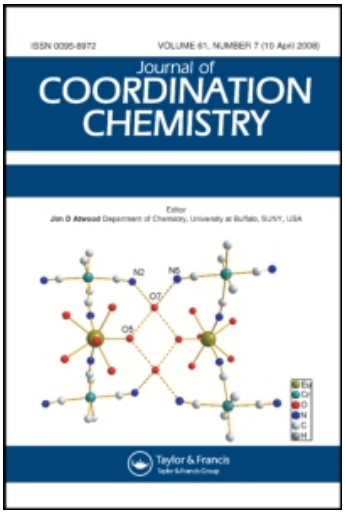

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PROPERTIES OF METAL COMPLEXES IN THE INTERPHASE OF AN OIL CONTINUOUS MICROEMULSION. 3. INTERACTION OF COPPER(II) WITH THE SIDE CHAIN OF TRYPTOPHAN[12]

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PROPERTIES OF METAL COMPLEXES IN THE INTERPHASE OF AN OIL CONTINUOUS MICROEMULSION.3. INTERACTION OF COPPER(II) WITH THE SIDE CHAIN OF TRYPTOPHAN[1,2]

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INTRODUCTION

In earlier work we have demonstrated the utility of oil continuous microemulsions for investigating ligand-metal interactions in cases where the ligand is an organic molecule sparingly soluble in water. Thus far, the interaction of several amino acid side-chains (histidine, lysine, glutamine, methionine) with Cu(II) has been investigated.[2,4] The oil continuous microemulsion used in these studies is composed of hexane, water, 2-propanol and hexadecyltrimethylammonium perchlorate.[5] The side chain is added to the system as a surface active derivative, i.e. an N^{α}-dodecanoylamino alcohol, which ensures that the side chain is located at the interface of the water-rich dispersed droplets. To date, the primary concern of our research has been to investigate the properties of metal complexes located in an interfacial environment. Our selection of ligands for these studies reflects an additional interest in bioinorganic chemistry. (Fendler and co-workers have previously argued that a host solution of the type used in our work is a suitable model for metal-protein interactions.)[6]

We are now reporting the results of investigations on the interaction of Cu(II) and the side chain of tryptophan. This system is of particular interest since the indole group in the side chain of tryptophan is the major chromophore contributing to the uv absorption spectrum of proteins. Furthermore, the indole group in tryptophan is quite sensitive to changes in its micro-environment, and as a consequence uv difference spectroscopy has been frequently used to follow chemical processes involving proteins,[7,8] including the reversible binding of metals.[9]

The affinity of the indole group in the side chain of tryptophan for transition metals is quite weak; indeed, the metal-indole interaction has not been investigated in simple solutions of small molecules, to our knowledge. However, reducing the water content of our oil continuous microemulsion has the effect of forcing the metal ion to interact with weak ligands present in the interphase portion of the dispersed droplets.[2] With such a system a significant interaction between Cu(II) and N^{α}-dodecanoyl-L-tryptophanol is clearly indicated by electron paramagnetic resonance spectroscopy.

EXPERIMENTAL

Organic solvents, water, and hexadecyltrimethylammonium perchlorate were prepared as described previously.[2] $Cu(ClO_4)_2 \cdot 6H_2O$ was purchased from G. F. Smith. N^{α}-dodecanoyl-L-tryptophanol was prepared as follows using published reaction conditions:[10,11]

a) L-tryptophan was N-acylated with dodecanoyl chloride,

b) N^{α}-dodecanoyl-L-tryptophan was esterified with methanol, and

c) the ester was reduced to an alcohol with $LiBH_4$.

Electron paramagnetic resonance spectra were measured with a Varian E-12 K-band spectrometer and a Varian E-3 X-band spectrometer. Absorption spectra were recorded with a Cary 14 spectrophotometer.

The microemulsion used as a host solvent for these studies was composed of hexane (10 ml), water (0.3 ml), 2-propanol (3.6 ml), and hexadecyltrimethylammonium perchlorate (15 mg). This composition is characterized by the relatively small volume of water present. The existence of an oil continuous microemulsion was confirmed by ultracentrifugation experiments, as described elsewhere.[1,2] N^{α}-dodecanoyl-L-tryptophanol is not soluble to a significant extent in either water or hexane. Thus, the quantity of ligand solubilized by the microemulsion is dependent on the amount of interfacial area present. However, in this microemulsion the interfacial area per unit volume is limited because the water content had been decreased to force an interaction between the metal and side chain. Consequently, in order to solubilize sufficient ligand for measurements at high mole ratios of ligand to metal, it was necessary to increase the volume of the microemulsion. In increasing the volume components were added according to the ratios presented above.

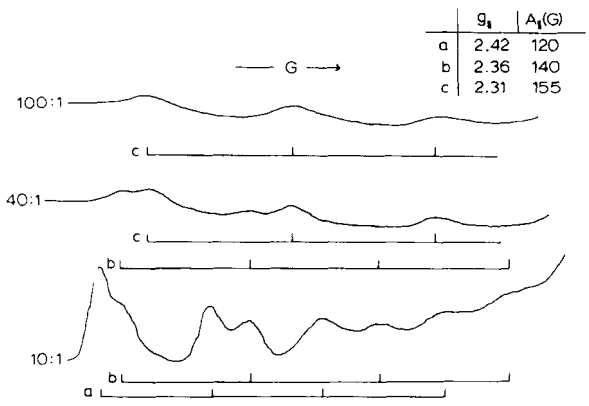

FIGURE 1 Electron paramagnetic resonance spectra of microemulsions containing N^{α}-dodecanoyl-L-tryptophanol and Cu(II). The ligand to metal mole ratios are indicated by the labels on the spectra. These spectra were measured at liquid nitrogen temperature following quick-freezing. Only the parallel signals are shown since overlap averages out the remainder of the signal. The epr parameters for the three observed species are shown on the figure. (See text for further details).

RESULTS AND DISCUSSION

Microemulsions containing 28.6 mg (0.11 mmole) of $Cu(ClO_4)_2 \cdot 6H_2O$ and varying amounts of N^{α}-dodecanoyl-L-tryptophanol were "quick-frozen" with liquid nitrogen and their epr spectra recorded. Evidence for three different species was obtained, as the mole ratio of ligand to metal was increased to 100:1. The epr parameters for the three species are listed in Figure 1, which shows illustrative examples of spectra recorded at different ligand to metal mole ratios. In the "10:1" spectrum, pattern *a* is that of aquated Cu(II). In the "40:1" spectrum, a CuL^{++} species (pattern *b*) and a CuL_2^{++} species (pattern *c*) can be identified, while at a mole ratio of 100:1, only the CuL_2^{++} pattern (i.e. pattern *c*) remains. Thus, the CuL_2^{++} species appears to be the limit complex for this system. The epr parameters for pattern *c* ($g_{\parallel} = 2.31$, $A_{\parallel} = 155$ *G*) are very close to those previously reported for the limit complex (also CuL_2^{++}) formed between Cu(II) and N^{α}-dodecanoyl-L-histidinol.[4]

The room temperature spectrum of the microemulsion containing a 100:1 mole ratio of ligand to metal showed considerable averaging and particular features in the spectrum could not be discreetly defined. We believe the averaging is due primarily to ligand exchange since the complexes are so weakly formed.

Absorption spectroscopy

A freshly prepared microemulsion containing Cu(II) and N^{α}-dodecanoyl-L-tryptophanol is light green in color. There are two regions of interest in the uv-vis spectra of Cu(II)/N^{α}-dodecanoyl-L-tryptophanol complexes. The first region is associated with the $\pi \rightarrow \pi^*$ transition of the indole chromophore which, for N^{α}-dodecanoyl-L-tryptophanol in 2-propanol, exhibits a maximum at ~2800 Å. The location of this maximum does not change when the ligand is incorporated into the interphase of the microemulsion, but the intensity of the band is diminished 2–3%. The uv difference spectroscopy of protein solutions depends on pertubation of the tryptophan side chain, to a large extent.[7,8] However, in our studies uv difference spectroscopy of microemulsions containing 0.11 mmole of Cu(II) and increasing amounts of ligand was not informative. This result could have been anticipated since the limit complex is so weakly formed that only one indole of each 50 (or so) is complexed. It is highly unlikely that the pertubation of a complexed indole could be detected against the "background" of a large number of non-complexed indoles. Attempts to study microemulsions containing a fixed amount of ligand and increasing amounts of Cu(II) were also unsuccessful; at high concentrations, the charge transfer band of $Cu(ClO_4)_2$ obscured the $\pi \rightarrow \pi^*$ transition of the indole ring.

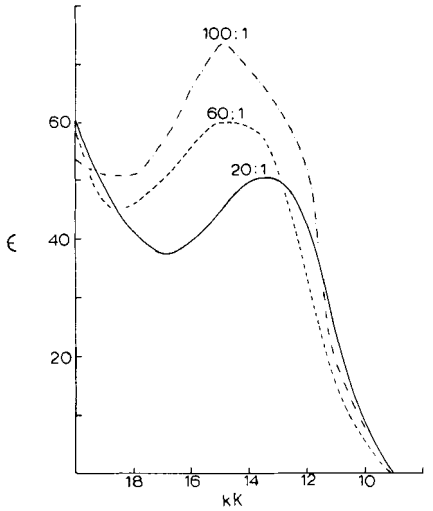

FIGURE 2 Optical spectra of the *d-d* transition of Cu(II) in microemulsions containing N^{α}-dodecanoyl-L-tryptopanol. The spectra, obtained at room temperature, are labeled with the appropriate ligand to metal mole ratios. The molar absorptivity is based on the concentration of Cu(II) which was 0.0055 M, 0.0018 M, and 0.0014 M for the 20:1, 60:1, and 100:1 curves, respectively.

The second region of the spectrum of interest is the *d-d* transition of Cu(II). Spectra for this region, obtained at several ligand to metal mole ratios, are shown in Figure 2. The limiting transition energy was actually attained at a ligand to metal mole ratio of 80:1, while the maximum molar absorptivity occurred at a ratio of 90:1. Thus, a microemulsion hosting a ligand to metal mole ratio of 100:1 contains only one species, i.e. the limit complex. In the 100:1 case the value of D_q (1490 cm^{-1}) is ~250 cm^{-1} greater than for aquated Cu(II).[13]

CONCLUSION

The epr and optical spectra of the limit complex formed in the Cu(II)/N^{α}-dodecanoyl-L-tryptophanol system indicate that Cu(II) is in an essentially square planar geometry. The strength of the crystal field (D_q = 1490 cm^{-1}) suggests participation of nitrogen atoms as donors.[13] Based on the value of D_q and the similarity of the observed epr spectra (Figure 1) to those reported for the Cu(II)/N^{α}-dodecanoyl-L-histidinol system,[4] we suggest that the structure shown in Figure 3 represents the limiting CuL_2^{++} complex. This model includes the formation of a nine-membered ring which, when coupled to the

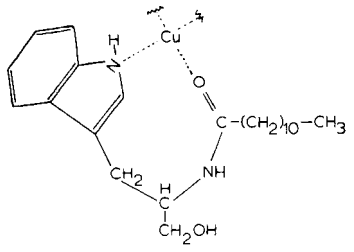

FIGURE 3 An illustration of the bonding which is postulated to occur between Cu(II) and N^{α}-dodecanoyl-L-tryptophanol.

fact that the indole N is a much weaker donor than the imidazole N, explains at least in part why the Cu(II)/N^{α}-dodecanoyl-L-tryptophanol interaction is so weak when compared to the interaction between Cu(II) and N^{α}-dodecanoyl-L-histidinol previously reported.[4]

It appears that the affinity Cu(II) shows for N^{α}-dodecanoyl-L-tryptophanol is quite similar to its affinity for N-dodecanoyl-L-methioninol.[2] The indole group has not as yet been implicated as a ligand in a metalloprotein, however, whereas the thioether group is believed to coordinate *Fe* in cytochrome *c*.[14] Presumably, future investigations of metalloproteins will implicate tryptophan as a ligand in metalloproteins.

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