

Magnetic Investigations on some Copper(II) N-Acetyl- and N-Benzoyl-alaninates

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The magnetic properties of $\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{Bz-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{Bz-}\beta\text{-ala})_2$ ($\text{Ac-}\alpha\text{-ala}$ = N-acetyl-DL-alaninate, $\text{Bz-}\alpha\text{-ala}$ = N-benzoyl-DL-alaninate, $\text{Bz-}\beta\text{-ala}$ = N-benzoyl- β -alaninate ion) have been investigated by means of variable-temperature magnetic and ESR measurements. The magnetic behaviour of the compounds suggests binuclear structures with exchange integrals typical of copper acetate monohydrate-like complexes. Low-temperature ESR spectra of powdered samples show triplet absorptions characteristic of axially symmetric ($\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{Bz-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$) or rhombically distorted ($\text{Cu}(\text{Bz-}\beta\text{-ala})_2$) copper(II) carboxylate dimers. A polymeric structure is proposed for $\text{Cu}(\text{Bz-}\beta\text{-ala})_2$ due to the detection of interdimer exchange between triplet states.

Introduction

Metal complexes of N-substituted amino-acids provide simple but appropriate model compounds for the understanding of metal-protein interactions.

Unlike amino-acids, small peptides such as N-acetyl-glycine [1, 2], N-benzoyl-glycine [3], N-acetyl- β -alanine [4] and N-acetyl-DL-tryptophan [5] do not coordinate copper(II) ions through the peptide nitrogen atom. Indeed, they act as simple carboxylic acids causing, under certain conditions, strong antiferromagnetic coupling between the Cu^{2+} ions within the pairs [4–9].

As bridging carboxylate groups of the peptide chains have recently been proposed to explain the antiferromagnetic behaviour of type 3 copper enzymes [9], copper(II) complexes of N-substituted amino-acids seem to be highly appropriate for an investigation of the correlation between magnetic properties and structure. For this reason we have carried out an ESR and magnetic investigation on N-acetyl- α -, N-benzoyl- α - and N-benzoyl- β -alaninate

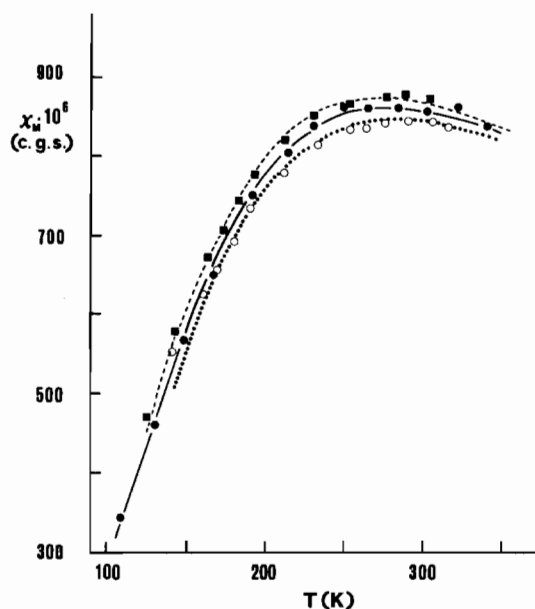


Fig. 1. Corrected molar susceptibilities and best fit-curves of $\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ (○ ○ ○), $\text{Cu}(\text{Bz-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ (● ● ●) and $\text{Cu}(\text{Bz-}\beta\text{-ala})_2 \cdot \text{H}_2\text{O}$ (■ ■ ■).

copper(II) complexes, which were suggested on the basis of previous reports to be dimeric [10].

Experimental

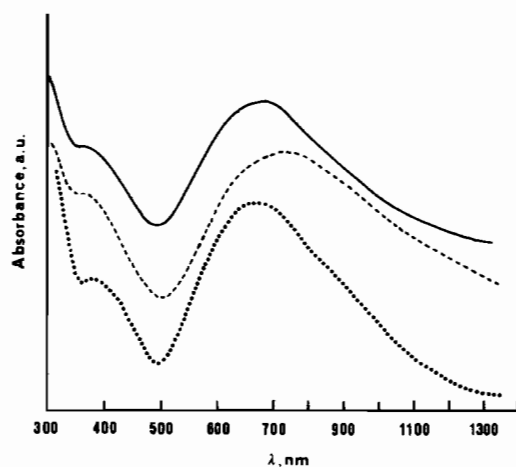
Preparation of the Complexes

$\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{Bz-}\beta\text{-ala})_2$ were prepared as previously described [10a, c].

$\text{Cu}(\text{Bz-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ could be prepared as reported in ref. [10b], but was better obtained in crystalline form by adding copper(II) perchlorate hexahydrate to an ethanolic solution of N-benzoyl- α -alanine, neutralized with ethanolic potassium hydroxide.

TABLE I. Magnetic Parameters for Copper(II) N-Acetyl- α -, N-Benzoyl- α - and N-Benzoyl- β -alaninate Complexes.

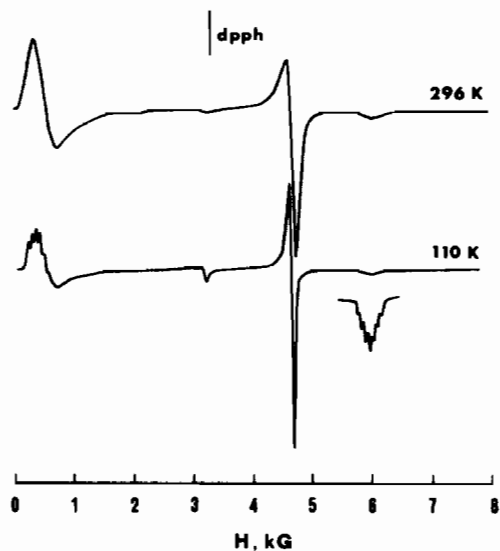
	$\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$	$\text{Cu}(\text{Bz-}\beta\text{-ala})_2$	$\text{Cu}(\text{Bz-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$
<i>Dimer</i>			
g_{\parallel}	2.375	2.374	2.395
g_{\perp}	2.080	2.074	2.087
\bar{g}	2.183	2.179	2.194
D, cm^{-1}	0.354	0.346	0.368
$2J, \text{cm}^{-1}$	-316	-303	-313
$A_{\parallel}, \text{cm}^{-1}$	78×10^{-4}	^a	74×10^{-4}
<i>Monomer</i>			
g_{\parallel}	2.379	2.368	2.379
g_{\perp}	2.071	2.058	2.068
$A_{\parallel}, \text{cm}^{-1}$	162×10^{-4}	164×10^{-4}	155×10^{-4}

^aNot detected.Fig. 2. Solid state electronic spectra of $\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ (—), $\text{Cu}(\text{Bz-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ (---) and $\text{Cu}(\text{Bz-}\beta\text{-ala})_2$ (.....).

The solution was allowed to stand at 4–5 °C overnight and potassium perchlorate was filtered off. A green crystalline compound was separated after a few days.

Physical Measurements

Variable-temperature magnetic susceptibilities were measured with a Newport Instruments Magnetic (Gouy) Balance using $\text{HgCo}(\text{SCN})_4$ for calibration; correction for diamagnetism was made using the appropriate Pascal constants. ESR spectra were obtained on a Varian E 9 X-band spectrometer. Electronic spectra were recorded on a Beckman

Fig. 3. ESR spectra of polycrystalline $\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$.

Acta M IV spectrophotometer equipped with a reflectance unit, using BaSO_4 as the reference sample.

Thermal analyses, carried out with a Perkin-Elmer TGS-2 apparatus, were used to monitor the water content of $\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ ($\Delta W_{\text{exp}} = 5.1$ wt.%, $\Delta W_{\text{theor.}} = 5.27$ wt.%) and $\text{Cu}(\text{Bz-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ ($\Delta W_{\text{exp.}} = 4.0$ wt.%, $\Delta W_{\text{theor.}} = 3.86$ wt.%).

Results

The magnetic susceptibility data obtained for powdered samples of $\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{Bz-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$

ala)₂·H₂O and Cu(Bz-β-ala)₂ in the 110–350 K temperature range are indicative of binuclear species with strong antiferromagnetic exchange. The experimental data (Fig. 1) were closely fitted by the Bleaney–Bowers equation for magnetically coupled pairs of copper(II) ions [11] and the exchange integrals, $2J$, were calculated on the basis of the $\bar{g} = [(g_{\parallel}^2 + 2g_{\perp}^2)/3]^{1/2}$ factor determined by ESR (*vide infra*) and the Van Vleck temperature-independent constant $N\alpha = 60 \times 10^{-6}$ c.g.s. units. The best fit-values (Table I) indicate that the magnitude of the exchange interaction between the copper(II) ions within the pairs is very similar for the three complexes.

The electronic spectra (Fig. 2) are also alike, being characteristic of dimeric carboxylate-bridged structures. In fact, a $d-d$ maximum is observed in the 725–665 nm (13.8–15.0 kK) range with a shoulder at about 27.0 kK, characteristic of the bridging system [12]. The observed shift of the $d-d$ maximum towards higher energy in Cu(Bz-β-ala)₂ indicates a more planar environment at the copper(II) ion.

Only the ESR spectra allowed us to differentiate the magnetic properties of the hydrates from those of the anhydrous complex. At room temperature both Cu(Ac-α-ala)₂·H₂O and Cu(Bz-α-ala)₂·H₂O reveal the same features, typical of axially symmetric binuclear copper(II) carboxylates in the triplet state (Fig. 3). The weak absorption at g ca. 2, which becomes more intense as the temperature is lowered, is assigned to mononuclear impurities present in each of the samples. At low temperatures copper(II) hyperfine splitting is detected and the 1:2:3:4:3:2:1 septets, expected for two equivalent $I = 3/2$ nuclei, are clearly evident in the parallel absorptions of the $S = 1$ species. The hyperfine structure does not appear in the signals at ca. 4900 G, presumably due to much smaller A_{\perp} values, as expected for such complexes. On the other hand, as a consequence of the exchange interaction, the A_{\parallel} values of the triplet state compounds are just half those of the corresponding $S = 1/2$ species (Table I).

Unlike the hydrate complexes, Cu(Bz-β-ala)₂ at room temperature exhibits only broad signals with the main absorption being centered at g ca. 2.15 (Fig. 4). Similar spectral features have been found for some dimeric copper(II) carboxylates [13, 14] and were explained in terms of exchange interactions between excited triplet states. According to such theory [13], triplet states are not localized, but interact between each other due to the ability to migrate throughout the crystal lattice. In the fast exchange limit, not only the temperature but even the fine structure of the $S = 1$ spectrum are averaged. As the temperature is lowered, the exchange frequency becomes smaller and the usual triplet absorptions, accompanied by the monomeric

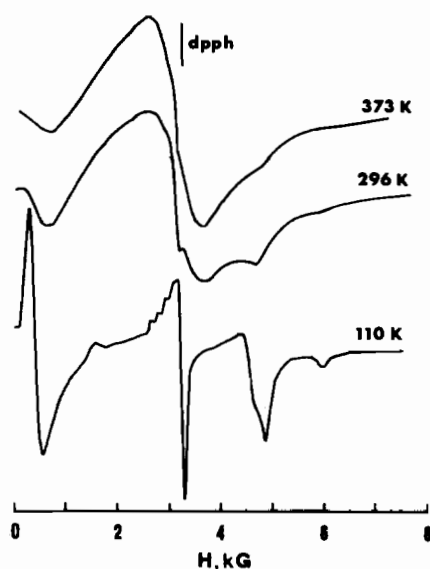


Fig. 4. ESR spectra of polycrystalline Cu(Bz-β-ala)₂. The spectra at 296 and 373 K were recorded with the same instrumental settings.

signals, show up in the spectra (Fig. 4). In this instance no evidence of hyperfine splitting of the triplet resonances was obtained. An indication of a non-zero value of E , the zero-field splitting parameter accounting for the rhombic distortion, is given by the splitting of the H_{12} signal (at ca. 4900 G), even though only one g_{\perp} value was calculated.

Using the singlet–triplet splitting value determined from the susceptibility measurements, the activation energy for the interdimeric exchange (~ 480 cm⁻¹) was evaluated from the temperature-dependence of the ESR spectrum (Fig. 4) according to ref. [14]. Again, the value exceeds the singlet–triplet separation. This is considered indicative of distinct contributions governing the migration of the triplet spin density in a crystal lattice [14].

Discussion and Conclusions

Our findings support the view that the compounds investigated possess dimeric arrangement of the copper(II) acetate type with strong antiferromagnetic exchange in the solid state. The $2J$ values lie in the range typical of several other binuclear carboxylates.

Inspection of the data summarized in Table II shows that within the series of copper(II) acetate type dimers no direct correlation of the exchange integrals with the Cu–Cu distances or the apical coordination is apparent. Instead, the magnetic parameters are more sensitive to modifications of the positive charge on the copper(II) ions produced by

TABLE II. Comparison of Magnetic Exchange Parameters for Hydrate and Anhydrous Binuclear Copper(II) Complexes.

Complex	$ -2J $ (cm^{-1})	Cu-Cu (Å)	Cu-L apical (Å)	Ref.
$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	275-305	2.64	2.16	19-21
$\text{Cu}(\text{CH}_3\text{COO})_2$	302			11
$\text{Cu}(\text{C}_2\text{H}_5\text{COO})_2 \cdot \text{H}_2\text{O}$	300			22
$\text{Cu}(\text{C}_2\text{H}_5\text{COO})_2$	300	2.578	2.28	22, 23
$\text{Cu}(\text{Acetu})_2 \cdot \text{H}_2\text{O}^a$	272	2.666	2.108	2, 6
$\text{Cu}(\text{Acetu})_2^a$	292			6
$\text{Cu}(\text{Hippu})_2^a$	327			9
$[\text{Cu}(\text{Ac-}\beta\text{-ala})_2 \cdot \text{H}_2\text{O}]_2 \cdot 2\text{H}_2\text{O}$	324	2.613	2.156	4
$\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$	316			This work
$\text{Cu}(\text{Bz-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$	313			This work
$\text{Cu}(\text{Bz-}\beta\text{-ala})_2$	303			This work

^aAcetu = N-acetylglucinate, Hippu = N-Benzoylglucinate ion.

suitable substitutions in the bridging system, as shown recently [15].

In our case the magnitude of the interdimeric interaction and the symmetry of the copper(II) coordination geometry clearly distinguish the hydrate species from the anhydrous one. Since hyperfine structure is resolved in $\text{Cu}(\text{Ac-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{Bz-}\alpha\text{-ala})_2 \cdot \text{H}_2\text{O}$, it follows that the interdimeric exchange is small. In this case the axial coordination of water molecules hinders close exchange between dimers favoring isolated copper(II) acetate monohydrate-like molecules. As the three complexes display comparable 2 J values, the occurrence of triplet excitons exchange in case of $\text{Cu}(\text{Bz-}\beta\text{-ala})_2$ is not attributable to higher population in the triplet state but to the presence of suitable paths allowing spin exchange. It thus appears that anhydrous $\text{Cu}(\text{Bz-}\beta\text{-ala})_2$ can be regarded as a coordination polymer provided with conducting bridges between binuclear clusters. Such an arrangement is suggested by both its insolubility in common organic solvents and by its IR spectrum [10c]. In fact, the only significant difference displayed by $\text{Cu}(\text{Bz-}\beta\text{-ala})_2$ with respect to the green $\text{Cu}(\text{Bz-}\beta\text{-ala})_2 \cdot 3\text{pic}$ (3-pic = 3-methylpyridine), with a caged dimer structure, is the shift of the $\nu(\text{OCO})_{\text{asym}}$ carboxylate stretching frequency from 1627 cm^{-1} (as in most metal-carboxylate dimers [4, 16, 17]) to 1583 cm^{-1} . As this behaviour has previously been found in dimeric $\text{Mo}(\text{CF}_3\text{COO})_2$, where intermolecular interactions occur through a carboxylate oxygen [18], a similar structure may be reasonably suggested for $\text{Cu}(\text{Bz-}\beta\text{-ala})_2$.

Also the rhombic distortion detected for the complex is likely related to the intermolecular bonding. It is likely that the sterical requirements of the inter-

dimeric bonds allow the complex to retain the acetate-like structure only at the expense of the in-plane symmetry, thus resulting in asymmetrical bridging of the carboxylate groups.

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