Notes

Magnetic and Spectroscopic Properties of Dimeric Copper(II) *N*-Benzoylvalinates †

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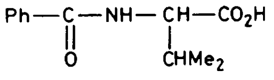
The e.s.r. spectra and temperature-dependent magnetic susceptibility of some complexes of the type $[Cu(bzValO)_2]$, $[Cu(bzValO)_2]\cdot H_2O$, and $[Cu(bzValO)_2L]$ (bzValO = *N*-benzoylvalinate anion; L = pyridine and 3- or 4-methylpyridine) are reported. Results suggest a dimeric structure for all the complexes with strong antiferromagnetic interactions between the Cu^{2+} ions within the pairs through a superexchange mechanism *via* the bridging carboxylate groups. A correlation between the values of $|2J|$ for a series of copper(II) amino-acid complexes and monoamine adducts and a comparison with $|2J|$ values of binuclear copper(II) carboxylates are presented.

It has previously been stated [1] that magnetic exchange interactions are important in a number of metalloprotein systems, including some copper-containing proteins. Consequently the knowledge of the possible pathways through which such interactions can be transmitted may be pertinent to the study of electron-transfer processes. A superexchange mechanism of interaction occurring *via* the bridging carboxylate groups is now preferred, rather than *via* a direct metal–metal bond.[2,3]

Amino-acids *N*-protected by an acyl or benzoyl group were often found to act as bridging bidentate ligands, *via* the carboxylate group, toward two copper ions, forming dimeric or polymeric complexes;[4] therefore the study of these systems may help us to understand the inter-relationships between structure and metal–metal interaction.

In this paper we report magnetic and spectroscopic results for the simple and mixed copper(II) amine complexes of



$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}NH{-}\underset{\underset{CHMe_2}{|}}{CH}{-}CO_2H}$$

bzVal

N-benzoyl-DL-valine (bzVal), which, being more complicated than the previously investigated *N*-protected amino-acids, enable us to extend our investigation also to the effect of ligand size.

Experimental

All chemicals were reagent grade and used as received.

Preparation of the Complexes.—The green complex $[Cu(bzValO)_2]\cdot H_2O$ instantaneously precipitated by mixing an aqueous solution of $[Cu(O_2CMe)_2]\cdot H_2O$ (10^{-2} mol dm^{-3}) with a concentrated methanolic solution of bzVal (2×10^{-2} mol dm^{-3}). By standing the filtered solution of the above compound for several days at room temperature (20 °C), the dark green $[Cu(bzValO)_2]$ complex separated.

All the $[Cu(bzValO)_2L]$ adducts [L = py (pyridine), 3Me-py, and 4Me-py] were prepared by adding diethyl ether to an ethanolic solution containing $[Cu(bzValO)_2]\cdot H_2O$ (10^{-2} mol dm^{-3}) and the appropriate amine (2×10^{-2} mol dm^{-3}).

Table 1. Analytical data

Complex	Analysis (%) * C	H	N
$[Cu(bzValO)_2]\cdot H_2O$	54.6 (55.2)	5.8 (5.8)	5.3 (5.4)
$[Cu(bzValO)_2]$	56.7 (57.2)	5.8 (5.6)	5.5 (5.6)
$[Cu(bzValO)_2(py)]$	59.6 (59.7)	6.1 (5.7)	7.3 (7.2)
$[Cu(bzValO)_2(3Me\text{-}py)]$	60.4 (60.3)	6.0 (5.9)	7.1 (7.0)
$[Cu(bzValO)_2(4Me\text{-}py)]$	60.1 (60.3)	6.0 (5.9)	7.0 (7.0)

* Calculated values are given in parentheses.

Physical Measurements.—Electronic, i.r., and e.s.r. spectra of the compounds were recorded as previously described.[4d] 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 $\mu_{eff.} = 2.83(\chi_M \cdot T)^{\frac{1}{2}}$.

Analysis. C, H, and N analyses of the complexes were performed by Mr. G. Pistoni using a C. Erba Elemental analyser model 1106. The data are presented in Table 1.

Results

All the complexes are stable in air and soluble in common organic polar solvents.

The direct interaction between the copper(II) ion and the amino-acid gives rise to the formation of two green complexes, one monohydrate and one anhydrous, which react with amines (py, 3Me-py, and 4Me-py) forming green monoamine adducts. All the complexes show similar magnetic and spectroscopic properties (Table 2).

In the e.s.r. spectra (Figure 1) an absorption near 3 000 G, whose intensity increases as the temperature decreases, assigned to mononuclear impurities of spin $S = \frac{1}{2}$, is also observed for all the complexes and the corresponding g values are reported in Table 2.

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† *Supplementary data available* (No. SUP 23364, 7 pp.): observed and calculated molar susceptibilities. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: 1 B.M. = 0.927×10^{-23} A m^2.

Table 2. Magnetic parameters and electronic spectral data for copper(II) *N*-benzoylvalinates

	$[Cu(bzValO)_2]\cdot H_2O$	$[Cu(bzValO)_2]$	$[Cu(bzValO)_2(py)]$	$[Cu(bzValO)_2(3Me\text{-}py)]$	$[Cu(bzValO)_2(4Me\text{-}py)]$
(*a*) Dimer					
$g_\parallel$	2.393	2.362	2.393	2.389	2.403
$g_\perp$	2.089	2.119	2.093	2.098	2.081
$\bar{g}$ [a]	2.191	2.200	2.193	2.195	2.188
D/cm^{-1}	0.372	0.363	0.383	0.377	0.389
E/cm^{-1}		0.0025			0.0029
$10^{-4}A_\parallel$/cm^{-1}	61	72	72	61	67
$\lvert 2J\rvert$/cm^{-1}	302 ± 2	342 ± 3	308 ± 4	350 ± 6	335 ± 11
$-10^6\Delta$ [b]/c.g.s.u.	257.72	244.72	293.72	307.24	307.24
$\mu_{eff.}$ [c]/B.M.	1.46	1.39	1.49	1.37	1.38
Electronic spectra d–d/10^3 cm^{-1}	14.1	15.2	13.9	13.7	13.8
Electronic spectra c.t./10^3 cm^{-1}	25.6 (sh)	24.4 (sh)	25.6 (sh)	26.0 (sh)	25.6 (sh)
(*b*) Monomer					
Y [d]	0.028	0.019	0.058	0.002	
$g_\parallel$	2.343	2.333	2.298	2.292	
$g_\perp$	2.060	2.075	2.122	2.059	
$10^{-4}A_\parallel$/cm^{-1}	164	163	161	171	

[a] $\bar{g} = [(g_\parallel^2 + 2g_\perp^2)/3]^{\frac{1}{2}}$. [b] $-\Delta$ = diamagnetism of the complexes. [c] At 295 K. [d] Y = mol fraction of monomeric impurities.

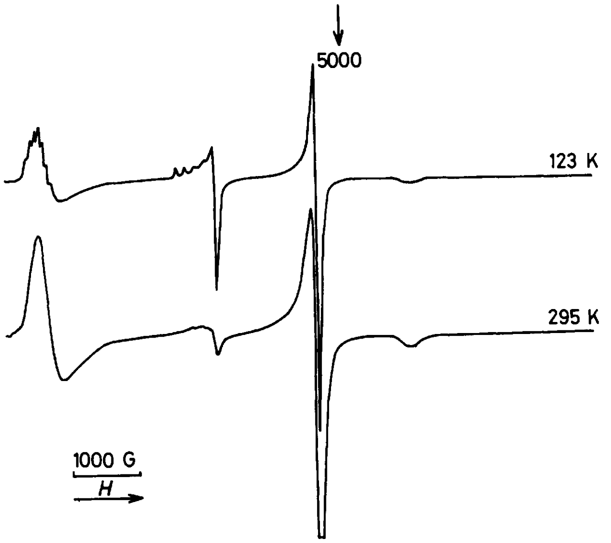

Figure 1. E.s.r. spectrum of $[Cu(bzValO)_2]\cdot H_2O$

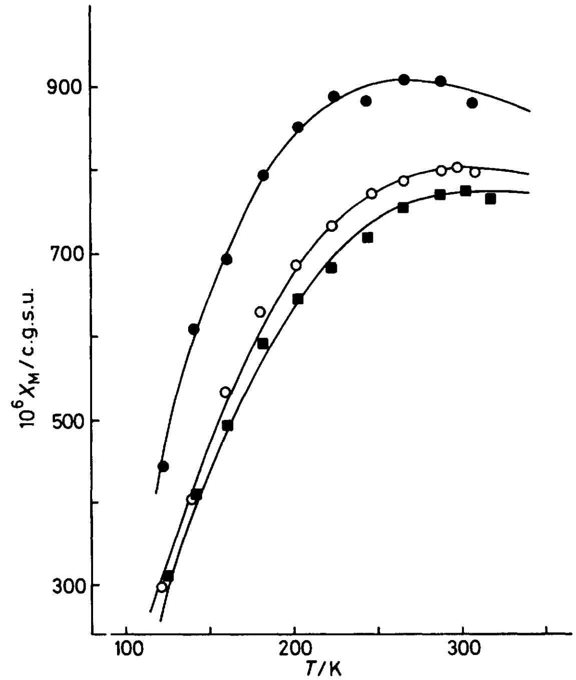

Figure 2. Corrected molar susceptibilities of $[Cu(bzValO)_2]$ (○), $[Cu(bzValO)_2]\cdot H_2O$ (●), and $[Cu(bzValO)_2(3Me\text{-}py)]$ (■); the full lines are the calculated best fit to the Bleaney-Bowers equation for $[Cu(bzValO)_2(3Me\text{-}py)]$, and to the corrected Bleaney-Bowers equation[8] for $[Cu(bzValO)_2]$ and $[Cu(bzValO)_2]\cdot H_2O$

The other absorptions are assigned to transitions in the triplet state. At 123 K, the absorption at the lowest magnetic field shows the seven-line hyperfine splitting from the two equivalent copper nuclei[5] and in the spectra of the 4Me-py and anhydrous compounds the $H_{\perp 2}$ band is split into two (H_x and H_y) implying that E is non-zero (but small). The transitions in the spectra at 123 K allow us to calculate the zero-field splitting parameters D and E and to obtain values for $g_\parallel$ and $g_\perp$.[6] The results are collected in Table 2.

The susceptibilities may be described by the usual Bleaney-Bowers equation for exchange coupled dimers[7] for the $[Cu(bzValO)_2L]$ (L = 3Me-py and 4Me-py), while for the other complexes it should be modified for the presence of monomeric impurities whose mol fraction is indicated as Y (Table 2) and estimated from the fitting process by using equation (4) of ref. 8.

The g values obtained from the e.s.r. spectra are used as constants in the fitting process (Table 2) and the temperature-independent paramagnetism, $N\alpha = 60 \times 10^{-6}$ c.g.s.u. The molar susceptibility data (Figure 2) support the hypothesis of isolated copper dimers with a negative intradimer exchange.

The electronic (Table 2) and i.r. data [$\nu(OCO)_{asym.} \simeq$ 1 630 cm^{-1}, $\nu(OCO)_{sym.} \simeq$ 1 420 cm^{-1}] of the hydrate and monoamine adducts are similar to those of structurally known binuclear copper(II) complexes.[3b,4d,4e] The spectroscopic data of $[Cu(bzValO)_2]$ are markedly different and require a further discussion.

Table 3. Structural and magnetic data for selected caged-dimer copper(II) complexes

Complex [a]	d(Cu–Cu)/Å	Bridge length [b]/Å	$\lvert 2J \rvert$/cm^{-1}	Ref.
$[\mathrm{Cu(O_2CMe)_2}]\cdot\mathrm{H_2O}$	2.616	6.458	275—305	2, *c*
$[\mathrm{Cu(acGlyO)_2}]\cdot\mathrm{H_2O}$	2.666	6.453	272	4*b*, *d*
$[\mathrm{Cu(acGlyO)_2}]$			292	*d*
$[\mathrm{Cu(bzGlyO)_2}]$			327	6
$[\mathrm{Cu(ac\text{-}\alpha\text{-}AlaO)_2}]\cdot\mathrm{H_2O}$			316	9
$[\mathrm{Cu(bz\text{-}\alpha\text{-}AlaO)_2}]\cdot\mathrm{H_2O}$			313	9
$[\mathrm{Cu(O_2CEt)_2}]$	2.578	6.44	300	2*b*, *e*
$[\mathrm{Cu(O_2CEt)_2}]\cdot\mathrm{H_2O}$			300	*e*
$[\mathrm{Cu(ac\text{-}\beta\text{-}AlaO)_2}]\cdot\mathrm{2H_2O}$	2.613	6.455	324	4*d*
$[\mathrm{Cu(bz\text{-}\beta\text{-}AlaO)_2}]$			303	9
$[\mathrm{Cu(O_2CPr^n)_2}]$	2.565	6.46	322	2*b*, *e*
$[\mathrm{Cu(O_2CPr^n)_2}]\cdot\mathrm{H_2O}$			339	*e*
$[\mathrm{Cu(acValO)_2}]\cdot\mathrm{H_2O}$			351	*f*
$[\mathrm{Cu(bzValO)_2}]\cdot\mathrm{H_2O}$			302	This work
$[\mathrm{Cu(bzValO)_2}]$			342	This work
$[\mathrm{Cu(acTrpO)_2}]\cdot\mathrm{H_2O}$			351	4*c*
$[\mathrm{Cu(O_2CMe)_2(py)}]$	2.630	6.44	325, 329	2*b*, *g*
$[\mathrm{Cu(O_2CMe)_2(3Me\text{-}py)}]$			322, 318	*g*
$[\mathrm{Cu(O_2CMe)_2(4Me\text{-}py)}]$			325, 318	*g*
$[\mathrm{Cu(O_2CEt)_2(2Me\text{-}py)}]$	2.647	6.425	364	2*a*
$[\mathrm{Cu(O_2CEt)_2(3Me\text{-}py)}]$	2.631	6.437	364	2*a*
$[\mathrm{Cu(bzValO)_2(py)}]$			308 ± 4 [h]	This work
$[\mathrm{Cu(bzValO)_2(3Me\text{-}py)}]$			350 ± 6	This work
$[\mathrm{Cu(bzValO)_2(4Me\text{-}py)}]$			335 ± 11	This work

[a] Abbreviations: acGlyO = *N*-acetylglycinate, ac-α-AlaO and bz-α-AlaO = *N*-acetyl- and *N*-benzoyl-DL-alaninate, ac-β-AlaO and bz-β-AlaO = *N*-acetyl- and *N*-benzoyl-β-alaninate, acValO = *N*-acetyl-DL-valinate; acTrpO = *N*-acetyl-DL-tryptophanate.

[b] The bridge length is defined as the mean Cu–O–C–O–Cu distance through the bridging carboxylate groups.

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[h] This $\lvert 2J \rvert$ value may be less precise because of the presence of monomeric impurities estimated as $Y = 5.8\%$ (Table 2).

Discussion

The $\lvert 2J \rvert$ values for the present complexes (Table 3) are quite comparable to those of other copper(II) dimers of *N*-protected amino-acids and carboxylic acids, and may account for an interaction *via* a superexchange mechanism. The comparison of the data available at present on similar complexes enables us to draw several conclusions.

First of all it should be noted that since hyperfine structure is resolved, the singlet–triplet separation must be much larger than the hyperfine components and interdimer exchange must be smaller than 0.1 cm^{-1}; only for the anhydrous complex does the broadening of the signal suggest that relevant interdimeric exchange is present. The $[\mathrm{Cu(bzValO)_2}]$ complex also shows in the electronic spectrum (Table 2) a higher energy shift of the *d–d* band due to a more planar arrangement of the CuO$_4$ chromophore and a lower energy shift of $\nu(\mathrm{OCO})_{\mathrm{asym.}}$ (1 598 cm^{-1}), as found in other anhydrous binuclear compounds,[3b,4d,9] due to a diminishing of copper–oxygen bond strength [9] as a consequence of intermolecular interactions *via* a carboxylate oxygen atom.[9]

Secondly, it may be observed that according to a theoretical treatment [10] on similar systems, the electronegativity of the substituent on the nitrogen atom affects $\lvert 2J \rvert$ which is lower for the benzoyl derivatives than for the corresponding acetyl compounds (Table 3). The $\lvert 2J \rvert$ reported value [6] for $[\mathrm{Cu(bzGlyO)_2}]$ (bzGlyO = *N*-benzoylglycinate) which is contrary to this trend was due to an overestimation of $g_{\parallel}$.

Furthermore, we compare the Cu–Cu distance, the mean Cu–O–C–O–Cu bridging pathway, and the $\lvert 2J \rvert$ values (Table 3) for structurally known dimers and we note that none of these factors may by itself exert a substantial effect upon the magnitude of $\lvert 2J \rvert$. If we consider the aforementioned factors together with the polarizability of the alkyl group attached to carboxylate [11] and the presence of an electron-withdrawing substituent on the nitrogen atom it should be feasible to rationalize the experimental results, as previously no theory has unequivocally explained the factors which determine the magnetic behaviour of such compounds.[2,10,11] The lack of sufficient structural data does not enable this correlation to be verified, but provides a rational direction for further experiments.

In view of all the above, we can state that *N*-protected amino-acid systems are efficient transmitters of spin, like the simple carboxylic acids (Table 3).[2]

Also, the $\lvert 2J \rvert$ values for the monoamine adducts (Table 3) parallel the behaviour of analogous carboxylate compounds. In fact, $\lvert 2J \rvert$ increases for these complexes in comparison with those for the hydrated and anhydrous ones because of the greater basicity of the apical ligand.

Acknowledgements

We thank the Centro Strumenti of the University of Modena for the recording of the i.r. spectra, the Centro di Calcolo Elettronico of the University of Modena for the computing facilities, and the Consiglio Nazionale delle Ricerche (C.N.R.) of Italy for financial support.

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Received 9th March 1982; *Paper* 2/413