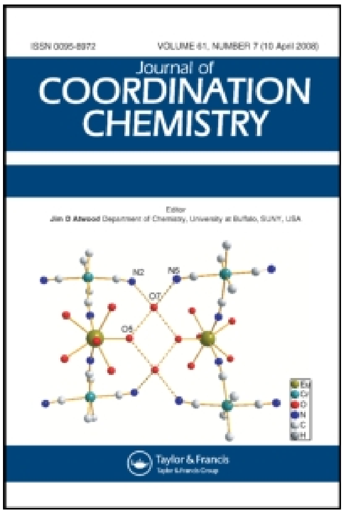

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SHORT COMMUNICATION

EPR OF COPPER(II) HIPPURATE AND ACETYLGLYCINE COMPLEXES

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The epr spectrum of the green anhydrous copper(II) hippurate complexes suggests a dimer structure similar to copper acetate monohydrate. The blue tetrahydrate copper(II) hippurate complex exhibits exchange narrowed lines and a simple analysis of the data points to a low-dimensional interaction. This is generally consistent with earlier x-ray data. The tetrahydrate complex of copper(II) acetylglycine is believed to be structually similar to the blue hippurate complex and exhibits a similar epr spectrum.

The copper(II) hippurate tetrahydrate ($Cu(Hip)_2 \cdot 4H_2O$ is of considerable stereochemical interest because it is a five coordinate tetragonal pyramidal copper(II) dimer.[1,2]. This complex, the related anhydrous complex, $Cu(Hip)_2$,[3] and the presumably analogous copper(II) acetylglycinate tetrahydrate, $Cu(Ace)_2 \cdot 4H_2O$, complex are of interest because they provide model systems for the interaction of metal ions with penicillins.[4] From the X-ray crystal structure results on $Cu(Hip)_2 \cdot 4H_2O$ one might expect appreciable metal–metal interaction but the room temperature moment is normal. Hyde and co-workers[3] found a Curie–Weiss behavior in the magnetic susceptibility data with a Weiss constant of about 33 ± 10°K. However, since the data were taken in the range from 115°K to room temperature, this value must be regarded with some caution due to the long extrapolation involved. Other magnetic susceptibility studies[4,5] which have been carried out at temperatures below 77°K indicate this value is too high but not by more than an order of magnitude and possibly less than that. The anhydrous $Cu(Hip)_2$ complex on the other hand exhibited a temperature variation in the magnetic susceptibility[3] curves which is similar to copper acetate and the J value was estimated to be 327 cm^{-1} from the maximum in the temperature-susceptibility plot. The purpose of this note is to report the epr parameters for these two complexes as well as a tetrahydrate copper(II) complex of acetylglycine which is believed to be structurally similar to the $Cu(Hip)_2 \cdot 4H_2O$ complex.

EXPERIMENTAL

The complexes were prepared and characterized as previously reported.[3] Considerable care was taken to isolate the tetrahydrate (blue) form of each of the complexes from the anhydrous (green) form. The epr data were obtained at X-band (9 GHz) at room temperature and liquid nitrogen temperature. The epr lineshapes for the tetrahydrate complexes were of the simple polycrystalline form described by Hathaway and Billings[6] and the g values and linewidths were analyzed according to the procedure outlined in their review. The linewidth in the perpendicular direction was determined assuming a Lorentzian lineshape and

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this procedure results in a possible uncertainty of the order of 20% since the actual lineshape may be diffusive (intermediate between Lorentzian and Gaussian). In the parallel direction the linewidth was taken as one half the width at half height. The values are $g_{\parallel} = 2.356$, $g_{\perp} = 2.068$, $\Delta H_{\parallel} = 70$ gauss, $\Delta H_{\perp} = 21$ gauss for the room temperature epr spectra of $Cu(Hip)_2 \cdot 4H_2O$ and $g_{\parallel} = 2.369$, $g_{\perp} = 2.069$, $\Delta H_{\parallel} = 18$ gauss, $\Delta H_{\perp} = 7$ gauss for the room temperature spectra of $Cu(Ace)_2 \cdot 4H_2O$. For the liquid nitrogen temperature data no significant changes were apparent but some small variations in the shape were noted. The overall uncertainty should be less than 0.01 in the g factors.

The anhydrous (green) $Cu(Hip)_2$ complex produced an X-band spectrum which was nearly identical to copper acetate. The analysis we employed is based on the equations of Wasson, Shyr and Trapp.[7] We find $g_{\parallel} = 2.348$, $g_{\perp} = 2.060$, $D = 0.247\ cm^{-1}$ and $E < 0.001\ cm^{-1}$. The overall uncertainty is less than 0.01 in the g factor and $\pm\ 0.005\ cm^{-1}$ in D.

DISCUSSION

The data presented above are consistent with the proposal by Hyde[3] that the green anhydrous complex is similar in structure to the copper acetate complex. The magnetic properties of the blue tetrahydrate systems are rather less well understood. The rather narrow epr line in the blue complexes is suggestive of an effective high temperature exchange field which is intermolecular in nature while the actual g values measured are those of a typical isolated complex. On the other hand the crystallographic structure would seem to imply dimer interactions as a major factor. We believe that these three observations are not inconsistent and we suggest the following model to account for these observations. The g factors being the same in the complex as in typical monomers is consistent with the idea that the exchange interactions, both inter and intramolecular, occur between copper(II) ions whose principal magnetic axes are parallel. These invididual copper ions are exchange coupled into dimeric species but the intramolecular exchange is sufficiently strong to exchange narrow the overall epr pattern. In order to put these suggestions on a more quantitative basis we will convert this exchange field into a critical temperature. The temperature can then be compared to the value found from the magnetic susceptibility results.

The measured esr linewidth in the "perpendicular" direction of the spectrum is about 21 gauss. In the simple three-dimensional line narrowing theory[8] this value may be related to an effective exchange field through the relation:

$$\Delta H = \frac{M_2}{H_e}$$

where M_2 is the second moment of the line and is the square of the linewidth which would be expected if no exchange narrowing were present. In this case we expect that M_2 has both inter and intramolecular dipolar contributions but that the effect of a hyperfine or pseudo-exchange contribution would be rather small. The latter two assumptions are based on the experimental evidence that the hyperfine field is usually quite small in the "perpendicular" direction[6] and that the pseudodipolar term is proportional to the exchange constant J.[9] Since J here is at least an order of magnitude smaller than in copper acetate we might expect that the corresponding pseudodipolar term to be smaller by roughly that much as well. In any event the inclusion of a small contribution from either of these effects would not greatly alter the overall estimate of M_2 made below. The intramolar contribution to M_2 may be estimated from the point dipolar approximation for H_d:

$$M_2 \cong H_d^2 \quad \text{and} \quad H_d \sim \frac{\mu}{r^3}$$

The value for H_d is about 250 gauss between unpaired electrons situated 3.3Å away from one another. The intermolecular dipolar contribution to M_2 may be roughly estimated from Van Vleck's isotropic formula

$$M_2' = 5.74 \times 10^4 \sqrt{(S)(S+1)}\ \frac{d}{M}$$

where d is the density of the sample, M is the molecular weight of the paramagnetic species and S is the effective spin, here taken as 1 for the dimer. We obtain $M_2' \cong 2 \times 10^4$ gauss.[2] With these results and the Richards equations[8] for one-dimensional exchange narrowing:

$$\Delta H \cong \frac{M_2^{2/3}}{H_e^{1/3}}$$

two-dimensional exchange narrowing:

$$\Delta H \cong \frac{M_2}{H_e} \ln \frac{H_e}{H_d}$$

and the equation for three-dimensional exchange is given above, we may estimate the range for the high temperature exchange field based on the three possible choices for magnetic dimensionality.

The results are $H_e \sim 60 \times 10^4$ gauss for one-dimensional exchange, 3×10^4 gauss for the two-dimensional interactions. In order to relate these to an effective Curie–Weiss temperature we can use $k\phi \cong g\beta H_e$ and obtain the values of $\phi = 80°K$, 4°K, and 0.5°K for the one, two and three-dimensional cases. A comparison with the present susceptibility data would suggest low-dimensional interactions, a result of which is generally consistent with the crystallographic data.[2] The tentative nature of these conclusions and the relatively crude approximations employed, however, must be reemphasized and the principal conclusion is that these systems should be carefully studied at low temperatures for evidence of low dimensional behavior.

For the acetylglycine complex narrower lines have been observed and these suggest rather stronger exchange fields or changes in molecular geometry as compared to the hippurate complex.

In conclusion we find that the anhydrous copper (hippurate) complex is a simple dimer and that the tetrahydrate complex possibly exhibits interaction between dimers in a low-dimensional pattern. The last complex, the blue $Cu(Ace)_2 \cdot 4H_2O$ may well be similar in structure to the $Cu(Hip)_2 \cdot 4H_2O$ but with a somewhat stronger exchange field.

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