Contribution from the Consiglio Nazionale delle Richerche of Italy, the Istituto di Chimica Generale,
Centro di Studio per la Strutturistica Diffrattometrica del CNR, University of Parma, 43100 Parma, Italy,
Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy,
and Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, Italy

# Copper(II) Complexes of N-Protected Amino Acids: Synthesis and Spectroscopic, Magnetic, and Structural Properties of Bis(*N*-acetyl-$\beta$-alaninato)diaquacopper(II) and Tetrakis[$\mu$-(*N*-acetyl-$\beta$-alaninato)]-diaquadicopper(II) Dihydrate. A Case of Structural Isomerism

L. P. BATTAGLIA,[1a] A. BONAMARTINI CORRADI,[1a] G. MARCOTRIGIANO,[1b] L. MENABUE,[1c]
and G. C. PELLACANI*[1c]

*Received September 16, 1980*

A blue and a green compound of the type $Cu(Ac\text{-}\beta\text{-}ala)_2\cdot 2H_2O$ and $[Cu(Ac\text{-}\beta\text{-}ala)_2\cdot H_2O]_2\cdot 2H_2O$ (Ac-$\beta$-ala = *N*-acetyl-$\beta$-alaninato ion) and a green compound of the type $[Cu(Ac\text{-}\beta\text{-}ala)_2]_2$ (obtained by dehydrating the two compounds above mentioned) were prepared and characterized by means of room-temperature electronic and infrared spectroscopy, low- and room-temperature magnetic and EPR measurements and DSC analysis. For the blue and green hydrate compounds the crystal structure was also determined by single-crystal X-ray diffraction methods. The blue $Cu(Ac\text{-}\beta\text{-}ala)_2\cdot 2H_2O$ complex crystallizes in the monoclinic space group $P2_1/n$ with two molecules in a unit cell of dimensions $a = 5.0135$ (2) Å, $b = 8.415$ (1) Å, $c = 17.952$ (2) Å, $\beta = 91.186$ (3)°, $d_{calcd} = 1.58$ g cm$^{-3}$, and $d_{measd} = 1.59$ g cm$^{-3}$. Least-squares refinement of the 137 variables led to a value of the conventional $R$ index of 0.062 for 1353 independent reflections having $I > 2\sigma(I)$. The copper environment consists of two centrosymmetrically related carboxylic oxygens and two water molecules in a square-planar arrangement. Two weak interactions involving the uncoordinated carboxylic oxygen atoms complete the coordination to a severely distorted tetragonal bipyramid. The green $[Cu(Ac\text{-}\beta\text{-}ala)_2\cdot H_2O]_2\cdot 2H_2O$ complex crystallizes in the monoclinic space group $P2_1/c$ with two molecules in a unit cell of dimensions $a = 9.120$ (1) Å, $b = 18.527$ (3) Å, $c = 8.978$ (3) Å, $\beta = 98.61$ (1)°, $d_{calcd} = 1.59$ g cm$^{-3}$, and $d_{measd} = 1.59$ g cm$^{-3}$. Least-squares refinement of the 226 variables had led to a value of the conventional $R$ index of 0.068 for 2509 independent reflections having $I > 2\sigma(I)$. The structure consists of centrosymmetric dimeric units. Coordination around each metal atom is elongated octahedrally with the carboxyl oxygen atoms at the equatorial sites and a water molecule and a copper atom in the axial positions. The importance of hydrogen bonding in the packing of the molecules is also discussed. These complexes represent an example of structural isomerism depending on the influence of the solution media. The spectroscopic and magnetic properties are interpreted on the basis of the crystal structures, in particular the hydrate and anhydrous green compounds, which present similar physical properties, show an exchange integral ($-2J$) of 324 ± 15 and 285 ± 15 cm$^{-1}$, respectively, and show a zero field splitting $D$ of 0.37 cm$^{-1}$. The thermal extrusion of two water molecules from the blue compound is accompanied by a structural change (irreversible thermochromism).

## Introduction

Our interest in the coordination properties of N-protected amino acids, in which the protecting group is an acetyl or a benzoyl group, derives from the fact that they are the more simple systems in which one peptide linkage is present. From the interactions among the *N*-acetyl derivatives and the copper(II) ion two simple compounds were generally separated, one blue from aqueous solutions and one green from ethanolic or methanolic solutions, which present different structures.[2] From the *N*-benzoyl derivatives, which are insoluble in water, generally only one green compound separated.[3,4]

In order to rationalize the influence of the formation conditions on the coordination and structure of the two simple copper(II) complexes obtained with the *N*-acetyl amino acids, in this paper we have investigated the coordination behavior of *N*-acetyl-$\beta$-alanine (hereafter abbreviated as Ac-$\beta$-alaH) toward the copper(II) ion. The synthesized compounds were characterized by means of electronic, infrared, and EPR spectroscopy, magnetic moment measurements, differential scanning calorimetric analysis, and X-ray analysis.

## Experimental Section

All chemicals were reagent grade and were used as received.

**Preparation of Blue Bis(*N*-acetyl-$\beta$-alaninato)diaquacopper(II), $Cu(Ac\text{-}\beta\text{-}ala)_2\cdot 2H_2O$.** The complex was prepared by direct reactions of *N*-acetyl-$\beta$-alanine (2 mmol) and copper(II) hydroxide (1 mmol), freshly prepared, in water or by mixing sodium *N*-acetyl-$\beta$-alaninato (2 mmol) and copper(II) perchlorate hexahydrate (1 mmol) in water. The solutions were stirred and warmed to 40-50 °C until the reagents were dissolved; then the blue solutions were slowly evaporated, yielding at room temperature (~20 °C) blue crystals. Anal. Calcd for $C_{10}H_{20}CuN_2O_8$: C, 33.36; H, 5.60; N, 7.79. Found: C, 33.32; H, 5.68; N, 7.82.

**Preparation of the Green Tetrakis[$\mu$-(*N*-acetyl-$\beta$-alaninato)]-diaquadicopper(II) Dihydrate, $[Cu(Ac\text{-}\beta\text{-}ala)_2\cdot H_2O]_2\cdot 2H_2O$.** By recrystallizing the $Cu(Ac\text{-}\beta\text{-}ala)_2\cdot 2H_2O$ complex in aqueous methanolic (1:1) solution, green crystals separated. The same compound was also obtained by repeatedly recrystallizing the blue $Cu(Ac\text{-}\beta\text{-}ala)_2\cdot 2H_2O$ in water. Anal. Calcd for $C_{10}H_{20}CuN_2O_8$: C, 33.36; H, 5.60; N, 7.79. Found: C, 33.29; H, 5.57; N, 7.77.

**Preparation of Green Tetrakis[$\mu$-(*N*-acetyl-$\beta$-alaninato)]-dicopper(II), $[Cu(Ac\text{-}\beta\text{-}ala)_2]_2$.** The compound was obtained by heating green $[Cu(Ac\text{-}\beta\text{-}ala)_2\cdot H_2O]_2\cdot 2H_2O$ at a temperature greater than 80 °C or blue $Cu(Ac\text{-}\beta\text{-}ala)_2\cdot 2H_2O$ at a temperature greater than 90 °C. Anal. Calcd for $C_{10}H_{16}CuN_2O_6$: C, 37.07; H, 4.98; N, 8.65. Found: C, 37.19; H, 4.94; N, 8.75.

**Physical Measurements.** The electronic spectra of the solid compounds were recorded as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. The infrared spectra were recorded

---

(1) (a) University of Parma. (b) University of Bari. (c) University of Modena.

(2) See for example: (a) Marcotrigiano, G.; Pellacani, G. C. *Can. J. Chem.* **1974**, *52*, 3607. (b) Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1897. (c) Marcotrigiano, G.; Pellacani, G. C.; Battaglia, L. P.; Bonamartini Corradi, A. *Cryst. Struct. Commun.* **1976**, *5*, 923 (identical (no better) structural results for the same compound have been successively also reported by Udupa, M. R.; Krebs, B. *Inorg. Chim. Acta* **1978**, *31*, 251). (d) Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chim. Acta* **1980**, *46*, 107. (e) Battaglia, L. P.; Bonamartini Corradi, A.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Am. Chem. Soc.* **1980**, *102*, 2663.

(3) (a) Brown, J. N.; Eichelberger, H. R.; Schaeffer, E.; Good, M. L.; Trefonas, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 6290. (b) Brown, J. N.; Trefonas, L. M. *Inorg. Chem.* **1973**, *12*, 1730. (c) Marcotrigiano, G.; Pellacani, G. C. *Z. Anorg. Allg. Chem.* **1975**, *413*, 171. (d) Sharrock, P.; Thibaudeau, C. H.; Caille, A. *Inorg. Chem.* **1979**, *18*, 510 and references therein.

(4) (a) Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chim. Acta* **1976**, *19*, 133. (b) Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Chem. Soc., Dalton Trans.* **1976**, 1627. (c) Marcotrigiano, G.; Menabue, L.; Morini, P.; Pellacani, G. C. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2249.

0020-1669/81/1320-1075$01.25/0

**Table I.** Crystal Data for $[Cu(Ac\text{-}\beta\text{-ala})_2 \cdot H_2O]_2 \cdot 2H_2O$ (I) and $Cu(Ac\text{-}\beta\text{-ala})_2 \cdot 2H_2O$ (II)

| | I | II |
|---|---|---|
| molecular formula | $C_{20}H_{40}Cu_2N_4O_{16}$ | $C_{10}H_{20}CuN_2O_8$ |
| mol wt | 719.6 | 359.8 |
| *a*, Å | 9.120 (1) | 5.0153 (2) |
| *b*, Å | 18.527 (3) | 8.415 (1) |
| *c*, Å | 8.978 (3) | 17.952 (2) |
| *β*, deg | 98.61 (1) | 91.186 (3) |
| *V*, Å$^3$ | 1499.9 (6) | 757.5 (1) |
| *Z* | 2 | 2 |
| $d_{calcd}$, g cm$^{-3}$ | 1.59 | 1.58 |
| space group | $P2_1/c$ | $P2_1/n$ |
| cryst dimens, mm | 0.30 × 0.08 × 0.62 | 0.39 × 0.10 × 0.68 |
| radiatn (λ, Å) | Cu Kα (λ = 1.541 78) (Ni filtered) | Cu Kα (λ = 1.541 78) (Ni filtered) |
| 2θ limits, deg | 4–140 | 4–140 |
| temp, °C | 20 | 20 |
| abs coeff, cm$^{-1}$ | 23.9 | 23.7 |
| *F*(000) | 748 electrons | 374 electrons |
| unique data used ($I > 2\sigma(I)$) | 2509 | 1353 |
| no. of variables | 226 | 137 |
| *R* | 0.068 | 0.062 |

with a Perkin-Elmer 180 spectrophotometer in KBr pellets or in Nujol mulls on KBr pellets as support in the 4000–250-cm$^{-1}$ spectral range. The low- and room-temperature magnetic moments were measured by the Gouy method using $Ni(en)_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The room-temperature EPR spectra were recorded on a JEOL PE-3X spectrometer; quartz sample tubes were employed for polycrystalline samples, and the spectra were calibrated with diphenylpicrylhydrazyl (DPPH, *g* = 2.0036) as a field marker. Differential scanning calorimetric analysis (DSC) was performed with a Perkin-Elmer DSC-1 instrument.

**X-ray Data Collection.** For both compounds, preliminary cell dimensions were determined from rotation and Weissenberg photographs; subsequently these values were refined by least squares using 2θ values of 15 high-angle reflections (120° < 2θ < 140°) accurately measured on an "on line" single-crystal automated Siemens AED diffractometer with Cu Kα radiation (λ = 1.541 78 Å). The refined cell constants and other relevant crystal data are given in Table I. The crystals were mounted with [010] and [001] axis along the $\phi$ axis of the diffractometer for $Cu(Ac\text{-}\beta\text{-ala})_2 \cdot 2H_2O$ and $[Cu(Ac\text{-}\beta\text{-ala})_2 \cdot H_2O]_2 \cdot 2H_2O$, respectively. For both compounds intensity data were collected with use of Ni-filtered Cu Kα radiation at a takeoff angle of 4°. The moving counter–moving crystal scan technique was employed with a drive speed related to the number of counts on the peak (lowest speed 2.5°/min). After every 20 reflections one reflection was measured as a check of alignment and crystal and instrument stability. No significant change in the measured intensity of this reflection was observed during data collection. Measurements were made with the "five-points technique" for 1426 independent reflections for $Cu(Ac\text{-}\beta\text{-ala})_2 \cdot 2H_2O$ and 2886 for $[Cu(Ac\text{-}\beta\text{-ala})_2 \cdot H_2O]_2 \cdot 2H_2O$. For $[Cu(Ac\text{-}\beta\text{-ala})_2 \cdot H_2O]_2 \cdot 2H_2O$ 2509 of these, having $I > 2\sigma(I)$, were considered as observed and used in the analysis; for $Cu(Ac\text{-}\beta\text{-ala})_2 \cdot 2H_2O$ the reflections observed were 1353 ($\sigma^2(I)$ = (total counts) + (0.01 × intensity)$^2$). The structure amplitudes were obtained after the usual Lorentz and polarization reduction and put on absolute scale by least squares. No correction for absorption was applied, as the $\mu r$ values are very low (0.29 for $Cu(Ac\text{-}\beta\text{-ala})_2 \cdot 2H_2O$ and 0.23 for $[Cu(Ac\text{-}\beta\text{-ala})_2 \cdot H_2O]_2 \cdot 2H_2O$). Therefore, on the assumption of cylindrical shapes for both crystals, the absorption correction coefficients are practically unchanged in the 4–70° θ range.

**Solution and Refinement of the Structures.** For $Cu(Ac\text{-}\beta\text{-ala})_2 \cdot 2H_2O$ a structure factor calculation with the contribution of copper atom at the origin of the cell gave a conventional *R* = 45.8%. The subsequent Fourier synthesis revealed the positions of all nonhydrogen atoms. The refinement was carried out isotropically and anisotropically by several full-matrix least-squares cycles to *R* = 8.3%. The final refinement including hydrogen atoms, found from a Δ*F* map, improved the final *R* to 6.2%. Two reflections (101 and 112) probably affected by counting error were rejected. The effects of anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found.

**Table II.** Fractional Atomic Coordinates ×10$^4$ for Cu, O, N, and C and ×10$^3$ for H Atoms with Esd's in Parentheses for the $Cu(Ac\text{-}\beta\text{-ala})_2 \cdot 2H_2O$ Complex

| | *x* | *y* | *z* |
|---|---|---|---|
| Cu | 0 | 0 | 0 |
| O(1) | 2871 (4) | 821 (3) | −615 (1) |
| O(2) | 287 (5) | −502 (4) | −1414 (1) |
| O(3) | 5614 (7) | −1288 (4) | −3637 (2) |
| O(4) | 2193 (4) | −1861 (3) | 249 (1) |
| N | 4699 (6) | 1186 (4) | −3232 (2) |
| C(1) | 2278 (8) | 340 (5) | −1284 (2) |
| C(2) | 4125 (7) | 850 (5) | −1893 (2) |
| C(3) | 2867 (8) | 696 (5) | −2657 (2) |
| C(4) | 5927 (10) | 181 (5) | −3679 (3) |
| C(5) | 7805 (9) | 902 (6) | −4230 (2) |
| H(1) | 438 (13) | 196 (7) | −185 (3) |
| H(2) | 602 (13) | 23 (5) | −181 (3) |
| H(3) | 114 (8) | 137 (5) | −267 (2) |
| H(4) | 258 (10) | −64 (6) | −274 (3) |
| H(5) | 503 (9) | 220 (6) | −333 (3) |
| H(6) | 856 (15) | 194 (8) | −417 (4) |
| H(7) | 702 (9) | 83 (5) | −475 (3) |
| H(8) | 945 (12) | 31 (4) | −424 (3) |
| H(9) | 387 (11) | −156 (6) | 44 (3) |
| H(10) | 138 (11) | −250 (6) | 61 (3) |

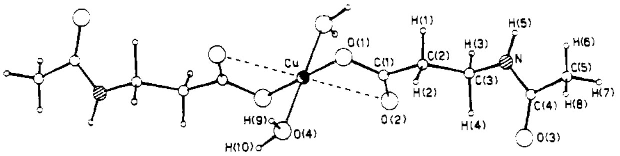

**Figure 1.** Projection along [100] of the blue $Cu(Ac\text{-}\beta\text{-ala})_2 \cdot 2H_2O$ complex.

The function minimized was $\sum w|\Delta F|^2$ with use of the weighting scheme $w^{-1} = [\sigma^2(F_o) + 0.0247(F_o)^2]$. The atomic scattering factors are those from ref 5 for Cu, O, N, and C and those of Stewart, Davidson, and Simpson[6] for H. The final atomic coordinates are quoted in Table II.

The structure of $[Cu(Ac\text{-}\beta\text{-ala})_2 \cdot H_2O]_2 \cdot 2H_2O$ was solved by the heavy-atom technique, with the copper atom located from a Patterson map. Successive Fourier synthesis yielded the positions of all nonhydrogen atoms, which were refined first isotropically and then anisotropically by several full-matrix least-squares cycles to give *R* = 0.082. A subsequent difference Fourier map revealed all hydrogen atoms which were refined isotropically, improving the *R* index to 6.8%. The effects of anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. The function minimized in the least-squares calculation was $\sum w|\Delta F|^2$ where $w^{-1} = [\sigma^2(F_o) + 0.01041(F_o)^2]$. The atomic scattering factors are the same used previously.[5,6] The final atomic coordinates are listed in Table III.

For both compounds all the calculations were performed with use of CYBER 76 of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, with the SHELX system of programs.[7] A listing of the observed and calculated structure factors for the reflections used in the structural analyses and a table of thermal parameters are available in the supplementary material.

**Analyses.** Nitrogen, carbon, and hydrogen were analyzed with a Perkin-Elmer 240 elemental analyzer by Mr. Giuseppe Pistoni.

## Results and Discussion

**Description of the Structures.** The blue crystals of $Cu(Ac\text{-}\beta\text{-ala})_2 \cdot 2H_2O$ consist of monomeric units, in which the copper atom lies on a symmetry center (Figure 1). Bond distances and angles are reported in Table IV. The copper environment consists of two centrosymmetrically related

---

(5) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(6) Stewart, R. R.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(7) Sheldrick, G. M. "A Program for Crystal Structure Determination"; University Chemical Laboratory: Cambridge, England, 1976.

**Table III.** Fractional Atomic Coordinates $\times 10^4$ for Cu, O, N, and C and $\times 10^3$ for H Atoms with Esd's in Parentheses for the $[Cu(Ac\text{-}\beta\text{-ala})_2 \cdot H_2O]_2 \cdot 2H_2O$ Complex

| | *x* | *y* | *z* |
|---|---|---|---|
| Cu | −63 (1) | 4609 (1) | 6200 (1) |
| O(1) | 1937 (4) | 5020 (2) | 6757 (4) |
| O(2) | 2058 (4) | 5684 (2) | 4712 (4) |
| O(3) | 2026 (5) | 6246 (2) | 10037 (5) |
| O(4) | 789 (4) | 3833 (2) | 5086 (4) |
| O(5) | 932 (4) | 4510 (2) | 3073 (4) |
| O(6) | 4975 (4) | 2531 (2) | 3480 (4) |
| O(7) | 192 (4) | 4010 (2) | 8282 (4) |
| O(8) | 2071 (5) | 4719 (2) | 10374 (5) |
| N(1) | 3485 (5) | 6589 (2) | 8356 (5) |
| N(2) | 2689 (5) | 2046 (2) | 3246 (5) |
| C(1) | 2591 (5) | 5437 (2) | 5988 (5) |
| C(2) | 4156 (5) | 5662 (3) | 6627 (6) |
| C(3) | 4274 (5) | 5908 (3) | 8273 (6) |
| C(4) | 2468 (6) | 6712 (3) | 9227 (6) |
| C(5) | 1879 (7) | 7478 (3) | 9170 (8) |
| C(6) | 1119 (5) | 3925 (2) | 3800 (5) |
| C(7) | 1803 (6) | 3306 (3) | 3070 (6) |
| C(8) | 2068 (7) | 2641 (3) | 4002 (7) |
| C(9) | 4116 (6) | 2023 (3) | 3058 (6) |
| C(10) | 4620 (6) | 1367 (3) | 2343 (7) |
| H(1) | 442 (6) | 606 (3) | 596 (7) |
| H(2) | 482 (6) | 523 (3) | 660 (7) |
| H(3) | 374 (7) | 550 (3) | 882 (7) |
| H(4) | 533 (6) | 602 (3) | 873 (6) |
| H(5) | 389 (6) | 704 (3) | 802 (7) |
| H(6) | 93 (7) | 758 (3) | 935 (8) |
| H(7) | 260 (7) | 779 (3) | 999 (8) |
| H(8) | 194 (7) | 769 (3) | 805 (8) |
| H(9) | 113 (6) | 323 (3) | 211 (7) |
| H(10) | 278 (6) | 349 (3) | 284 (7) |
| H(11) | 112 (6) | 247 (3) | 433 (7) |
| H(12) | 279 (7) | 273 (3) | 496 (7) |
| H(13) | 221 (6) | 158 (3) | 303 (6) |
| H(14) | 398 (7) | 101 (3) | 197 (8) |
| H(15) | 528 (7) | 111 (3) | 281 (8) |
| H(16) | 504 (7) | 153 (3) | 146 (8) |
| H(17) | −50 (7) | 384 (3) | 893 (8) |
| H(18) | 57 (7) | 437 (3) | 887 (8) |
| H(19) | 204 (6) | 521 (3) | 1021 (7) |
| H(20) | 150 (7) | 465 (3) | 1106 (8) |

**Table IV.** Bond Distances (Å) and Angles (Deg) for $Cu(Ac\text{-}\beta\text{-ala})_2 \cdot 2H_2O$ with Esd's in Parentheses

| Distances | | | |
|---|---|---|---|
| Cu–O(1) | 1.958 (2) | Cu–O(2) | 2.580 (2) |
| Cu–O(4) | 1.960 (2) | C(3)–N | 1.456 (5) |
| O(1)–C(1) | 1.296 (4) | N–C(4) | 1.326 (6) |
| O(2)–C(1) | 1.243 (5) | C(4)–O(3) | 1.249 (5) |
| C(1)–C(2) | 1.510 (5) | C(4)–C(5) | 1.507 (7) |
| C(2)–C(3) | 1.503 (5) | | |
| **Angles** | | | |
| O(1)–Cu–O(4) | 89.7 (1) | C(2)–C(3)–N | 111.3 (3) |
| O(1)–C(1)–O(2) | 121.4 (3) | C(3)–N–C(4) | 123.8 (4) |
| O(1)–C(1)–C(2) | 116.7 (3) | N–C(4)–O(3) | 122.3 (4) |
| O(2)–C(1)–C(2) | 121.9 (3) | N–C(4)–C(5) | 116.4 (4) |
| C(1)–C(2)–C(3) | 112.6 (3) | O(3)–C(4)–C(5) | 121.3 (4) |

carboxyl oxygens and two water molecules in a square-planar arrangement. Two weak interactions in the out-of-plane axial positions, involving uncoordinated carboxyl oxygen atoms, complete the coordination to the distorted tetragonal bipyramid. This kind of structure is typical of copper(II) carboxylates, in which the carboxylic group behaves as an essentially unidentate ligand.[8] A similar situation has been previously found in bis(*N*-acetylglycinato)diaquacopper(II) dihydrate.[2c] It is interesting to observe that the Cu–O (carboxylic) distance is not shorter than the Cu–O(4)(water) distance, as found in the *N*-acetylglycinate complex.[2c] Likewise these values 1.958 (2) and 1.960 (2) Å are in the range of those observed in other carboxylate complexes.[8] In *N*-acetylglycinate–copper complex,[2c] Cu–O(carboxylic) and Cu–O(water) distances were 1.955 (3) and 1.947 (3) Å, respectively. The angle between the Cu–O(2) vector and the normal to the O(1)O(4)O(1)′O(4)′ plane is 99.3°. As shown in Table V the carboxylic group (O(1)O(2)C(1)C(2)) and the peptidic group (C(3)NC(4)C(5)O(3)) are planar, and the maximum deviation from planarity is 0.01 Å for C(4). The dihedral angle between these planes is 55.7°.

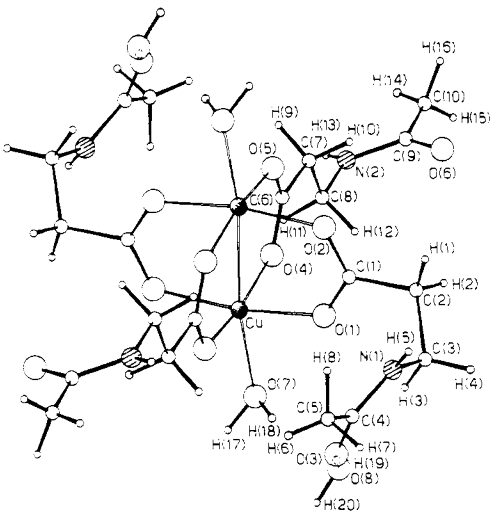

Figure 2. Projection along [010] of the green $[Cu(Ac\text{-}\beta\text{-ala})_2 \cdot H_2O]_2 \cdot 2H_2O$ complex.

The crystal structure of the green $[Cu(Ac\text{-}\beta\text{-ala})_2 \cdot H_2O]_2 \cdot 2H_2O$ complex consists of centrosymmetric dimeric units (Figure 2) in which four carboxylate groups bridge two copper atoms. Coordination around each metal atom is tetragonal bipyramidal with the carboxylic oxygens at the equatorial sites and a water molecule and a copper atom in the axial positions, in a similar way to that observed in dimeric copper(II) acetate monohydrate. The peptide groups are not involved in the coordination. The structural features of $[Cu(Ac\text{-}\beta\text{-ala})_2 \cdot H_2O]_2 \cdot 2H_2O$ are given in Table VI. The Cu–O(carboxylic) bond lengths are in good agreement with those found in tetrakis[$\mu$-(acetylglycinato)-diaquadicopper(II)[9] and in other dimeric copper(II) carboxylate complexes.[10,11] The Cu–O(1)C(1)O(2)–Cu′ and Cu–O(4)–C(4)O(5)–Cu′ bridge lengths, 6.436 and 6.455 Å, respectively, are in the range of 6.40–6.50 Å observed for carboxylate adducts.[10,11] Coordination planes in the dimer, Cu–O(1)C(1)O(2)–Cu′–O(2)′C(1)′O(2)′–Cu and Cu–O(4)C(4)O(5)–Cu′–O(4)′C(4)′O(5)′–Cu, are nearly perpendicular, the dihedral angle being 89.4° (prime indicates centrosymmetric atoms). Also the Cu–Cu distance (2.62 Å) is in the range of those observed for copper(II) acetate monohydrate and normal dimeric carboxylate complexes. The carboxylic and peptidic groups are planar within the experimental errors, the dihedral angles between O(1)O(2)C(1)C(2) and O(3)N(1)C(4)C(5)O(3) being 71.1° and that between O(4)O(5)C(6)C(7) and C(8)N(2)C(9)C(10)O(6) being 73.4° (Table V).

The distances involving hydrogen atoms are available as supplementary material.

Conformation of the ligands in both complexes can be described with use of torsion angles quoted in Table VII. The

---

(8) Muir, K. W. "Molecular Structure by Diffraction Methods"; The Chemical Society: London, 1973; Vol. 1, p 631 and references therein.

(9) Udupa, M. R.; Krebs, B. *Inorg. Chim. Acta* **1979**, *37*, 1.

(10) Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209.

(11) Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291.

Table V. Equations of Least-Squares Planes through Various Atoms in the Form $AX + BY + CZ = D$, with Deviations (Å) of Each Atom from the Plane in Square Brackets ($X$, $Y$, $Z$, are the orthogonal coordinates)[a]

| | *A* | *B* | *C* | *D* |
|---|---|---|---|---|
| (a) Cu(Ac-β-ala)$_2$·2H$_2$O Complex | | | | |
| plane: O(1), O(2), C(1), C(2), C(3)*<br>[O(1) 0.00, O(2) 0.00, C(1) 0.01, C(2) 0.00, C(3)* 0.43] | −0.54899 | 0.82169 | −0.15309 | −0.06628 |
| plane: C(3), N, C(4), C(5), O(3), C(2)*<br>[C(3) −0.007, N 0.006, C(4) 0.012, C(5) −0.008, O(3) 0.00, C(2)* −1.257] | −0.74462 | 0.06531 | −0.66429 | 2.06887 |
| (b) [Cu(Ac-β-ala)$_2$·H$_2$O]$_2$·2H$_2$O Complex | | | | |
| plane O(1), O(2), C(1), C(2), C(3)*<br>[O(1) 0.000, O(2) 0.00, C(1) −0.002, C(2) 0.001, C(3)* −1.050] | 0.43336 | −0.78610 | −0.44075 | −9.58357 |
| plane O(4), O(5), C(6), C(7), C(8)*<br>[O(4) −0.001, O(5) −0.001, C(6) 0.005, C(7) 0.002, C(8)* −0.063] | −0.86043 | −0.30571 | −0.40768 | −4.04140 |
| plane C(3), N(1), C(4), C(5), O(3), C(2)*<br>[C(3) −0.020, N(1) 0.020, C(4) 0.004, C(5) −0.025, O(3) 0.003, C(2)* 1.136] | −0.59964 | −0.27085 | −0.75304 | −10.1450 |
| plane C(8), N(2), C(9), C(10), O(6), C(7)*<br>[C(8) −0.027, N(2) 0.018, C(9) 0.004, C(10) −0.020, O(6) 0.002, C(7)* 1.263] | −0.10860 | −0.43686 | −0.89295 | −1.15399 |

[a] The atoms marked with an asterisk are not included in the planarity.

Table VI. Bond Distances (Å) and Angles (Deg) for [Cu(Ac-β-ala)$_2$·H$_2$O]$_2$·2H$_2$O with Esd's in Parentheses[a]

| | | | |
|---|---|---|---|
| Distances | | | |
| Cu–O(1) | 1.971 (4) | Cu–O(5)$^i$ | 1.968 (4) |
| Cu–O(2)$^i$ | 1.957 (3) | Cu–O(7) | 2.156 (4) |
| Cu–O(4) | 1.976 (4) | Cu–Cu$^i$ | 2.613 (1) |
| O(1)–C(1) | 1.246 (6) | O(4)–C(6) | 1.248 (6) |
| O(2)–C(1) | 1.262 (5) | O(5)–C(6) | 1.263 (5) |
| C(1)–C(2) | 1.515 (6) | C(6)–C(7) | 1.502 (7) |
| C(2)–C(3) | 1.535 (8) | C(7)–C(8) | 1.489 (8) |
| C(3)–N(1) | 1.460 (7) | C(8)–N(2) | 1.453 (7) |
| N(1)–C(4) | 1.319 (8) | N(2)–C(9) | 1.338 (7) |
| C(4)–O(3) | 1.235 (7) | C(9)–O(6) | 1.247 (6) |
| C(4)–C(5) | 1.516 (8) | C(9)–C(10) | 1.480 (8) |
| Angles | | | |
| O(1)–Cu–O(4) | 89.5 (1) | O(2)$^i$–Cu–O(4) | 89.9 (2) |
| O(1)–Cu–O(2)$^i$ | 168.7 (2) | O(7)–Cu–Cu$^i$ | 171.0 (1) |
| O(1)–Cu–O(5)$^i$ | 89.9 (2) | O(7)–Cu–O(1) | 90.2 (1) |
| O(5)$^i$–Cu–O(2)$^i$ | 88.5 (2) | O(7)–Cu–O(5)$^i$ | 97.8 (1) |
| O(5)$^i$–Cu–O(4) | 168.5 (2) | O(7)–Cu–O(2)$^i$ | 101.1 (1) |
| O(5)$^i$–Cu–Cu$^i$ | 83.3 (1) | O(7)–Cu–O(4) | 93.7 (1) |
| O(2)$^i$–Cu–Cu$^i$ | 87.8 (1) | O(4)–Cu–Cu$^i$ | 85.2 (1) |
| O(1)–C(1)–O(2) | 125.2 (4) | O(1)–Cu–Cu$^i$ | 80.9 (1) |
| O(1)–C(1)–C(2) | 117.6 (4) | O(4)–C(6)–O(5) | 124.2 (4) |
| O(2)–C(1)–C(2) | 117.2 (4) | O(4)–C(6)–C(7) | 118.2 (4) |
| C(1)–C(2)–C(3) | 111.9 (4) | O(5)–C(6)–C(7) | 117.5 (4) |
| C(2)–C(3)–N(1) | 110.0 (4) | C(6)–C(7)–C(8) | 115.5 (5) |
| C(3)–N(1)–C(4) | 125.1 (4) | C(7)–C(8)–N(2) | 114.0 (5) |
| N(1)–C(4)–O(3) | 123.3 (5) | C(8)–N(2)–C(9) | 122.5 (4) |
| N(1)–C(4)–C(5) | 114.8 (5) | N(2)–C(9)–O(6) | 121.1 (5) |
| O(3)–C(4)–C(5) | 122.0 (5) | N(2)–C(9)–C(10) | 116.9 (5) |
| | | O(6)–C(9)–C(10) | 122.0 (5) |

[a] $i = \bar{x}, 1 - y, 1 - z$.

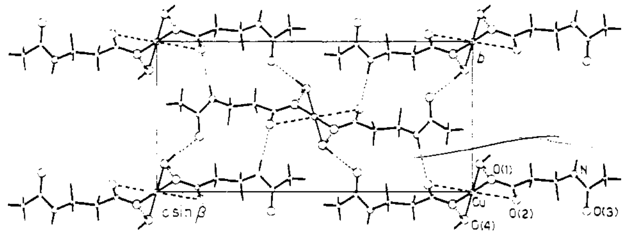

**Figure 3.** Packing of the structure of the blue Cu(Ac-β-ala)$_2$·2H$_2$O complex.

*N*-acetyl-β-alaninato ligands show different conformations. In the blue compound the ligand is present in an extended form; in the green complex the ligands are present in the folded (O(1)O(2)C(1)C(2)C(3)N(1)C(4)C(5)O(3)) and in the extended form (O(4)O(5)C(6)C(7)C(8)N(2)C(9)O(6)C(10)). The folded form shows around the C′–C$^\alpha$ and C$^\alpha$–C$^\beta$, conformation similar to that found in pyruvidene-β-alaninato,[12] in which the torsion angles around C′–C$^\alpha$ and C$^\alpha$–C$^\beta$ bonds are 52.4 and 68.5°, respectively. Corresponding torsion angles in β-alanine[13] are 9.3 and 83.7° and in nickel β-alaninate are 30.3 and 73.7°.[14]

In both complexes packing (Table VIII and IX) is determined by hydrogen bonds involving water molecules, carboxylic oxygens, and peptide groups. In the blue complex the ligand molecules are hydrogen bonded in a manner such that layers in the (010) plane are formed in a more regular arrangement than that found in the green complex. The water molecule acts as a hydrogen donor to the peptide oxygen and to the coordinated carboxylic oxygen atom. Further hydrogen bonding also occurs between peptide nitrogen and a slightly coordinated carboxylic oxygen.

In the green complex the structure can be described as layers along (010) connected by NH···O hydrogen bonds involving two different peptide nitrogens (N(1) and N(2)), one connected with the carboxylate group and the other with the coordinated water molecule.

Also noteworthy is the importance of the uncoordinated water molecule, which joins two adjacent dimers along the [001] axis through hydrogen bonds involving simultaneously carboxylic and peptidic oxygens and a coordinated water molecule. In Figures 3 and 4 packing of the complexes is illustrated.

**Electronic, Infrared, and EPR Spectroscopy and Magnetic Measurements.** The blue Cu(Ac-β-ala)$_2$·2H$_2$O complex, which has a "normal" room-temperature magnetic moment ($\mu_B$ = 1.88 $\mu_B$), shows at room temperature a typical axial EPR spectrum with two $g$ values ($g_\parallel$ = 2.322, $g_\perp$ = 2.067) which indicate a predominantly $d_{x^2-y^2}$ ground state and an essentially square-planar arrangement around the copper(II) ion.[15,16] In particular, the $g$ crystal values perfectly agree with the structural data as they are characteristic of compounds having a CuO$_4$ chromophore.[16,17]

The room-temperature electronic spectrum, which exhibited a maximum near 15.9 × 10$^3$ cm$^{-1}$ and a shoulder at about 12.7 × 10$^3$ cm$^{-1}$ for shape and d–d band position, agrees with those reported for tetragonal copper(II)–oxygen systems.[16,18] The

---

[12] Ueki, T.; Ashida, T.; Sasada, Y.; Kakudo, M. *Acta Crystallogr., Sect. B* **1968**, *B24*, 1361.

[13] Jose, P.; Pant, L. M. *Acta Crystallogr.* **1965**, *18*, 806.

[14] Jose, P.; Pant, L. M.; Biswas, A. B. *Acta Crystallogr.* **1964**, *17*, 24.

[15] Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143 and references therein.

[16] Billing, D. E.; Hathaway, B. J.; Nicholls, P. *J. Chem. Soc. A* **1969**, 316.

[17] Smith, D. W. *J. Chem. Soc. A* **1970**, 3108.

**Table VII.** Torsion Angles (Deg) for the $Cu(Ac\text{-}\beta\text{-}ala)_2 \cdot 2H_2O$ (I) and $[Cu(Ac\text{-}\beta\text{-}ala)_2 \cdot H_2O]_2 \cdot 2H_2O$ (II) Complexes

| complex I | | complex II | | | |
|---|---|---|---|---|---|
| O(1)C(1)C(2)C(3) | 161.8 (3) | O(2)C(1)C(2)C(3) | 132.6 (4) | O(5)C(6)C(7)C(8) | 177.1 (4) |
| O(2)C(1)C(2)C(3) | 18.3 (5) | O(1)C(1)C(2)C(3) | 47.9 (6) | O(4)C(6)C(7)C(8) | 2.0 (7) |
| C(1)C(2)C(3)N | 179.6 (3) | C(1)C(2)C(3)N(1) | 68.9 (5) | C(6)C(7)C(8)N(2) | 178.3 (4) |
| C(2)C(3)NC(4) | 106.0 (4) | C(2)C(3)N(1)C(4) | 127.8 (5) | C(7)C(8)N(2)C(9) | 76.1 (6) |
| C(3)NC(4)O(3) | 0.5 (6) | C(3)N(1)C(4)O(3) | 3.0 (8) | C(8)N(2)C(9)O(6) | 2.7 (8) |
| C(3)NC(4)C(5) | 178.6 (4) | C(3)N(1)C(4)C(5) | 176.7 (4) | C(8)N(2)C(9)C(10) | 176.7 (5) |

**Table VIII.** Hydrogen-Bonding Distances (Å) and Angles (Deg) of the $Cu(Ac\text{-}\beta\text{-}ala)_2 \cdot 2H_2O$ Complex[a]

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $O(4)\cdots O(1)^{i}$ | 2.694 (3) | O(4)–H(9) | 0.94 (5) | $H(9)\cdots O(1)^{i}$ | 1.77 (5) | $O(4)–H(9)\cdots O(1)^{i}$ | 168 |
| $O(4)\cdots O(3)^{ii}$ | 2.668 (4) | O(4)–H(10) | 0.94 (5) | $H(10)\cdots O(3)^{ii}$ | 1.75 (5) | $O(4)–H(10)\cdots O(3)^{ii}$ | 167 |
| $N\cdots O(2)^{iii}$ | 2.859 (5) | N–H(5) | 0.88 (5) | $H(5)\cdots O(2)^{iii}$ | 2.00 (5) | $N–H(5)\cdots O(2)^{iii}$ | 165 |

[a] $i = 1 - x, \bar{y}, \bar{z}$; $ii = x - {}^1/_2, -y - {}^1/_2, {}^1/_2 + z$; $iii = {}^1/_2 - x, {}^1/_2 + y, -z - {}^1/_2$.

**Table IX.** Hydrogen-Bonding Distances (Å) and Angles (Deg) of the $[Cu(Ac\text{-}\beta\text{-}ala)_2 \cdot H_2O]_2 \cdot 2H_2O$ Complex[a]

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $O(8)\cdots O(5)^{ii}$ | 2.806 (6) | O(8)–H(20) | 0.87 (7) | $H(20)\cdots O(5)^{ii}$ | 1.97 (7) | $O(8)–H(20)\cdots O(5)^{ii}$ | 160 (1) |
| $O(7)\cdots O(8)$ | 2.688 (5) | O(7)–H(18) | 0.88 (6) | $H(18)\cdots O(8)$ | 1.89 (6) | $O(7)–H(18)\cdots O(8)$ | 149 (1) |
| $O(8)\cdots O(3)$ | 2.844 (5) | O(8)–H(19) | 0.92 (6) | $H(19)\cdots O(3)$ | 1.92 (6) | $O(8)–H(19)\cdots O(3)$ | 175 (1) |
| $O(7)\cdots O(3)^{iii}$ | 2.740 (6) | O(7)–H(17) | 0.97 (7) | $H(17)\cdots O(3)^{iii}$ | 1.80 (7) | $O(7)–H(17)\cdots O(3)^{iii}$ | 164 (1) |
| $N(1)\cdots O(6)^{iv}$ | 2.836 (6) | N(1)–H(5) | 0.97 (6) | $H(5)\cdots O(6)^{iv}$ | 1.98 (6) | $N(1)–H(5)\cdots O(6)^{iv}$ | 145 (1) |
| $N(2)\cdots O(7)^{v}$ | 3.006 (5) | N(2)–H(13) | 0.98 (5) | $H(13)\cdots O(7)^{v}$ | 2.18 (5) | $N(2)–H(13)\cdots O(7)^{v}$ | 141 (1) |

[a] $ii = x, y, 1 + z$; $iii = \bar{x}, 1 - y, 2 - z$; $iv = 1 - x, 1 - y, 1 - z$; $v = x, {}^1/_2 - y, z - {}^1/_2$.

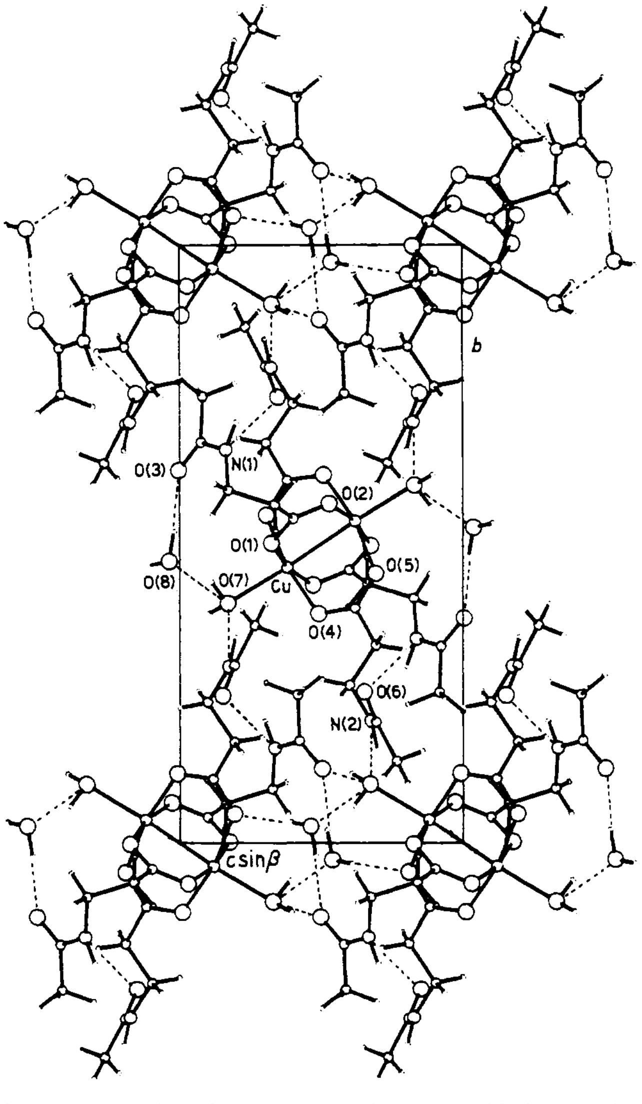

**Figure 4.** Packing of the structure of the green $[Cu(Ac\text{-}\beta\text{-}ala)_2 \cdot H_2O]_2 \cdot 2H_2O$ complex.

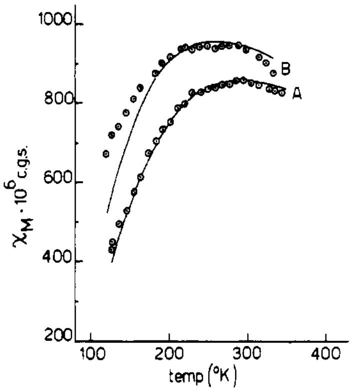

**Figure 5.** Variations of magnetic susceptibilities with temperature for the solid green $[Cu(Ac\text{-}\beta\text{-}ala)_2 \cdot H_2O]_2 \cdot 2H_2O$ (A) and $[Cu(Ac\text{-}\beta\text{-}ala)_2]_2$ (B) complexes: O, experimental susceptibility; ---, calculated susceptibility.

observed spectrum can be interpreted in terms of $d_{x^2-y^2} \leftarrow d_{xz}$, $d_{yz}$ ($15.9 \times 10^3$ cm$^{-1}$) and $d_{x^2-y^2} \leftarrow d_{xy}$ ($12.7 \times 10^3$ cm$^{-1}$) excitations in agreement with the EPR data and the results of crystal field calculations. The reasonable calculated values of the molecular orbital coefficients ($k_\parallel = 0.72$ and $k_\perp = 0.73$) confirm the d–d band assignment.[16]

The EPR spectra of the green complexes ($g_z = 2.429$ and $g_\perp = 2.106$ for the hydrate complex and $g_z = 2.411$ and $g_\perp = 2.109$ for the anhydrous one), typical of dimeric carboxylates,[10,11,19] show a zero field splitting of 0.37 cm$^{-1}$. The presence of magnetically dilute copper(II) impurities ($g_\parallel = 2.328$ and $g_\perp = 2.067$) is only observed for the hydrate compound. The observed and calculated magnetic susceptibilities (available as supplementary material) are shown graphically in Figure 5. A maximum in the curve is observed at 285 and 260 K (the Neel temperature) for the hydrate and anhydrous green compounds, respectively. The experimental data are closely fitted by the usual dimer equations.[20,21] By using for the Landé splitting factor ($\bar{g} = [(g_\parallel^2 + 2g_\perp^2)/3]^{1/2}$[22,23] the

---

(18) Cotton, F. A.; Wilkinson, G. "Advances Inorganic Chemistry", 2nd ed.; Interscience: New York, 1966; p 902.
(19) Moreland, J. A.; Doedens, R. J. *Inorg. Chem.* **1978**, *17*, 674.
(20) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.
(21) Kokot, E.; Martin, R. L. *Inorg. Chem.* **1964**, *3*, 1306.
(22) Jotham, R. W.; Kettle, S. F. *J. Chem. Soc. A* **1969**, 2816.
(23) Dehand, J.; Jordanov, J.; Keck, F.; Mosset, A.; Bonnet, J. J.; Galy, J. *Inorg. Chem.* **1979**, *18*, 1543.

EPR-determined values of 2.219 and 2.214 for the hydrate and anhydrous complex, respectively, and, for the temperature-independent paramagnetism ($N\alpha$), a value of $60 \times 10^{-6}$ emu/mol, $-2J$ (exchange integral) values of $324 \pm 15$ and $185 \pm 15$, respectively, may be calculated. These values, indicating a relatively strong magnetic interaction between the two copper(II) ions, which diminishes when the axial water is lost, fall in the range found for dimeric copper(II) carboxylates.[10,11]

Their electronic spectra show two bands around $14 \times 10^3$ (band I) and $27 \times 10^3$ (band II) $cm^{-1}$. Band I may be considered to be the "ordinary copper(II) band",[11] while band II is taken to be diagnostic of a dimeric structure.[11,24-26]

The DSC studies of the hydrate blue and green complexes show two strong endothermic peaks in the temperature ranges 368–375 and 350–367 K, respectively. The weight loss corresponds to the complete loss of the water molecules. In particular in the green compound both coordinated and uncoordinated water molecules are lost within the temperature range reported above. The thermal extrusion of the water molecules from the blue compound is accompanied by a change in the coordination geometry (irreversible thermochromism) from a monomeric distorted tetragonal-bipyramidal structure (blue compound) to a dimeric quadruply bridged copper(II) acetate-like structure (green compound). Differences in energies between these two structural types should be very low. In fact the $Cu(Ac\text{-}\beta\text{-}ala)_2\cdot 2H_2O$ and $[Cu(Ac\text{-}\beta\text{-}ala)_2\cdot H_2O]_2\cdot 2H_2O$ complexes may be directly obtained depending on the preparation conditions. In the green compound obtained from aqueous alcoholic or alcoholic solutions, the metal ion:coordinated water ratio is lower than in the blue compound, separated from aqueous solution. This may be related to the different hydrogen-bonding interactions that the water molecules undergo in the two cases. These complexes represent a quite evident example of structural isomerism determined by the influence of the solution media on the coordination interactions.

Studies in the IR spectral region are peformed by comparing the spectra of the amino acid, its alkali salts, the complexes, and their deuterated analogues. While the IR spectra of the anhydrous and hydrated green complexes are quite similar to one another, some diffferences are observed with the hydrate blue complex. In fact in the blue complex one sharp band, assignable to NH stretching vibration, appears to 3338 $cm^{-1}$, which may be associated with the peptidic NH group involved in only one type of hydrogen bonding with a slightly coordinated carboxylic oxygen (N–H(5)···O(2)$^{iii}$; see Table VIII), while in the hydrate green complex the two bands at 3393 and 3300 $cm^{-1}$, shifted at 3398 and 3255 $cm^{-1}$ in the anhydrous one, assignable to NH stretching vibrations, are directly connected with the two different types of hydrogen bonds in which the peptidic NH group is involved (N(2)–H(13)···O(7)$^{v}$ and N(1)–H(5)···O(6)$^{iv}$, respectively; see Table IX). A difference in the N···O distance of about 0.2 Å results in a separation of 93 $cm^{-1}$ of the two NH frequencies.

Differences are also observed in the 1700–1350-$cm^{-1}$ spectral range in which the intense CO ketonic and antisymmetric and symmetric carboxylate stretching frequencies must appear. In the blue complex these band appear at 1634, 1592, and 1408 $cm^{-1}$, respectively, while in the hydrate and anhydrous green complexes they appear at 1640, 1618, and 1435 $cm^{-1}$ and 1653, 1609, and 1440 $cm^{-1}$, respectively. This agrees with our previous suggestion[2e] on the importance of examining the position of the symmetric carboxylate stretching vibration, which is the band directly connected with the oxygen atom linked to the copper(II) ion, together with the $\Delta\nu$ ($\nu(OCO)_{as} - \nu(OCO)_s$) separation,[11,27] to get a correct assignment of the way in which the carboxylate group coordinates.

An attempt to assign the Cu–O stretching vibrations in the far-infrared region may be performed, although it is difficult to distinguish these bands clearly. However in the hydrate green complex the band at 334 $cm^{-1}$ should be prevalently assigned to the IR-active antisymmetric metal–ligand stretch (the symmetric stretch is only Raman active in centrosymmetric complexes[28]). This may be confirmed as in the anhydrous one this band appears at 357 $cm^{-1}$, probably as a consequence of an increased Cu–O bond order since the axial water molecules are absent, and as the band appears in the spectral range in which this vibration should lie.[11]

In the blue compound in the same spectral region two bands may be associated with the copper–oxygen frequencies at 394 and 323 $cm^{-1}$; in particular the band at 394 $cm^{-1}$ is found in the expected range for $\nu(Cu\text{–}OH_2)$.[29,30]

**Acknowledgment.** The authors are grateful to Professor M. Nardelli for helpful discussion and to the Centro Strumenti dell'Università di Modena for the recording of the IR spectra.

**Registry No.** I, 76037-20-2; II, 76037-19-9; $[Cu(Ac\text{-}\beta\text{-}ala)_2]_2$, 76037-18-8.

**Supplementary Material Available:** A listing of observed and calculated structure factor amplitudes and tables of thermal parameters, distances involving hydrogen atoms, and observed and calculated magnetic susceptibilities (12 pages). Ordering information is given on any current masthead page.

---

(24) Hibdon, D. H.; Nelson, J. H. *Inorg. Chim. Acta* **1973**, *7*, 629.

(25) Harrison, W.; Rettig, S.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1972**, 1852 and references therein.

(26) Wasson, J. R.; Chin-I-Shyr; Trapp, C. *Inorg. Chem.* **1968**, *7*, 469.

(27) Freeman, H. C. In "Inorganic Biochemistry"; Eichhorn, G. L.; Ed.; Elsevier: Amsterdam, 1973; Vol. 1, p 121 and references therein.

(28) Tsivadze, A. Yu.; Kharitonov, Yu. Ya.; Smirnov, A. N.; Tsintsadze, G. V.; Gverdtsiteli, L. V. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *25*, 705.

(29) Ferraro, J. R. "Low-Frequency Vibrations of Inorganic and Coordination Compounds"; Plenum Press: New York, 1971; Chapter 5.

(30) Cariati, F.; Morazzoni, F.; Zanderighi, G. M.; Marcotrigiano, G.; Pellacani, G. C. *Inorg. Chim. Acta* **1977**, *21*, 133.