# Notes

## Magnetic and Spectroscopic Properties of Dimeric Copper(II) Complexes of *N*-Benzyloxycarbonyl-substituted Amino Acid Anions †

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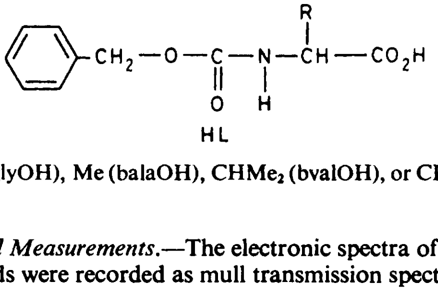
*N*-Benzyloxycarbonyl-substituted amino acids (HL) react with the copper(II) ion to form simple green complexes of formula $[\{CuL_2(H_2O)_n\}_2]$ (L = *N*-benzyloxycarbonyl-glycinate, -valinate, or -leucinate, $n = 1$ ; L = *N*-benzyloxycarbonylalaninate, $n = 0$), which show physical properties indicating a dimeric structure with strong antiferromagnetic interactions between the copper(II) ions within the pairs through a superexchange mechanism *via* bridging carboxylate groups. Exchange integrals ($-2J$) in the range 295—350 $cm^{-1}$ were calculated.

Amino acids N-protected by an acyl or benzoyl group have been found to co-ordinate the metal ions invariably only through the carboxylate group.[1] In all these ligands the presence of a carboxylate group as primary ligating group, presenting very weak co-ordinative properties also in solution,[2] is unable to promote the peptide nitrogen atom into chelation to the metal ion. In basic media, metal hydroxide precipitates before hydrogen deprotonation occurs. Further typical behaviour of these amino acids is the separation from alcoholic media of dimeric compounds, of the copper(II) acetate type, with strong antiferromagnetic exchange.[3]

In this paper we report magnetic and spectroscopic results for dimeric copper(II) complexes of some *N*-benzyloxycarbonyl-substituted amino acids (HL), in order to compare the influence of the substituent on the exchange integral values.



HL

R = H (bglyOH), Me (balaOH), $CHMe_2$ (bvalOH), or $CH_2CHMe_2$ (bleuOH)

### Experimental

*Preparation of the Complexes.*—The compounds $[\{CuL_2(H_2O)\}_2]$ [L = *N*-benzyloxycarbonyl-glycinate (bglyO), -valinate (bvalO), or -leucinate (bleuO)] and $[\{CuL_2\}_2]$ [L = *N*-benzyloxycarbonylalaninate (balaO)] were prepared by mixing NaL and copper(II) perchlorate hexahydrate with a ligand to metal molar ratio of 2 : 1 in ethanol. From the green solutions, after slow evaporation, green compounds precipitated (Found: C, 48.8; H, 4.50; N, 5.65; $H_2O$, 3.90. Calc. for $[\{Cu(bglyO)_2(H_2O)\}_2]$, $C_{40}H_{44}Cu_2N_4O_{18}$: C, 48.2; H, 4.45; N, 5.65; $H_2O$, 3.60%. Found: C, 51.45; H, 4.90; N, 5.40. Calc. for $[\{Cu(balaO)_2\}_2]$, $C_{44}H_{48}Cu_2N_4O_{16}$: C, 52.0; H, 4.75; N, 5.50%. Found: C, 54.0; H, 5.85; N, 5.00; $H_2O$, 3.10. Calc. for $[\{Cu(bvalO)_2(H_2O)\}_2]$, $C_{52}H_{68}Cu_2N_4O_{18}$: C, 53.6; H, 5.90; N, 4.80; $H_2O$, 3.10%. Found: C, 54.95; H, 6.50; N, 4.65; $H_2O$, 2.90. Calc. for $[\{Cu(bleuO)_2(H_2O)\}_2]$, $C_{56}H_{76}Cu_2N_4O_{18}$: C, 55.1; H, 6.30; N, 4.60; $H_2O$, 2.95%).

*Physical Measurements.*—The electronic spectra of the solid compounds were recorded as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. The i.r. spectra were recorded with a Perkin-Elmer 180 spectrophotometer as KBr pellets, and as Nujol mulls on KBr pellets, in the range 4 000—250 $cm^{-1}$. The magnetic susceptibilities of powdered samples were determined at different temperatures on a Gouy balance (Newport Instruments Ltd.) standardized with $Hg[Co(SCN)_4]$. The molar susceptibilities were corrected for diamagnetism using Pascal constants. The effective magnetic moments were calculated using the expression $\mu_{eff.} = 2.83(\chi_m \cdot T^{\frac{1}{2}})$. E.s.r. spectra were obtained on a Varian E9 *X*-band spectrometer on polycrystalline samples with diphenylpicrylhydrazyl (dpph, $g = 2.0036$) as calibrating field marker. Thermal analyses were performed on a Mettler TA3000 instrument with a scan speed of 5 °C $min^{-1}$.

Carbon, hydrogen, and nitrogen were analysed with a C.Erba Elemental Analyser model 1106 by Mr. G. Pistoni. The water content was determined gravimetrically by thermal analysis.

### Results and Discussion

The copper(II)–amino acid interactions in alcoholic solution (the amino acids HL are insoluble in water) give rise to the formation of green microcrystalline compounds, stable in air, which all show similar magnetic (temperature range 120—315 K) and spectroscopic properties (Table) suggestive of binuclear species with strong antiferromagnetic exchange.

The magnetic susceptibilities of the complexes are satisfactorily described by the usual Bleaney–Bowers equation for exchange-coupled dimers.[4] The $\langle g \rangle$ values obtained from the

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† *Supplementary data available* (No. SUP 56003, 4 pp.): experimental and calculated molar susceptibilities and magnetic moments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

*Non-S.I. unit employed:* B.M. = $9.274 \times 10^{-24}$ J $T^{-1}$.

**Table.** Weight-loss temperature ranges, decomposition temperatures, low-temperature (123 K) magnetic parameters, and room-temperature (298 K) electronic and i.r. data for the copper(II) complexes

| | $[\{Cu(bglyO)_2(H_2O)\}_2]$ | $[\{Cu(balaO)_2\}_2]$ | $[\{Cu(bvalO)_2(H_2O)\}_2]$ | $[\{Cu(bleuO)_2(H_2O)\}_2]$ |
|---|---|---|---|---|
| Temp. range for loss of water (K) | 358—403 | | 323—395 | 323—407 |
| Decomposition temp. (K) | 413 | 423 | 419 | 409 |
| $g_{\parallel}$ | 2.371 | 2.344 | 2.384 | 2.337 |
| $g_{\perp}$ | 2.065 | 2.071 | 2.083 | 2.074 |
| $\langle g \rangle$ * | 2.168 | 2.165 | 2.188 | 2.165 |
| $D$/cm$^{-1}$ | 0.33 | 0.36 | 0.38 | 0.36 |
| $\mu_{eff.}$/B.M. (298 K) | 1.41 | 1.35 | 1.33 | 1.37 |
| $\lvert 2J \rvert$/cm$^{-1}$ | 295 ± 5 | 343 ± 9 | 350 ± 6 | 335 ± 7 |
| *d–d* transition, ν/cm$^{-1}$ | 14 600 | 14 700 | 14 800 | 14 300 |
| Charge transfer, ν/cm$^{-1}$ | 27 000 (sh) | 26 300( sh) | 26 300 (sh) | 26 700 (sh) |
| ν(NH)/cm$^{-1}$ | 3 340ms | 3 358s | 3 340m<br>3 280ms | 3 340ms |
| $\nu(OCO_{ester})_{asym}$/cm$^{-1}$ | 1 725s<br>1 690vs | 1 690vs | 1 720vs<br>1 680vs | 1 725vs<br>1 690vs |
| $\nu(OCO_{ester})_{sym}$/cm$^{-1}$ | 1 290vs<br>1 260vs | 1 280s<br>1 250s | 1 268s<br>1 218s | 1 240s<br>1 215ms |
| $\nu(OCO_{carboxylate})_{asym}$/cm$^{-1}$ | 1 615vs | 1 605vs | 1 630vs | 1 625vs |
| $\nu(OCO_{carboxylate})_{sym}$/cm$^{-1}$ | 1 405vs | 1 420vs | 1 420vs | 1 415s |

* $\langle g \rangle = [(g_{\parallel}^2 + 2g_{\perp}^2)/3]^{\frac{1}{2}}$.

e.s.r. spectra and the temperature-independent paramagnetism, $N\alpha = 60 \times 10^{-6}$, are used as constants in the fitting process. The best-fit values (Table) support the hypothesis of isolated copper dimers with a negative intradimer exchange very similar for all the complexes. Furthermore, the $\lvert 2J \rvert$ values for the present complexes are comparable to those of other copper(II) dimers of N-protected amino acids (272—351 cm$^{-1}$) [3,5–10] and carboxylic acids (275—340 cm$^{-1}$),[11–13] and may account for an interaction *via* a superexchange mechanism and for a copper acetate type structure.

The spectroscopic results also agree with the presence of dimeric structures and with an amino acid co-ordination only through the carboxylate group. In fact the electronic spectra show two bands at 14 300—14 800 [the 'ordinary copper(II) band' (*d-d*)[14]] and 26 300—27 000 cm$^{-1}$ (charge-transfer band; considered as diagnostic of a dimeric structure [14–17]) very similar in shape and positions to those found for the structurally known tetrakis-[μ-(*N*-acetylglycinato)]-diaquadicopper(II) [18,19] and tetrakis-[μ-(*N*-acetyl-β-alaninato)]-diaquadicopper(II) dihydrate.[6]

The absorptions in the i.r. spectra of the complexes assigned to the most significant ligand functions are reported in the Table. Several aspects are worth noting. (*a*) The position of the NH stretching vibration in the complexes (3 340—3 358 cm$^{-1}$) is unchanged from that in the corresponding alkali-metal salts (3 315—3 340 cm$^{-1}$), which confirms the inability of this group to participate in the co-ordination, if undeprotonated. In the structurally known N-protected amino acid complexes of copper(II) the NH group is found to be involved only in intermolecular hydrogen bonding, generally among peptide groups.[1] (*b*) The positions and separations of the intense antisymmetric and symmetric carboxylate stretching frequencies indicate the presence of *syn–syn* bridging co-ordinated carboxylate groups.[5,6,10] (*c*) The $\nu(OCO_{ester})_{asym}$ band in aqueous complexes is split, which may be explained as due to the probable involvement of half of these groups in hydrogen bonding with water molecules (one amino acid for one water molecule).

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