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Note

# Hydrothermal Synthesis and Structural Characterization of a Two-Dimensional Polymeric Copper(II) Complex Containing an Unusual Bridged $H_2edta^{2-}$ Ligand

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## Introduction

The coordination chemistry of ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid ($H_4$edta) with first-row transition metal ions has been widely studied and structurally well characterized. The mono- and diprotonated ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate ($Hedta^{3-}$ and $H_2edta^{2-}$) can act either as a pentadentate ligand to form a six-coordinate octahedron or as a hexadentate ligand to form a seven-coordinate distorted monocapped trigonal prism or pentagonal bipyramid, often with a water molecule as a sixth or seventh ligand, respectively. Some examples are six coordination of $[M^{III}(Hedta)(H_2O)]$ (M = Cr,[1] Fe,[2] Co[3]), $\{[Ni^{II}(Hedta)(H_2O)]^-\}$,[4] and $[M^{II}(H_2edta)(H_2O)]$ (M = Ni,[5] Cu[6]), and seven coordination of $[M^{III}(Hedta)(H_2O)]$ (M = Ti, V),[7] $\{[Mn^{II}(Hedta)(H_2O)]^-\}$,[8] and $[Co^{II}(H_2edta)(H_2O)]$.[9] Other related structures containing hexadentate $edta^{4-}$ are $[Fe^{II}(edta)(H_2O)]\cdot 2NaClO_4\cdot 6H_2O$,[10] $Na[Ti^{III}(edta)(H_2O)]\cdot 2H_2O$,[11] $[Ti^{IV}(edta)(H_2O)]$,[12] $K[Ti^{III}(edta)(H_2O)]\cdot 2.5H_2O$,[13] and $NH_4[Co^{III}edta]\cdot 2H_2O$.[14] However, no six-coordinate [M(Hedta)] and $[M(H_2edta)]$ type complexes are known in which these ligands act as a hexadentate ligand. In this work, we examine the hydrothermal synthesis of the first $[M^{II}(H_2edta)]$ type complex with the $H_2edta^{2-}$ bridging ligand coordinating to the copper(II) ions. The synthesis, X-ray single-crystal structure, and magnetic property of $[Cu(edtaH_2)]_n$ complex are reported herein.

## Experimental Section

**Materials and Physical Techniques.** All chemicals were of reagent grade and were used as commercially obtained without further purification. The infrared spectrum was recorded on a Nicolet Fourier transform IR, MAGNA-IR 500 spectrometer in the range 500−4000 cm$^{-1}$ using the KBr disk technique. Magnetic measurement was carried out on polycrystalline samples with a SQUID magnetometer. Molar magnetic susceptibility was recorded every 5 K in the range 5−300 K with 10 000 G external field.

**Preparation of $[Cu(EDTAH_2)]_n$.** A mixture of $CuCl_2\cdot 2H_2O$ (0.341 g, 2 mmol), $H_4$edta (0.2292 g, 1 mmol), 5% $HNO_3$ (2 drops), and $H_2O$ (5 mL) was put into a 23 mL poly(tetrafluoroethylene)-lined stainless steel autoclave container and heated for 24 h at 80 °C under auto generous pressure. After the mixture was cooled to room temperature, violet crystals were collected in 44% yield along with unreacted $H_4$edta. IR (KBr) $\nu$/cm$^{-1}$: 1734 (s), 1605 (vs), 1564 (s), 1388 (s), 1313, 1207, 1174, 1122 (m), 1010, 977, 934, 892, 861, 751, 699, 641, 587 (w). Anal. Calcd: C, 33.95; H, 3.99; N, 7.92. Found: C, 33.68; H, 3.35; N, 7.85.

**X-ray Crystallography.** A violet crystal of approximately 0.20 × 0.15 × 0.10 mm$^3$ was mounted on a glass capillary. Data collection was carried out on a Bruker SMART CCD diffractometer with Mo radiation at room temperature. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 15 frames each, each frame corresponding to a 0.3° scan in 15 s, followed by spot integration and least-squares refinement. Data were measured using an $\omega$ scan of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART[15] software and refined with SAINT on all observed

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**Table 1.** Crystallographic Data and Details of the Structure Determination for $[Cu(H_2Edta)]_n$

| | | | |
|---|---|---|---|
| chemical formula | $C_{10}H_{14}N_2O_8Cu$ | fw | 353.77 |
| cryst syst | orthorhombic | space group | $P2_12_12_1$ |
| $a$ [Å] | 6.9085(2) | temp (K) | 295(2) |
| $b$ [Å] | 11.9893(3) | $\lambda$ (Mo Kα) [Å] | 0.710 73 |
| $c$ [Å] | 15.6103(4) | $\mu$ [mm$^{-1}$] | 1.733 |
| $V$ [Å$^3$] | 1292.97(6) | $R(F_o)^a$ $(I > 2\sigma(I))$ | 0.0360 |
| $\rho_{calc}$ [g/cm$^3$] | 1.817 | $R_w(F_o)^b$ $(I > 2\sigma(I))$ | 0.0869 |
| $Z$ | 4 | GOF | 1.028 |

[a] $R = \sum||F_o|^2 - |F_c|^2|/\sum|F_o|^2$. [b] $R_w = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$.

**Table 2.** Selected Bond Lengths (Å) and Bond Angles (deg) of $[Cu(H_2edta)]_n$

| | | | |
|---|---|---|---|
| Cu(1)−O(1) | 1.943(2) | Cu(1)−O(5) | 1.952(2) |
| Cu(1)−O(6) | 1.985(2) | Cu(1)−N(1) | 2.106(2) |
| Cu(1)−N(2) | 2.400(2) | Cu(1)−O(3) | 2.459(2) |
| O(1)−C(4) | 1.277(3) | O(2)−C(4) | 1.234(4) |
| O(3)−C(6) | 1.210(4) | O(4)−C(6) | 1.318(3) |
| O(5)−C(8) | 1.259(3) | O(6)−C(8)#[a] | 1.257(3) |
| O(7)−C(10) | 1.326(4) | O(8)−C(10) | 1.193(4) |
| N(1)−C(1) | 1.498(3) | N(2)−C(2) | 1.485(3) |
| N(1)−C(3) | 1.485(4) | N(2)−C(7) | 1.464(4) |
| N(1)−C(5) | 1.480(4) | N(2)−C(9) | 1.466(4) |
| | | | |
| O(1)−Cu(1)−O(5) | 176.18(8) | O(1)−Cu(1)−O(6) | 86.72(9) |
| O(5)−Cu(1)−O(6) | 97.00(8) | O(1)−Cu(1)−N(1) | 84.80(8) |
| O(5)−Cu(1)−N(1) | 91.38(9) | O(6)−Cu(1)−N(1) | 164.20(9) |
| O(1)−Cu(1)−N(2) | 99.67(8) | O(5)−Cu(1)−N(2) | 79.63(8) |
| O(6)−Cu(1)−N(2) | 113.46(8) | N(1)−Cu(1)−N(2) | 81.16(8) |
| O(1)−Cu(1)−O(3) | 91.56(8) | O(5)−Cu(1)−O(3) | 87.42(8) |
| O(6)−Cu(1)−O(3) | 93.30(8) | N(1)−Cu(1)−O(3) | 73.67(8) |
| N(2)−Cu(1)−O(3) | 151.36(8) | | |

[a] Symmetry transformation (#): $x - 1/2, -y + 1/2, -z + 2$.

reflections. Data reduction was performed with the SAINT[16] software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[17] The structures were solved by direct methods with the SHELX-93[18] program and refined by full-matrix least-squares methods on $F^2$ with SHEXLTL-PC V 5.03.[18] All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms of the acetate group were located in difference Fourier maps and refined isotropically, and other hydrogen atoms were placed in their geometrically generated positions. Detailed data collection and refinement of the complex are summarized in Table 1, and selected bond distances and angles are listed in Table 2. Other crystallographic data are given as Supporting Information.

## Results and Discussion

**Synthesis.** The $[Cu(H_2edta)]_n$ compound can be obtained using only the hydrothermal method, where the acidic aqua solution of $CuCl_2{\cdot}2H_2O$ and $H_4$edta were put into the stainless steel autoclave container and heated for 24 h at 80 °C under auto generous pressure. The compound was identified by infrared spectra and elemental analysis, and its structure was determined by single-crystal X-ray diffraction.

**Structural Description.** Figure 1a shows a perspective drawing of $[Cu(H_2edta)]_n$ and the labeling of the atoms. Selected bond distances and angles are given in Table 2. The molecular structure of $[Cu(H_2edta)]_n$ is similar to the corresponding six-coordinated edta-related complexes of $[M^{III}(Hedta)(H_2O)]$ (M = Cr,[1] Fe,[2] Co[3]), $\{[Ni^{II}(Hedta)(H_2O)]^-\}$,[4] and $[M^{II}(H_2edta)(H_2O)]$ (M = Ni,[5] Cu[6]), but the sixth water coordinated site is replaced by the oxygen atom of the nonprotonated acetate group in the neighboring complex to form a polymeric helical chain. A clear view is shown in Figure 1b. This is the first structure in which a helically polymeric chain is constructed by the bridging $H_2edta^{2-}$ ligand. The nearest Cu···Cu distance is 5.221(2) Å which is shorter than 5.517, 5.581, and 5.578 Å of Ni···Ni, Co···Co, and Zn···Zn distances, respectively, found in the series of $[MM'(edta)(H_2O)_4]{\cdot}2H_2O$ complexes (M, M′ = Ni, Co, Zn).[19−21] The environment about the copper atom involves a tetragonally distorted octahedral geometry with four coplanar bonds of nearly equivalent length (Cu(1)−N(1) 2.106(2), Cu(1)−O(1) 1.943(2), Cu(1)−O(5) 1.952(2), Cu(1)−O(6) 1.985(2) Å) and two longer tetragonal bonds (Cu(1)−N(2) 2.400(2), Cu(1)−O(3) 2.459(2) Å). Comparable bond distances found in the tetragonally distorted octahedral compounds, $[Cu(H_2edta)(H_2O)]$[6] and Ag[Cu(Hedta)(H$_2$O)]·H$_2$O,[22] are as follows: Cu−N 2.066(2), 2.291(2); Cu−O 1.970(2), 1.929(2), and 2.467(2); and Cu−O(water) 1.978(3) Å for $[Cu(H_2edta)(H_2O)]$, and Cu−N 2.073(4), 2.344(5); Cu−O 1.933(4), 1.942(4), and 2.528(4);

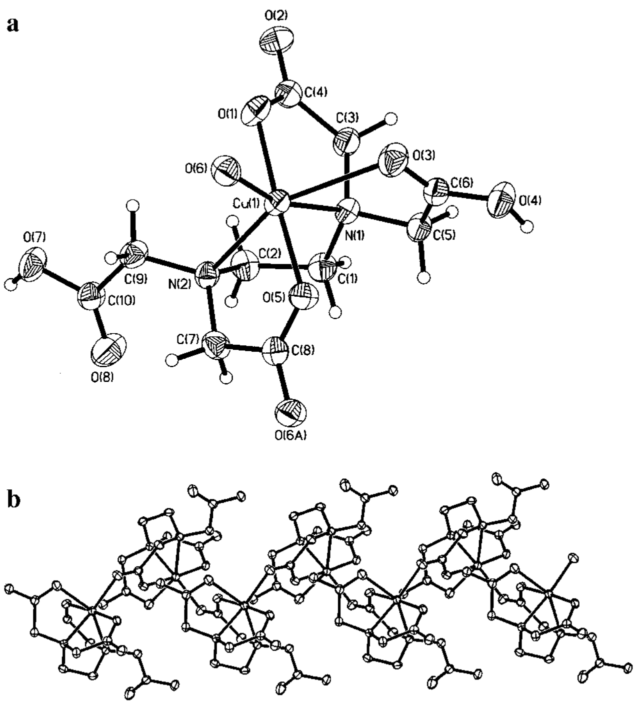

**Figure 1.** (a) Molecular structure of $[Cu(H_2edta)]_n$. (b) Helical polymeric chain of $[Cu(H_2edta)]_n$. Ellipsoids are drawn at the 50% probability level.

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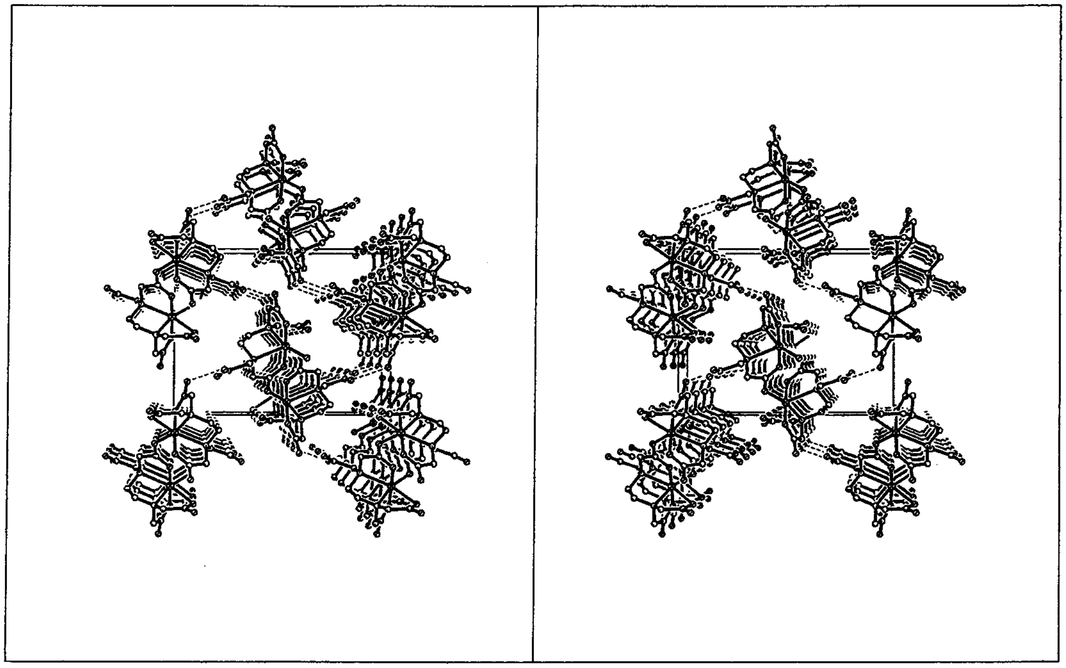

**Figure 2.** Packing pictures viewing along *a* axes of $[Cu(H_2edta)]_n$. Dash lines indicate the interchain hydrogen bonds.

and Cu−O(water) 1.994(4) Å for $Ag[Cu(Hedta)(H_2O)]\cdot H_2O$. The $H_2edta^{2-}$ ligand acts as a hexadentate bridging ligand in which two nitrogen donors (N(1), N(2)), two oxygens of two acetate groups (O(1), O(5)), and one acetatic group O(3) coordinate to one copper(II) ion and the sixth acetate oxygen atom O(6) coordinates to the other copper(II) ion. The hydrogens for acetic acid groups were located in the difference map. These positions are supported by the C−O bond lengths in the acetate groups.[23] The protonated C(6)−O(4) and C(10)−O(7) bond lengths of 1.318(4) and 1.326(4) Å are obviously longer than other acetate C−O bond lengths of an average value of 1.238 Å. The C(6)−O(3) distance of 1.210(4) Å with the long Cu(1)−O(3) distance (2.459(2) Å) is also shorter than the other three coordinated C−O bond distances (C(4)−O(1) 1.277(3), C(8)−O(5) 1.259(3), and C(8)−O(6) 1.257(3) Å). Other C−N (av 1.479 Å) and C−C (av 1.520 Å) bond lengths in $H_2edta^{2-}$ ligand are normal and consistent with other M−edta related complexes, like 1.478 and 1.518 Å in $[Cu(H_2edta)(H_2O)]$[6] and 1.476 and 1.516 Å in $Ag[Cu(Hedta)(H_2O)]\cdot H_2O$.[22]

**Ring Strain.** The $H_2edta^{2-}$ ligand forms four chelate rings with the Cu atom involving three glycinate and one ethylenediamine rings. The strain of the chelate rings could be measured by the sums of the angles of the five-membered chelate rings, as has been proposed by Hoard et al.[22] The idealized angle sums are 527.9° and 538.9° for the ethylenediamine and glycinate backbone, respectively. The sums of the angles of the five-membered chelate rings for some six-coordinate M−edta complexes are given in Table 3. The angle sums of E ring (Cu(1)−N(1)−C(1)−C(2)−N(2)) obtained from $[Cu(H_2edta)]_n$ are 513.7(2)°. This result reveals that the E ring exhibits a "strain" similar to that of other metal−edta complexes listed in Table 3. The sums of the R rings for Cu(1)−O(1)−C(4)−C(3)−N(1) chelation, 538.6(3)°, and Cu(1)−O(5)−C(8)−C(7)−N(2) chelation, 538.5(3)°, are not significantly different from that of 540.0° for a pentagon, but the sum of G ring for Cu(1)−O(3)−C(6)−C(5)−N(1) chelation, 525.1(2)°, deviates quite markedly. These sum values are also comparable with those of some six-coordinate M−edta complexes (Table 3).

**Table 3.** Comparisons of Ring Bond Angle Sums (deg) for Some Six-Coordinate Metal−edta Complexes

| compound | E ring | R ring | G ring | ref |
|---|---|---|---|---|
| $NH_4[Co^{III}edta]\cdot 2H_2O$ | 520.9 | 537.8 | 523.5 | 14 |
| $[Cr^{III}(Hedta)(H_2O)]$ | 521.6 | 536.2, 539.5 | 524.3 | 1 |
| $[Fe^{III}(Hedta)(H_2O)]$ | 513.7 | 539.7, 535.0 | 526.4 | 2 |
| $[Co^{III}(Hedta)(H_2O)]$ | 517.2 | 537.8 | 523.5 | 3 |
| $[Ni^{II}(H_2edta)(H_2O)]$ | 514.5 | 538.4 | 524.9 | 5 |
| $[Cu^{II}(H_2edta)(H_2O)]$ | 513.9 | 538.9, 539.5 | 527.0 | 6 |
| $[Cu^{II}(H_2edta)]_n$ | 513.7 | 538.6, 538.5 | 525.1 | this work |

**Hydrogen Bonding.** There are two intermolecular hydrogen bonds existing between the $[Cu(H_2edta)]_n$ polymeric chains. The protonated carboxylic group O(4)−H(4) forms an intrachain hydrogen bond with the coordinated oxygen, O(1), and the other protonated acetic group, O(7)−H(7), forms an interchain hydrogen bond with the uncoordinated oxygen, O(2). The O···O distances of intrachain O(4)···O(1) and interchain O(7)···O(2) are 2.696(3) and 2.674(4) Å, with the O(4)−H(4)···O(1) and O(7)−H(7)···O(2) angles 165.2(8)° and 168.4(8)°, respectively. The packing diagram of $[Cu(H_2edta)]_n$, illustrated in Figure 2, shows the interaction (dashed line) of hydrogen bonds between the $[Cu(H_2edta)]_n$ chains.

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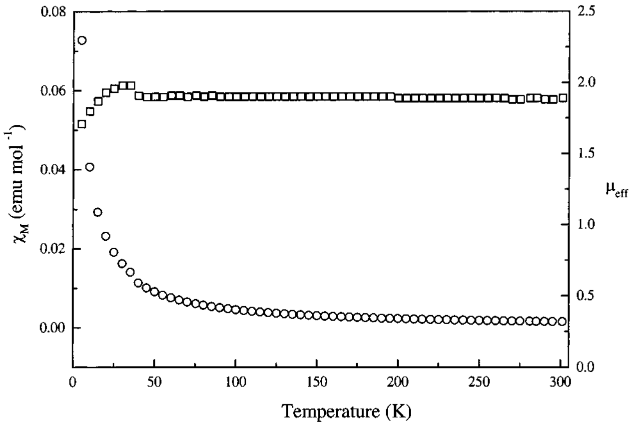

**Figure 3.** Magnetic data of [Cu($H_2$edta)]$_n$. Legend: ○, indicates the molar magnetic susceptibility, $\chi_M$, and □, the effective magnetic moment, $\mu_{eff}$.

**Magnetic Susceptibility.** The experimental curves of the molar magnetic susceptibility $\chi_M$ (○) and effective magnetic moment ($\mu_{eff}$) (□) with respect to temperature ($T$) for [Cu($H_2$edta)]$_n$ is displayed in Figure 3. The temperature dependence basically follows the Curie−Weiss law, and very weak antiferromagnetic interaction has been observed below 25 K.

## Conclusion

In summary, we have synthesized a new Cu(II) coordination network based on the $H_2$edta$^{2-}$ bridging ligand to form a helically polymeric chain. The structural characterization and ring strain of [Cu($H_2$edta)]$_n$ complex has been completely described and compared with other related metal−edta complexes. The magnetic property has been satisfactorily explained.

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**Supporting Information Available:** X-ray crystallographic files for the compound in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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