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Spectral and Magnetic Properties of Linear-Chain Aminoacid Complexes of Copper(II), Bis(d,l-α-aminobutyrato)- and Bis(l-asparaginato)copper(II)

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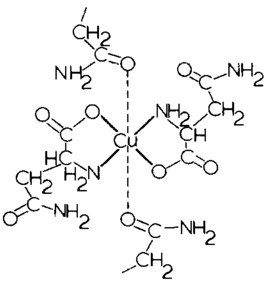
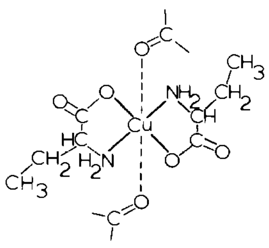
The electronic structures of the linear-chain aminoacid complexes, bis(l-asparaginato)copper(II), Cu(aspg)$_2$, and bis(d,l-α-aminobutyrato)copper(II), Cu(aba)$_2$, have been elucidated using variable temperature magnetic susceptibility measurements and electronic and electron paramagnetic resonance (EPR) spectroscopy. Despite established linear chain structures, no evidence was found for metal–metal spin exchange coupling to 1.8 °K. EPR spectra demonstrated that metal–ligand covalency is minimal. The g- and hyperfine anisotropy of copper(II)-doped Cd(aspg)$_2$ were completely resolved.

Introduction

The importance of studying coordination complexes of aminoacids and peptides as an aid to understanding the more complex protein and enzyme systems has been emphasized by Österberg [1] and others. Undoubtedly, this is in response to the biological significance that has been attached to such complexes in recent years [2–9]. The crystal structures of two aminoacid complexes, bis(l-asparaginato)copper(II) [10], Cu(aspg)$_2$, Ia, and bis-(d,l-α-amino butyrato)copper(II) [3, 11], Cu(aba)$_2$, Ib, have been reported. In both compounds the copper(II) ion is hexacoordinated and bridged by the aminoacids to form linear chains. Magnetic susceptibility and electron paramagnetic resonance (EPR) studies [12, 13] of polymeric bis(l-tyrosinato)-copper(II) have demonstrated the presence of spin-spin interactions between the copper(II) ions. Such interactions, along with the current interest shown in metal–aminoacid complexes, have prompted our investigation of the spectral and magnetic properties of Cu(aspg)$_2$ and Cu(aba)$_2$. Variable temperature magnetic susceptibility data, EPR and electronic spectra are presented and discussed with a particular focus on the structural, rather than biological, properties of the complexes.



Ia



Ib

Experimental

Both complexes were prepared by standard methods reported in the literature [10, 11]. Elemental analyses: Bis(l-asparaginato)copper(II), $C_8H_{14}N_4O_6Cu$: Calc'd: 29.5, %C; 4.3, %H; 17.2, %N; 19.3, %Cu. Found: 29.6, %C; 4.5, %H; 17.1, %N; 19.4, %Cu. Bis(d,l-α-aminobutyrato)copper(II), $C_8H_{16}N_2O_4Cu$: Calc'd: 35.89, %C; 6.02, %H; 10.46, %N. Found: 34.49, %C; 5.66, %H; 9.67, %N. C, H and N analyses were performed by Integral Microanalytical Laboratories, Raleigh, North Carolina, and copper was determined by titration with EDTA [14].

Magnetic susceptibilities were determined with a Foner-type vibrating sample magnetometer [15] operating at a field strength of 10 kGauss. Calibration of the magnetometer was checked using HgCo-(NCS)$_4$ [16] with the more recent correction to the Weiss constant [17] being applied and then recalibrated with $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$ [18]. Both standards agreed within 2%. The magnetic field was calibrated as previously reported [19] and is accurate to better than 0.15% at 10 kGauss. The sample temperature was measured with a GaAs diode that had been calibrated against a commercially calibrated diode [20]. A value of 60 × 10^{-6} cgs units was employed for the temperature-independent paramagnetism of the copper(II) ion and diamagnetic corrections of all of the substituents were estimated from Pascal's constants [21]. The EPR spectra were taken with JEOLCO Me-ESR and Varian E-3 X-band spectrometers. The magnetic field and klystron frequency and field sweep were checked using double standards (a) DPPH free radical (g = 2.0036) and vanadyl(IV) acetylacetonate in benzene [22] and (b) DPPH free radical and Mn(II)-doped MgO. Quartz

3 mm i.d. tubes were employed to contain polycrystalline samples. Electronic spectra were obtained with a Cary Model 17 recording spectrophotometer using a mull (transmission) technique described previously [23]. Crystal field calculations were performed using the explicit method of Companion and Komarynsky [24] and a computer program previously described [25]. Details of this method [24], its simplification using elementary group theory, and evaluation of ligand crystal field parameters are discussed elsewhere [25, 26].

Results

The magnetic susceptibilities of both $Cu(aspg)_2$ and $Cu(aba)_2$ were determined in the temperature range 1.8–150 °K. Qualitatively, the plots of magnetic susceptibility, χ, *vs.* temperature are characteristic of a spin S = 1/2 paramagnet [27]. The reciprocal susceptibilities (Figures 1 and 2) appear to obey the Curie–Weiss law ($\chi = [N_A g^2 \beta^2 / 3k(T - \theta)]\,S(S + 1)$, where S = 1/2, θ is the Weiss constant, and the other symbols have their usual meanings) to temperature as low as 1.8 °K. The Curie–Weiss g-values and Weiss constants were evaluated using a Simplex linear least squares routine [28] in which the best fits to data were obtained by minimizing the quantity

$$p = \sum_{i=1}^{n} \frac{(\chi_c - \chi_o)^2}{n}$$

All data points were weighted equivalently. A g-value of 2.11 was obtained for both complexes and θ values of –0.76 and –0.55 were obtained for $Cu(aba)_2$ and $Cu(aspg)_2$, respectively.

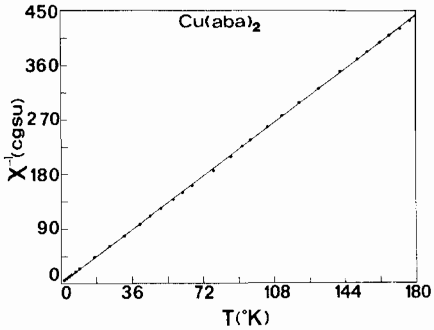


Figure 1. Reciprocal molar susceptibilities *vs.* temperature for $Cu(aba)_2$. The solid line is the best least-squares fit to the Curie–Weiss law.

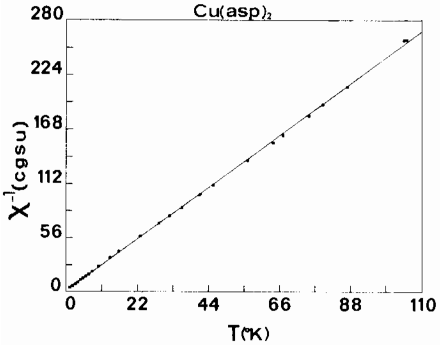


Figure 2. Reciprocal molar susceptibilities *vs.* temperature for $Cu(aspg)_2$. The solid line is the best least-squares fit to the Curie–Weiss law.

The EPR spectra of $Cu(aba)_2$ and $Cu(aspg)_2$ are shown in Figures 3 and 4, respectively. Blue $Cu(aba)_2$, itself, is not magnetically dilute but the g-anisotropy is resolved (Figure 3). Polycrystalline $Cu(aspg)_2$ exhibits an EPR spectrum characteristic of axial symmetry although crystallographic data [10] leads to the expectation of three g-values.

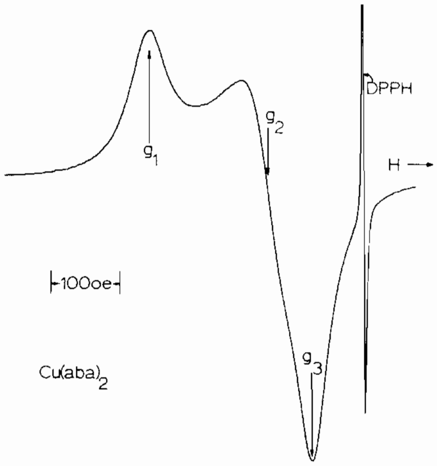


Figure 3. X-band ESR spectrum of polycrystalline $Cu(aba)_2$. Room temperature.

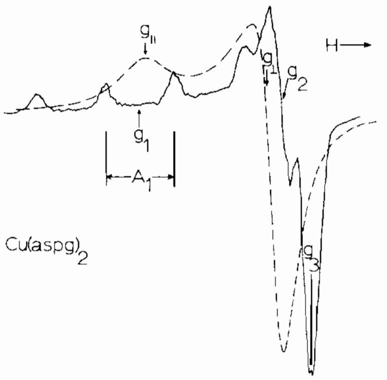


Figure 4. X-band ESR spectra of pure polycrystalline $Cu(aspg)_2$ (---) and $Cu(aspg)_2$ doped into the corresponding cadmium(II) complex (——). Room temperature.

The EPR spectrum of copper(II)-doped $Cd(aspg)_2$, whose structure has been reported [29], is shown in

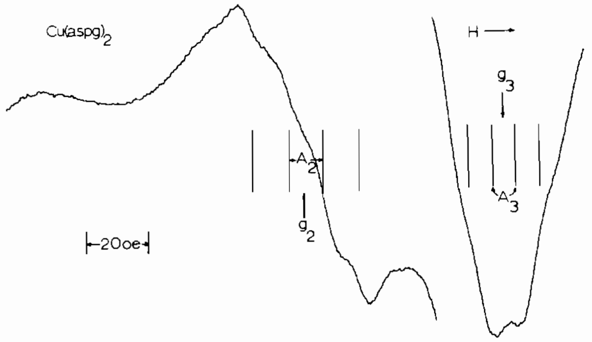


Figure 5. Expanded scale presentation of the high-field part of the ESR spectrum of Cu(aspg)$_2$ doped into the cadmium-(II) complex. The first-order analysis of the copper nuclear hyperfine splitting is indicated.

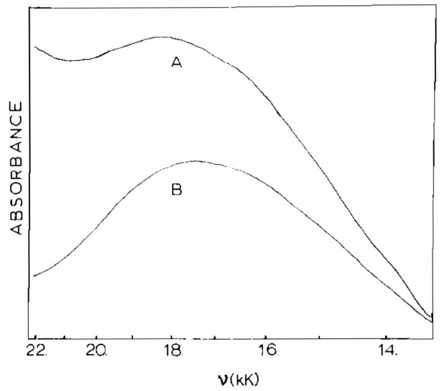


Figure 6. Mull (transmission) electronic spectra of Cu(aba)$_2$ (A) and Cu(aspg)$_2$ (B).

TABLE I. EPR and Electronic Spectral Data.

Compound	Lattice	±0.005				(±2.0) × 10^4 cm^{-1}				ν(kK)^c
		g_1	g_2	g_3	$<g>^a$	A_1	A_2	A_2	$<A>^b$	
Cu(aba)$_2$	pure	2.206	2.081	2.050	2.112	–	–	–	–	18.5 (17.0)
Cu(aspg)$_2$	pure	2.241	2.068	2.068	2.127	–	–	–	–	17.5
Cu(aspg)$_2$	Cd(II)	2.284	2.072	2.035	2.130	151.6	11.2	6.9	56.6	–

[a] $<g> = 1/3\ (g_1 + g_2 + g_3)$ or $<g> = 1/3\ (2g_\perp + g_\parallel)$. [b] $<A>$ is calculated similarly to $<g>$. [c] Mull (transmission) data. 1kK = 1000 cm^{-1}.

Figures 4 and 5. The g and metal nuclear hyperfine anisotropy is completely resolved. The data can be fit to a spin-Hamiltonian of the form:

$$\hat{H} = (g_x\hat{S}_xH_x + g_y\hat{S}_yH_y + g_z\hat{S}_zH_z)\beta$$
$$+ A_x\hat{S}_x\hat{I}_x + A_y\hat{S}_y\hat{I}_y + A_z\hat{S}_z\hat{I}_z$$

where the symbols have their usual meanings. Repeated attempts to grow crystals of copper(II)-doped Cd(aspg)$_2$ were without success. It has thus been assumed that the g and A tensors share the same principal axis system. EPR and electronic spectral data are summarized in Table I. The electronic spectra of Cu(aba)$_2$ and Cu(aspg)$_2$ are shown in Figure 6.

Discussion

Historically, magnetic data have often been employed to predict gross structural features of various compounds [30, 31] . Unusual magnetic behavior, *e.g.*, subnormal moments, has often been used as a criterion for structural studies [32]. Currently, the emphasis being placed on detailed structural analyses of complexes of biological significance [1, 3] has led to a proliferation of crystal structures of complexes which have not been characterized by other techniques. The latter studies are vital if the possible contributions of a given compound in biological processes, say, electron and energy transport [33], are to be properly assessed. Both Cu(aba)$_2$ and Cu(aspg)$_2$ were of interest because their novel linear chain structures [10, 11] could lead to cooperative phenomena among the magnetic ions.

The magnetic susceptibility data as low as 1.8 °K show that both systems are best described as a linear array of S = 1/2 monomers in the ground state. The spins are electrostatically independent of one another to the limits of our measurements. The reciprocal susceptibilities *versus* temperature (Figures 1 and 2) for the complexes show little deviation from Curie–Weiss behavior [34].

The copper–copper separations in Cu(aba)$_2$ [3, 11] and Cu(aspg)$_2$ [10] are ~4.5 and 6.17 Å, respectively. Antiferromagnetic exchange interactions in linear chain complexes of copper(II) have been detected by magnetic susceptibility measurements in compounds with copper–copper separations on the order of 12 Å [35]. However, a delocalized π-system provided the pathway for spin exchange. For Cu(aspg)$_2$ a σ-pathway for exchange exists, extended electron delocalization is minimal and there is essentially no metal–metal interaction. For Cu(aba)$_2$ the metal–metal separation is ~4.5 Å and there is a possibility of π-interaction through the carboxylate group. The reason that spin-coupling is not observed rests with the spatial configuration of the orbitals involved. The EPR spectrum of Cu(aba)$_2$ Figure 3 is consistent with a predominantly $d_{x^2-y^2}$ ground state [36]. The unpaired electron is constrained to lie in the plane of the four short copper–ligand bonds. The superexchange pathway provided by the ligands connects two short in-plane bonds of one copper ion to an out-of-plane bond on an adjacent copper ion. No superexchange pathway is provided that allows $d_{x^2-y^2}$–$d_{x^2-y^2}$ overlap which would result in an antiferromagnetic interaction. Through space or direct bond interactions [37, 38] between the copper ions would be severely attenuated over such distances.

The electronic spectrum (Figure 6) of Cu(aba)$_2$ exhibited a maximum near 18.5 kK with a shoulder at about 17 kK in good accord with the results of single crystal data [39]. The observed spectrum can be interpreted in terms of $d_{x^2-y^2} \leftarrow d_{xz}$ and d_{yz} (18.5 kK) and $d_{x^2-y^2} \leftarrow d_{xy}$ (17 kK) excitations in accord with the EPR data and the results of crystal field calculations. The lack of significant exchange coupling militates against the excitonic interpretation proposed by Dijkgraaf [39]. Cu(aspg)$_2$ exhibited a broad maximum ~17.5 kK. Using donor atom coordinates determined from the crystal structure data and the following α_4 parameters (donor atom in parentheses: 9 kK (in-plane N), 8.1 kK (in plane-O) and 3.15 kK (*trans*-O), the energy level sequence: $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \gtrsim d_{yz}$ was obtained. Since the site symmetry about the copper(II) ion in Cu(aspg)$_2$ is only approximately D_{2h}, the "d" orbitals listed in the preceding sequence are only those which are dominant (>77%). Using the same crystal field parameters and the geometry about the ion in the cadmium complex [29], the same energy level sequence is calculated. The d_{xz}–d_{yz} level separation remains 0.57 kK but the parentage of the d_{xy} level changes. We attribute the g-anisotropy ($g_x - g_y = 0.037$) observed in the EPR spectrum of copper(II)-doped Cd(aspg)$_2$ to this population difference.

The low site symmetry of the copper(II) ion in Cd(aspg)$_2$ is evident in the EPR spectrum of the complex (Figures 4 and 5). Three g-values, which indicate no three-fold or higher rotation axis, are resolved as is the nuclear hyperfine anisotropy. The A_2 and A_3 hyperfine coupling constants are of about the same magnitude as expected for nitrogen superhyperfine splitting. However, for tetragonal type copper(II) complexes the perpendicular hyperfine splitting is generally 1/10 or less the parallel splitting. Two equivalent nitrogen atoms (I = 1) are expected to lead to a fine-line splitting pattern with an intensity distribution differing from that observed. Even under high gain conditions, no evidence for nitrogen superhyperfine splitting was found.

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