The dysprosium analogue was solved first, and its final fractional coordinates were used as a starting point in the refinement the Y compound. The dysprosium positions were determined via inspection of a Patterson function map. A difference Fourier map phased on the dysprosium atoms readily revealed the positions of the non-hydrogen atoms.

Disorder in the structures was immediately obvious from unrealistically close contacts between some of the atoms related by the 2-fold axis containing M(2). Because of the presence of disorder, an attempt was made to refine these structures in the noncentrosymmetric *Ia*. High correlations between atoms related by the center of symmetry in *I*2/*a* and the continued presence of disorder led us to conclude that *I*2/*a* was in fact the correct choice.

There are four pairs of 2-fold-related general positions in *I*2/*a*. The disorder model used has two atoms in general positions, half-weighted, such that each of these atoms occupies only one position of each 2-fold-related pair of general positions. The two atoms may not reside on the same side of the 2-fold axes. The pairs of atoms involved are as follows: Cl(4), O(13); Cl(5), O(14); Cl(6), C(13); O(12), O(12)′. In addition, the M(2) position may be fractionally disordered about the 2-fold axis. Although the M(2) atom would not refine properly off the 2-fold axis, noticeable anisotropy of the M(2) thermal parameters are noted for both compounds. The resulting atom orientations and hydrogen-bonding network were described earlier. Least-squares refinement with isotropic thermal parameters led to $R = 0.104$ (M = Dy) and 0.109 (M = Y). The crown hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The methyl and water hydrogen atoms were not located because of the disorder. Refinement of the non-hydrogen atoms (except for O(12), M = Y) with anisotropic temperature factors led to the final R values. The final values of the positional parameters are given in Tables VI and VII.

A low-temperature and a room-temperature structure determination were also carried out on the higher melting form of the Y compound. These determinations were isostructural with the two complexes reported above except for the atoms relating to O(12) and O(12)′. Whereas only two positions were found for O(12) in the low-melting forms, a third refinable position was found in the higher melting form. Two features were found unique to this form of the Y complex. First, different hydrogen-bonding patterns were noted for the three positions related to O(12). In addition, the disorder resulted in two different geometries observed for the $[M(OH_2)_7(OHMe)]^{3+}$ cation: one a bicapped trigonal prism and the other a square antiprism. The occupancy factors (50% O(12)/50% O(12)′ in the structures reported above) refined to 45% O(12), 40% O(12)′, and 15% O(12)P.

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Supplementary Material Available: Figures A and B, showing a view of the unit cell contents and H-bonding contacts around $[M(OH_2)_7(OHMe)]^{3+}$, and Tables SI–SIX, listing derived hydrogen atom coordinates, thermal parameters, bond distances and angles, and least-squares planes results for geometry calculations (31 pages); Tables SX and SXI, listing observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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An Unusual Six-Membered Chelate Ring Involving Carboxylic Function to Copper(II) Coordination: Synthesis, Crystal Structure, and Properties of Aqua(((2-carboxyethyl)imino)diacetato)copper(II)

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The complex $[Cu^{II}(H_2O)(HNPDA)]$ (HNPDA = ((2-carboxyethyl)imino)diacetate) has been synthesized and characterized by X-ray diffraction. The title compound crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 10.559$ (3) Å, $b = 8.715$ (2) Å, $c = 11.217$ (2) Å, $\beta = 111.85$ (3)°, $Z = 4$, $V = 958.1$ Å^3, and $D_{\text{measd}} = 1.998$ g cm^{-3}. Final $R = 0.031$ and $R_w = 0.029$ for 1663 independent observed reflections. Each tetradentate HNPDA^{2-} ligand chelates one copper(II) ion with three nearly coplanar and short bonds (Cu–N = 1.997 (3) Å, Cu–O(13) = 1.963 (3) Å, and Cu–O(23) = 1.972 (3) Å) and a fourth longer bond (Cu–O(5) = 2.488 (3) Å), making up an interesting β-aminopropionic acid–copper(II) six-membered chelate ring, which is puckered in a boat-type conformation. The in-plane short bond Cu–O(H_2O) = 1.924 (2) Å and a trans-apical long bond Cu–O(14^i) = 2.494 (3) Å, involving an O donor atom of the bidentate-bridged acetate arm of a second HNPDA^{2-} ligand (referred to by the superscript i), complete the tetragonally elongated octahedral coordination of each copper(II) ion. Thus, each ligand molecule links two copper atoms and each copper(II) is bonded to two ligands. The 2_1-axis-related copper complexes share one oxygen atom, thus forming infinite polynuclear zigzag chains, reinforced by O(4)–H(O4)···O(24^{iv}) (symmetry code iv: $x, -1 + y, z$) intrachain hydrogen bonds (linking alternating complex entities). In addition, both hydrogen atoms of the coordinated water molecule are involved in interchain hydrogen bonds with two different homologous chains, making up tunnels of irregular hexagonal cross section that run parallel to the [010] axis in the tridimensional network. The potentiometric and conductometric titrations, thermal stability, spectral (IR, reflectance, ESR) properties, and magnetic susceptibility data are interpreted in light of the known crystal structure of this complex.

Introduction

The studies on amino polycarboxylic acid–metal ion systems in aqueous solution often point out the formation of metal–proton–ligand species $M_pH_qL_r$. The literature concerning these ternary complexes in the solid state is clearly less extensive. Even for the most common amino polycarboxylic acids such as ethylenediaminetetraacetic acid (H_4EDTA)[2-7] or nitrilotriacetic

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Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement

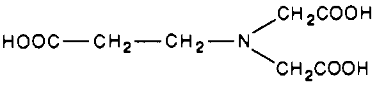
formula: $CuC_7H_{11}NO_7$
$M_r = 282.71$
monoclinic space group: $P2_1/c$
$a = 10.559\ (3)$ Å
$b = 8.715\ (2)$ Å
$c = 11.217\ (2)$ Å
$\beta = 111.85\ (3)°$

$V = 958.1$ Å^3
$Z = 4$
$D_{measd} = 1.99$ g cm^{-3}
$D_{exptl} = 1.96$ g cm^{-3}
$\mu = 2.392$ mm^{-1} (Mo Kα)
$F(000) = 580$

scan type: $\omega - 2\theta$
scan range: $1.6° < \theta < 28°$
octants collecd: $0 \leqslant h \leqslant 13$; $0 \leqslant k \leqslant 11$; $-14 \leqslant l \leqslant 14$
no. of indep reflns measd: 2458
final $R = 0.031^a$
final $R_w = 0.029^a$

[a] For 1663 independent observed reflections with $I > 3\sigma(I)$.

acid,[8,9] only a few crystallographic studies of their "acid" metal chelates have been made. Nevertheless, metal–hydrogen–EDTA compounds show an interesting variety of chemical structures. In these compounds, five-membered aminoacetic acid–metal chelate rings of nearly planar configuration are described. Homologous six-membered β-aminopropionic acid–metal chelate rings can be expected, for example, in the acid chelate MHL of ((2-carboxyethyl)imino)diacetic acid (H_3NPDA), which can also be called *N*,*N*-bis(carboxymethyl)-β-alanine:


$$HOOC{-}CH_2{-}CH_2{-}N\begin{matrix}CH_2COOH\\CH_2COOH\end{matrix}$$

This ligand has been extensively studied in solution for a wide variety of metal ions,[10-20] but not in the solid state by X-ray diffraction. Three papers also refer to Cr(III)[21] or Co(III)[22,23] with this amino polycarboxylic acid in the solid state, but in the compounds $[Cr(OH)(HNPDA)(H_2O)_2]$[21] and $\{[Co(HNPDA)(dien)]ClO_4\}$,[23] the β-aminopropionic acid–metal chelate ring is not formed. Long ago, Chaberek and Martell[11] suggested the formation of [Cu(HNPDA)] species in aqueous solution and discussed its structure on the basis of a tridentate ((2-carboxyethyl)imino)diacetate form of the ligand, with the propionic arm being free. The present paper deals with the synthesis, crystal structure, and properties of the compound aqua(((2-carboxyethyl)imino)diacetato)copper(II),[24] in which we had suspected the existence of a six-membered β-alanine–copper(II) chelate ring.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters with Esd's Given in Parentheses[a]

	x	y	z	B_{eq}, Å^2
Cu	0.69238 (5)	0.49258 (7)	0.42077 (4)	1.38 (1)
OW	0.6571 (3)	0.5190 (4)	0.5765 (2)	1.84 (8)
N	0.7405 (3)	0.4688 (3)	0.2651 (3)	1.11 (9)
C(1)	0.8818 (4)	0.4025 (5)	0.3020 (4)	1.4 (1)
C(2)	0.8934 (4)	0.2362 (5)	0.3461 (4)	1.5 (1)
C(3)	0.8729 (4)	0.2102 (5)	0.4711 (4)	1.5 (1)
O(4)	0.8520 (3)	0.0680 (3)	0.4978 (3)	2.22 (9)
O(5)	0.8789 (3)	0.3133 (3)	0.5456 (3)	1.94 (9)
C(11)	0.6317 (4)	0.3711 (5)	0.1735 (3)	1.6 (1)
C(12)	0.5746 (4)	0.2620 (5)	0.2487 (4)	1.4 (1)
O(13)	0.5845 (3)	0.3041 (3)	0.3608 (3)	1.6 (8)
O(14)	0.5207 (3)	0.1402 (3)	0.1974 (3)	2.07 (9)
C(21)	0.7397 (4)	0.6289 (4)	0.2188 (4)	1.5 (1)
C(22)	0.7885 (4)	0.7382 (5)	0.3326 (4)	1.5 (1)
O(23)	0.7904 (3)	0.6900 (3)	0.4406 (3)	1.63 (8)
O(24)	0.8187 (3)	0.8718 (3)	0.3122 (3)	1.99 (9)

[a] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}\vec{a}_i\cdot\vec{a}_j$

Experimental Section

Ligand Synthesis. *N*,*N*-Bis(carboxymethyl)-β-alanine, or ((2-carboxyethyl)imino)diacetic acid ($H_3NPDA = H_3L$), was prepared by the method of González García and Niclós Gutiérrez.[25] Analogous procedures have been reported in the literature.[10,12,14,21]

Synthesis of Aqua(*N*,*N*-bis(carboxymethyl)-β-alaninato(2–))copper(II), $[Cu(HNPDA)(H_2O)]$. This complex is obtained in aqueous solution by reaction of ((2-carboxyethyl)imino)diacetic acid and $Cu_2CO_3(OH)_2$ (Merck) in a 2:1 molar ratio. In a typical reaction, to 48.74 mmol of H_3NPDA in 400 mL of CO_2-free water is slowly added 24.37 mmol of $Cu_2CO_3(OH)_2$, the reaction mixture being heated (60 °C) and stirred and the CO_2 (byproduct of the synthesis) removed under vacuum. The dark blue solution obtained is left to cool slowly and then is filtered to remove insoluble byproducts. The clear blue solution is allowed to evaporate at room temperature for some days, and the dark blue crystals formed are filtered and washed with cool water, ethanol, and acetone and then air-dried. The product is purified by recrystallization in a minimum amount of hot water (70 °C); yield 12.5 g (90%). Anal. Calcd for $C_7H_{11}CuNO_7$: C, 29.53; H, 3.90; N, 4.92; Cu, 22.32. Found: C, 30.03; H, 3.90; N, 4.68; Cu, 22 ± 1 (complexometry).

X-ray Structure Determination. Diffraction data for $[Cu(HNPDA)(H_2O)]$ were collected at room temperature on a four-circle Enraf-Nonius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The crystals were shaped as parallelepipeds. Details on crystal data, intensity collection, and refinement are reported in Table I. Lattice constants were obtained by a least-squares fit of 25 reflections in the range $5.1 < \theta < 17.9°$. The intensities of three standard reflections measured every 90 min showed no systematic variation. Intensities were corrected for Lorentz and polarization effects; absorption correction was not necessary. Direct methods (MULTAN 80)[26] were used to solve the structure, by locating the copper atoms. Carbon, nitrogen, and oxygen atoms were found by Fourier and difference Fourier synthesis. The structure was then refined by a full-matrix least-squares method[27] to final residuals $R = 0.031$ and $R_w = 0.029$ with $w = 1/\sigma^2(F)$. H atoms could be located from difference maps. Final atomic positional parameters and equivalent isotropic temperature factors are listed in Table II. All calculations were performed with the local system of programs adapted to the UNIVAC 1110 computer.[28] Scattering factors

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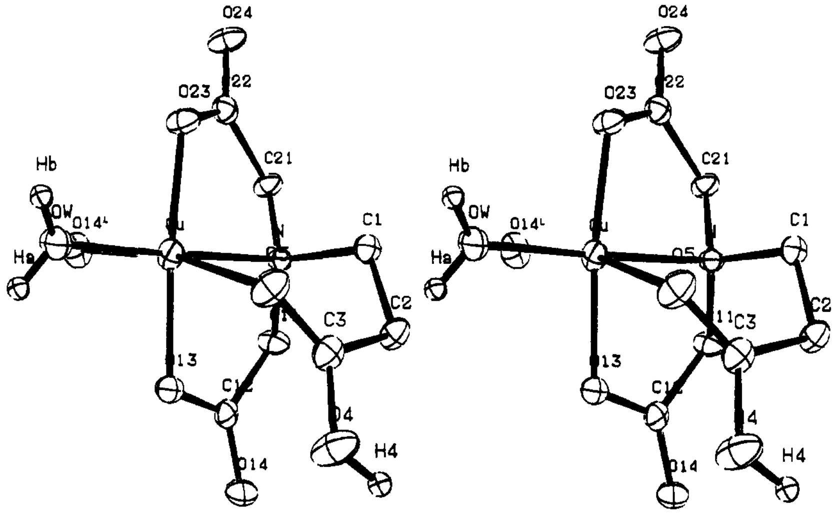

Figure 1. ORTEP stereoscopic view of the copper(II) complex showing the unusual six-membered chelate ring, along with the numbering scheme.

and the anomalous dispersion correction terms were taken from ref 29. The highest peak in the last difference Fourier map calculated at the end of the refinement was less than 0.12 e Å^{-3}. Tables of anisotropic thermal parameters, positional parameters for the hydrogen atoms, distances from the atoms to the mean planes, torsion angles, van der Waals distances and structure factors have been deposited as supplementary material.

Physical Measurements. The potentiometric and conductometric titration curves of a solution of [Cu(HNPDA)(H$_2$O)] (4 × 10^{-3} mol L^{-1}) in water with CO$_2$-free KOH solution (1.088 mol L^{-1}) were recorded under an N$_2$ atmosphere and at 298 K with a Radiometer RTG-622 recording titration system supplied with a Radiometer CDM-3 conductimeter. TG and DTA diagrams were recorded on a Rigaku thermal analysis system, Thermoflex model, under a static air atmosphere. IR spectra were recorded with a Beckman IR-4260 spectrophotometer using the KBr disk technique. The near-IR–vis–UV diffuse-reflectance spectra (4000–40 000 cm^{-1}) were recorded with a Beckman 5240 spectrophotometer equipped with an integrating sphere. The sample (10%) was diluted with "white Kodak" (BaSO$_4$) used as a reference. The spectra represent the variations of the Kubelka function,[30] KUB = $(1 - R_\infty)^2/2R_\infty$, equivalent to the absorbance in transmission spectra, as a function of the wavenumber ($\bar{\nu}$). The ESR spectra of the powdered sample have been obtained with a Varian V4500 X-band spectrometer (9300 MHz) at 77 and 300 K, and the use of a double cavity allows the simultaneous observation of the sample and of the Varian reference "strong pitch" (g = 2.0028). The magnetic susceptibility was measured at room temperature with a Gouy balance and in the temperature range of 115–300 K with a Faraday magnetic torsion balance equipped with a low-temperature device.

Results and Discussion

Description of the Structure. An ORTEP view of the complex [Cu(HNPDA)(H$_2$O)] showing the atom labeling is given in Figure 1. Bond lengths and angles are given in Table III.

Coordination Polyhedron. The copper(II) ion is bonded to one nitrogen and five oxygen donor atoms, thus forming an elongated distorted octahedral polyhedron of coordination. The oxygen atom OW of the water molecule and the N, O(13), and O(23) atoms, belonging to the doubly ionized bis(carboxymethyl)amino moiety, or iminodiacetato group (–N(CH$_2$COO$^-$)$_2$) of the ligand HNPDA^{2-} are roughly placed at the corners of the square cross section of the tetragonally elongated octahedral polyhedron; the apical sites are occupied by the oxygen atom O(5) unbonded to the acid proton in the 2-carboxyethyl substituent of the same ligand HNPDA^{2-}, previously mentioned, and by the oxygen atom O(14^{i}) of the bidentate carboxylate group of one ionized carboxymethyl group of the neighboring HNPDA^{2-} ligand related by the 2$_1$ screw axis. Thus, the crystal structure of the studied complex has no discrete complex molecules but is polymeric (as described below). The copper(II) ion lies 0.0381 (6) Å off the least-squares mean plane P(1) defined by the donor atoms N, C(13), O(23), and OW; it is displaced toward the apical position occupied by the atom O(5). The short Cu–N, Cu–O(13), and Cu–O(23) bonds conform with those observed in other octahedral copper(II) amino poly-

Table III. Bond Lengths (Å) and Angles (deg) with Esd's Given in Parentheses[a]

(a) Copper Environment			
Cu–OW	1.924 (2)	Cu–N	1.997 (3)
Cu–O(13)	1.963 (3)	Cu–O(5)	2.488 (3)
Cu–O(23)	1.972 (3)	Cu–O(14^{i})	2.494 (3)
OW–Cu–O(13)	97.3 (1)	O(13)–Cu–O(5)	84.5 (1)
OW–Cu–O(23)	93.7 (1)	O(13)–Cu–O(14^{i})	87.5 (1)
OW–Cu–N	176.6 (1)	O(23)–Cu–O(5)	102.2 (1)
O(13)–Cu–O(23)	167.5 (1)	O(23)–Cu–O(14^{i})	86.7 (1)
O(13)–Cu–N	85.3 (1)	N–Cu–O(5)	91.2 (1)
O(23)–Cu–N	84.0 (1)	N–Cu–O(14^{i})	93.5 (1)
OW–Cu–O(5)	86.8 (1)	O(5)–Cu–O(14^{i})	170.4 (1)
OW–Cu–O(14^{i})	88.8 (1)		
(b) Ligand HNPDA^{2-}			
N–C(1)	1.503 (5)	C(11)–C(12)	1.530 (5)
N–C(11)	1.486 (5)	C(12)–O(13)	1.273 (4)
N–C(21)	1.483 (5)	C(12)–O(14)	1.237 (5)
C(1)–C(2)	1.517 (5)	C(21)–C(22)	1.516 (5)
C(2)–C(3)	1.508 (5)	C(22)–O(23)	1.271 (5)
C(3)–O(4)	1.309 (5)	C(22)–O(24)	1.246 (5)
C(3)–O(5)	1.209 (5)		
Cu–N–C(1)	110.3 (2)	C(11)–C(12)–O(13)	117.3 (3)
Cu–N–C(11)	106.2 (2)	C(11)–C(12)–O(14)	118.8 (3)
Cu–N–C(21)	103.7 (2)	O(13)–C(12)–O(14)	123.9 (4)
C(1)–N–C(11)	113.6 (3)	N–C(21)–C(22)	109.8 (3)
C(1)–N–C(21)	109.4 (3)	C(21)–C(22)–O(23)	118.1 (3)
C(11)–N–C(21)	113.1 (3)	C(21)–C(22)–O(24)	117.3 (3)
N–C(1)–C(2)	113.9 (3)	O(23)–C(22)–O(24)	124.4 (4)
C(1)–C(2)–C(3)	115.0 (3)	Cu–O(13)–C(12)	113.6 (2)
C(2)–C(3)–O(4)	116.6 (3)	Cu–O(5)–C(3)	104.5 (2)
C(2)–C(3)–O(5)	122.6 (4)	Cu–O(14^{i})–C(12^{i})	148.6 (3)
O(4)–C(3)–O(5)	120.8 (4)	Cu–O(23)–C(22)	110.9 (3)
N–C(11)–C(12)	109.6 (3)		

(c) Hydrogen Bonds

	dist	angles
OW–HA(OW)···O(14^{ii})	2.693 (4)	159
OW–HB(OW)···O(24^{iii})	2.722 (4)	173
O(4)–H(O4)···O(24^{iv})	2.607 (4)	169

[a] Symmetry code: (i) $1 - x, {}^1/_2 + y, {}^1/_2 - z$; (ii) $x, {}^1/_2 - y, {}^1/_2 + z$; (iii) $x, {}^3/_2 - y, {}^1/_2 + z$; (iv) $x, -1 + y, z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $x, {}^1/_2 - y, -{}^1/_2 + z$; (vii) $2 - x, 1 - y, 1 - z$; (viii) $2 - x, -y, 1 - z$.

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carboxylates having glycinate chelate rings, with both donor atoms placed in equatorial coordination sites.[5,9,31,32] On the other hand, the Cu–OW bond is the shortest one in this new complex. The strength of this Cu(II)–OH_2 linkage is noteworthy. Comparable, although longer, Cu–OW bonds (1.956 (7) Å) are found in the complex $\{[Cu_2L(H_2O)_2]\cdot 4H_2O\}_n$ of the ligand L^{4-} = *N,N,N′,N′*-tetrakis(carboxymethyl)cystamine(4–) ion.[32] Also, in the related complex aqua(ethylenediaminetetraacetic acidato(2–))-copper(II), $[Cu(H_2EDTA)(H_2O)]$, there is a longer Cu(II)–OH_2 bond (1.978 (3) Å).[5] The two trans-axial bonds Cu–O(5) and Cu–O(14^i) are similar to but much longer than the other four quasi-in-plane coordination bonds to the equatorial donor atoms. The Cu–O(5) bond, due to the apical un-ionized carboxyl group coordination of the β-aminopropionic acid moiety of the ligand, has a length similar to that of the apical Cu–O bonds of the homologous aminoacetic acid–copper(II) chelate ring in the related compounds $[Cu(H_2EDTA)(H_2O)]$[5] (2.467 (2) Å) and $[Cu(H_3DTPA)](H_2O)$[31] (2.518 (2) Å), where H_5DTPA is diethylenetriaminepentaacetic acid. That is also of interest, keeping in mind the remarkable difference between the conformations of these chelate rings (see below). The distances of the atoms O(5) and O(14^i) from the square mean plane P(1) are 2.494 (3) and 2.454 (3) Å, respectively, and the angles between the normal to P(1) and the directions of Cu–O(5) and Cu–O(14^i) are 9.18 and 2.08°, respectively. Thus, although very strong, the octahedral distortion of the coordination polyhedron of Cu(II) approaches D_{4h} symmetry.

Chelate Rings and Ligand Conformation. The ligand $HNPDA^{2-}$ chelates one copper(II) ion as a tetradentate complexing agent and supplies the O(14) atom to form an additional long coordination bond with a second Cu(II) ion. The chelation of the former Cu(II) ion takes place by means of two five-membered glycinate–copper(II) rings (both slightly distorted) and by formation of a singular six-membered aminopropionic acid–Cu(II) chelate ring, which is puckered in a boat-type conformation. In this chelate ring, the Cu, N, C(2), and C(3) atoms define the mean plane P(2) with a maximum deviation for these atoms lower than 0.05 Å, the atoms C(1) and O(5) lying on the same side and at a considerable distance of this plane. Such a boat-type conformation does not differ very much from those in bis(β-alaninato) complexes of Co(II), Ni(II), and Cu(II) and in bis(D,L-β-aminobutyrato)copper(II) dihydrate,[33] but we know of no structural data of other complexes with a β-aminopropionic acid–metal chelate ring. In the complex studied, the angle N–Cu–O(5) conforms with the 91 ± 1° of the angles N–M–O in β-alaninate–metal and related six-membered amino carboxylate–metal chelate rings.[33]

The internal geometry of the $HNPDA^{2-}$ ligand correlates well with the literature concerning the lengths of the C–C and C–O bonds. In particular, the distance C(3)–O(5), the shortest example of this type of bond in the molecule, corresponds well to the value for the CO double bond of a carboxyl group while the longest distance C(3)–O(4) corresponds to that of the single bond with a hydrogen bonded to the oxygen. Among the CO lengths of the carboxylate groups (which have a partial double-bond character), the values of C(12)–O(13) and C(22)–O(23) correspond to weaker bonds correlating with the relatively strong Cu–O interactions. The conformation of the $HNPDA^{2-}$ ligand may be described by the endocyclic torsion angles and, in particular, those around the C–N bond in each of the three arms; these angles are 68.8 (3), –29.5 (4), and 33.7 (4)°, respectively. For C(2)–C(1)–N–Cu, C(12)–C(11)–N–Cu, and C(22)–C(21)–N–Cu, the values are related to different environments, according to the associated functional group: 2-carboxyethyl or ionized carboxymethyl. These last two values can be compared with those found for the sodium nitrilotriacetate–copper(II) hydrate compound,[9] for which the homologous torsion angles were 39.0, 45.8, and 12.9°, respectively. Furthermore, the dihedral angles formed by each COO group with the C(1)C(2)C(3), NC(11)C(12), and NC(21)C(22) planes have the values 15.6 (4), 154.9 (3), and 164.9 (4)°, respectively. They characterize, in the same manner, the conformation of the NTA ligand in the complex $NaCuNTA\cdot H_2O$: –30.9, 24.3, and 16.7°.

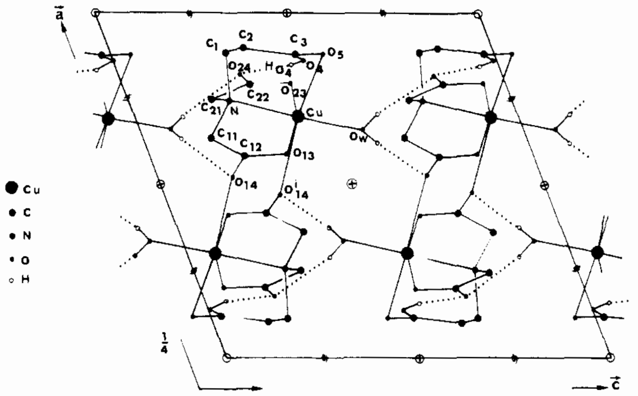

Figure 2. Projection of the crystal structure along the $\vec{b}$ axis. The hydrogen bonds are indicated by dashed lines.

The $HNPDA^{2-}$ ion acts with Cu(II) as a multidentate ligand in which the nitrogen atom constitutes one of the anchorage sites. Thus, it does not act as a zwitterion; the acidic hydrogen atom remains bonded to the 2-carboxyethyl group (see Solution Properties), thus leaving the electron pair of the nitrogen available. On the other hand, the zwitterion form has been described in the acid calcium nitrilotriacetate, $Ca(HNTA)\cdot 2H_2O$.[8]

Crystal Packing. Figure 2 shows that each ligand $HNPDA^{2-}$ is coordinated to two copper(II) ions, which are themselves bonded to two different ligands $HNPDA^{2-}$, thus forming infinite polynuclear zigzag chains of the complex. In the crystal, two homologous chains are related by the glide plane *c* and remain almost parallel to the plane ($\bar{1}02$). Every one of these zigzag chains is reinforced by intrachain hydrogen bonds O(4)–H(O4)···O(24^{iv}) (2.607 (4) Å, 169°), linking two alternate complex entities, each related by a translation parallel to the [010] axis. In addition, the coordination water molecules make up the two interchain hydrogen bonds OW–HA(OW···O(14^{ii}) (2.693 (4) Å, 159°) and OW–HB(OW)···O(24^{iii}) (2.722 (4) Å, 173°), thus linking the referred water molecule with oxygen atoms of two alternate $HNPDA^{2-}$ ligands belonging to homologous chains. This arrangement leads to the formation of tunnels of irregular hexagonal cross section about the centers of symmetry ($^1/_2$, 0, 0) and ($^1/_2$, 0, $^1/_2$), which run parallel to the [010] axis.

We can observe that the different infinite polymeric layers parallel to the plane (100) are linked only by weak van der Waals forces.

Other intermolecular contacts (of which the shortest, O(23)–O(14^i), has the value 3.088 (4) Å) contribute equally to the stability of the crystalline form.

The existence of tunnels formed by the very special arrangement of different helix chains permits us to consider an insertion of molecules possessing little volume, compatible with the size of these canals.

Properties of the Complex $[Cu(HNPDA)(H_2O)]$. Solution Properties. The potentiometric and conductometric titrations of dilute aqueous solutions of $[Cu(HNPDA)(H_2O)]$ (ca. 4 × 10^{-4} M) against KOH (0.1 M) show two independent steps, each involving 1 equiv of base/mol of complex. First, an acid (carboxyl) group (with pK_a = 2.85 ± 0.05 at 298 K) is neutralized, after which, in alkaline medium, a hydroxo complex could be formed. Both processes can be correlated in part with the structure of the studied complex in the solid state and with the most probable structure of its related species in the solution state. This latter structure can be inferred by keeping in mind the following aspects. (1) Both the solid compound and its aqueous solutions have the same color and similar electronic spectra, and thus, we would expect a tetragonally elongated octahedral coordination around

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the copper(II) ion in the $[CuNO_5]$ chromophore of the acid complex in solution. (2) It is reasonable to assume that the apical site of the $O(14^{i})$ atom in the solid $[Cu(HNPDA)(H_2O)]$ would be replaced by the oxygen atom of a water molecule in the related species. (3) The pK_a value of this solution complex species is higher than the pk_1 constant for the dissociation of an acetic arm from glycine hydrochloride (2.36)[34] and iminodiacetic acid (2.54)[11] but lower than pk_1 for the dissociation of a propionic arm from β-alanine hydrochloride (3.55)[34] or iminopropionic and iminodipropionic acids (3.61 and 4.11, respectively),[11] and also it lies between the pK_1 (2.00–2.24) and pK_2 (3.60–3.96) values corresponding to one acetic arm and the propionic arm of free ((2-carboxyethyl)imino)diacetic acid.[10,11,13,19] All these data strongly suggest that the studied complex dissociates the hydrogen ion from its propionic arm,[11] which would be weakly coordinated to the copper(II) ion. The above insights allow us to write the first titration step as

$$[Cu(HNPDA)(H_2O)_2] + OH^- \rightleftarrows [Cu(NPDA)(H_2O)_2]^- + H_2O$$

Thus, the propionic acid arm rather than an acetate arm of the $HNPDA^{2-}$ ligand remains the protonated group because the propionate arm has higher basicity than the acetate arm in this ligand and other analogous amino carboxylate ligands.[11,19,35] In addition, it is well-known that the five-membered glycinate copper(II) chelate rings are more stable than its homologous six-membered β-aminopropionate chelate rings in solution complexes.[11,17,35] Then, the most probable structure of $[Cu(HNPDA)(H_2O)_2]$ in the solution state agrees reasonably well with the crystal structure of $[Cu(HNPDA)(H_2O)]$ (the most striking difference being the occupation of an apical site of the copper(II) coordination by an additional water molecule in the solution species and by the $O(14^{i})$ atom in the solid compound).

Thermal Stability. TG and DTA diagrams of $[Cu(HNPDA)(H_2O)]$ first show the loss of a water molecule at 438–483 K, as expected for its coordination to the copper(II) ion (Figure 3, supplementary material). This step is followed by two other ones corresponding to the decarboxylation and pyrolysis of the organic ligand, perhaps to give a basic nitrate of copper(II).

IR Spectrum. The IR spectrum of $[Cu(HNPDA)(H_2O)]$ (Figure 4, supplementary material) shows a well-defined $\nu(C{=}O)$ band of the –COOH group at 1718 cm^{-1}, in spite of the intrachain hydrogen bond formation, as referred to above. This band appears at 1700 cm^{-1} in the related complex $[Ni(HNPDA)(H_2O)]\cdot 3H_2O$.[36] The deformation mode of H_2O and the antisymmetric stretching modes of bidentate-bridged and monodentate carboxylato groups (at 1625, 1600, and 1595 cm^{-1}, respectively) as well as the symmetric modes of the bidentate and monodentate carboxylate groups (1400 and 1380 cm^{-1}) appear unresolved in the spectrum.

Reflectance Spectra. In the near-infrared region (Figure 5a, supplementary material) we can detect narrow bands of weak intensity. These bands are harmonics and combination bands of fundamental vibrations observable in classic infrared spectra. In these regions, the assignation of bands is delicate and gives little supplementary information on the structure of the compound. However, the vis–UV spectrum (Figure 5b, supplementary material) allows us to confirm the absence of binuclear species. In principle, the binuclear copper(II) complexes[37] show a characteristic band at about 28 000 cm^{-1}, a band we did not observe. The spectrum displays only an asymmetric band, easily visible at 13 690 cm^{-1}. This agrees with the hypothesis of a complex with a distorted octahedral structure as confirmed by the X-ray structure analysis. From 30 000 cm^{-1} onward, a charge-transfer band, probably due to an electron transfer of the ligand toward the transition-metal ion, can be observed.

Electron Spin Resonance (Figure 6, Supplementary Material). X-Band spectra have been obtained for a powdered sample at room and low temperature. The lowering of the temperature to 77 K results in a slight increase of the apparent line width. The slightly asymmetrical line indicates that copper(II) ions are at least in axial symmetry. No hyperfine structure can be seen, hence indicating the presence of interactions between the copper(II) ions. However, we have not observed any supplementary line in the low- or high-field part of the spectrum that would indicate the presence of a copper dimer species. Practically, axial spectra with $g_{\parallel}$ (2.22) > $g_{\perp}$ (2.06) are consistent with an elongated octahedral configuration, in good agreement with the typical g factors given by Hathaway.[38]

Magnetic Data. The paramagnetism of $[Cu(HNPDA)(H_2O)]$ follows the Curie law (115–300 K) with a Curie constant of $C = 0.50$ K emu mol^{-1}, and the temperature-independent magnetic moment for copper(II) ion is $\mu = 2.02\ \mu_B$ (Figure 7, supplementary material). These data represent the usual behavior for a mononuclear and distorted octahedral copper(II) complex with ionic or weakly covalent metal–ligand bonds.

Conclusion

The crystallographic study of the complex $[Cu(HNPDA)(H_2O)]$ shows the existence of a β-aminopropionic acid–copper(II) six-membered chelate ring with boat-type conformation. The 2-carboxyethyl group of the ligand $HNPDA^{2-}$ forms this chelate ring with a conformation similar to those in bis(β-alaninate) complexes of Co(II), Ni(II), and Cu(II). The un-ionized carboxyl coordination takes place through the linkage of the unbonded to proton oxygen atom at the apical site of the elongated octahedral coordination polyhedron of the copper(II) ion. This structural feature also applies to the carboxymethyl–copper(II) coordination in the related compounds $[Cu^{II}(H_2EDTA)(H_2O)]$[5] and $[Cu(H_3DTPA)]\cdot H_2O$.[31]

Supplementary Material Available: Tables SI–SVI, giving anisotropic thermal parameters, hydrogen parameters, least-squares mean plane equations and dihedral angles, torsion angles, and van der Waals distances less than 3.60 Å, respectively, and Figures 3–7, giving TG and DTA diagrams, the IR spectrum, reflectance spectra (near-IR spectrum and vis–UV spectrum), ESR spectra, and inverse molar susceptibilities vs. temperature, respectively (11 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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