on benzene solutions of the dihalides and the diazide, it was found in the present work that the 220-230-cm^{-1} band is very strongly polarized but the 260-cm^{-1} band is depolarized. Therefore the 220-230-cm^{-1} band should be assigned to the symmetric Sb-C_6H_5 stretching vibration. Accordingly, the strong Raman band at *ca.* 230 cm^{-1} is assigned to the symmetric Sb-C_6H_5 stretching frequency and the 290-cm^{-1} band, which appears strong in the infrared but is weak in Raman, is assigned to the antisymmetric Sb-C_6H_5 stretching frequency. Thus the vibrational spectra for triphenylantimony diazide and the diisocyanate are also in accord with a trigonal-bipyramidal skeleton.

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Registry No. $Me_3Sb(N_3)_2$, 51019-36-4; $Ph_3Sb(N_3)_2$, 51019-33-1; $Me_3Sb(NCO)_2$, 51019-34-2; $Ph_3Sb(NCO)_2$, 51019-35-3.

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Electronic Studies of Copper(II) Complexes of Amino Acids. IV. The Copper-Carnosine System, a Magnetically Dilute Copper Dimer

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Great interest has developed in the last several years in the study of coordination compounds of amino acids and peptides.[1-3] The general purpose in this field has been to try to elucidate the special physical properties of the larger protein and enzyme metal complexes, a problem which at this time still remains unresolved. Several very interesting aspects have been brought forward by investigators such as Gray,[4] Vallee and Williams,[5] and Malmstrom and Vanngard.[6] In particular, Villa and Hatfield[7,8] have demonstrated the possibility of spin interactions in dimeric Cu(II) compounds of amino acids such as the tyrosinato system. In this paper, the magnetic, epr, and spectral properties of the copper(II)-β-alanyl-L-histidine (carnosine) complex will be presented and discussed. The interest in this compound was prompted by its structure,[9] shown in Figure 1, where it can be seen that two carnosine molecules bridge between two copper ions forming a strict dimeric structure. The Cu(II) is pentacoordinated by an amino, a peptide, and an imidazole (3) nitrogen, by a carboxyl oxygen, and by a water molecule. There exist possibilities of spin interaction *via* the bridging ligands or through space, as well as interdimer interactions.

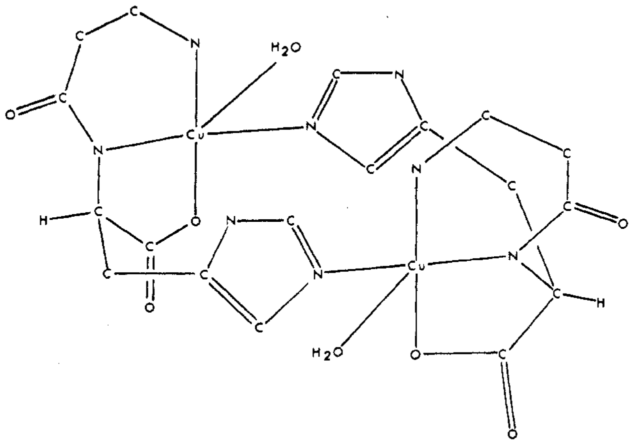

Figure 1. Structure of the (carnosine)copper dimer.

Experimental Section

The compound, (β-alanyl-L-histidinato)copper(II) dihydrate, was prepared according to Freeman[9] by dissolving 2 mmol of carnosine with excess freshly prepared $Cu(OH)_2$ in about 10 ml of H_2O, filtering off the excess hydroxide, and adjusting the final pH to 10 with 10% NaOH. Dark blue crystals formed within 1 hr. *Anal.* Calcd for $Cu(C_9H_{16}N_4O_5)$: C, 33.38; H, 4.98; N, 17.30. Found: C, 33.12; H, 4.78; N, 17.32. The magnetic measurements were made as previously described[10] in a Faraday susceptibility setup down to 77°K and in a vibrating-sample magnetometer from 77 to 4°K. The epr measurements were carried out in Varian Associates E-3 and EM-500 spectrometers at the X band. The visible-near-infrared spectra were obtained as Nujol mulls between glass plates in a DK-2A spectrophotometer. Analyses were commercially done by Galbraith, Inc.

Results

The epr spectrum of the copper-carnosine compound is shown in Figure 2, which can be described with an $S = {}^1/_2$ spin Hamiltonian. Under close scrutiny it can be observed that the spectrum is not symmetrical and can be interpreted as being composed of a $g_{\parallel} = 2.20$ and $g_{\perp} = 2.08$. The solid spectrum of the pure material at 77°K corroborates this interpretation. A solid solution spectrum at 77°K of the mother liquor (from the preparation of the compound) gave a completely symmetrical spectrum with $g_{\text{av}} = 2.11$, again indicating the presence of an $S = {}^1/_2$ species.

The magnetic susceptibility for this compound was measured from room temperature to 4°K and is shown in Figure 3. The X's are the experimental points while the lines are the theoretical χ and $1/\chi$ expected from a Curie law with $\mu = 1.80$ BM. It is evident from the figure that the fit of the data to the Curie law is excellent and that the temperature axis intercept is 0.

The solid-state electronic spectrum consisted of one broad band at 14,000 cm^{-1} which can be assigned to the $E \leftarrow B_1$ transition.

Discussion

Two different types of magnetic interactions have been postulated in copper(II) compounds: (1) through-space interactions, such as in the $[Cu(ac)_2]_2$ dimer, and (2) interactions *via* the bridging ligands, such as in the copper-tyrosine compounds. The Cu-Cu distance in the first type of compounds is less than 3 Å while in the second

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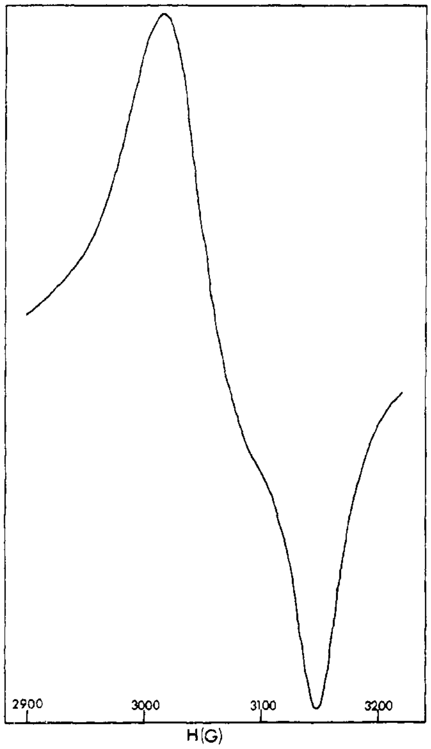

Figure 2. Epr spectrum of (carnosine)copper; R, T, and X bands.

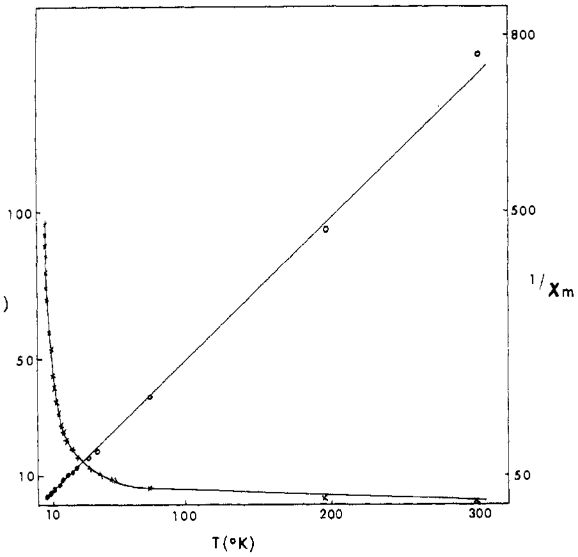

Figure 3. Magnetic susceptibility dependence on T of (carnosine)-copper.

it is 3-3.5 Å. The copper–carnosine compound that we report here has a Cu-Cu separation of about 4 Å.

The room-temperature and 77°K epr spectra are consistent with a C_{4v} symmetry for each Cu(II) ion in the dimer. The electronic spectrum is also consistent with an axial symmetry approximately D_{4h} or C_{4v}. There is no evidence of spin interactions from these spectra nor from the frozen solution epr spectrum. H_{min}, usually in the 1500-G region of the epr spectra of spin-coupled copper compounds, was also absent for the copper–carnosine system.

The magnetic susceptibility is most revealing. This compound follows the Curie law from room temperature to 4°K. This is indicative of no spin interactions between the Cu(II) ions in the dimer. Furthermore, the usual Weiss constant Θ is 0 in this case which can be interpreted as a lack of spin interactions among Cu(II) ions in different dimers.

Apparently, the Cu-Cu separation in the dimer is too large for intradimer spin coupling through space since the dipolar coupling increases as an inverse function of distance. Also, the possible spin delocalization through the bridging ligands is not effective in this case because there are two successive carbon atoms with sp^3 hybridization which will stop any π type spin delocalization (see Figure 1). The σ-bond type coupling is expected to be negligible in this case where there are six intervening atoms between the two Cu(II) ions. Finally, the organic skeleton and water molecules surrounding the Cu(II) ions are bulky enough to dictate large separations among the metal ions in different dimers, therefore, stopping any intermolecular interactions.

This is, then, the first well-documented example of a completely magnetically dilute Cu(II) dimer free from intra- and interionic spin coupling, rather different from the now well-known cases of spin-coupled (dimethylglyoxime)copper and (diethyldithiocarbamato)copper dimers.

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Registry No. (Carnosine)copper dimer, 51095-95-5.

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Resonance Raman Effect and Far-Infrared Spectra of Rhodium-Doped Silver Bromide Crystals

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Considerable interest has been shown in the study of impurity-induced vibrational spectra, particularly in alkali halides, silicon, and some group III-V compounds. Similar studies on silver halides have not been extensive owing to difficulties in instrument sensitivities, sample handling, and the solubilities of impurities in the host lattice. With improved instrumentation for the far-infrared spectrum and taking advantage of a resonance Raman effect, we have been able to observe the far-infrared and laser Raman spectra in rhodium-doped silver bromide crystals.

Large boules of high-purity silver bromide doped with 200 ppm of rhodium tribromide were grown by the standard Bridgman method. These impurity-doped silver bromide samples were light sensitive and corrosive and were handled with care under red light. The Rh ion concentration was determined by atomic absorption spectroscopy. The far-infrared absorption spectrum has been measured in the 10-500-cm^{-1} spectral region using a Fourier transform spectrometer, Polytec Model 30, at a resolution of ~0.5 cm^{-1}. The Raman spectra were recorded with a Spex Ramalog spectrom-