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

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ABSTRACT: Copper(II) complexes of hexadentate ethylenediaminetetracarboxylic acid type ligands H4eda3p and H2eddadp (H4eda3p = ethylenediamine-N-acetic-N,N',N'-tri-3-propionic acid; H2eddadp = ethylenediamine-N,N'-diacetic-N,N'-di-3-propionic acid) have been prepared. An octahedral trans(O6) geometry (two propionate ligands coordinated in axial positions) has been established crystallographically for the Ba[Cu(eda3p)]·8H2O compound, while Ba[Cu(eddadp)]·8H2O is proposed to adopt a trans(O3) 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 strained chelate rings (R rings) has been established. A natural bonding orbital analysis of the series of complexes is also presented.

INTRODUCTION

A large and diverse set of ethylenediaminetetracetic acid (H4edta) 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 matrices,2 for diagnostic X-ray and magnetic resonance imaging,3 and as bleaching agents in the photographic industry.4 A wealth of amino-ions in biological and environmental matrixes,2 for diagnostic reagents for determination of the concentration of many metal interests in Medta-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-monohalogenocarboxylic 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(H2edta)(H2O)] 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
ligands (ethane or 1,3-propanediamine-N,N′-diacetate-N,N′-di-
3-propionate ions ([[eddadp]]^2⁻ or [pdadap]^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(O₅) and trans(O₆) refers to axial acetato and propionate groups, respectively. The six-membered carboxylate rings of ethylenediamine-N,N′-diaceto-
N,N′-dipropionato ion ([eddadp])^2⁻ serve better for the formation of less-strained G rings favoring the trans(O₅) 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

It is worth noting that, for Co^{III} and Rh^{III}, the less stable trans(O₅O₆) isomer is also found and characterized. The optically active S,S-eddad ligand (S,S-ethylenediamine-N,N′- diisuccinate ion) produces only the trans(O₅) isomer but does so stereospecifically with the Λ configuration. 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(O₅) or trans(O₆) and trans(O₅O₆) (Figure 1). For M = Co^{III},29,30 Cr^{III},31,32 or Cu^{II},33 the favored less-
strained trans(O₅) 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(O₅O₆) 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(O₅O₆) isomer (Figure 1, middle) with the larger (six-membered) chelate rings in the G plane should form preferentially relative to the corresponding trans(O₅) 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. As formulated by Kohn and Sham, 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 method and ligand-field molecular mechanics (LFMM) 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 (eddadp, 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. Ethylenediamine and 3-chloropropionic and chloro-
acetic acids were purchased from Fluka and used as supplied. Ethylenediamine-N-acetic-N,N′,N′-tri-3-propionic acid (H₄ed3ap) was prepared by a previously described procedure. Ethylenediamine-N,N′-diacetic-N,N′-di-3-propionic acid (H₄edadp) was prepared by the method of Byers and Douglas.

Preparation of Barium (Ethylenediamine-N-aceto-
N,N′-tri-3-propionato)cuprate(II) Octahydrate, Ba[Cu(eda3p)]·8H₂O

A total of 5.01 g (0.015 mol) of H₄ed3ap was dissolved in 40 mL of water, and 2.52 g (0.030 mol) of NaHCO₃ was added in small portions. This solution was added to a solution of 2.56 g (0.015 mol) of CuCl₂·2H₂O in 15 mL of water. The resulting mixture was stirred at 65 °C for 1 h. At the end of the reaction, NaHCO₃ 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 0.1 M solution of BaCl₂. 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)]·8H₂O. Elemental analysis

Figure 1. Geometrical isomerism of six-coordinate [M(edta-type)]^n⁻ complexes. The trans(O₅) nomenclature refers to the size of the carboxylate chelate rings for the axial donors; i.e., trans(O₅) represents two axial acetate groups, trans(O₆) two axial propionate groups, and trans(O₅O₆) one axial acetate and one axial propionate ligand.
is consistent with the composition of $\text{Ba}[\text{Cu}({\text{eda}3\text{p}})] \cdot 8\text{H}_2\text{O}$: $\text{C}_6\text{H}_{12}\text{N}_6\text{O}_8\text{BaCu}$, $M_r = 661.26$. Anal. Calc. for the complex salt: C, 21.8; H, 4.4; N, 4.6. Found: C, 21.9; H, 4.4; N, 4.6.

## Physical Measurements.
Suitable blue crystals of the $[\text{Cu}({\text{eda}3\text{p}})]^{2-}$ complex were obtained by recrystallization from a mixture of methanol/water. A prism-shaped crystal with dimensions of $0.52 \times 0.37 \times 0.31 \text{ mm}^3$ 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 $\text{K}α$ 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.\(^{43}\) 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 Belgrad, 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.

## 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-$N,N,N′,N′′$-tetraacetate-$N′$-3-propionate (ed3ap), ethylenediamine-$N,N$-diacetate-$N′,N′′$-di-3-propionate (edddap), ethylenediamine-$N$-acetate-$N′,N′′$-tri-3-propionate (ed3p), and ethylenediaminetriacetopropionate (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

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

### Description of the Crystal Structure of $\text{Ba}[\text{Cu}({\text{eda}3\text{p}})] \cdot 8\text{H}_2\text{O}$.
A structural diagram of the $\text{trans}(\text{O}_{6}) - [{\text{Cu}({\text{eda}3\text{p}}})]$\(^{2-}\) 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 $\text{trans}(\text{O}_{6}) - [{\text{Cu}({\text{eda}3\text{p}}})]$\(^{2-}\) complex, a $\text{Ba}^{2+}$ 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 $\text{Ba}^{2+}$ 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.
The trans(O$_{ba}$) geometry of the [Cu(eda3p)]$^{2-}$ entity contains a Jahn–Teller distorted octahedral N$_2$O$_4$ Cu$^{II}$ ion with axial propionates (see Figure 2).

The Cu–L distances range from 1.951(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 ($\rho = 0.082$ Å). The cis angles at the Cu$^{II}$ ion range from 79.26(6) to 105.62(8)$^\circ$ and the trans angles from 162.44(9) to 174.68(8)$^\circ$ 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 $\Phi_2$, which relate to the deviations of the atoms from the mean plane of the ring, are $q_2 = 0.462(3)$ Å, $\Phi_2 = 273.5(2)^\circ$ and $q_2 = 0.389(18)$ Å, $\Phi_2 = 158.2(3)^\circ$, respectively. These should be compared to the ideal values of $q_2 > 0$ and $\Phi_2 = 0$ for the envelope conformation versus $q_2 > 0$ and $\Phi_2 = 90^\circ$ 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, $\Phi^2 = 223.99(14)^\circ$, and $\Theta = 103.09(12)^\circ$ and Q(2) = 0.844(2) Å, $\Phi^2 = 231.31(15)^\circ$, and $\Theta = 94.19(14)^\circ$] 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, $\Phi^2 = 111.8(3)^\circ$, and $\Theta = 125.49(19)^\circ$] adopts a half-chair conformation (ideal puckering parameters: chair with values for $\Theta = 0^\circ$ and $\Phi = 0^\circ$; boat for $\Theta = 90^\circ$, $\Phi = 0^\circ$; twist boat for $\Theta = 90^\circ$ and $\Phi = 90^\circ$; the half-chair is intermediate between the chair and skew boat; the half-boat is intermediate between

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

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<tr>
<th>ligand (number of isomers)</th>
<th>Relative Energies (kcal mol$^{-1}$)</th>
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<td>edta$^a$ (1)</td>
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<td>ed3ap$^b$ (2)</td>
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<td>eddadp$^c$ (3)</td>
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**Table 1.** Comparison of the Experimental and DFT Data for edta-Type Copper(II) Complexes

- **$^a$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$^{-1}$.

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Figure 2. X-ray crystal structure Ba[Cu(eda3p)]$^{2-}$·8H$_2$O: (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.
the chair and boat69). 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(O5) 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(O5) isomer as the most favorable one for the [Cu(eddadp)]2− anion. Hence, we will take parameters from the DFT-calculated trans(O5)−[Cu(eddadp)]2− anion (Figure 3) for a structural comparison with similar complexes. The trans(O5)−[Cu(eddadp)]2− anion adopts C2 molecular symmetry with a distorted octahedral N2O4 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-workers59 have reported stability constant data for edta-type copper(II) complexes. The measured log β values (water/KNO3 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 decreases, although the experimental measurements were unable to establish the precise CN of the Cu2+ 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.

The bond dissociation energy (BDE) for all polarizable continuum model (PCM)/water-optimized species was estimated via the expression $\text{BDE} = E(\text{CuL}) - E(\text{Cu}) - E(L)$. The BDEs are approximately 238.80, 240.65, 238.80, 240.86, −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)(H2O)] species 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$^{2+}$.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$^{2+}$-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
Cu the average equatorial Cu complex. The tetragonality parameter and depends on its structure as well as the geometry of the distortion is restricted by chelation of the multidentate ligand connectors. (d) the bond angles that a coordinated N atom makes with its angle from 109.5°. The IR data (carboxylate region) are in agreement with the IR spectrum of the edta-type chelates deviate 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. ‘Δ(M−O−C)(ring)’ is the mean value of the deviation of the corresponding rings’ M−O−C bond angle from 109.5°. ‘ΔΣ(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(O5)−[Cu(ed3ap)]2− where both values are recorded because they are significantly different from each other. ‘Tetragonality.

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) decreases in the order Cu(edta) > Cu(ed3ap) > Cu(dddadp) > 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 copper(II) chelates deviate from the ideal of the corresponding chelate rings (Figure 4). indicating covalency changes from moderate to 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-propionate rings [trans(O5)−[Cu(edta)]2−], indicating covalency changes from moderate to minimal as the number of 3-propionate rings decreases. As explained before, the G-ring strain of edta-type chelates arises when the effect of chelation distorts the tetrahedral bonding geometry of the N atoms. trans(O5)−[Cu(ed3ap)]2− shows the greatest ΔΣ(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).

A further measure of the distortion from ideal octahedral coordination is the average equatorial N−Cu−O angles (Figure 5). trans(O5)−[Cu(dddadp)]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 MnN2O2 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(O5)−[Cu(dddadp)]2− complex of C2 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-
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, \textit{trans}(O₆)-[\textit{Cu}(eda₃p)]²⁻ has C₁ 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 lies at higher energy than the corresponding frequency of six-membered chelate rings. 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. 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>
<thead>
<tr>
<th>complex</th>
<th>(10^3 \text{ cm}^{-1})</th>
<th>(\varepsilon)</th>
<th>TDDFT ((\times10^3) cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cu}(edta)]^{2-})</td>
<td>13.66 97</td>
<td>15.38 13.89</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu}(ed3ap)]^{2-})</td>
<td>13.62 102</td>
<td>15.17 13.69</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu}(eddadp)]^{2-})</td>
<td>13.99 149</td>
<td>15.01 13.59</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu}(eda3p)]^{2-})</td>
<td>14.18 157</td>
<td>15.50 14.20</td>
<td></td>
</tr>
<tr>
<td>([\text{Cu}(edtp)]^{2-})</td>
<td>14.49 204</td>
<td>15.67 14.08</td>
<td></td>
</tr>
</tbody>
</table>

All of the complexes are blue and experimentally exhibit one asymmetric absorption band irrespective of the underlying approximate C₁ or C₂ symmetry. The computed absorption curve is composed of electronic transitions from the d⁰, dₓᵧ, dₓz, and dᵧz orbitals to dₓ, 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 \([\text{Cu}(edta)]^{2-}\) to \([\text{Cu}(eda3p)]^{2-}\). The correlation between tetragonality and the experimental absorption maximum is given in Figure 7, where the calculated value of \(T\) for the \([\text{Cu}(edtp)]^{2-}\) 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 d⁰ orbital energy and lowering dₓᵧ 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.
**CONCLUSIONS**

The preparation of barium (ethylenediamine-N-acetato-N,N′,N″-tri-3-propionato)cuprate(II) octahydrate, Ba[Cu(edta3p)]·8H2O (for which we report a crystal structure), and barium (ethylenediamine-N,N′-diametaceto-N,N″-di-3-propionato)cuprate(II) octahydrate, Ba[Cu(eddadp)]·8H2O, completes the series of copper(II) ethylenediaminetetraacboxylate 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(O6) geometry for Ba[Cu(edta3p)]·8H2O and a trans(O5) geometry for Ba[Cu(eddadp)]·8H2O. The crystallographically observed isomer for [Cu(edta3p)]2− also corresponds to the lowest-energy structure computed using DFT. The proposed trans(O6) geometry for the [Cu(edta3p)]2− ion and trans(O5) 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 deviations 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 H3eddadp, H3eda3p, and H4edtp 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**

5 Supporting Information

X-ray crystallographic 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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