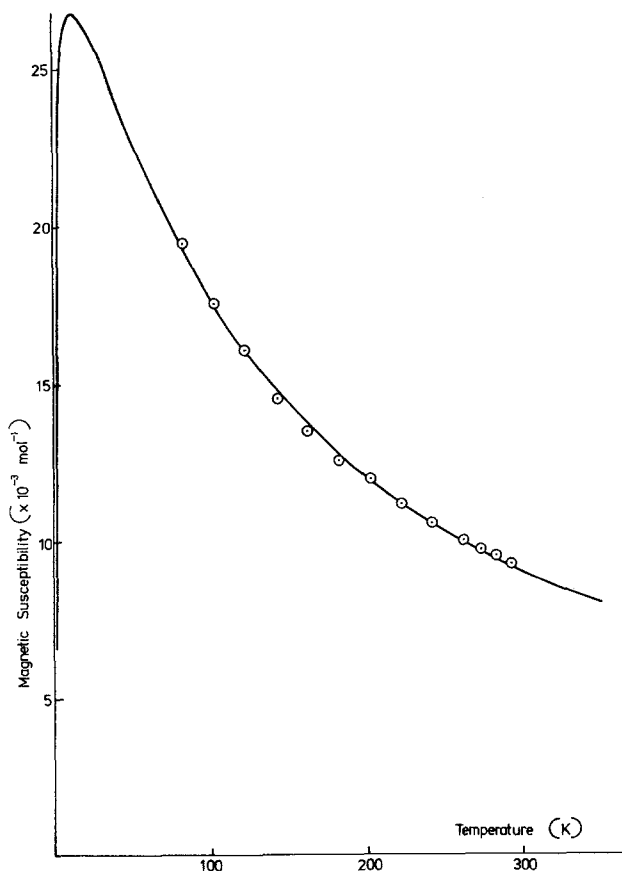


Fig. 4. Magnetic susceptibility data ( $\circ$ ) for Fe(III)- $\beta$ -CD. Solid line was calculated with  $g = 1.79$  and  $J = -3.24$  cm $^{-1}$ .

The susceptibility versus temperature data, however, fitted the Bleaney-Bowers equation well [9] for a tetrahedron of equivalent Fe(III) centres, with  $S_1 = S_2 = S_3 = S_4 = 5/2$  (Table I). This model assumes interaction occurs only between adjacent centres and gives rise to the  $g$  and  $J$  values for the Fe(III) complex shown in Table II.

#### 4. Discussion

The sign and values obtained for the coupling constant ( $J$ ) in each case indicates the nature and extent of the coupling in the complex. Values reported [10–15] for other complexes known to contain the binuclear hydroxy-bridged system (Table III) show that the coupling constants obtained for the metallo- $\beta$ -CD complexes can be described as having small negative values. This is indicative of antiferromagnetic character in these complexes with the energy difference between the ground singlet state and paramagnetic triplet excited state ( $2J$ ) being comparable to  $kT$ , even at liquid nitrogen temperatures. The paramagnetic triplet state is therefore appreciably

Table III. Values of  $J$  for  $[\text{ML}(\text{OH})]_2^{2+}$  type complexes

Complex	$J$ ( $\text{cm}^{-1}$ )	Ref.
$[\text{Cr}(\text{phen})_2\text{OH}]_2\text{I}_4 \cdot 4 \text{H}_2\text{O}$	-6.5	[10]
$[\text{Cr}(\text{gly})_2\text{OH}]_2$	-4.2	[10]
$[\text{Fe}(\text{picol})_2\text{OH}]_2$	-8.0	[11]
$[\text{Cu}(\text{EAEP})\text{OH}]_2(\text{ClO}_4)_2$	-65.2	[12]
$[\text{Cu}(\text{MAEP})\text{OH}]_2(\text{ClO}_4)_2$	-64.5	[13]
$[\text{Cu}(\text{bipy})\text{OH}]_2\text{SO}_4 \cdot 5 \text{H}_2\text{O}$	+24.0	[14]
$[\text{Cu}(\text{bipy})\text{OH}]_2(\text{NO}_3)_2$	+86.0	[15]

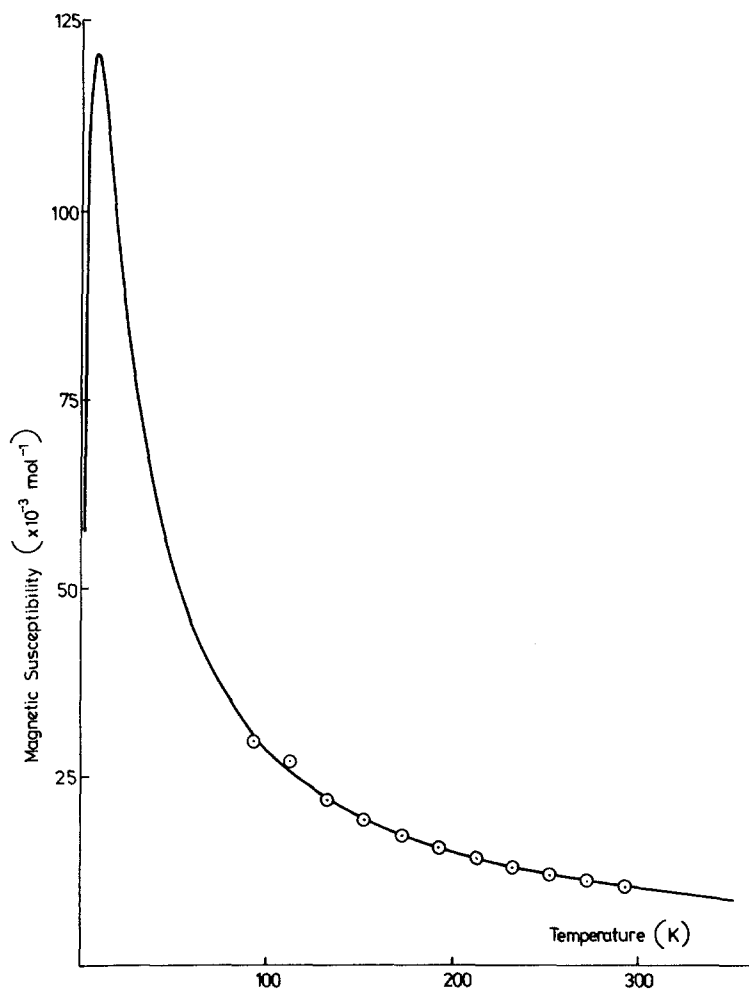


Fig. 5. Magnetic susceptibility data (○) for Co(II)- $\beta$ -CD. Solid line was calculated with  $g = 1.80$  and  $J = -2.03 \text{ cm}^{-1}$ .

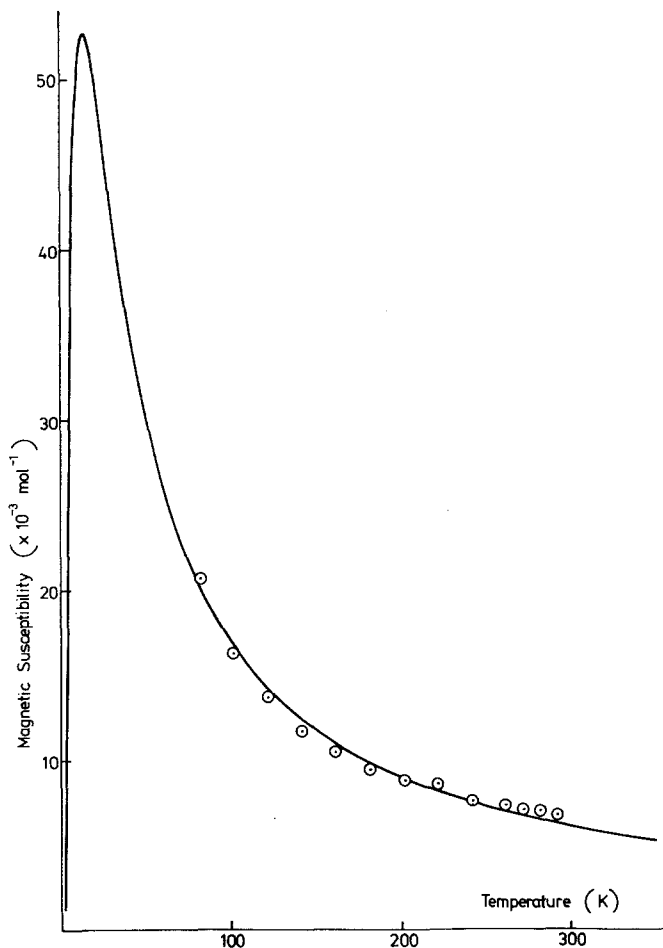


Fig. 6. Magnetic susceptibility data (○) for Ni(II)- $\beta$ -CD. Solid line was calculated with  $g = 1.94$  and  $J = -4.89 \text{ cm}^{-1}$ .

populated, thus giving rise to very low Néel points (Table II) and accounting for the magnitude of the room temperature magnetic moments [4]. This super-exchange mechanism [16] can be considered as occurring through the overlap of the  $sp^m$  hybrid orbitals of the bridging oxygens with the  $t_{2g}$  and  $e_g$  orbitals of the pseudo-octahedral metal ion centres. The greater the M—O—M bond angle ( $\Theta$ ) the larger the percentage  $s$  character required to accommodate bonding.

A molecular orbital approach [17] suggests that for the  $\text{Cu}_2\text{O}_2$  ring in Cu(II) hydroxy-bridged complexes, assuming  $D_{2h}$  symmetry, the degeneracy of the HOMO is lifted when the Cu—O—Cu bond angle is greater than  $90^\circ$ , thus giving rise to a singlet ground state. The experimental approach of Hatfield *et al.* [18] suggests that the critical angle is closer to  $97.6^\circ$ . The magnitude of the magnetic susceptibility at any given temperature and the Néel point temperature for a given complex is determined by the magnitude of the energy gap between the singlet ground state and the triplet excited state for that complex.

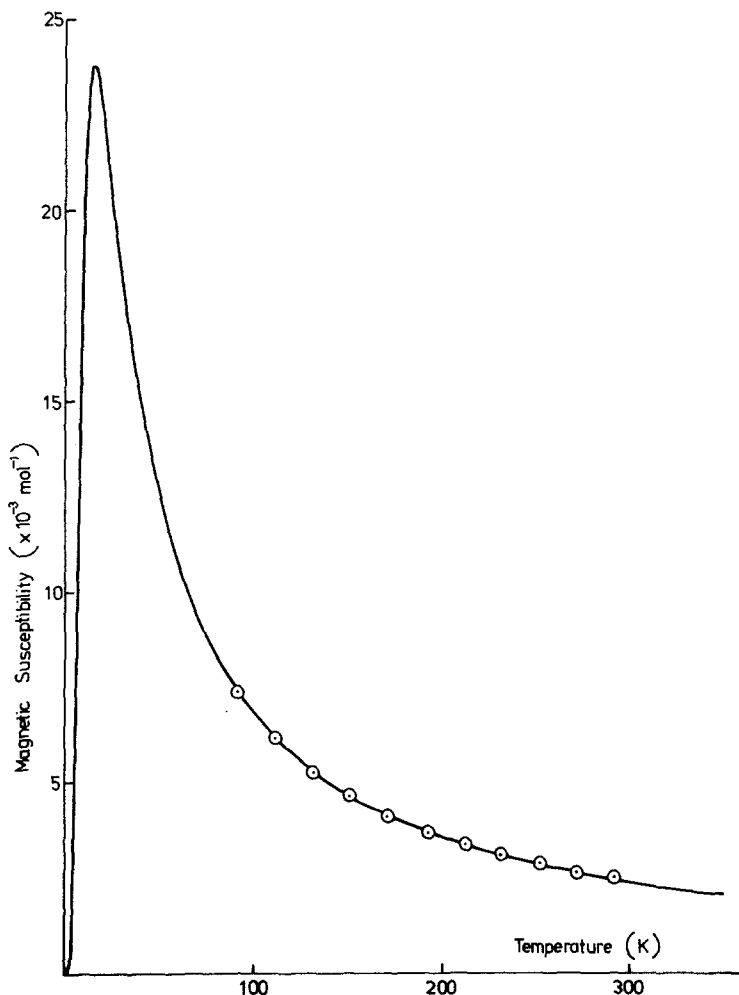


Fig. 7. Magnetic susceptibility data ( $\circ$ ) for  $\text{Cu(II)}-\beta\text{-CD}$ . Solid line was calculated with  $g = 1.98$  and  $J = -8.59 \text{ cm}^{-1}$ .

Binuclear hydroxy-bridged copper(II) complexes have been studied extensively. Hatfield *et al.* [18] have reported linear correlations between the coupling constant ( $J$ ) and the  $\text{Cu}-\text{O}-\text{Cu}$  bond angle ( $\Theta$ ) on the one hand, and the copper-to-copper distance ( $R_{\text{Cu}-\text{Cu}}$ ) on the other, for a series of well-characterised  $\text{Cu(II)}$  complexes.

Best fit lines resulted in the following relationships:

$$2J(\text{cm}^{-1}) = 74.53\Theta + 7270 \quad (1)$$

$$2J(\text{cm}^{-1}) = -450R_{\text{Cu}-\text{Cu}} + 13018 \quad (2)$$

Substituting the exchange coupling constant value obtained here for the  $\text{Cu(II)}-\beta\text{-CD}$  complex,  $J = -8.59 \text{ cm}^{-1}$ , into Equations 1 and 2 gives values for  $\Theta$  and  $R_{\text{Cu}-\text{Cu}}$  of  $97.77^\circ$  and  $2.891 \text{ \AA}$ , respectively. The latter value agrees well with  $R_{\text{Cu}-\text{Cu}}$  values for other hydroxy-bridged  $\text{Cu(II)}$  complexes [18]. Using these values



the Cu—O (bridge) bond distance was calculated as 1.919 Å. This agrees very well with the value of 1.92 Å reported by Hatfield *et al.* [18] for the complex  $[\text{Cu}_2(\text{OH})_2(\text{bipy})_2]\text{SO}_4 \cdot 5 \text{H}_2\text{O}$ . Values of  $J$  obtained by this technique cannot be taken as accurate, however: the authors were guided by the severe restriction on the acceptable range for the  $g$  parameter.

Similar studies carried out for binuclear hydroxy-bridged chromium(III) complexes [19, 20] did not reveal corresponding linear correlations, partly due to the lack of sufficient crystallographic data for these complexes.

In this case the unpaired electrons are in the  $t_{2g}$  orbitals which have a non-bonding character in the sigma-only system. Super-exchange via sigma bonding is therefore inhibited compared to the case for the Cu(II) complexes. Electronic spectra [4] indicated that substantial distortion from an octahedral environment exists for the metal ions in the Cr(III)- $\beta$ -CD complex. This would facilitate an alternative pathway for magnetic coupling involving the  $d_{xy}$  metal orbitals and the  $p_x$  and  $p_y$  orbitals of the bridging oxygens. This may account for the value of  $J = -5.21 \text{ cm}^{-1}$ , which is comparable to that obtained for the Mn(III)- $\beta$ -CD complex.

The results obtained here for the Mn(III)- $\beta$ -CD complex agree with those obtained by Boucher and Coe [21] for dimeric Mn(III)-Schiff base complexes containing oxygen bridging units. Similarly many Fe(III) [11] and Ni(II) [22] complexes have been reported which show an antiferromagnetic character and are known to contain bridged systems. As mentioned earlier, the magnetic data for the Fe(III)- $\beta$ -CD complex fit the equation describing coupling between four Fe(III) centres (Table I) each having  $S = 5/2$  and arranged in a tetrahedral fashion with bridging hydroxyl groups (Figure 1). The best fit values for  $g$  and  $J$  are  $g = 1.790$  and  $J = -3.241 \text{ cm}^{-1}$ . The coupling constant compares well with that obtained by Thornton *et al.* [9] for a series of iron carboxylate complexes. The complex  $\text{Fe}_4(\text{OME})_6(\text{O}_2\text{CMe})$  gave a reported  $J$  value of  $-4 \text{ cm}^{-1}$ . The respective magnetic moments per mole of complex, 4.61 BM for the Fe(III)- $\beta$ -CD complex at 293 K and 4.98 BM for the iron carboxylate complex at 298 K, are also in excellent agreement. The presence of tetrahedral Fe(III) clusters with sulphur bridges is well established in redox proteins, such as *bacterium clostridium botulinum* [23].

## 5. Conclusion

These results provide support for the proposed hydroxy-bridged structures of the metallo- $\beta$ -CD complexes; Cr(III), Mn(III), Co(II), Ni(II) and Cu(II) complexes having binuclear moieties, while the Fe(III) complex is more likely to be tetranuclear with a pseudo-tetrahedral arrangement of iron(III) centres. The presence of coupling through the super-exchange mechanism, rather than by direct spin-spin coupling, is supported by the fact that the diameter of the  $\beta$ -CD cavity (6.7 Å) would not allow sufficiently close proximity of the metal ion centres to facilitate the latter mechanism.

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