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The syntheses and structures of two hexanuclear copper(II) complexes with amino acids†

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Hexanuclear copper(II) complexes with amino acids have been synthesized and the structures can be described as cages with pseudocubic O_h symmetry in which six copper ions are bound by eight tridentate amino acids with one Na^+ in the center of the cage.

Copper complexes of amino acids are of continuing interest since they are simple model systems for the study of metal–protein interactions.[1,2] Amino acids are ubiquitous ligands in biology as well as being the basic building units of proteins. They can coordinate *via* the carboxylate or amino groups. Meanwhile, copper is an essential element, particularly for oxygen transportation *e.g.* in hemocyanin, existing widely in organisms such as molluscs and shellfish. Therefore study of the interaction between copper and amino acids may be useful in understanding the action of metal ions in organisms.

The investigation of copper–amino acid complexes started in the 1960s. Many 1 : 1 or 1 : 2 complexes between copper(II) and amino acids have been reported in the last two decades, most of them being either mononuclear, chain or netted structures.[3–12]

In this paper we wish to report the syntheses of two hexanuclear copper(II) complexes $Na[NaCu_6(Gly)_8(H_2O)_2](ClO_4)_6\cdot2H_2O$, (**1**) and $[NaCu_6(Pro)_8(OH)](ClO_4)_4\cdot H_2O$ (**2**) in which the ratio of copper to amino acid is 6 : 8.‡ The cationic structures of $[NaCu_6(Gly)_8(H_2O)_2]^{5+}$ (**1a**) and $[NaCu_6(Pro)_8(OH)]^{4+}\cdot H_2O$ (**2a**) are shown in Fig. 1 and 2, respectively.§

The metal framework of both complexes may be described as a cage with pseudocubic O_h symmetry. Each amino acid group acts as a tridentate ligand by utilizing its amino and carboxylate groups to chelate one Cu^{2+} and bridge another, as shown in Scheme 1. Four chelated Cu^{2+} are located at the equatorial vertices of a regular non-bonding octahedron. Each Cu^{2+} has a coordination number (CN) of 4 and its coordination geometry can be described as square planar. The average Cu_e–O and Cu_e–N distances are 1.952 Å and 1.995 Å, respectively and the Cu_e–Cu_e distance is 5.052 Å for complex **1** and 5.000 Å for complex **2**. The other two Cu^{2+} ions are situated at the axial vertices and bind the other oxygen atom of the carboxyl group with a Cu_a–O distance of 1.950 Å. The average distance between axial and equatorial coppers is 5.041 Å (complex **1**) and 4.983 Å (complex **2**).

There is one Na^+ in the center of the cation cage for **1a** and **2a**. There are electrovalent bonds between the Na^+ and the surrounding eight oxygen atoms of the amino acids. The average Na–O distance is 2.604 Å for complex **1** and 2.552 Å for complex **2**.

In complex **1**, each Cu_a is also bonded to one H_2O beside the amino acids, and the Cu_a–O_w distance is 2.353 Å (as shown in Fig. 1). As a result, the Cu^{2+} has a CN of 5 and forms a tetrapyramid. In complex **2**, one Cu_a is coordinated by one OH, and the Cu_a–O_h distance is 2.314 Å. There is one H_2O beside the other Cu_a, but the Cu_a–O_w distance is quite long (3.612 Å) (as shown in Fig. 2).

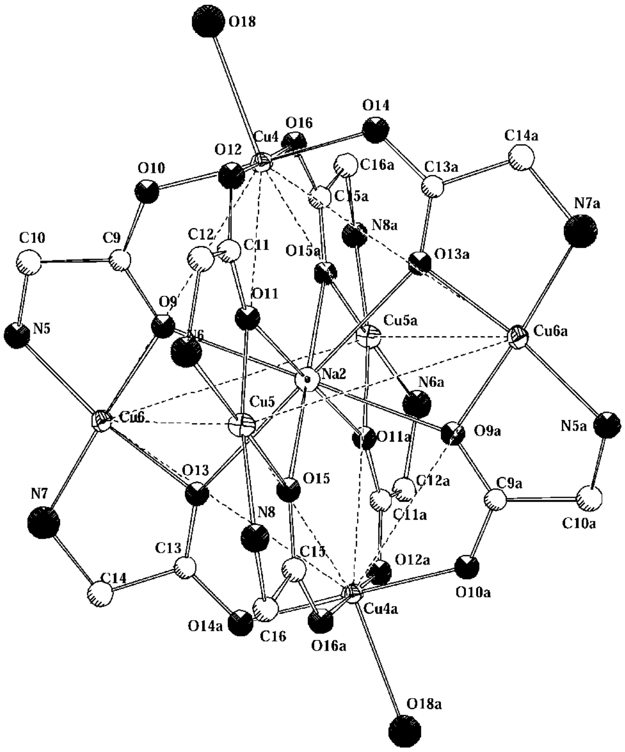
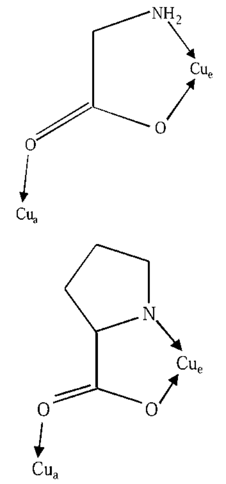


Fig. 1 The cation $[NaCu_6(Gly)_8(H_2O)_2]^{5+}$ (**1a**).



Scheme 1 Chelation and bridging by glycine (top) and proline (bottom).

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† Electronic supplementary information (ESI) available: packing diagrams for **1** and **2**. See http://www.rsc.org/suppdata/dt/b1/b105383n/

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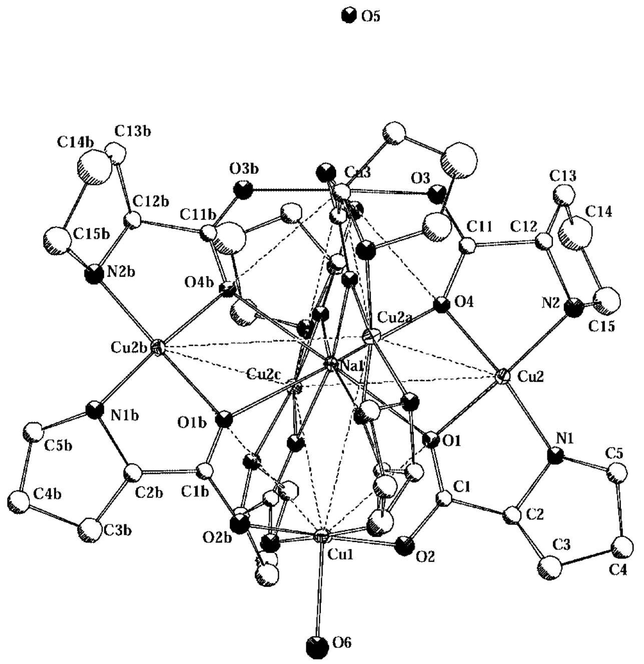

Fig. 2 The cation $[NaCu_6(Pro)_8(OH)]^{4+}\cdot H_2O$ (**2a**).

There is a remarkable difference between the two complexes. There are two Na^+ in complex **1**, one inside the octahedral cage, the other outside the cage, but there is only one Na^+ in the cage for complex **2**. There are two possible reasons for this observation: firstly the different amino acids in **1** and **2** lead to differences in the isoelectric point in solution and secondly there is a different steric interaction between the two amino acids. The difference in the number of Na ions in the two complexes was confirmed by elemental analysis.§

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Notes and references

‡ Preparation of **1**. $Cu(ClO_4)_2\cdot 5H_2O$ (0.353 g, 1 mmol) was dissolved in 10 mL of H_2O, then glycine (0.075 g, 1 mmol) was added. The pH value of the above solution was then carefully adjusted by slow addition of 0.1 M aqueous NaOH until the precipitate thus formed remained (*ca.* pH 5.5). The mixture was then filtered and the filtrate was placed in a desiccator with phosphorus pentaoxide. Blue rhombic crystals were then collected by filtration several weeks later (Found: C, 10.83; H, 2.662; N, 6.164; O, 42.51; Na, 2.84. Calc. for $Na_2Cu_6C_{16}H_{40}N_8O_{44}Cl_6$: C, 11.38; H, 2.388; N, 6.636; O, 41.69; Na, 2.72%).

Preparation of **2**. $Cu(ClO_4)_2\cdot 5H_2O$ (0.353 g, 1 mmol) was dissolved in 10 mL of H_2O, then proline (0.114 g, 1 mmol) was added. The pH value of the above solution was then carefully adjusted by slow addition of 0.1 M aqueous NaOH until the precipitate thus formed remained (*ca.* pH 5.5). The mixture was then filtered and the filtrate was placed in a desiccator with phosphorus pentaoxide. Blue octahedral crystals were collected by filtration several weeks later (Found: C, 27.48; H, 4.096; N, 6.350; O, 32.58; Na,1.36. Calc. for $NaCu_6C_{40}H_{67}N_8O_{34}Cl_4$: C, 27.45; H, 3.859; N, 6.403; O, 31.08; Na,1.31%).

§ Crystal data for $Na[NaCu_6(Gly)_8(H_2O)_2](ClO_4)_6\cdot 2H_2O$ (**1**): Crystal dimensions 0.24 × 0.18 × 0.10 mm, $M = 1688.48$, triclinic, space group $P\bar{1}$, $a = 11.3736(2)$, $b = 12.75600(10)$, $c = 19.5416(3)$ Å, $\alpha = 92.5050(10)$, $\beta = 94.2820(10)$, $\gamma = 114.5420(10)°$, $V = 2563.05(6)$ Å^3, $Z = 2$, $\rho_{calc.} = 2.188$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 2.901 mm^{-1}, $2.10 \le 2\theta \le 50.06°$, $T = 293$ K. Of 13077 reflections collected, 8836 were independent and 6326 observed $[I > 2\sigma(I)]$. The structure was solved by direct methods using SHELXTL-Plus.[13] The final cycle of full-matrix least-squares refinement[14] converged with $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.0666$ and $wR = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma w[(F_o^2)^2]\}^{0.5} = 0.1515$, $w = \{[\sigma^2 F_o^2] + (0.0633P)^2 + 21.5696P\}^{-1}$, $P = (F_o^2 + 2F_c^2)/3$. Largest difference peak and hole: 1.483 and −1.113 e Å^{-3}. CCDC reference number 165331.

Crystal data for $[NaCu_6(Pro)_8(OH)](ClO_4)_4\cdot H_2O$ (**2**): Crystal dimensions 0.38 × 0.36 × 0.34 mm, $M = 1750.05$, tetragonal, space group $I4$, $a = b = 13.6500(3)$, $c = 18.1900(5)$ Å, $V = 3389.21(14)$ Å^3, $Z = 2$, $\rho_{calc.} = 2.105$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 4.057 mm^{-1}, $3.94 \le 2\theta \le 50.10°$, $T = 293$ K. Of 6928 reflections collected, 2561 were independent and 2150 observed $[I > 2\sigma(I)]$. The structure was solved by direct methods with the SHELXTL-97 program. The final cycle of full-matrix least-squares refinement converged with $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.0666$ and $wR = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma w[(F_o^2)^2]\}^{0.5} = 0.1992$, $w = \{[\sigma^2 F_o^2] + (0.1604P)^2 + 2.2465P\}^{-1}$, $P = (F_o^2 + 2F_c^2)/3$. Largest difference peak and hole: 1.664 and −0.570 e Å^{-3}. CCDC reference number 165332. See http://www.rsc.org/suppdata/dt/b1/b105383n/ for crystallographic data in CIF or other electronic format.

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