Synthesis, Structure and Properties of Poly-[(N-(2-Hydroxyethyl)-N'-carboxymethyl-1,2-ethylenediamine-N, N'-Diacetato)copper(II) Hydrate], \{[Cu(Hhedta)] \cdot H_2O\}_n

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Copper(II) Chelate, Crystal Structure, Amino-polycarboxylates, Ethanolamine

The stoichiometric reaction of \(N\)-(2-hydroxyethyl)-1,2-ethylenediamine-\(N, N'\)-triaceitic acid [H₃hedt = (HOC₂H₂CH₂)₁₂HC₃H₂N(CH₂CO₂H)₂] and copper(II) hydroxy-carbonate in water yields crystalline samples of poly-[(N-(2-hydroxyethyl)-N'-carboxymethyl-1,2-ethylenediamine-N,N'-diacetato)copper(II) hydrate], \{[Cu(Hhedta)] \cdot H_2O\}_n (I). The compound was studied by TG analysis (with FT-IR study of the evolved gases), IR, electronic and ESR spectra, magnetic susceptibility data and single crystal X-ray diffraction methods. It crystallises in the orthorhombic system, space group Fdd2 (\(a = 21.906(2)\), \(b = 36.602(4)\), \(c = 6.928(1)\) Å, \(Z = 16\), and final \(R_1 = 0.029\) for 1554 independent reflections). The Cu(II) atom exhibits a \(N, N', O, O'\)-pentadentate chelating role as well as a \(O, O'\)-carboxylate bridging one and has a free \(N'\)-carboxymethyl arm. The bridging carboxylate group of the Hhedta ligand leads to polymeric chains \{[Cu(Hhedta)] \cdot H_2O\}_n parallel the \(c\) axis. A hydrogen bonding network involves all \(O-H\) polar bonds (non-ionised carboxylic and alcoholic hydroxyl groups and water molecules). The structure reveals the preferred formation of a copper(II)-(\(N\)-2-hydroxyethylamino) or copper(II)-(ethanolamino) versus a copper(II)-(\(N\)-carboxymethylamino) chelate ring.

Introduction

Studies of amino-polycarboxylate metal chelates offer the possibility of obtaining complexes with partially protonated forms of the ligands. In such ‘acid’ compounds the non-ionised group(s) of the ligand can take part in the chelation or can remain non-coordinated. Even both possibilities can arise in a given compound. Structural reports have shown a tendency of the metal ion to allow remarkable distortions in its coordination polyhedra [1, 2]. This coordinative flexibility offers discrimination possibilities for different donors involved in a given copper(II) complex. For example, in the crystal structure of aqua\{[N,N'-bis(carboxymethyl)-1,2-ethylenediamino-N,N'-diacetato]copper(II) [Cu(H₂edta)(H₂O)]\}, reported by Stephens in 1969 [3], the diprotonated form (H₂edta(2-) ion) is pentadentate and the aqua ligand completes the distorted octahedral coordination of the metal, having a free \(N\)-carboxymethyl-amino arm on the ligand. Both metal-glycinate rings are of R type (that is nearly perpendicular to the plane CuNN) whereas the metal-aminoacetic ring is of G type (nearly coplanar to this plane). The details of this and all other structural reports of compounds having copper(II)-amino-acetic and closely related chelate rings [3 - 25] always show the formation of a rather long Cu-O(carboxylic) bond, of 2.29 - 2.52(1) Å. Nevertheless, it is generally assumed that the ionized carboxylate group is a better metal-binding group than the non-ionised carboxylic one.

Pertinent studies may afford new and concluding insights about the conformational flexibility of polydentate ligands and/or concerning to metal-coordinating preferences of specific donor groups which
are frequently present in biological molecules. There is structural evidence that the N-2-hydroxyethyl-iminodiacetate(2-) ion (heida) [26 - 44] and the N,N-bis(hydroxyethyl)glycinate(1-) ion (bicinc) [45 - 53] display such conformational flexibility in their metal chelates, which seems enhanced in distorted environments of their copper(II) complexes [35 - 37, 48 - 53]. In copper(II)-bicinc complexes [48 - 53] O-hydroxyl donors are among the four closest donors and/or at an apical/distant coordination position. However, whether the O-hydroxyl donor is stronger than the O-carboxyl donor of a non-ionised carboxylic group or not seems to remain unclear. In order to answer this question we have synthesised and studied an ‘acid’ copper(II) complex of the divalent anion [H2hedta(2-)] of N-(2-hydroxyethyl)-1,2-ethylenediamine-N,N,N′-triacetic acid (H2hedta). The structure of this aminopolycarboxylic acid [54] and those of several chelates with trivalent (Fe, Co, La, Ce, Er) [55 - 60] and tetravalent (as VO2+) [61] metal ions have been reported. Surprisingly no structural evidence concerning the complexes having a metal in an oxidation state lower than three seems to be available.

**Experimental**

All chemicals were commercially available products of reagent grade and used without further purification.

**Synthesis of title compound I**

\[
\left[\text{Cu(Heida)}\right]_n \cdot \text{H}_2\text{O} \quad (I)
\]

was obtained by reaction of H2hedta (1000 mg, 3.59 mmol, Sigma) and Cu2CO3-(OH)2 (397 mg, 1.80 mmol, Merck) in water (100 ml) in a Kitasato flask, with heating (t < 50 °C) and stirring under reduced pressure (to remove the CO2 by-product). The resulting blue solution was stirred and heated at 60°C for 30 min. Then it was left to cool to r.t. and slowly filtered to remove a very small amount of CuO. By slow evaporation (3 - 4 weeks) of the clear solution at r.t., well-shaped crystals of the product appeared. The crystals were collected by filtration, washed with cold water and air-dried. The blue compound is stable at r.t. without apparent water loss. It can be re-crystallised at r.t. from its solution in hot water (60°C). Yield: ≥ 85%. C10H14CuNa2O5: Calcd H 5.07, C 33.57, N 7.83%. Found H 5.25, C 33.48, N, 7.91%. Calcd Cu 17.76%. Found Cu 17.54% (EDTA complexometry [62]).

**Crystal structure determination**

A blue prismatic crystal of \([\text{Cu(Heida)}] \cdot \text{H}_2\text{O}\)_n was mounted on a glass fibre and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of 15.37 < θ < 24.96° in an Enraf Nonius CAD4-automatic diffractometer [63]. Data were collected at 233(2) K using CuKα radiation (λ = 1.54184 Å) and the ω-scan technique, and corrected for Lorentz and polarization effects [64]. A semi-empirical absorption correction was made (Psi scan) [65]. The structure was solved by direct methods [66] which have revealed the position of all non-hydrogen atoms, and refined on F2 by a full-matrix least-squares procedure using anisotropic displacement parameters [67]. All hydrogen atoms were located from difference maps and included as fixed contributions riding on attached C atoms with isotropic thermal parameters 1.2 times those of the respective C atoms. The H atoms of the water molecule, O(1), and the H atom linked to O(31) were refined isotropically. The absolute configuration was established [68]. Atomic scattering factors were from ‘International Tables for X-ray Crystallography’ [69], molecular graphics prepared with the programs ZORTEP [70] and PLUTON [71]. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

**Physical measurements**

Infrared spectra were obtained by the KBr disc technique on a Beckman IR 4260 spectrophotometer. The TG (pyrolysis) and analysis of evolved gases were recorded (295 - 875 K) in air flow (100 ml/min) using a Shimazu Thermobalance TGA-DTG-50H coupled with an IR-FT Nicolet Magma 550 instrument (and a mass spectrometer Fison Thermolab). The electronic (reflectance) spectrum (175 - 3300 nm) was obtained in a Cary 5E spectrophotometer. The ESR spectrum of a polycrystalline sample was recorded without magnetic dilution in a spectrophotometer Bruker ESP 300E (X band, 9300 MHz) at
Table 1. Crystal data and structure refinement for compound I.

<table>
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<th>Property</th>
<th>Value</th>
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<td>Empirical formula</td>
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<td>Fdd2</td>
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<tr>
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<tr>
<td></td>
<td>b = 36.602(4) Å</td>
</tr>
<tr>
<td></td>
<td>c = 6.928(1) Å</td>
</tr>
<tr>
<td></td>
<td>V = 5554.5(11) Å</td>
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<tr>
<td>Z, Calculated density</td>
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<tr>
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<tr>
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<tr>
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<td>Reflections collected</td>
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<tr>
<td>Compl. to 2θ = 66.96°</td>
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<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices</td>
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<tr>
<td>— [I &gt; 2 sigma (I)]</td>
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<tr>
<td>Largest diff. peak / hole</td>
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</table>

*Supplementary data:* Crystallographic data has been deposited with the CCDC (12 Union Road, Cambridge, CB2 1EZ, UK) and are available on request by quoting the deposition number CCDC-136013 ([Cu(Hhedta)]-H₂O, I).

Results and Discussion

Figure 1 shows a plot of the complex molecule in the asymmetric unit with the labelling of atoms. Selected bond lengths and angles are listed in Table 2. Two amino nitrogen atoms N(11) and N(21), two carboxylate oxygen atoms O(11), O(21) and the hydroxyl atom O(31) of the same Hhedta ligand and the carboxylate O(22) from an adjacent Hhedta, which is symmetry related by the code ii = -x + 1/2, -y, z + 1/2, define an asymmetrically elongated octahedral copper(II) coordination (type 4+1+1) [1, 2]. The main source of distortion arises not only from the unequal coordination bond lengths, but also from differences in the trans-angles O(11)-Cu(1)-O(21) = 177.5(1)°, N(11)-Cu(1)-O(22) = 162.0(1)° and O(31)-Cu(1)-N(21) = 150.8(1)°. Each Hhedta ligand has a free N-carboxymethyl arm. The water
molecule is not bonded to the metal. The donor atoms N(11), O(11), O(21) and O(22) define a square with mean plane P(1), from which copper(II) is displaced by 0.122(1) Å toward O(31). The bond lengths and angles of the coordination polyhedron have normal values in agreement with those reported for closely related compounds [3-10, 35-37, 48-53]. That is particularly true for Cu-O(31, hydroxyl) = 2.357(3) Å which is clearly similar to the corresponding bond in the polymeric compound [{Cu(heida)(H_2O)}_2H_2O]_n (Cu-O(hydroxyl) = 2.35(1) Å [35]. It falls between two Cu(II)-O(hydroxyl) apical bonds reported for the octahedral Cu(II) chelate [{CuBr(bheg)(H_2O)}] (2.29(1) and 2.67(1) Å [51]).

The internal geometry of the Hhedta ligand has normal bond lengths and angles [54-61]. Each ligand chelates a copper(II) atom and acts as a bridge between this and another metal ion Cu(1') throughout the O(22') donor atom (symmetry code i = -x + 1/2, -y, z - 1/2). The bridging carboxylate group -C(22)O(21)O(22') has roughly a \textit{syn-anti} conformation. This bridging leads to the formation of mono-dimensional polymeric chains [Cu(Hhedta)]_n which extend in parallel to the c axis of the crystal (Fig. 2).

The pentadentate chelation of the Hhedta(2-) ligand yields four five-membered rings. One is of the metal-(ethylendiamine) type (Table 3) and has the usual asymmetric skew conformation with different and opposite deviations of the C(1) (0.47(1) Å) and C(2) (-0.19(1) Å) atoms from the plane N(11)Cu(1)O(31) [73]. Two other rings are metal-glycinate like and have a rather planar unsymmetrical envelope conformation (both C atoms lying at the same side of the N-Cu-O plane [73] and a deviation of 0.14(1) Å for C(21) atom). These rings are of the R type, that is they lie nearly perpendicular to the plane Cu(1)N(11)N(21). The Cu-(glycinate) ring involving the shortest Cu(1)-N(11) bond is nearly coplanar with the mean plane P(1) of the four closest donor atoms (angle between mean planes of 63(2)°). In contrast, the Cu-(glycinate) ring containing the longest Cu(1)-N(21) bond is nearly perpendicular to P(1). The remaining Cu(II)-(ethanolamine) chelate ring also has an asymmetric skew conformation [73] with different and opposite deviations of the C(31) (0.46(1) Å) and C(32) (-0.26(1) Å) atoms from the plane N(11)Cu(1)O(31).

The crystal is built up by a hydrogen bonding network where the polar O-H bonds of the [Cu(Hhedta)]_n chains and those of water molecules are involved (Fig. 2). The hydrogen atom of the free carboxyl arm interacts with a neighbouring water molecule (O(41)-H(410)...O(14): 2.65(1) Å, 173(7)°, v = -x, -y, 1z). The water molecule acts twice as donor for the carboxylate atom O(12) of the same asymmetric unit (O(1)-H(102)...O(12), 2.79(1) Å, 171(9)°) and with O(111iiii) of an adjacent Hhedta ligand (O(1)-H(101)...O(111iiii), 2.97(1) Å, 173(8)°, iii = x - 1/4, -y + 1/4, z - 1/4). The alcoholic proton is linked to a carboxylate acceptor of an adjacent complex unit (O(31)-H(310)...O(12iiii), 2.68(1) Å, 164(8)°, iv = x - 1/4, -y + 1/4, z + 1/4).

The TG/DTG analysis of I (5.156 mg, 20 °C/min., in air-flow) reveals its thermal decomposition in three steps. The first one (90 - 205 °C, max. rate of weight loss at 135 °C, expl. weight loss 4.398%, calcd. for H_2O 5.035 %) is mainly due to the dehydration process. The two remaining ones overlap (205 - 550 °C) and they correspond to the pyrolysis of the organic ligand. The composition at the residue at 560 °C is close to the data for CuO (found 22.08%, calcd. 22.23%). The IR spectrum has the bands expected for the Hhedta(2-) ligand and the water molecule [74]. The electronic spectrum shows an unsymmetrical d-d band with \( \nu_{\text{max}} = 12500 \) and a shoulder near 8700 cm\(^{-1}\) in agreement with the elongated octahedral chromophore.
CuN\textsubscript{2}O\textsubscript{4} (or CuNO\textsubscript{3}+N+O). The powder ESR spectrum at room temperature is of axial type with $g_{||} = 2.17 > g_{\perp} = 2.13 > 2.03$ and shows the coupling effect of the nuclear spin of copper ($^{63}$Cu and $^{65}$Cu with $I = 3/2$) on the $g_{||}$ moiety with a coupling constant $A_{||} = 101.3$ gauss. These data are in accordance with a $d_{x^2-y^2}$ Cu(II) ground state and the relatively short metal-metal separation ($Cu(1)-Cu(1') = Cu(1)-Cu(1'') = 5.194(1)$ Å) in the polymeric complex chain. A plot of $\chi$ data versus $T/(K)$ ($T = 80 - 298$ K) is linear ($\chi = (1/C)T - (\theta/C)$) with a statistical $r^2$ factor of 0.9998) according to a Curie-Weiss behaviour, $\chi = C/(T - \theta)$ [72]. The Curie constant is $C = 0.41$ K·emu·mol$^{-1}$ with a Weiss constant of $\theta = 6.07$. The estimated value of $\mu_{\text{eff}}$ for Cu(II) atom is 1.82 BM, in accordance with the structure reported here.

It is worth noting the preference of the Hhedta(2-) ligand to involve the hydroxyl O(31) donor atom in the copper(II) chelation instead of the non-protonated carboxyl O(42) of the free N-carboxymethyl arm. In this connection it seems instructive to make an structural comparison of I and the related complex [Cu(H\textsubscript{2}edta)(H\textsubscript{2}O)] [3]. Both compounds have a similar composition (with formula type Cu(HL)-H\textsubscript{2}O or Cu(H\textsubscript{2}L)-H\textsubscript{2}O respectively), pentadentate chelating ligands and a distorted octahedral copper(II) coordination (type 4+1+1). The compounds differ in the way in which the hexa-coordination is effectively reached. The former gives polymeric chains, the latter one forms complex molecules involving the aqua ligand. However, this difference has no significance in the metal coordination as it becomes evident for its similar bond lengths and angles. Indeed the corresponding bonds [Cu(1)-O(22) 1.955(3) Å in I and Cu-O(aqua) 1.978(2) Å in the H\textsubscript{2}edta derivative] have very similar values. Moreover, the 1,2-ethylene diamino-N,N'-diacetato moieties of the Hhedta and H\textsubscript{2}edta ligands give three similar chelate rings. The Cu-ethanolamino) ring of I has its counterpart in the Cu-(N-carboxymethylamino) ring in the related H\textsubscript{2}edta complex. The structure of I can be regarded as a consequence of replacing the nearly planar and rather rigid Cu-(N-carboxymethylamino) chelate ring in [Cu(H\textsubscript{2}edta)(H\textsubscript{2}O)] [3] by a skewed Cu-(N-2-hydroxyethylamino) ring in [Cu(Hhedta)]-H\textsubscript{2}O. This preference may be related to the opportuni
ties for puckering in the latter. As a consequence, the Cu(1)-O(31, hydroxyl) bond (2.357(3) Å in I is significantly shorter than the ‘corresponding’ Cu-O(9, carboxyl) (2.467(2) Å). Conversely, the Cu(1)-N(21) bond in I (2.433(3) Å) is remarkably longer than the corresponding Cu-N(1) bond (2.291(2) Å) in the H\textsubscript{2}edta derivative [3]. The introduction of N-2-hydroxyethyl-amino arms into amino-polycarboxylate ligands is a source of conformational flexibility as it can also be inferred from the structural consequences for the incoming bidentate N-heterocyclic ligands (bipyridine or phenantroline) to [Cu(heida)(H\textsubscript{2}O)]-H\textsubscript{2}O [36]. In the latter, the ‘Cu(IDA)’ chelate moiety exhibits a mer-conformation (with two G rings) whereas it shows a fac-conformation (with one G and one R ring) in the bipy and phen derivatives, [Cu(heida)(bipy)]·4H\textsubscript{2}O [36] and [Cu(heida)(phen)]·7H\textsubscript{2}O [37]. A significant conformational flexibility can be inferred in some copper(II) complexes of bicine or bheg [48 - 53]. Bicine gives [Cu(bheg)]ClO\textsubscript{4}, H\textsubscript{2}O [53] and compounds of general formula [Cu(bheg)L']·nH\textsubscript{2}O (L’ = Cl, Br or NCS mbox[50 - 52]) having distorted trigonal bipyramidal Cu(II) coordination, as well as [Cu(bheg)Br(H\textsubscript{2}O)] (asymmetrically elongated octahedron, type 4+1+1) [51]. In all these compounds bheg acts as tripodal tetradentate ligand and L’ is linked trans to the Cu-N(bheg) bond. In the five-coordinated compounds (above) the two O(hydroxyl) donors give Cu-O bonds with different lengths, one of 2.00 - 2.05 Å, and the other one of 2.18 - 2.20 Å. The aqua ligand transforming [Cu(bheg)(Br)] into the six-coordinated derivative [Cu(bheg)Br(H\textsubscript{2}O)] does not modify the tetradentate role of bheg but it produces a significant lengthening of the Cu(II)-N(amino) bond (from 2.024(6) to 2.07(1) Å) and both Cu(II)-O(hydroxyl) bonds (from 2.048(6) and 2.194(7) Å to 2.29(1) and 2.67(1) Å) [51].

Acknowledgements

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