Solution and Solid State Investigation of the Cu(II)–*N*-Acetyl-L-Glutamine System and its *N*-Methylimidazole Adduct

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Abstract

The interactions of *N*-acetyl-L-glutamine (AcglnH) with copper(II) ion in aqueous and water–methanol (50% *v/v*) solutions and in solid state have been investigated. It was found that the *N*-acetyl-L-glutaminate anion (Acgln) is unable to form stable complexes in solution on varying the pH values, before copper(II) hydroxyde precipitation occurs. In the solid state two compounds of the formulas $Cu(Acgln)_2 \cdot 2H_2O$ and $Cu(Acgln)_2(MeIm)_2 \cdot 2H_2O$ (MeIm = *N*-methylimidazole) are separated; for the latter complex the crystal and molecular structure was determined by means of the single crystal X-ray diffraction method. The compound crystallizes in the monoclinic space group *C*2, with cell dimensions: $a = 15.606(7)$, $b = 7.353(2)$, $c = 13.951(2)$ Å, $\beta = 110.69(3)^\circ$ and $Z = 2$. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares to an *R* value of 0.026. The structure consists of $[Cu(Acgln)_2(MeIm)_2]$ units and uncoordinated water molecules. The Cu(II) atom lying on the twofold axis exhibits a square-planar N_2O_2 environment from ligation by two symmetry-related carboxylate oxygens and *N*-methylimidazole nitrogens. The second non-bonding carboxylate oxygens are 2.813(3) Å from the Cu(II) atom and both are placed under the coordination plane. Spectroscopic and thermal results agree with the crystal structure, while for binary $Cu(Acgln)_2 \cdot 2H_2O$ a CuO_4 chromophore is suggested.

Introduction

Investigation of copper(II)–*N*-protected amino acid systems has provided a great deal of information which may help in understanding the reaction mechanism between peptides or sulfonamides and copper(II) ion in biological substrates [1]. The results for *N*-acetyl-, *N*-benzoyl-, *N*-benzyloxycarbonyl-, *N*-tosyl- (= 4-toluensulfonyl-) and *N*-dansyl- (= 5-dimethylaminonaphthalene-1-sulfonyl-) aminoacids [2–4] revealed that only *N*-tosyl-α-, and *N*-dansyl-α-derivatives form stable complexes in aqueous solution, acting as carboxylate ligands; as a consequence NH deprotonation is reached before metal hydroxide precipitation and very stable chelate complexes are formed.

Asparagine and glutamine are known to form stable complexes with copper(II) ion both in the solid and solution state [5–7]. In particular, the crystal structure of bis(L-asparaginato)copper(II) complex [5] shows that the terminal amidic oxygen atom may also be an active coordination site.

For *N*-acetyl derivatives of the same ligands, no investigations have hitherto been performed, and it should be of interest to compare their coordination behavior, both in the solid and solution states, with that of the parent aminoacids in order to verify if the presence of an acetyl group on the α-nitrogen atom may further activate the coordination ability of terminal amide group. Therefore, in this paper we discuss the results of an investigation of the copper(II)–*N*-acetyl-L-glutamine system, in solution and solid state. For better information on the coordinative ability of the amino acid, the crystal and molecular structure of bis(*N*-methylimidazole)bis(*N*-acetyl-L-glutaminato)copper(II) dihydrate is also reported.

Experimental

Materials

N-acetyl-L-glutamine was purchased from the Sigma Chemical Co. $Cu(ClO_4)_2 \cdot 6H_2O$ and *N*-methylimidazole were from Fluka and used as received. The solution of NaOH (10^{-1} mol/dm^3) was Normex, C. Erba; 9.84×10^{-3} mol/dm^3 was titrated with potassium hydrogen phtalate. The concentrations of copper(II) solutions were determined with EDTA.

Potentiometric pH Measurements

Potentiometric studies were performed at 25 ± 0.1 °C with a Crison 501 potentiometer using an Ingold 104023316 combined glass electrode. The electrode system was calibrated by the method in ref. 8. The dissociation constant of the ligand [9]

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TABLE I. Composition (mol/dm^3) of Solutions of Copper(II)–*N*-acetylglutamine (HL) Systems Used in pH-Titration (I = 0.1 $NaClO_4$, 25 °C)

Solvent	$[Cu^{2+}]$	[HL]
H_2O	0	1.98×10^{-3}
	4.04×10^{-3}	1.98×10^{-3}
	1.615×10^{-2}	2.05×10^{-3}
50% (v/v) Methanol	0	1.11×10^{-3}
	0	9.88×10^{-3}
	0	1.007×10^{-2}
	3.03×10^{-3}	1.048×10^{-3}
	2.56×10^{-3}	9.99×10^{-3}
	2.56×10^{-3}	1.038×10^{-2}
	1.70×10^{-3}	1.022×10^{-2}

TABLE II. Negative Logarithm of the Acidity Constants of the Ligand and Logarithm of Stability Constants of its Binary Cu^{2+} Complexes (I = 0.1 $NaClO_4$, 25 °C)

Solvent	pK_{HL}^{H}	$\log K_{CuL}^{Cu}$	$\log \beta_{CuL_2}^{Cu}$
H_2O	3.35 ± 0.02	1.35 ± 0.05	
50% (v/v) Methanol	4.13 ± 0.01	2.31 ± 0.04	4.25 ± 0.04

and stability constants of the metal–ligand complexes were determined at ionic strength adjusted to 0.1 by adding $NaClO_4$. The concentrations of the metal and ligand used in calculations are collected in Table I.

All metal:ligand molar ratios were tested by at least three titrations and the data were collected until the beginning of the hydrolysis of Cu^{2+} ion. The stability constants were determined as reported in refs. 10 and 11, by taking into account the species H^+, HL, L^-, Cu^{2+} and CuL^+ for metal:ligand molar ratios 2:1 and 8:1 (aqueous solution) and 3:1 (50% v/v aqueous methanol) and considering also the species CuL_2 for the metal to ligand molar ratio 1:4 in 50% aqueous methanol. For the mixed methanol solutions no corrections were applied for the change in solvent from water to aqueous methanol (Table II).

Preparation of Complexes

$Cu(Acgln)_2 \cdot 2H_2O$

An aqueous ethanolic (1:4) solution containing copper(II) acetate monohydrate (10^{-2} mol/dm^3) and *N*-acetyl-L-glutamine (2×10^{-2} mol/dm^3) was slowly concentrated until a small volume was obtained. By adding ethanol and cooling at 0 °C, a green compound was obtained, but analysis did not give interpretable results. By dissolving this compound in H_2O and subsequent evaporation, a light blue compound separated. *Anal.* Found: C, 35.60; H, 5.47; N, 11.89; H_2O, 7.60. $C_{14}H_{26}CuN_4O_{10}$ requires: C, 35.46; H, 5.53; N, 11.83; H_2O, 7.60%.

$[Cu(Acgln)_2(MeIm)_2] \cdot 2H_2O$

The complex was prepared by mixing 10^{-3} mol of the binary complex to 2×10^{-3} mol of the amine in 2×10^{-2} dm^3 of methanol. By slow evaporation at room temperature (~20 °C) after 12 h, blue crystals separated. *Anal.* Found: C, 41.43; H, 5.99; N, 17.53; H_2O, 5.75. $C_{22}H_{38}CuN_8O_{10}$ requires: C, 41.41; H, 6.00; N, 17.56; H_2O, 5.65%.

Physical Measurements

The reflectance spectra of the complexes were recorded with a Varian Cary 2300 spectrophotometer. The infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer as KBr pellets and as Nujol mull on KBr as support in the 4000–250 cm^{-1} spectral range. The EPR spectra were recorded with a Bruker ER 200-SRC spectrometer. Thermogravimetric analysis was performed at a speed rate of 5 °C/min with a Mettler TA3000 instrument.

X-ray Data Collection and Structure Determination

Crystal data for $[Cu(Acgln)_2(MeIm)_2] \cdot 2H_2O$. $C_{22}H_{38}CuN_8O_{10}$, M_r = 637.908, monoclinic, space group $C2$ (C_2^3, No. 5), a = 15.606(7), b = 7.353(2), c = 13.951(2) Å, β = 110.69(3)°, U = 1497.64 Å^3, D_m = 1.40 g cm^{-3} (by flotation), Z = 2, D_c = 1.41 g cm^{-3}, $F(000)$ = 669.97, Mo Kα radiation, λ = 0.71069 Å, μ(Mo Kα) = 7.41 cm^{-1}, 293 K.

A blue crystal of approximate dimensions 0.40 × 0.30 × 0.20 mm was mounted on an Enraf-Nonius CAD4 automated single crystal diffractometer. The unit cell dimensions were determined from least-squares fit to the setting angles of 25 reflections in the range $8 < \vartheta < 15°$. A single data set ($2.5 < \vartheta < 25°$, $\pm h, k, l$) was recorded by the ω–2ϑ scan technique (scan width 0.60 + 0.35 tan ϑ, scan speed 1.5–8.2 deg min^{-1}). The intensities of two standard reflections, monitored every 1 h, showed no significant changes. Data were corrected by Lorentz and polarization effects, and an empirical absorbtion correction, based on the ψ scan [12], was applied (maximum minimum transmission factors 0.999, 0.920). The final set of data consisted of 1438 unique reflections, of which 1416 had $I > 3\sigma(I)$ and were used in the structural analysis.

The structure was solved by conventional Patterson and Fourier methods; full-matrix least-squares refinement of positional and isotropic thermal parameters for all non-hydrogen atoms led to convergence at R = 0.042*.

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

TABLE III. Final Positional Parameters

Atom	*x/a*	*y/b*	*z/c*
Cu	0.0	0.25[a]	0.0
N(1)	0.1341(2)	0.2324(6)	0.0306(2)
C(1)	0.1755(2)	0.2361(8)	−0.0377(2)
N(2)	0.2652(2)	0.2180(4)	0.0071(2)
C(2)	0.2839(2)	0.1977(6)	0.1100(3)
C(3)	0.2029(2)	0.2063(6)	0.1237(3)
C(4)	0.3319(3)	0.2216(7)	−0.0460(3)
O(1)	0.0215(1)	0.2369(5)	0.1482(2)
O(2)	0.0199(2)	0.5355(5)	0.1405(2)
C(5)	0.0267(2)	0.3937(5)	0.1892(2)
C(6)	0.0433(2)	0.4000(5)	0.3047(2)
N(3)	0.0211(2)	0.2306(6)	0.3430(2)
C(7)	−0.0662(2)	0.1812(6)	0.3235(2)
O(3)	−0.1300(1)	0.2835(7)	0.2759(2)
C(8)	−0.0801(3)	−0.0048(9)	0.3603(4)
C(9)	0.1423(2)	0.4527(5)	0.3668(2)
C(10)	0.1530(2)	0.4969(7)	0.4782(3)
C(11)	0.2516(2)	0.4896(6)	0.5512(2)
O(4)	0.3148(2)	0.5374(6)	0.5236(2)
N(4)	0.2652(2)	0.4370(6)	0.6458(2)
Ow	0.0467(3)	−0.1271(5)	0.2237(3)

[a]The origin of the unit cell was arbitrarily defined by assigning the value of 1/4 to the *y* coordinate of the Cu atom.

Hydrogen atoms were located on a Fourier difference map, and refined isotropically by some least-squares cycles; they were then treated as fixed contributors in the final anisotropic cycles of refinement. Final convergence was reached at $R = 0.026$ and $R_w = 0.030$ ($w = 1.0/\sigma^2(F_o) + 0.00132F_o^2$). A final difference map showed no residual electron density greater than 0.4 e Å^{-3}. There was no evidence for secondary extinction. The enantiomeric model was chosen by assigning the known *S*-configuration, according to the Cahn–Ingold notation, to L-glutaminate ion.

Complex neutral atom scattering factors [13] were used throughout; major calculations were carried out on a Vax-11/750 computer using the SHELX-76 system of programs [14] and ORTEP plotting program [15].

Final positional parameters for non-hydrogen atoms are given in Table III. Lists of anisotropic temperature factors, of hydrogen atom parameters, and of observed and calculated structure factors are available see 'Supplementary Material'.

Analysis

Nitrogen, carbon and hydrogen were analysed with a C. Erba Model 1106 Elemental Analyser Instrument by Mr. G. Goldoni. The water content was determined thermogravimetrically with a Mettler TA3000 instrument.

Results and Discussion

Solution Behavior

The pK_a of the ligand and the logarithm of the stability constants for the binary copper(II) complex are reported in Table II.

The values for the aqueous system are close to those of *N*-acetylglycine [16] and follow the trend of a decrease in complex stability with a decrease of pK_a of parent ligand [17].

The potentiometric titrations of the metal:ligand system can be almost exactly superimposed on that of the free ligand up to pH ≃ 6 (also for 50% *v/v* methanol), excluding any significant interactions between copper(II) and *N*-acetyl-L-glutamine. This is confirmed by the stability constant value of 1:1 complex which is lower than the corresponding pK_a of *N*-acetyl-L-glutamine.

In both systems, by adding NaOH to the solution at pH > 6, no increase in pH was found until complete precipitation of copper(II) hydroxide occurred, and the equivalents of NaOH necessarily correspond to the total copper(II) equivalents in solution.

For the water–methanol (50% *v/v*) solution, the slight increase in $\log K_{CuL}^{Cu}$ is accompanied by a similar increase in pK_a of the ligand, due to the diminishing donor properties of methanol with respect to water [4], but the metal–ligand interactions are practically the same as in water.

This behavior of the solution rules out the deprotonation of the terminal nitrogen of the $-CO-NH_2$ group either before or after metal hydroxide precipitation, and consequently the only active site is the weakly basic carboxylate group. As a result it was possible to separate a solid microcrystalline binary compound of empirical formula $Cu(Acgln)_2 \cdot 2H_2O$ only from a very concentrated solution.

Solid State Behavior

The thermogravimetric analysis of the light blue binary complex shows a sharp peak corresponding to the complete loss of two water molecules at very high temperature (393–453 K), indicating that the water molecules are directly involved in metal ion coordination. Its electronic and EPR data ($d-d_{max}$ = 14 500 cm^{-1}, $g_\parallel = 2.33$, $g_\perp = 2.12$) are similar to those of structurally known copper(II)–N-protected aminoacidate complexes having CuO_n ($n = 5$, 6) chromophore [18–20]. In the infrared region its most relevant feature is the splitting of $\nu(C-O)_{ket}$ (1650, 1670 cm^{-1}; free ligand = 1670 cm^{-1}), which may be attributed to the involvement of the terminal amidic oxygen in the metal ion coordination, such as in the bis(L-glutaminato)copper(II) [5], or to hydrogen bonding in crystal packing.

The coordination ability of *N*-acetyl-L-glutamine through the carboxylate group is also demonstrated by the easy reaction of this compound with *N*-

TABLE IV. Bond Distances (Å) and Bond Angles (deg)[a]

Cu–N(1)	1.987(3)	C(5)–C(6)	1.540(5)
Cu–O(1)	1.976(2)	C(6)–N(3)	1.444(6)
N(1)–C(1)	1.326(4)	N(3)–C(7)	1.342(5)
C(1)–N(2)	1.323(4)	C(7)–O(3)	1.238(6)
N(2)–C(2)	1.368(5)	C(7)–C(8)	1.503(8)
N(2)–C(4)	1.476(5)	C(6)–C(9)	1.531(4)
C(2)–C(3)	1.345(5)	C(9)–C(10)	1.537(5)
C(3)–N(1)	1.375(4)	C(10)–C(11)	1.518(5)
C(5)–O(1)	1.276(5)	C(11)–O(4)	1.229(5)
C(5)–O(2)	1.228(5)	C(11)–N(4)	1.318(5)
O(1)–Cu–N(1)	89.7(1)	O(2)–C(5)–C(6)	120.2(3)
O(1)–Cu–O(1')	174.4(1)	C(5)–C(6)–N(3)	112.7(3)
O(1)–Cu–N(1')	89.9(1)	C(5)–C(6)–C(9)	111.3(3)
N(1)–Cu–N(1')	172.5(2)	N(3)–C(6)–C(9)	109.6(3)
C(3)–N(1)–C(1)	105.3(3)	C(6)–N(3)–C(7)	121.2(3)
N(1)–C(1)–N(2)	111.2(3)	N(3)–C(7)–O(3)	120.7(5)
C(1)–N(2)–C(2)	107.7(3)	O(3)–C(7)–C(8)	123.4(4)
C(1)–N(2)–C(4)	125.3(3)	N(3)–C(7)–C(8)	115.8(4)
C(2)–N(2)–C(4)	127.0(3)	C(6)–C(9)–C(10)	110.6(3)
N(2)–C(2)–C(3)	106.3(3)	C(9)–C(10)–C(11)	113.1(3)
C(2)–C(3)–N(1)	109.4(3)	C(10)–C(11)–O(4)	121.0(4)
O(1)–C(5)–O(2)	122.7(3)	C(10)–C(11)–N(4)	116.6(3)
O(1)–C(5)–C(6)	117.2(3)	O(4)–C(11)–N(4)	122.3(3)

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

methylimidazole, giving rise to a crystalline blue ternary complex of the formula $Cu(Acgln)_2(MeIm)_2 \cdot 2H_2O$. The determination of the crystal and molecular structure of this compound was performed in order to obtain certain information on the coordinative sites of the ligand.

Description of the Structure of [Cu(Acgln)$_2$(MeIm)$_2$]·2H$_2$O

Bond distances and angles are given in Table IV with atoms labelled as in Fig. 1.

The structure consists of $[Cu(Acgln)_2(MeIm)_2]$ units and uncoordinated water molecules that provide crystalline stability through a network of hydrogen-bond interactions. The Cu(II) atom, which lies on a twofold axis, exhibits a square-planar N_2O_2 geometry from ligation by two symmetry-related Acgln molecules acting as simple carboxylate ligands through an oxygen atom of the α-carboxylate group and two MeIm molecules.

Planarity analysis, quoted in the supplementary material, shows that the four donor atoms deviate from their least-squares mean-plane in the pattern of a slight tetrahedral distortion (from −0.016 to 0.16 Å) while the Cu atom deviates 0.113 Å from the plane.

Two weak non-bonding interactions with copper(II) ion involve the second carboxylic oxygen atom (Cu···O(2) = 2.813(3) Å), both placed under the coordination plane of 51.7(1)°; whereas in bis(L-asparaginato)zinc(II) complex, the second oxygen atom of the carboxylate group of two neighboring molecules completes the octahedral coordination geometry of the metal ion [21].

The Cu–O and Cu–N bond lengths are similar to those found in other copper(II) N-protected amino acidato-imidazole complexes [2, 22].

The terminal amide group, which exists in the keto form, is only involved in hydogen bond formation, contrary to what occurs in bis(L-asparaginato)-copper(II) in which the amidic oxygen coordinates the metal ion and establishes polymeric structures

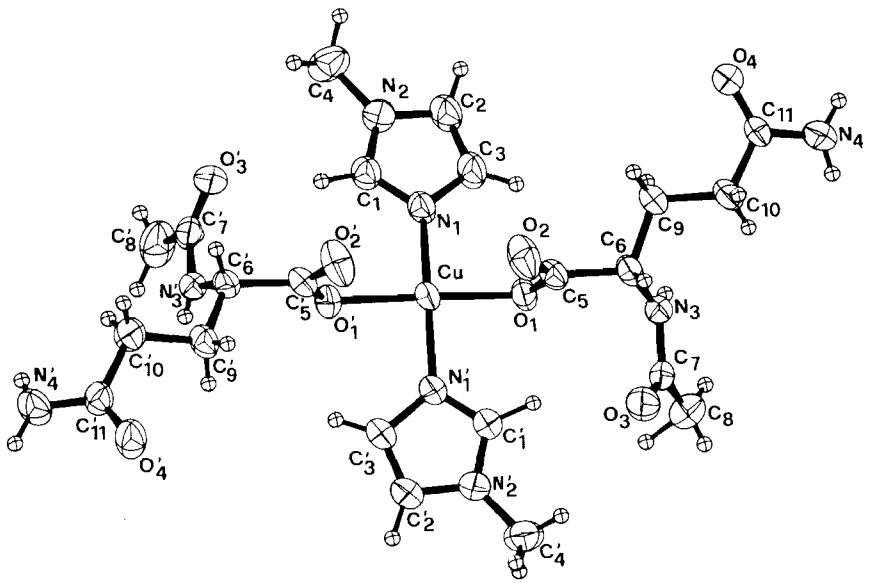

Fig. 1. ORTEP view of $[Cu(Acgln)_2(MeIm)_2]$ showing the atom numbering and thermal motion ellipsoids (40%) for non-hydrogen atoms. The hydrogen atoms are represented as a sphere of arbitrary radius.

[5]. The π-back bonding donation from Cu^{2+} to aromatic amine may explain the stability of such a CuN_2O_2 chromophore despite the very weak coordinating ability of *N*-acetyl-L-glutamine, as in previously investigated N-protected amino acids.

Bond distances and angles with the Acgln are consistent with those previously observed with the free ligand [23]. The near planarity of the α-peptidic group prevents nitrogen coordination toward the copper(II) ion as has been found in *N*-acetyl-, *N*-benzoyl- and *N*-benzyloxycarbonyl-aminoacidate complexes [21].

The *N*-methylimidazole ligand is planar with no deviation from the least-squares plane through the five atoms by more than 0.007 Å, and it is also nearly coplanar with the coordination plane with a dihedral angle of 7.64°.

The crystal packing is determined by intermolecular hydrogen bonds involving the water molecules, coordinated and uncoordinated carboxylic oxygens and both amide groups.

In accord with the presence of uncoordinated water molecules, the dehydration process begins almost at room temperature (321 K) and is completed at 393 K.

The electronic and EPR data ($d-d_{max}$ = 17 500 cm^{-1}, $g_{\parallel} = 2.29$, $g_{\perp} = 2.06$, $A_{\parallel} \times 10^4$ $cm^{-1} = 160$) are in the range expected for an essentially square-planar CuN_2O_2 chromophore [22].

We may conclude that despite the presence of several potentially active coordination sites, the coordinating ability of *N*-acetyl-L-glutamine closely resembles that of other *N*-acetyl-aminoacids. Secondly, the ligation from the *N*-methylimidazole molecules enhances the affinity of Cu^{2+} ion toward oxygen donor ligands.

Supplementary Material

List of observed and calculated structure factors, anisotropic temperature factors, hydrogen atom parameters, bond distances and angles involving hydrogen atoms and selected least-squares planes (13 pages) are available on request.

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