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Synthetic, Crystallographic, and Computational Study of Copper(II) Complexes of Ethylenediaminetetracarboxylate Ligands

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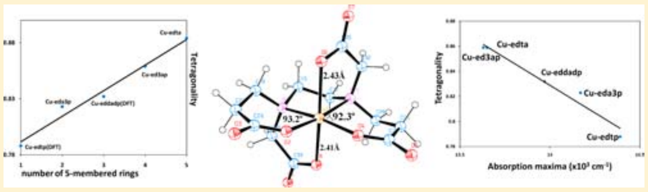
S *Supporting Information*



ABSTRACT: Copper(II) complexes of hexadentate ethylenediaminetetracarboxylic acid type ligands H_4eda3p and H_4eddadp (H_4eda3p = ethylenediamine-*N*-acetic-*N*,*N*′,*N*′-tri-3-propionic acid; H_4eddadp = ethylenediamine-*N*,*N*′-diacetic-*N*,*N*′-di-3-propionic acid) have been prepared. An octahedral trans(O_6) geometry (two propionate ligands coordinated in axial positions) has been established crystallographically for the Ba[Cu(eda3p)]·$8H_2O$ compound, while Ba[Cu(eddadp)]·$8H_2O$ is proposed to adopt a trans(O_5) geometry (two axial acetates) on the basis of density functional theory calculations and comparisons of IR and UV−vis spectral data. Experimental and computed structural data correlating similar copper(II) chelate complexes have been used to better understand the isomerism and departure from regular octahedral geometry within the series. The in-plane O−Cu−N chelate angles show the smallest deviation from the ideal octahedral value of 90°, and hence the lowest strain, for the eddadp complex with two equatorial *β*-propionate rings. A linear dependence between tetragonality and the number of five-membered rings has been established. A natural bonding orbital analysis of the series of complexes is also presented.

■ INTRODUCTION

A large and diverse set of ethylenediaminetetraacetic acid (H_4edta) and related chelates have been synthesized. Such aminopolycarboxylate ligands and/or their corresponding metal complexes have been used: as environmental protectors for the removal of heavy metals from soil and water,[1] as analytical reagents for determination of the concentration of many metal ions in biological and environmental matrixes,[2] for diagnostic X-ray and magnetic resonance imaging,[3] and as bleaching agents in the photographic industry.[4] A wealth of aminopolycarboxylate ligands and their corresponding metal (mostly iron) complexes have been investigated industrially for processing silver halide photographic light-sensitive material (Fuji, Konica, etc.).[5,6] Some edta derivatives and their metal complexes have also been shown to be very promising as therapeutic superoxide dismutase mimetics.[7] Our interest in edta-type ligands concerns their potential medicinal use for the treatment of Wilson's disease (WD).[8]

Over the past decade, our group has worked on the synthesis, structures, and biological/environmental activity of new edta derivatives and their metal complexes, particularly focusing on divalent metals such as copper(II) and nickel(II).[9−14] Our interest in M^{II}edta-type complexes is related to their stereochemistry and to the study of the factors determining coordination numbers (CNs) and structural types. edta-type chelates have been prepared via several methods: by condensation from neutralized *α*- or *β*-monohalogencarboxylic acid and the corresponding diamine,[14,15] by condensation of acrylic acid and diamine (to obtain chelates with propionate arms),[16] and by condensation of dihalogen derivatives of diamine with diverse amino acids.[17]

Structural variations of the edta-type framework involve increasing the size or rigidity of the chains or omitting one or more of the carboxylate arms. Geometrical isomerism is possible for complexes of the hexadentate edta-type ligands where the carboxylate arms are replaced so as to form nonequivalent chelate rings.[9,10] Structural parameters of the $[M(edta)]^{n-}$ chelate systems show notable departures from regular octahedral coordination and imply that the system is strained.[18−20] The equatorial chelate rings (G rings) and the diamine backbone ring (E ring) of the complex are more strained than the axially coordinated chelate rings (R rings). Another ligand displaces a G-ring donor more easily than an R ring,[21] and as a consequence, in the case of copper(II), the pentadentate aminocarboxylate ligand coordination in $[Cu(H_2edta)(H_2O)]$ has been well established.[22] For the edta-type ligands having mixed (five- and six-membered) carboxylate arms, geometrical isomers are possible that differ in the number (0, 1, 2, or 3) of six-membered rings lying in the G plane. Such

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ligands (ethane or 1,3-propanediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ions ({$[eddadp]^{4-}$ or $[pddadp]^{4-}$, respectively}) relieve in-plane strain, thus allowing the complexes to attain bite angles closer to the octahedral ideal with apparently less strain in the M−L bonds. With respect to the carboxylate donors, the three possible isomers are shown in Figure 1, where the nomenclature trans(O_5) and trans(O_6) refers to axial acetato and propionate groups, respectively.[9,10] The six-membered carboxylate rings of ethylenediamine-*N*,*N*′-diacetato-*N*,*N*′-dipropionato ion ($[eddadp]^{4-}$) serve better for the formation of less-strained G rings favoring the trans(O_5) isomer of $[M(eddadp)]^{n-}$ complexes when M = Co^{III},[23,24] Cr^{III},[25,26] and Rh^{III} or Ni^{II}.[11,27,28]

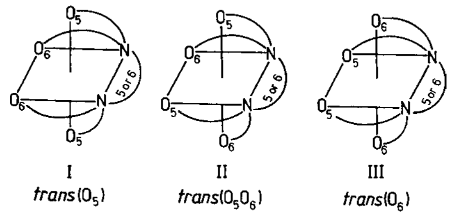

I trans(O_5)
II trans(O_5O_6)
III trans(O_6)

Figure 1. Geometrical isomerism of six-coordinate $[M(edta\text{-}type)]^{n-}$ complexes. The trans(O_n) nomenclature refers to the size of the carboxylate chelate rings for the axial donors; i.e., trans(O_5) represents two axial acetate groups, trans(O_6) two axial propionate groups, and trans(O_5O_6) one axial acetate and one axial propionate ligand.

It is worth noting that, for Co^{III} and Rh^{III}, the less stable trans(O_5O_6) isomer is also found and characterized. The optically active *S*,*S*-edds ligand (*S*,*S*-ethylenediamine-*N*,*N*′-disuccinate ion) produces only the trans(O_5) isomer but does so stereospecifically with the Λ configuration.[9] The unsymmetrical ed3ap (ethylenediamine-*N*,*N*,*N*′-triacetate-*N*′-3-propionate ion) and eda3p (ethylenediamine-*N*-acetate-*N*,*N*′,*N*′-tri-3-propionate ion) ligands can yield two geometrical isomers differing in the position of the six- and five-membered rings, respectively: trans(O_5) or trans(O_6) and trans(O_5O_6) (Figure 1). For M = Co^{III},[29,30] Cr^{III},[31,32] or Cu^{II},[33] the favored less-strained trans(O_5) isomer of $[M(ed3ap)]^{n-}$ was isolated and characterized. In the case of $[M(eda3p)]^{n-}$ (M = Co^{III} [15] or Cr^{III} [31,32]), only the trans(O_5O_6) isomer was reported. Because of the supposed larger strain for the G glycinate rings compared to the corresponding R rings, the authors claimed it was reasonable to expect that the trans(O_5O_6) isomer (Figure 1, middle) with the larger (six-membered) chelate rings in the G plane should form preferentially relative to the corresponding trans(O_6) isomer.[15,31,32,34] The five-coordinate square-pyramidal copper(II) complex of the ethylenediaminetetrapropionate anion $[edtp]^{4-}$ has been isolated and crystallographically verified.[35] Here the usually hexadentate edtp-type ligand acts as a pentadentate ligand with one free β-propionate arm.

To help make sense of these experimental observations, we turn to theoretical calculations, which can provide further insight into the structural and electronic properties of metal complexes. The relative energies of the various structural forms of M-edta-type complexes would be of use to experimental chemists. However, the accurate calculation of the electronic structure of transition-metal complexes remains a challenging task for quantum chemistry. Fortunately, density functional theory (DFT) often yields results in good agreement with experimental data and at a relatively low computational cost compared to comparable wave-function methods. In addition to structures and total energies, DFT can also access the magnetic and d−d spectral properties of metal complexes.[36] As formulated by Kohn and Sham,[37] DFT has become the method of choice for calculations of transition-metal systems.

A possible alternative to DFT is to use classical force fields. For Cu^{II}edta-like complexes, the two most promising approaches are Comba and co-workers' molecular mechanics/angular overlap model[38] method and ligand-field molecular mechanics (LFMM)[39] developed by one of the current authors. Both offer the possibility of rapid, accurate calculations of the structural and spectral properties of coordination complexes. However, both approaches are parametric, and we are not aware of any existing force-field parameters for copper(II) aminocarboxylates. We intend to develop a LFMM force field for this type of system, but the construction of new force fields requires good training data and we often resort to DFT to provide them. The results of the current study will thus feed into this future project.

Here, we focus on an experimental and DFT analysis of the copper(II) complexes of a series of aminopolycarboxylates. The complexes with eddadp and eda3p ligands have not yet been reported. We have therefore prepared both the $[Cu(eddadp)]^{2-}$ and $[Cu(eda3p)]^{2-}$ compounds (although we remain unable to obtain X-ray-quality crystals for the $[Cu(eddadp)]^{2-}$ complex), which completes a series of copper(II) complexes with ethylenediaminetetracarboxylate ligands containing five-membered acetate and/or six-membered β-propionate chelate rings.

This paper covers their structural, configurational, and electronic properties including unsymmetrical (ed3ap and eda3p) and symmetrical (edta, eddadp, and edtp) edta-type ligands. The IR (carboxylate region) and UV−vis spectra of all complexes have been recorded and are discussed in relation to the structure of the whole series. This work aims to elucidate the different geometrical isomers and electronic structure properties including an extensive molecular orbital analysis based on DFT and natural bonding orbitals (NBOs).

■ EXPERIMENTAL DETAILS

Reagent-grade, commercially available chemicals were used without further purification. Ethanediamine and 3-chloropropionic and chloroacetic acids were purchased from Fluka and used as supplied. Ethylenediamine-*N*-acetic-*N*,*N*′,*N*′-tri-3-propionic acid (H_4eda3p) was prepared by a previously described procedure.[15] Ethylenediamine-*N*,*N*′-diacetic-*N*,*N*′-di-3-propionic acid ($H_4eddadp$) was prepared by the method of Byers and Douglas.[23]

Preparation of Barium (Ethylenediamine-*N*-acetato-*N*,*N*′,*N*′-tri-3-propionato)cuprate(II) Octahydrate, Ba[Cu(eda3p)]·8H$_2$O. A total of 5.01 g (0.015 mol) of H_4eda3p was dissolved in 40 mL of water, and 2.52 g (0.030 mol) of $NaHCO_3$ was added in small portions. This solution was added to a solution of 2.56 g (0.015 mol) of $CuCl_2\cdot 2H_2O$ in 15 mL of water. The resulting mixture was stirred at 65 °C for 1 h. At the end of the reaction, $NaHCO_3$ was added to give the reaction mixture a pH of ~7, and the solution was stirred for 1 h. The blue suspension was then filtered and desalted by passage through a G-10 Sephadex column, with distilled water as the eluent. The resulting blue solution was poured into a 4 × 40 cm column containing a Dowex 1-X8 (200−400 mesh) anion-exchange resin in the Cl^- form. The column was then washed with water and eluted with a 0.1 M solution of $BaCl_2$. Two bands were obtained. The second eluate was evaporated to 10 mL and desalted by passage through a G-10 Sephadex column, with distilled water as the eluent. The eluate was concentrated to a volume of 3 mL and stored in a desiccator over methanol for several days. The blue crystals were collected and air-dried. Yield: 1.1 g (11%) of $Ba[Cu(eda3p)]\cdot 8H_2O$. Elemental analysis is consistent with the composition of Ba[Cu(eda3p)]·8H_2O: $C_{13}H_{34}N_2O_{16}BaCu$, M_w = 675.29. Anal. Calcd for the complex salt: C, 23.1; H, 5.1; N, 4.2. Found: C, 23.2; H, 4.5; N, 4.6.

Preparation of Barium (Ethylenediamine-*N*,*N*′-diacetato-*N*,*N*′-di-3-propionato)cuprate(II) Octahydrate, Ba[Cu-(eddadp)]·8H_2O. A solution of copper(II) chloride hexahydrate $CuCl_2$·2H_2O; 3.41 g, 0.020 mol in 30 mL of water) was added to an aqueous solution of H_4eddadp (6.41 g, 0.02 mol) and $NaHCO_3$ (3.36 g, 0.040 mol) in 30 mL of water with heating and stirring (65 °C). Heating with stirring at the same temperature was continued for 1 h. The pH of the mixture was then adjusted to approximately 7 by the gradual addition of $NaHCO_3$, and the blue solution was then heated with stirring at the same temperature for a further 1 h (the volume of the solution was maintained by the periodic addition of hot water). The solution was then evaporated to 10 mL, desalted by passage through a G-10 Sephadex column, eluted with distilled water, and then introduced into a 5 × 60 cm column containing a Dowex 1-X8 (200−400 mesh) anion-exchange resin in the Cl^- form. The column was then washed with water and eluted with a 0.1 M solution of $BaCl_2$ (∼0.5 mL min^{-1}). The blue eluate was evaporated to 10 mL and desalted again by passage through a G-10 Sephadex column, with distilled water as the eluent. After that, the eluate was concentrated to a volume of 3 mL and stored in a desiccator over methanol for several days. The light-blue powder was collected and air-dried. Yield: 0.95 g (7.2%) of Ba[Cu(eddadp)]·8H_2O. Elemental analysis is consistent with the composition of Ba[Cu(eddadp)]·8H_2O: $C_{12}H_{32}N_2O_{16}BaCu$, M_w = 661.26. Anal. Calcd for the complex salt: C, 21.8; H, 4.9; N, 4.2. Found: C, 21.9; H, 4.4; N, 4.6.

Physical Measurements. Suitable blue crystals of the $[Cu(eda3p)]^{2-}$ complex were obtained by recrystallization from a mixture of methanol/water. A prism-shaped crystal with dimensions of 0.52 × 0.37 × 0.31 mm^3 was mounted on top of a glass fiber and aligned on a Bruker (40) SMART APEX CCD diffractometer (platform with a full three-circle goniometer).[40] The crystal was cooled to 100(1) K. Intensity measurements were performed using graphite-monochromated Mo Kα radiation from a sealed ceramic diffraction tube (Siemens). The final unit cell was obtained from the *xyz* centroids of 6754 reflections after integration. The structure was solved by Patterson methods, and extension of the models was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[41] Final refinement on F^2 was carried out by full-matrix least-squares techniques. Crystallographic and experimental details for the structures are summarized in Table S1 in the Supporting Information. CCDC 891689 contains the CIF file for this manuscript. All data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_requests/cif.

Carbon, hydrogen, and nitrogen analyses were performed at the Microanalytical Laboratory, Faculty of Chemistry, University of Belgrade, Belgrade, Serbia. IR spectra in the 400−4000 cm^{-1} region were recorded on a Perkin-Elmer SpectrumOne Fourier transform IR spectrophotometer, using the KBr pellet technique. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrophotometer. For these measurements, 1 × 10^{-3} M aqueous solutions of the complexes under investigation were used.

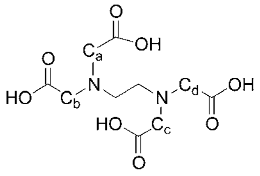
■ COMPUTATIONAL DETAILS

All DFT calculations used the Amsterdam Density Functional code version ADF2007.01.[42−44] After various combinations of functional and basis set were tested, the geometries for copper(II) complexes were optimized using the Becke−Perdew (BP86) functional in a spin-unrestricted formalism with no symmetry constraints on the structure. Starting geometries either were taken from experimental X-ray structures or were preoptimized using the MM+ force field implemented in *Hyperchem 7.01*,[45] with the latter yielding a very rough starting point for the DFT geometry refinement. For C, H, N, and O atoms, Slater-type orbital basis sets of triple-ζ quality with polarization functions (TZP) have been used. The triple-ζ with two polarization functions TZ2P+ basis set was used for the Cu center. This basis set is available for the transition metals Sc−Zn only (Z = 21−30) and is nearly identical with TZ2P except for a better description of the d space (four radial functions for the d orbitals instead of three). Condensed-phase effects were treated using the conductor-like screening model of solvation (COSMO, vide infra) because the obtained geometries are far more realistic than those from in vacuo optimization.[46] A dielectric constant of ε = 78.4 (water-like) was chosen together with a solvent radius of 1.4 Å. The division level was increased to ND = 4. ADF default parameters were used for all of the COSMO solvation parameters, together with a nonoptimized Cu^{II} atom radius of 2.33 Å. Because Cu^{II} is surrounded by five or six ligands, it is not expected to contribute significantly to the solvent-accessible surface.[47−49] The inner shells were represented by the frozen-core approximation (1s for C, N, and O and 1s2p for Cu). Subsequent frequency calculations at the same level of theory verified that the optimized structures were true local minima on the potential energy surface; i.e., there were no imaginary frequencies. The time-dependent DFT (TDDFT) method for computing the electronic transitions and NBO output file.47 employed the *Gaussian09A01* program.[50] For these calculations, we used the unrestricted B3LYP hybrid functional and Ahlrich's TZVP basis set.[51] For molecular orbital analysis, we used *NBO 5.0*.[52]

■ RESULTS AND DISCUSSION

This paper deals with a series of copper(II) complexes with hexadentate edta-type ligands containing five- and/or six-membered carboxylate arms: ethylenediaminetetraacetate (edta), ethylenediamine-*N*,*N*,*N*′-triacetate-*N*′-3-propionate (ed3ap), ethylenediamine-*N*,*N*-diacetate-*N*′,*N*′-di-3-propionate (eddadp), ethylenediamine-*N*-acetate-*N*,*N*′,*N*′-tri-3-propionate (eda3p), and ethylenediaminetetrapropionate (edtp) (Scheme 1). It is our intention to show how structural and electronic effects influence the different behaviors of the members of such a series.

Scheme 1. Ethylenediaminecarboxylic Acids Considered in This Work[a]



pro-ligand	a	b	c	d	No 5-membered rings
H_4edta	1	1	1	1	5
H_4ed3ap	1	1	1	2	4
H_4eddadp	1	2	1	2	3
H_4eda3p	1	2	2	2	2
H_4edtp	2	2	2	2	1

[a] Of the 16 possible combinations, 9 give rise to unique copper complex structures (see Table 1).

Description of the Crystal Structure of Ba[Cu-(eda3p)·8H_2O. A structural diagram of the *trans*(O_6)-$[Cu(eda3p)]^{2-}$ anion, with its adopted atom-numbering scheme, and the packing of the molecules in the unit cell are shown in Figure 2. The unit cell contains two asymmetric units, with each unit comprising one formula unit of three moieties: an anionic *trans*(O_6)-$[Cu(eda3p)]^{2-}$ complex, a Ba^{2+} ion coordinated to four water molecules, and four additional water molecules of crystallization. A search of the distances yielded intermolecular and intramolecular contacts shorter than the sum of the van der Waals radii[53] for the atoms. Hence, the Ba^{2+} ions are linked either to water molecules or a complex anion, forming together with other complex anions an infinite two-dimensional network (Figure 2b). The Ba···Ba distance across the water connections is 4.615 Å, and that connected with the complex anion is 4.825 Å.

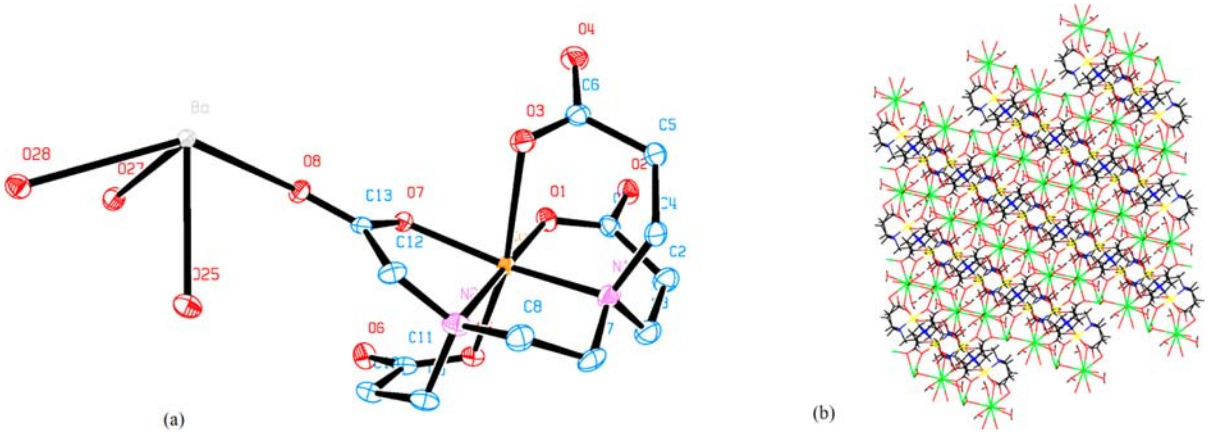


Figure 2. X-ray crystal structure Ba[Cu(eda3p)]·8H_2O: (a) structural detail of the $[Cu(eda3p)]^{2-}$ anion and its interactions with the Ba^{2+} counterion; (b) crystal packing view along the *c* axis.

Table 1. Comparison of the Experimental and DFT Data for edta-Type Copper(II) Complexes

Relative Energies (kcal mol^{-1})[f]

	ligand (number of isomers)				
	edta[a] (1)	ed3ap[b] (2)	eddadp[c] (3)	eda3p[d] (2)	edtp[e] (1)
trans(O_5)		0	0		
trans(O_5O_6)		1.3	0.8	2.3	
trans(O_6)			2.3	0	

Comparison of Experimental (X-ray) and Lowest-Energy DFT-Optimized Structures

	edta[a] (1)		ed3ap[b] (2)	eddadp[c] (3)		eda3p[d] (2)	edtp[e] (1)	
	C_1 symmetry	C_2 symmetry	C_1 symmetry	C_1 symmetry	C_2 symmetry	C_1 symmetry	C_1 symmetry	C_2 symmetry
Cu−N (Å) in-plane	*2.096:2.094*[g]	*2.096:2.057*	*1.986:2.076*	*:2.090*	*:2.254*	*2.026:2.061*	*2.008:2.060*	*2.008:2.066*
Exp: DFT	*2.094:2.052*	*2.094:2.057*	*2.070:2.079*	*:2.090*	*:2.254*	*2.023:2.065*	*2.044:2.090*	*2.044:2.066*
Cu−O (Å) in-plane	*2.023:2.094*	*2.023:2.011*	*1.929:2.029*	:2.018	:2.204	1.951:1.967	1.932:1.998	1.932:2.003
Exp: DFT	*1.933:2.006*	*1.933:2.011*	2.020:1.986	:2.009	:2.204	*2.013:2.015*	1.980:2.043	1.980:2.003
Cu−O (Å) axial	*2.381:2.362*	*2.381:2.455*	2.333:2.463	*:2.431*	*:1.994*	2.518:2.896	2.173:2.228	2.173:2.678
Exp: DFT	*2.224:2.319*	*2.224:2.455*	2.262:2.406	*:2.407*	*:1.994*	2.300:2.532		
Cu−O−C (deg) (av.)	111.0:110.8	111.0:110.0	116.4:115.0	:120.3	:124.71	112.4:112.4	129.7:129.0	129.7:126.2
Exp: DFT								
Cu−O−C−O(deg) (av.)	173.28:173.4	173.28:174.2	172.9:175.0	:178.4	:172.4	144.2:149.6	166.3:167.3	166.3:164.0
Exp: DFT								

[a] Reference 58. [b] Reference 33. [c] This work. [d] This work. [e] Reference 35. [f] The isomer with the lowest-energy minimum has been indicated with 0 kcal mol^{-1}. [g] Bond lengths for five-membered rings are in italics.

The trans(O_6) geometry of the $[Cu(eda3p)]^{2-}$ entity contains a Jahn−Teller distorted octahedral N_2O_4 Cu^{II} ion with axial propionates (see Figure 2).

The Cu−L distances range from 1.9515(18) to 2.5177(17) Å (see Table S1 in the Supporting Information) and are comparable with those in related Cu(edta)-type complexes.[54,55] As expected, the two axial Cu−O bonds are significantly longer [Cu−O3 2.5177(17) Å and Cu−O5 2.2991(17) Å] than the equatorial Cu−O distances [Cu−O7 2.0126(16) Å and Cu−O1 1.9515(18) Å]. The asymmetry in the axial bond distances could be due to the steric demands of the in-plane coordinated *β*-propionate ring or to crystalline effects such as electrostatic interactions between the metal complex and the Ba^{2+} ions or the water molecules of crystallization. The Cu^{II} ion is moderately displaced from the average plane defined by the donor atoms (ρ = 0.082 Å). The cis angles at the Cu^{II} ion range from 79.26(6) to 105.62(8)° and the trans angles from 162.44(9) to 174.68(8)° showing moderate distortion. The five-membered backbone ethylenediamine ring Cu−N1−C7−C8−N2 and in-plane acetate ring Cu−O7−C13−C12−N2 have similar twisted envelope conformations. Their puckering parameters q_2 and φ_2, which relate to the deviations of the atoms from the mean plane of the ring, are q_2 = 0.462(3) Å, φ_2 = 273.5(2)° and q_2 = 0.3898(18) Å, φ_2 = 158.2(3)°, respectively. These should be compared to the ideal values of $q_2 > 0$ and $\varphi_2 = 0$ for the envelope conformation versus $q_2 > 0$ and $\varphi_2 = 90°$ for the twisted conformation.

The six-membered chelate rings are significantly different. The two *β*-propionate rings Cu−O3−C6−C5−C4−N1 and Cu−O5−C11−C10−C9−N2 [with puckering parameters $Q(2)$ = 0.917(2) Å, Φ^2 = 223.99(14)°, and Θ = 103.09(12)° and $Q(2)$ = 0.844(2) Å, Φ^2 = 231.31(15)°, and Θ = 94.19(14)°] adopt a skew boat conformation, while the in-plane six-membered *β*-propionate ring Cu−O1−C1−C2−C3−N1 [with puckering parameters $Q(2)$ = 0.482(2) Å, Φ^2 = 111.8(3)°, and Θ = 125.49(19)°] adopts a half-chair conformation (ideal puckering parameters: chair with values for $\Theta = 0°$ and $\Phi = 0°$; boat for $\Theta = 90°$, $\Phi = 0°$; twist boat for $\Theta = 90°$ and $\Phi = 90°$; the half-chair is intermediate between the chair and skew boat; the half-boat is intermediate between the chair and boat[56]). See Table S2 in the Supporting Information showing the basic conformations of an *N*-membered ring.

Having prepared a series of edta-like complexes with five- and six-membered carboxylate chelates, we can now compare their experimental spectroscopic and geometric properties with the results of DFT calculations. We optimized the geometries of each of the possible geometric isomers in terms of the nature of the axial donors (Figure 1). Quantum-chemical calculations on anions often lead to occupied orbitals having physically unreasonable positive energies, but as pointed out by Deeth and Fey,[57] ionization and/or ligand dissociation is prevented by the finite size of the basis set. Therefore, we include a COSMO continuum dielectric solvation field as a convenient way of mitigating the structural effects of excess charge on transition-metal complexes such as excessively long M−L bonds.

Table 1 compares the theoretical and experimental bond distances, angles, and torsion angles for the series. The relative energies are obtained from the calculated total energies without corrections for basis set superposition error because these are not very large with DFT, especially with such a large basis set.

In general, the comparison between the theory and experiment is reasonably good. BP86/COSMO gives systematically longer Cu−L distances than those observed in solid-state structures by around 0.05 Å for equatorial contacts and up to 0.3 Å for axial bond lengths. The latter is to be expected given that the weakness of the axial interactions makes them much more sensitive to environmental or other effects. However, the energetic consequences of changing the axial bonds even by a few tenths of an angstrom are minimal.

The calculations also indicate that the crystallographically observed Jahn−Teller axis corresponds to the lowest-energy DFT structure, although the other elongation axes give structures that are quite close in energy. Because we were not able to prepare suitable crystals for an X-ray structure determination of the $[Cu(eddadp)]^{2-}$ complex, despite many crystallization techniques used (including exchange of the countercation), the proposed trans(O_5) structure is a prediction based on the DFT energies (Table 1). However, as described later, this prediction is consistent with the spectral results and our expectations from working with such systems.

Microanalysis, spectral analysis (IR and UV−vis), and a comparison of the experimental and DFT-calculated spectra provide further strong supporting evidence for the trans(O_5) isomer as the most favorable one for the $[Cu(eddadp)]^{2-}$ anion. Hence, we will take parameters from the DFT-calculated *trans*(O_5)-$[Cu(eddadp)]^{2-}$ anion (Figure 3) for a structural comparison with similar complexes. The *trans*(O_5)-$[Cu(eddadp)]^{2-}$ anion adopts C_2 molecular symmetry with a distorted octahedral N_2O_4 environment; two acetate rings are located in the axial positions, and the other two *β*-propionate rings and the backbone ethylenediamine ring are placed in the equatorial plane.

Martell and co-workers[59] have reported stability constant data for edta-type copper(II) complexes. The measured log *β* values (water/KNO_3 media; potentiometry) for $[Cu(edta)]^{2-}$, $[Cu(eddadp)]^{2-}$, and $[Cu(edtp)]^{2-}$ are 18.3, 16.3, and 15.4, respectively, indicating a trend toward less stable complexes as the number of six-membered chelate rings increases, although the experimental measurements were unable to establish the precise CN of the Cu^{II} center. However, on the assumption of hexadentate ligation, the experimental trend of a decrease in the stability constant with an increasing number of propionate donors also emerges from DFT.

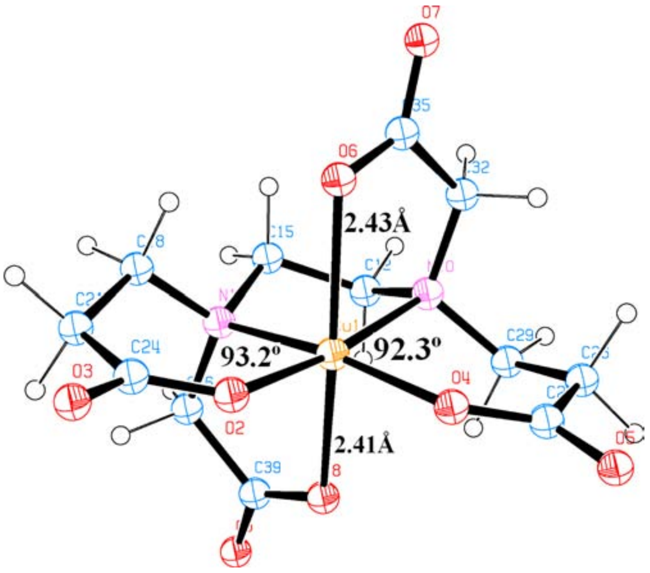


Figure 3. DFT-optimized structure of the *trans*(O_5)-$[Cu(eddadp)]^{2-}$ anion.

The bond dissociation energy (BDE) for all polarizable continuum model (PCM)/water-optimized species was estimated via the expression BDE = $E(CuL) - E(Cu) - E(L)$. The BDEs are −240.86, −240.65, −238.80, −230.90, and −223.41 kcal mol^{-1} for L = edta, ed3ap, eddadp, eda3p, and edtp, respectively. Both theory and experiment agree, at least qualitatively, that more glycinato rings lead to more stable complexes. In apparent contrast, however, more glycinato rings may lead to a reduction in the ligand denticity. Thus, while the edta complex has the largest formation constant, it is usually found as the pentadentate $[Cu(edta)(H_2O)]^-$ species[22] with one equatorial acetate substituted with a water molecule. In order to encourage the ligand to be hexadentate, more six-membered chelates are needed even though this leads to a drop in stability.

NBO Analysis. NBO output from the Gaussian calculations was analyzed using the *NBO 5.0* package.[52] Energy values based on the donor−acceptor (D−A) mechanism (a second-order perturbation theory analysis of the Fock matrix in the NBO basis) have been obtained (Supporting Information). NBO analysis does not find any strong directional metal−ligand covalent bonding. Rather, the interaction is mostly ionic, and the complex is fragmented in two separate units: copper(II) and a tetraanionic edta-type ligand. This fragmentation is particularly pronounced with the copper(II) chelates of ed3ap, eddadp, and eda3p ligands. The largest D−A energy transfers result from donation of electronic charge from the ligand (the carboxylate O-atom lone pairs as well as from the tetrahedral N atoms) to the one-center (lone) non-Lewis (excited) s* orbital of Cu^{II}.[52] This energy decreases as the number of five-membered rings decreases, thus paralleling the trends described above.

Structural Parameters of edta-Type Chelates and Their Octahedral Distortion in Relation to the Structure of the Ligand and Geometry of the Complex. To characterize the strain for Cu^{II}edta-type complexes, the following terms can be considered: (a) the cis and trans angles around the central ion; (b) the ring angle sums of the various

Table 2. Strain Analysis of Copper Complexes with edta-Type Ligands with Five- and/or Six-Membered Carboxylate Rings

complex	$\Sigma\Delta(O_h)$[a]	$\Delta\Sigma$(ring)[b]			Δ(M−O−C)[c]		$\Sigma\Delta$(N)[d]	T[e]	ref
		E(T)	R	G	R	G			
trans(O_5)-$[Cu(edta)]^{2-}$	83	−14	−1	−12	+1	+3	23	0.884 (0.859)	22 (60)
trans(O_5)-$[Cu(ed3ap)]^{2-}$	67	−12	−1 (−11)	+42	+2	+12	+37/+29	0.859	(33)
trans(O_5)-$[Cu(eddadp)]^{2-}$	54	−25.4	+1 (+14.5)	+72	+0.5	+21	15	0.832	this work
trans(O_6)-$[Cu(eda3p)]^{2-}$	61	−23.1	+9.2	−10 (+29.2)	+11	+5	18	0.823	this work

[a] $\Sigma\Delta(O_h)$ is the sum of the absolute values of the deviations from 90° of the L−M−L′ bite angles. All values are rounded off to the nearest degree. [b] $\Delta\Sigma$(ring) is the deviation from the ideal of the corresponding chelate rings' bond angle sum. Values in parentheses are when data for the two individual R or G rings are significantly different. [c] Δ(M−O−C)(ring) is the mean value of the deviation of the corresponding rings' M−O−C bond angle from 109.5°. [d] $\Sigma\Delta$(N) is the sum of the absolute values of the deviations from 109.5° of the six bond angles made by N atoms. A mean value for the two N atoms is reported except for *trans*(O_5)-$[Cu(ed3ap)]^{2-}$ where both values are recorded because they are significantly different from each other. [e] Tetragonality.

kinds of rings; (c) the Cu−O−C or Cu−N−C bond angles; (d) the bond angles that a coordinated N atom makes with its connectors.

The structural data correlating the stereochemistry of the copper(II) complexes are given in Table 2. The extent of distortion is restricted by chelation of the multidentate ligand and depends on its structure as well as the geometry of the complex. The tetragonality parameter T (taken as the ratio of the average equatorial Cu−O bond lengths to the average axial Cu−O bond lengths with values typically around 0.8 ± 0.02)[60] decreases in the order Cu(edta) > Cu(ed3ap) > Cu(eddadp) > Cu(eda3p) > Cu(edtp). Although this order correlates with the number of five-membered rings [the higher the number of five-membered rings, the higher the tetragonality (Figure 4)], the rationalization is complicated because T depends on both axial and equatorial bonds such that T will decrease if the equatorial bonds get relatively shorter or if the axial bonds get relatively longer. For example, the decrease in T from Cu(edta) to Cu(ed3ap) is due to a decrease in the average equatorial Cu−O bond lengths, with the average axial bond lengths remaining constant, while the subsequent drop from Cu(ed3ap) to Cu(eddadp) emerges from increases in both.

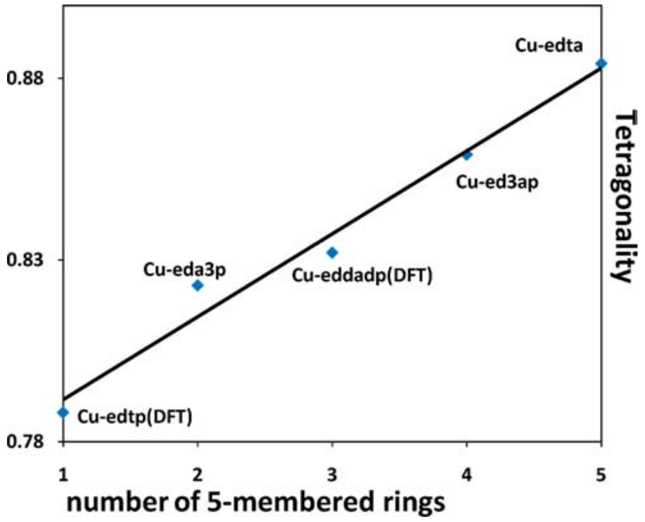


Figure 4. Tetragonality versus number of five-membered rings for Cu(edta)-type complexes.

The sum of the bite-angle deviations, $\Sigma\Delta$, varies from 54° in trans(O_5)-$[Cu(eddadp)]^{2-}$ to 83° in trans(O_5)-$[Cu(edta)]^{2-}$, with the latter having the greatest distortion of any complex in Table 2. The sums of 54° and 61° for trans(O_5)-$[Cu(eddadp)]^{2-}$ and trans(O_6)-$[Cu(eda3p)]^{2-}$ indicate moderate distortion. The bond angle chelate−ring sums for the five-membered G (in-plane) rings, as supposed, are less (the deviations are negative) than the ideal sum (538.5°). The complexes *trans*(O_5)-$[Cu(ed3ap)]^{2-}$, DFT-calculated *trans*(O_5)-$[Cu(eddadp)]^{2-}$, and *trans*(O_6)-$[Cu(eda3p)]^{2-}$ with values of +42, +72, and +19.6°, respectively, show larger deviations because of the presence of 3-propionate rings (Table 2).

The M−O−C fragment of the carboxylate rings is expected to attain a bond angle between 109.5 and 120° depending on the degree of covalency of the M−O bond. The Cu−O−C bond angles of the elongated copper(II) chelates deviate minimally when there is no 3-propionato rings [*trans*(O_5)-$[Cu(edta)]^{2-}$], indicating covalency changes from moderate to minimal as the number of 3-propionate rings decreases. As explained before,[61,62] the G-ring strain of edta-type chelates arises when the effect of chelation distorts the tetrahedral bonding geometry of the N atoms. *trans*(O_5)-$[Cu(ed3ap)]^{2-}$ shows the greatest $\Sigma\Delta$(N) deviation (+37/+29°), consistent with being the only complex with mixed five- and six-membered equatorial carboxylate rings. All of the other complexes show moderate distortion, although much larger than that established for trivalent transition metals like chromium(III) and cobalt(III).[63,64]

A further measure of the distortion from ideal octahedral coordination is the average equatorial N−Cu−O angles (Figure 5). *trans*(O_5)-$[Cu(eddadp)]^{2-}$ yields the closest value to 90°. A similar result is observed for iron(III) complexes, where having two six-membered propionate chelates in the MN_2O_2 plane in conjunction with axial five-membered acetate chelate rings allows the ligand to attain near-octahedral coordination in the equatorial plane. Interestingly, for copper(II), the BDEs reported above indicate that this geometrical feature does not translate into a more stable, less strained system overall. However, there could be important consequences for selectivity when considering other metal centers that show a different tendency for octahedral coordination.

Spectral Analysis. The complexes have been further analyzed by means of IR and UV−vis spectra (see Table S3 in the Supporting Information: IR vibrations for Cu(edta)-type complexes).

The IR data (carboxylate region) are in agreement with the structures and molecular symmetries. In the case of the *trans*(O_5)-$[Cu(eddadp)]^{2-}$ complex of C_2 symmetry, the IR spectrum contains only one wide band centered on 1598 cm^{-1}. Normally, two bands are expected because of the asymmetric vibrations of five-membered acetate and six-membered β-

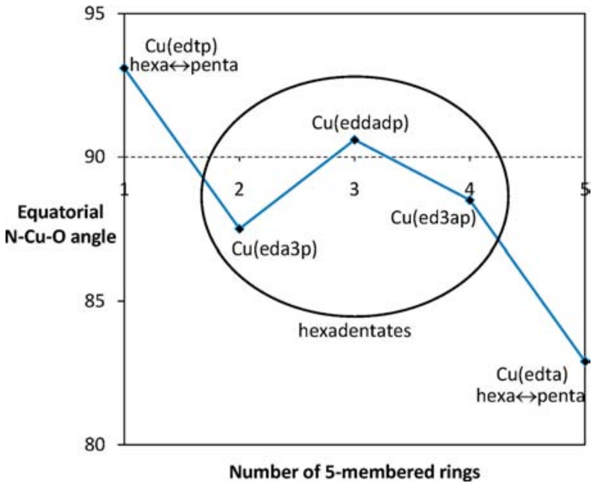


Figure 5. Comparison of the average N−Cu−O bond angles and the number of five-membered chelate rings.

propionate rings. However, because the packing in the crystal and thus the arrangements of the lattice water molecules are unknown, mixing with water vibrations may mask distinct vibrations. In contrast, *trans*(O_6)-$[Cu(eda3p)]^{2-}$ has C_1 molecular symmetry, and we obtain a nice correlation in that the spectrum contains one intense wider band positioned at 1575 cm^{-1} corresponding to asymmetric vibrations of three β-propionate rings and one shoulder of moderate intensity located at 1623 cm^{-1} due to asymmetric stretches of the acetate ring. This interpretation is in agreement with the generally accepted rule that the frequency assigned to five-membered rings[65] lies at higher energy than the corresponding frequency of six-membered chelate rings.[66] For protonated carboxylate groups (1700−1750 cm^{-1}) and for coordinated carboxylate groups (1600−1650 cm^{-1}), asymmetric carboxylate stretching frequencies have been well established.[67,68] Therefore, the absence of the band in the 1700−1750 cm^{-1} region confirms that all of the carboxylate groups are deprotonated.

The ligand-field absorption spectra are now considered for all of the complexes. Electronic absorption spectra of the complexes of known structure are shown in Figure 6.

Table 3 lists the relevant electronic absorption data of the whole series including the TDDFT calculations (*Gaussian09*) for the 10 lowest-energy transitions.

Table 3. Electronic Absorption and TDDFT Data for Cu^{II}edta-Type Complexes

	exptl value in		TDDFT ($\times 10^3$ cm^{-1})	
complex	10^3 cm^{-1}	ε	unscaled value	scaled by 0.9
$[Cu(edta)]^{2-}$	13.66	97	15.38	13.89
$[Cu(ed3ap)]^{2-}$	13.62	102	15.17	13.69
$[Cu(eddadp)]^{2-}$	13.99	149	15.01	13.59
$[Cu(eda3p)]^{2-}$	14.18	157	15.50	14.20
$[Cu(edtp)]^{2-}$	14.49	204	15.67	14.08

All of the complexes are blue and experimentally exhibit one asymmetric absorption band irrespective of the underlying approximate C_1 or C_2 symmetry. The computed absorption curve is composed of electronic transitions from the d_{z^2}, $d_{x^2-y^2}$, d_{xz}, and d_{yz} orbitals to d_{xy} assuming the Z direction lies along the axis of elongation while the X and Y directions bisect the in-plane bond angles. The energy absorption maxima for these octahedral complexes increase on going from $[Cu(edta)]^{2-}$ to $[Cu(eda3p)]^{2-}$. The correlation between tetragonality and the experimental absorption maximum is given in Figure 7, where the calculated value of T for the $[Cu(edtp)]^{2-}$ complex is 0.788.

This means that more six-membered rings increase the in-plane ligand-field strength, inducing a blue shift. The complexes with axial five-membered glycinate rings have a stronger axial interaction, raising the d_{z^2} orbital energy and lowering d_{xy} to compensate, leading to a general lowering of the energy of d−d transitions.

The TDDFT calculations do not provide as clear a correlation with tetragonality as the experiment. The 10 lowest-energy transitions were considered, and the transition with the largest oscillator strength was taken for comparison.

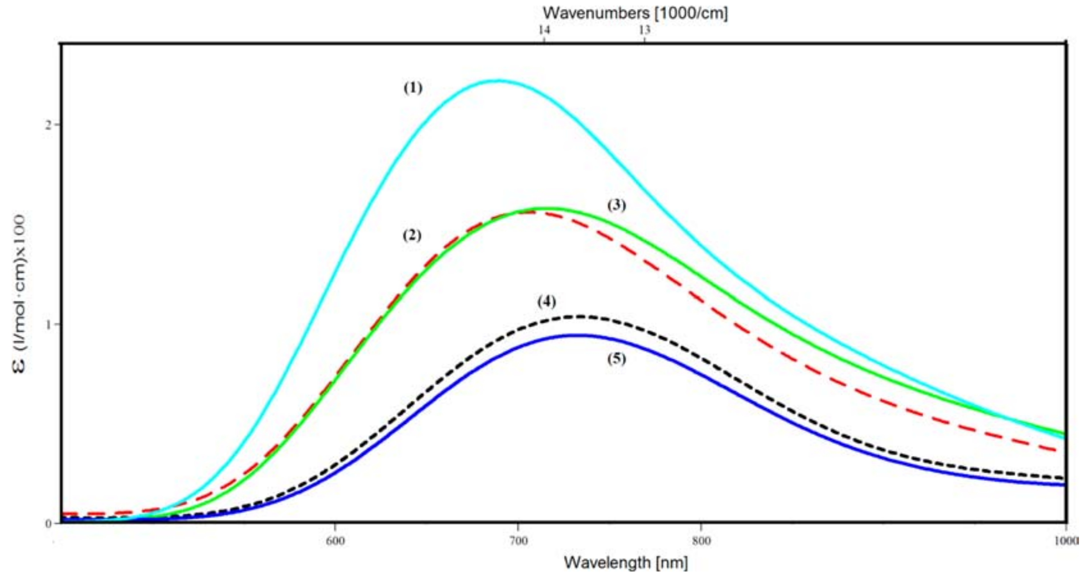


Figure 6. Electron absorption spectra of 10^{-3} dm^3 mol^{-1} aqueous solutions of Cu(edta)-type complexes: (1) Cu(edtp); (2) Cu(eda3p); (3) Cu(eddadp); (4) Cu(ed3ap); (5) Cu(edta).

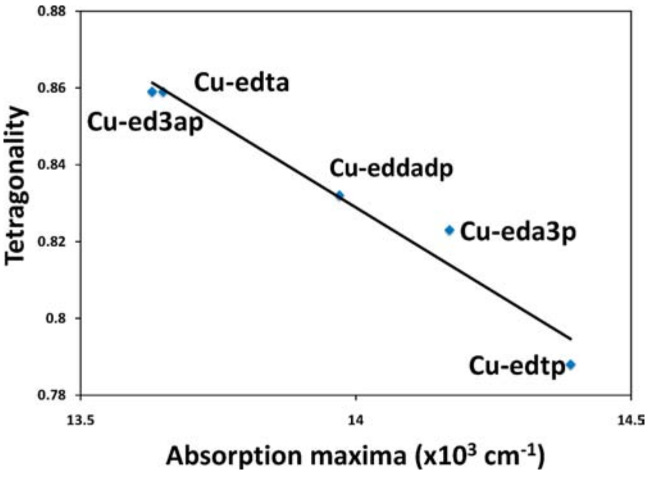


Figure 7. Correlation diagram between tetragonality and the experimental d−d absorption maxima ($\times 10^3$ cm^{-1}) for Cu(edta)-type complexes.

TDDFT appears systematically to overestimate the transition energy. A scaling factor of 0.9 improves the numerical agreement between the theory and experiment (see Table 3), but the sequence of complexes as a function of the band maximum is rather different from that of the experiment. For complexes such as $[Cu(edta)]^{2-}$ and $[Cu(edtp)]^{2-}$, it may be that, in solution, there is an equilibrium between hexadentate and pentadentate binding, although this would presumably impact on the tetragonality, which was based on a single contributor. Alternatively, given that the experimental band maxima only span a range of 800 cm^{-1}, the relatively small variations from complex to complex are too subtle for TDDFT.

Chelate Modeling against WD. WD is one of the very few forms of serious hepatic, neurological disease for which some pharmacological therapy is available. In virtually every patient who is asymptomatic, and in any of those who are ill, decoppering therapy can maintain or restore normal health and longevity. In the liver of patients with WD, imperfect biliary excretion of copper and a disturbance in the secretion of copper as holoceruloplasmin into the blood results in copper accumulation in the liver.[69] Treatments for WD have progressed from the intramuscular administration of dimercaprol (2,3-disulfanylpropan-1-ol or British anti-Lewisite) to the more easily administered oral penicillamine. Alternative agents to penicillamine, such as trientine, have been developed and introduced specifically for patients with adverse reactions to penicillamine. Zinc was developed separately, as was tetrathiomolybdate, which was used for copper poisoning in animals. Patients with WD should be treated with chelating agents, including penicillamine and trientine, and/or zinc. However, severe side effects, including immunological effects (lupus-like reactions, nephrotic syndrome, myasthenia gravis, and Goodpasture syndrome), as well as effects involving the skin (degenerative changes, elastosis perforans serpiginosa, etc.) and joints (arthropathy) are often observed in patients who are treated with penicillamine. Trientine shares some of penicillamine's side effects but appears to be significantly less toxic.[69]

In order to eliminate the side effects of chelate drugs, we are in the course of examining several edta-like ligands as copper immobilization agents. After investigating the current series of Cu^{II}edta-type complexes, we particularly intend to use those chelates that are more selective (such as chelates with more 3-propionic arms) to copper. Thus, H_4eddadp, H_4eda3p, and H_4edtp are of potential interest because, although their copper(II) complexes have somewhat weaker stability constants than Cu^{II}edta, the work of Chaberek et al.[59] suggests they are more selective toward the Cu^{II} ion compared to other metal ions like Ni^{II}, Co^{II}, Zn^{II}, or Mg^{II}.

■ CONCLUSIONS

The preparation of barium (ethylenediamine-*N*-acetato-*N*,*N*′,*N*′-tri-3-propionato)cuprate(II) octahydrate, Ba[Cu(eda3p)]·$8H_2O$ (for which we report a crystal structure), and barium (ethylenediamine-*N*,*N*′-diacetato-*N*,*N*′-di-3-propionato)cuprate(II) octahydrate, Ba[Cu(eddadp)]·$8H_2O$, completes the series of copper(II) ethylenediaminetetracarboxylate chelates with acetate and propionate groups. On the basis of the experimental data and DFT calculations, we find a stable hexadentate coordination with a trans(O_6) geometry for Ba[Cu(eda3p)]·$8H_2O$ and a trans(O_5) geometry for Ba[Cu(eddadp)]·$8H_2O$. The crystallographically observed isomer for $[Cu(eda3p)]^{2-}$ also corresponds to the lowest-energy structure computed using DFT. The proposed trans(O_6) geometry for the $[Cu(eda3p)]^{2-}$ ion and trans(O_5) geometry for the $[Cu(eddadp)]^{2-}$ are also consistent with the spectral results. The metal−ligand bonds (Cu−O and Cu−N) within the complexes investigated are essentially electrostatic in nature based on NBO calculations. We observe linear correlations between tetragonality and the number of five-membered rings in the complex anion and between tetragonality and the energy of the most intense d−d absorption. The latter correlation is observed with the experimental absorption spectra, while the calculated TDDFT transitions show a more scattered trend. In addition, the equatorial N−Cu−O angles show the smallest deviation from the ideal value of 90° when there is an equal number of glycinate and β-propionate rings and larger devitations when all of the carboxylate arms are the same. This could be a useful way of distinguishing different metal centers based on their propensity for octahedral coordination. The chelates H_4eddadp, H_4eda3p, and H_4edtp are thus of potential interest in curing WD because they have somewhat weaker stability constants than other edta-like ligands but are, in fact, more selective toward copper because they encourage the hexadentate form.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystalloraphic data in CIF format and Tables S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Sun, B.; Zhao, F. J.; Lombi, E.; McGrath, S. P. *Environ. Pollut.* **2001**, *113*, 111−120.

(2) Lin, H.; Chou, Y.; Yang, J. *Anal. Chim. Acta* **2008**, *611*, 89−96.

(3) Chang, A. C.; Kumar, K.; Tweedle, M. F. Dual functioning excipient for metal chelate contrast agents. U.S. Patent 7,385,041, June 10, 2008.

(4) Fushiki, I.; Koboshi, S.; Terada, S. Process for the treatment of photographic materials. U.S. Patent 4,138,257, Feb 6, 1979.

(5) Toshiro, N.; Akira, A. Processing method for silver halide color photosensitive materials. U.S. Patent EP0205121A2, Dec 17, 1986.

(6) Koboshi, S.; Kon, M.; Miyaoka, K. Method of storing photographic processing solution. U.S. Patent EP0250219B1, March 30, 1994.

(7) Fisher, A. E. O.; Naughton, D. P. *Biomed. Pharmacother.* **2005**, *59*, 158−162.

(8) Blanuša, M.; Varnai, V. M.; Piasek, M.; Kostial, K. *Curr. Med. Chem.* **2005**, *12*, 2771−2794.

(9) Radanović, D. J. *Coord. Chem. Rev.* **1984**, *54*, 159−261.

(10) Douglas, B. E.; Radanović, D. J. *Coord. Chem. Rev.* **1993**, *128*, 139−165.

(11) Radanović, D. J.; Ianelli, S.; Pelosi, G.; Matović, Z. D.; Tasić-Stojanović, S.; Douglas, B. E. *Inorg. Chim. Acta* **1998**, *278*, 66−75.

(12) Matović, Z. D.; Ianelli, S.; Pelosi, G.; Janićijević, S. K.; Ristanović, V. M.; Ponticelli, G.; Radanović, D. J. *Polyhedron* **2002**, *21*, 2667−2674.

(13) Matović, Z. D.; Miletić, V. D.; Samardžić, G.; Pelosi, G.; Ianelli, S.; Trifunović, S. *Inorg. Chim. Acta* **2005**, *358*, 3135−3144.

(14) Matović, Z. D.; Meetsma, A.; Miletić, V. D.; van Koningsbruggen, P. J. *Inorg. Chim. Acta* **2007**, *360*, 2420−2431.

(15) Radanović, D. J.; Đuran, M. I.; Miletić, V. D.; Maricondi, C.; Douglas, B. E. *Inorg. Chem.* **1988**, *27*, 1265−1269.

(16) Yutaka, U.; Kenji, K. Chemical compositions and a processing method using the same for processing silver halide photographic light-sensitive material. U.S. Patent EP0599620A1, June 1, 1994.

(17) Stanković, M. Z.; Radić, G. P.; Glođović, V. V.; Radojević, I. D.; Stefanović, O. D.; Čomić, Lj. R.; Klisurić, O. R.; Djinović, V. M.; Trifunović, S. R. *Toxicol. Appl. Pharmacol.* **2011**, *30*, 2203−2209.

(18) Weakliem, H. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 549−555.

(19) Okamoto, K.; Tsukihara, T.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3534−3539.

(20) Kushi, Y.; Morimasa, K.; Yoneda, H. Presented at the 49th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1984; Abstract 1N31.

(21) Ogino, H.; Shimura, M. *Adv. Inorg. Bioinorg. Mech.* **1986**, *4*, 107−135.

(22) Stephens, F. S. *J. Chem. Soc. A* **1969**, 1723−1734.

(23) Byers, W.; Douglas, B. E. *Inorg. Chem.* **1972**, *11*, 1470−1473.

(24) Radanović, D. J.; Douglas, B. E. *Inorg. Chem.* **1975**, *14*, 6−10.

(25) Radanović, D. J.; Douglas, B. E. *J. Coord. Chem.* **1975**, *4*, 191−198.

(26) Helm, F. T.; Watson, W. H.; Radanović, D. J.; Douglas, B. E. *Inorg. Chem.* **1977**, *16*, 2351−2537.

(27) Gailey, K. D.; Radanović, D. J.; Đuran, M. I.; Douglas, B. E. *J. Coord. Chem.* **1978**, *8*, 161−167.

(28) Radanović, D. J.; Gailey, K. D.; Đuran, M. I.; Douglas, B. E. *J. Coord. Chem.* **1980**, *10*, 115−123.

(29) Radanović, D. J.; Đuran, M. I.; Kostić, T. S.; Maricondi, C.; Douglas, B. E. *Inorg. Chim. Acta* **1993**, *207*, 111−119.

(30) Radanović, D. J.; Miletić, V. D.; Ama, T.; Kawaguchi, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1605−1614.

(31) Radanović, D. J.; Ristanović, V. M.; Stojčeva-Radovanović, B.; Todorovska, A. D.; Sakagami, N.; Lino, A.; Kaizaki, S. *Transition Met. Chem* **1999**, *24*, 403−408.

(32) Radanović, D. J.; Sakagami, N.; Ristanović, V. M.; Kaizaki, S. *Inorg. Chim. Acta* **1999**, *292*, 16−27.

(33) Radanović, D. J.; Ama, T.; Gurešić, D. M.; Ristanović, D. M.; Radanović, D. D.; Kawaguchi, H. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2283−2288.

(34) Miletić, V. D.; Meetsma, A.; van Koningsbruggen, P. J.; Matović, Z. D. *Inorg. Chem. Commun.* **2009**, *12*, 720−723.

(35) Rychlewska, U.; Radanović, D. D.; Dimitrijević, M. Đ.; Ristanović, D. M.; Vasojević, M. M.; Radanović, D. J. *Polyhedron* **2001**, *20*, 2523−2530.

(36) Neese, F. *Coord. Chem. Rev.* **2009**, *253*, 526−563.

(37) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, 1133−1138.

(38) Comba, P.; Remenyi, R. *Coord. Chem. Rev.* **2003**, *238*, 9.

(39) Deeth, R. J.; Anastasi, A.; Diedrich, C.; Randell, K. *Coord. Chem. Rev.* **2009**, *253*, 795.

(40) *Bruker, SMART, SAINTPLUS and XPREP Area Detector Control and Integration. Software Smart Apex Software Reference Manuals*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 2000.

(41) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Israël, R.; Smits, J. M. M. *The DIRDIF-99 Program System*; Crystallography Laboratory, University of Nijmengen: Nijmengen, The Netherlands, 1999.

(42) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931−967.

(43) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391−403.

(44) *ADF2007.01*; SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands,http://www.scm.com.

(45) *HyperChem (TM)*; Hypercube Inc.: Gainesville, FL, 2012.

(46) Hocking, R. K.; Deeth, R. J.; Hambley, T. W. *Inorg. Chem.* **2007**, *46*, 8238−8244.

(47) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 799−805.

(48) Klamt, A. *J. Phys. Chem.* **1995**, *99*, 2224−2235.

(49) Klamt, A.; Jones, V. *J. Chem. Phys.* **1996**, *105*, 9972−9981.

(50) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(51) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.

(52) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0*; Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001.

(53) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−452.

(54) Sakagami, N.; Kaizaki, S. *J. Chem. Soc., Dalton Trans.* **1992**, *No. 2*, 291−297.

(55) Matović, Z. D. Faculty of Science, Kragujevac, Serbia, unpublished work.

(56) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354−1358.

(57) Deeth, R. J.; Fey, N. *J. Comput. Chem.* **2004**, *25*, 1840−1848.

(58) Porai-Koshits, M. A.; Novozhilova, N. V.; Polynova, T. N.; Filippova, T. V.; Martynenko, L. I. *Kristallografiya* **1973**, *18*, 89−98.

(59) Courtney, R. C.; Chaberek, S., Jr.; Martell, A. E. *J. Am. Chem. Soc.* **1953**, *75*, 4814−4818.

(60) Tomlinson, A. A. G.; Hathaway, B. J.; Billing, D. E.; Nichols, P. *J. Chem. Soc. A* **1969**, 65−71.

(61) Solans, X.; Font-Altaba, M.; Oliva, J.; Herrera, J. *Acta Crystallogr., Sect. C* **1983**, *C39*, 435−438.
(62) Halloran, L. J.; Caputo, R. E.; Willett, R. D.; Legg, J. I. *Inorg. Chem.* **1975**, *14*, 1762−1768.
(63) Kaizaki, S.; Byakuno, M.; Hayashi, M.; Legg, J. I.; Umakoshi, K.; Ooi, S. *Inorg. Chem.* **1987**, *26*, 2395−2399.
(64) Parvez, M.; Maricondi, C.; Radanović, D. J.; Trifunović, S. R.; Miletić, V. D.; Douglas, B. E. *Inorg. Chim. Acta* **1996**, *248*, 89−92.
(65) Nakamoto, K.; Morimoto, Y.; Martell, A. E. *J. Am. Chem. Soc.* **1961**, *83*, 4528−4532.
(66) Ćelap, M. B.; Niketić, S. R.; Janjić, T. J.; Nikolić, V. N. *Inorg. Chem.* **1967**, *6*, 2063−2065.
(67) Busch, D. H.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 4574−4575.
(68) Morris, M. L.; Busch, D. H. *J. Am. Chem. Soc.* **1956**, *78*, 5178−5181.
(69) Walshe, J. M. *Mov. Disord.* **1999**, *4*, 545−550.