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CALORIMETRIC AND STRUCTURAL INVESTIGATION OF MONOMERIC AND DIMERIC COPPER(II)-*N*-PROTECTED AMINOACIDATES

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ABSTRACT

A calorimetric investigation of the dehydration of structurally-known binary copper(II)-*N*-protected aminoacidates is reported to compare their relative stability. In order to consider a series of strictly related compounds, the crystal and molecular structure of *N*-benzoyl-α-alaninate (bz-α-ala) complex is also determined. The compound crystallizes in the triclinic space group $P\bar{1}$ with 1 formula unit in a cell of dimensions $a = 9.425(3)$, $b = 9.579(3)$, $c = 12.644$ Å, $\alpha = 74.10(2)°$, $\beta = 78.95(2)°$, $\gamma = 88.32(3)°$. The structure was solved using the Patterson and Fourier methods and refined by least-squares calculations to a conventional R factor of 5.6% for 3134 counter data. It consists of centrosymmetric tetracarboxylato bridged binuclear molecules showing the copper(II) acetate structure.

The calorimetric analysis shows higher dehydration E_a values for dimeric species with respect to blue ones which assign a peculiar stability to dimeric structures. The crystal size strongly influences kinetic parameters because the proportion between water molecules on the surface and in the bulk varies with the crystal dimensions.

INTRODUCTION

Dimeric copper(II)acetate-like binary complexes are easily formed by most carboxylate ligands and *N*-protected aminoacids [1,2]. Using slightly different experimental methods, monomeric species may also be prepared for the second type of ligands, but they are seldom obtained from diluted aqueous solutions. In these cases, the blue monomers easily transform into the green hydrated dimers or anhydrous polymers when standing at room temperature in air, by recrystallizing from a hydroalcoholic mixture, or by heating to moderate temperatures [3]. On the other hand, the caged-dimer structure of the binary complexes is also retained in ternary adducts with

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aromatic amines of low p*Ka* (p*Ka* < 6) [4–6] such as pyridines, thus suggesting that a peculiar stability pertains to dimeric or polymeric species. Consequently, thermodynamic and kinetic parameters relative to the dehydration process would be very useful for the confirmation and quantification of this stability. In these transformations a role may also be played by the different kinds of water molecules present in the lattice. However coordinated and uncoordinated water molecules can be expected to be indistinguishable by thermal measurements since, according to the literature, they have comparable binding strength and will be eliminated simultaneously [7,8].

Hitherto, in this area no systematic studies exist on the dehydration and structure rearrangement of these compounds [9], in particular from a kinetic point of view. We report here the calorimetric and kinetic investigation on a series of strictly-related, structurally-known monomeric and dimeric copper(II)-*N*-protected aminoacidates. Furthermore, since the crystal structure is available in the literature only for *N*-acetylglycine and *N*-acetyl-β-alanine complexes, we also made a structural investigation of the *N*-benzoyl-α-alanine-copper(II) compound, to which dimeric structure has been previously assigned by means of magnetic and spectroscopic measurements [10].

EXPERIMENTAL

Preparation of complexes

The compounds were prepared as reported in refs. 2 and 10.

Thermal measurements

DSC measurements were carried out by employing a Perkin Elmer DSC-4, and TGA measurements were made using a Mettler TA 3000 instrument. Both thermograms were generally recorded at a rate of 3 K min^{-1}.

For DSC, closed pans in static air were used and sample size was always near 2 mg. For TGA, closed crucibles were used in air with sample size in the range 10–15 mg.

Kinetic parameters were computed from the DSC thermograms recorded by a standard DSC-4 kinetic program which operated in a range corresponding to the central 90% of the peak by default. For green compounds, which exhibited some superposition of the dehydration (endothermic) and decomposition peaks (exothermic), the choice of a proper baseline was made by selecting a slightly increasing one, that is by an assumption of the same thermal conductivity as that before the peak considered. The same measurements were performed on powders with different crystal size and different heating rate in order to ascertain their possible influence on the parameters computed. The measurements were repeated under nitrogen flow (10 cm^3 min^{-1}), but no significant differences were detected.

X-ray data collection

Crystal data for $[\{Cu(bz\text{-}\alpha\text{-}ala)_2(H_2O)\}_2]$

$C_{40}H_{44}Cu_2N_4O_{14}$, $M = 931.91$, triclinic, $a = 9.425(3)$, $b = 9.579(3)$, $c = 12.644(2)$ Å, $\alpha = 74.10(2)°$, $\beta = 78.95(2)°$, $\gamma = 88.32(3)°$, $U = 1077.14$ Å^3, Space group $\underline{P}_{l}^{-}$ (C_i^l, No. 2), $D_m = 1.44$ g cm^{-3} (by flotation), $Z = 1$, $D_c = 1.437$ g cm^{-3}, $F(000) = 481.97$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 9.99$ cm^{-1}.

A prismatic crystal of approximate dimensions 0.45 × 0.20 × 0.20 mm was used for data collection on an Enraf-Nonius CAD4 automated single-crystal diffractometer. Unit cell dimension determination and intensity data measurements were made at room temperature by using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Cell dimensions were determined from a least-squares fit to the setting angles of 25 intense reflections from diverse regions of reciprocal space. Intensity data for ±h, ±k, +l reflections were collected with the ω-2θ scan method in the $2.5 \leqslant \theta \leqslant 25.0°$ range, with a scan width of 1.4° + 0.35(tan θ) and a scan speed range of 2.06–3.30 deg min^{-1}. The intensities of two standard reflections, monitored at 1-h intervals, showed no significant changes. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on the ψ scan [11], was applied ($0.925 \leqslant T$ factor $\leqslant 0.999$). The final set of data consisted of 3808 unique reflections, of which 3134 had $I \geqslant 3\sigma(I)$ and were used in the structure analysis.

The centrosymmetric space group $\underline{P}_{l}^{-}$ was initially assumed and then confirmed by the subsequent refinement of the structure, which was solved by standard Patterson and Fourier methods, and refined through full-matrix least-squares calculations *. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were added to the model as fixed contributors at their observed positions, except those belonging to the methyl group, which were placed in calculated locations. Final convergence was reached at $R = 0.056$ and $R_w = 0.060$ ($w = 1.0/\sigma^2(F) + 0.0105\ F_0^2$). A final difference map had no significant features, with a maximum residual of 1.3 e Å^{-3} near the metal atom. There were no evidence for secondary extinction.

Complex neutral-atom scattering factors [12a,b] were used throughout; major calculations were carried out on a VAX-11/750 computer by using

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* The quantity minimized during refinement was $\Sigma w(|F_0| - |F_c|)^2$, where w is the weighting factor. The unweighted and weighted residuals are defined as follows: $R = (\Sigma|F_0| - |F_c|)/\Sigma|F_0|$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$.

TABLE 1

Final positional parameters

Atom	x/a	y/b	z/c
Cu	0.47400(4)	0.47199(4)	0.40801(3)
O(1)	0.2864(3)	0.4113(4)	0.5080(3)
O(2)	0.3268(3)	0.4560(3)	0.6639(2)
C(1)	0.2501(4)	0.4152(5)	0.6070(4)
C(2)	0.0950(6)	0.3618(9)	0.6607(5)
C(3)	0.078(1)	0.198(1)	0.6514(8)
N(1)	0.0626(4)	0.3616(5)	0.7770(3)
C(4)	−0.0740(4)	0.3609(4)	0.8309(3)
O(3)	−0.1761(3)	0.3648(4)	0.7817(3)
C(5)	−0.0991(4)	0.3453(4)	0.9542(4)
C(6)	−0.2356(5)	0.3826(6)	1.0042(4)
C(7)	−0.2671(6)	0.3653(6)	1.1175(5)
C(8)	−0.1650(7)	0.3114(6)	1.1817(4)
C(9)	−0.0344(6)	0.2740(7)	1.1341(4)
C(10)	−0.0010(5)	0.2909(6)	1.0199(4)
O(4)	0.4123(3)	0.6753(3)	0.3767(2)
O(5)	0.4492(4)	0.7197(3)	0.5340(3)
C(11)	0.4095(5)	0.7549(4)	0.4410(3)
C(12)	0.3579(7)	0.9080(5)	0.4036(4)
C(13)	0.224(1)	0.926(1)	0.4846(6)
N(2)	0.3346(5)	0.9393(4)	0.2896(3)
C(14)	0.3379(6)	1.0730(5)	0.2236(5)
O(6)	0.3438(7)	1.1765(4)	0.2624(4)
C(15)	0.3343(5)	1.0962(4)	0.1035(4)
C(16)	0.3872(6)	1.2232(5)	0.0291(5)
C(17)	0.3959(6)	1.2483(6)	−0.0850(5)
C(18)	0.3470(6)	1.1439(6)	−0.1244(4)
C(19)	0.2929(7)	1.0160(6)	−0.0512(5)
C(20)	0.2852(6)	0.9896(5)	0.0618(4)
Ow(7)	0.4005(3)	0.4479(3)	0.2644(2)

the SHELX-76 system of programs [13].

Final positional parameters for non-hydrogen atoms are given in Table 1. Lists of anisotropic temperature factors, of hydrogen atom parameters and of observed and calculated structure factors are available as supplementary material.

RESULTS AND DISCUSSION

Description of the structure

A drawing of the structure, showing the numbering scheme, is given in Fig. 1. Selected bond distances and bond angles are reported in Table 2. Lists of complete bond distances and bond angles, hydrogen bonding

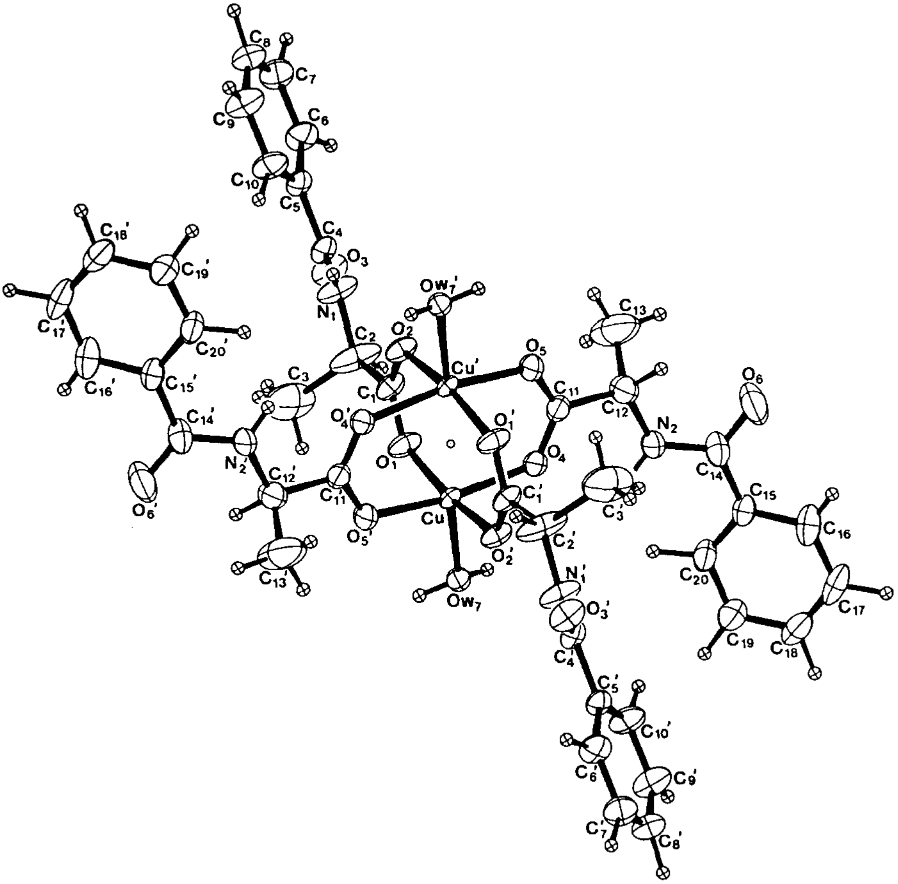

Fig. 1. ORTEP view of the complex molecule showing the atom numbering and thermal motion ellipsoids (40%) for non-hydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius. Primed atoms are related to unprimed by an inversion centre.

interactions and selected least-squares planes are available as supplementary material *.

The structure consists of centrosymmetric tetracarboxylato-bridged binuclear molecules showing the well-known dimeric cupric acetate monohydrate structure [14,15]. The dimensions of our coordination polyhedron compare very well with those reported for many bridged binuclear copper(II) carboxylates [4,5,16], whose structural features, updated to 1980, were recently reviewed by Melnik [5]. The Cu · · · Cu separation of 2.660(1) Å is in the range 2.563–2.666Å reported for the CuO_5 chromophore, and correlates well with the displacement of the metal atom from its basal coordina-

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* Lists of observed and calculated structure factors, anisotropic thermal parameters, hydrogen atom parameters, bond distances and angles involving carbon and hydrogen atoms, selected least-squares planes (23 pages) are available from Dr. P. Baraldi, Dipartimento di Chimica dell'Università di Modena, via G. Campi 183, 41100 Modena, Italy on request.

TABLE 2

Selected bond distances (Å) and bond angles (deg)

Cu-O(1)	1.966(3)	Cu-O(2′)	1.976(3)
Cu-O(4)	1.972(3)	Cu-O(5′)	1.955(3)
Cu-Ow(7)	2.134(3)	Cu · · · Cu′	2.660(1)
C(1)-O(1)	1.243(5)	Cu(11)-O(4)	1.253(5)
C(1)-O(2)	1.250(5)	C(11)-O(5)	1.257(5)
C(2)-N(1)	1.442(6)	C(12)-N(2)	1.448(6)
N(1)-C(4)	1.336(5)	N(2)-C(14)	1.321(6)
C(4)-O(3)	1.236(5)	C(14)-O(6)	1.227(6)
O(1)-Cu-O(4)	89.5(1)	O(1)-Cu-O(2′)	167.4(2)
O(1)-Cu-O(5′)	90.4(1)	O(1)-Cu-Ow(7)	93.5(1)
O(4)-Cu-O(2′)	88.5(1)	O(4)-Cu-O(5′)	167.4(2)
O(4)-Cu-Ow(7)	90.7(1)	O(2′)-Cu-O(5′)	88.9(1)
O(2′)-Cu-Ow(7)	98.9(1)	O(5′)-Cu-Ow(7)	101.9(1)
Ow(7)-Cu · · · Cu′	170.4(1)	C(1)-O(1)-Cu	127.1(3)
C(1)-O(2)-Cu′	118.5(3)	C(11)-O(4)-Cu	125.3(3)
C(11)-O(5)-Cu′	121.4(3)	C(2)-N(1)-C(4)	121.0(4)
C(12)-N(2)-C(14)	119.8(5)		

Primed atoms are related to unprimed by the symmetry transformation $1-x$, $1-y$, $1-z$ of the reference coordinates.

tion plane (planar within ±0.0002 Å) of 0.215 Å [5]. Our mean Cu-O equatorial bond distance of 1.967(3) Å is consistent with the almost constant reported value of 1.96 Å, as well as the Cu-O apical bond length of 2.134(3) Å, close to the averaged reported value of 2.11 Å [5]. The largest distortion from ideal C_{4v} geometry about the copper atom involves the Cu-O_{apical} bond direction, which deviates 6.2° from the normal to the basal coordination plane. Further interesting structural dimensions are the Cu-O-C-O-Cu bridge lengths (6.435 and 6.437 Å in our case), and the sum of all interatomic distances (including half value of the Cu · · · Cu separation) of 11.33 Å; their reported, almost constant mean values for the CuO_5 chromophore are 6.44 and 11.43 Å, respectively [5]. The corresponding bond distances and bond angles within the two crystallographically independent bz-α-ala ligands do not differ significantly, and are in the ranges expected.

The crystal packing is mainly determined by two strong intermolecular hydrogen bonding interactions, which involve water protons and benzoylic oxygens, with O · · · O distances of 2.68 and 2.78 Å, and subtended angles at H atoms of 167 and 166°, respectively. Weaker intramolecular, hydrogen-bonding interactions occur between aminic protons and carboxylate oxygens.

Thermal data

For the compounds examined the dehydration peaks are generally not simple; they exhibit a tail before or after them, or a not-well-resolved doubling even for low heating rates.

TABLE 3

Calorimetric and kinetic parameters for Cu(II)-*N*-protected aminoacidates [a]

	Dehydration temp. range (°C) (and peak temp. in parentheses)	Dehydration enthalpy (kJ mol^{-1})	$\log_{10} A$	Activation energy (kJ mol^{-1})	Reaction order	%H_2O weight loss
Green compounds						
$[Cu(acgly)_2(H_2O)_2]_2$	162–187 Dec. (179)	55.9	43.0	194±4	0.8	7.0
$[Cu(ac\text{-}\beta\text{-}ala)_2(H_2O)]_2 \cdot 2H_2O$	84– 95 (90)	51.5	159	273±6	1.72	10.5
$[Cu(bz\text{-}\alpha\text{-}ala)_2(H_2O)]_2$	160–186 Dec. (177)	65.4	41.3	176±4	0.9	4.2
Blue compounds						
$[Cu(acgly)_2(H_2O)_2]2H_2O$	79–107 (99)	51.9	38.1	66±1	0.9	18.0
$[Cu(ac\text{-}\beta\text{-}ala)_2(H_2O)_2]$	86–105 (98)	58.2	61.4	110±2	1	10.4

[a] Abbreviations: acgly, *N*-acetylglycinate anion; ac-β-ala, acetyl-β-alaninate anion; bz-α-ala, *N*-benzoylalaninate anion.

The data obtained from DSC and TGA measurements are summarized in Table 3. They show that the molar enthalpy values measured over the whole series of copper(II) compounds are almost constant, thus confirming that the presence of different kinds of water molecule placed in different sites of the crystal lattice has little effect on ΔH values. For this reason we do not attribute the peak separation to coordinated and uncoordinated water molecules, following literature observations on copper complexes [8].

Furthermore, the temperature at which dehydration takes place does not influence the observed ΔH values; in fact, values measured on the compounds dehydrating at about 90 or 180 °C are of the same order and are near those generally found for hydrated metal salts [8,17].

Measurements carried out on the same powders as a function of crystal size and of heating rate exhibit some effects on the TGA and DSC thermograms. Decreasing the heating rate only decreases the peak temperature, therefore leaving ΔH and the kinetic parameters unchanged, as expected [18]. Decreasing the crystal size increases the kinetic parameters, suppresses the multiplicity of peaks and enhances the peak at lower temperatures. A possible explanation of this behavior would be the different proportion of different kinds of water molecules escaping from the crystals. Water molecules on the surface of the crystals would escape more easily than molecules in the bulk, which must first migrate to the surface. The action of grinding certainly alters the relative proportion of water molecules on the surface and in the bulk of the crystals.

The higher activation energy values measured on higher crystal sizes support this interpretation too, since surface and bulk molecules are in different environments and dehydration processes must be activated differently.

Other interesting features can be also observed by comparing the activation energy for corresponding blue and green compounds. The value of E_a is found to be three times greater for dimeric compounds than for monomeric ones, and the latter dehydrate at a temperature about 100 °C lower, but no definite relationship could be identified between E_a and temperature on the basis of our present data. However we can underline that these data confirm the greater stability of green with respect to blue compounds.

By comparing the coordination behavior of *N*-protected aminoacids and simple carboxylic acids, it emerges that the ability to form blue monomeric hydrate species, found only for the first class of ligands, should be attributed to the strong hydrogen bonds involving water molecules and the peptidic group, which are lacking in carboxylic acids.

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