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Preparation and Crystal Structure of the *trans*(O^5) Isomer of Magnesium(ethylenediamine-*N*,*N*,*N*′-triacetato-*N*′-3-propionato)cuprate(II) Octahydrate, Mg[Cu(ed3ap)]·8H_2O. Stereochemistry of Octahedral Cu(II)–EDTA-Type Complexes in Relation to the Structure of the Ligand

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The hexadentate complex *trans*(O^5)-Mg[Cu(ed3ap)]·8H_2O (**1**) (ed3ap = ethylenediamine-*N*,*N*,*N*′-triacetate-*N*′-3-propionate (4−) ion) has been prepared and its structure established by X-ray crystallography. The complex crystallizes in space group $Pna2_1$ of the orthorhombic crystal system. The structure converged to $R = 0.076$ for 2213 observed reflections. The Cu(II) ion is surrounded by two nitrogen and four oxygen atoms of the ligand, making an elongated rhombic octahedron (tetragonality, $T = 0.859$). The conformations of the chelate rings of the complex anion were found to be an *envelope* (or *twist*) for the five-membered rings and a distorted *skew-boat* (*half-chair*) for the G2 β-alaninate ring. The extremely large total deviation observed for the R2 ring (−11°) is not common for axially coordinated glycinates in M–edta-type complexes. A comparison of the structures of octahedral Cu(II)–edta-type complexes shows an expected variation in their stereochemistry, depending on the structure of the ligand and the geometry of the complex. Data for the electronic absorption and reflectance spectra are also reported.

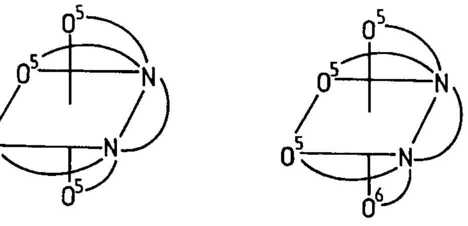
Many transition-metal ions take a coordination number of 6 when complexed with edta (ethylenediaminetetraacetate (4−) ion); such hexadentate structures of $[M(edta)]^{n-}$ are well known (M = Co(III),[1a,b] Cr(III),[2] Fe(III),[3] Mn(III),[4] Zn(II),[5a] Cu(II),[5a—d] Co(II)[6] or Ni(II).[7] The bonding angles exhibited by these complexes are strained, as shown by the significant deviation from ideal values. The ethylenediamine ring (E ring) and two in-plane glycinate rings (G rings) are more strained than the axially coordinated glycinate rings (R rings). Another ligand displaces a G ring more easily than an R ring,[8] and such a complex of $[Cu(H_2edta)(H_2O)]$ (the edta acting as a pentadentate) has been well established.[9]

The edta-like ligands with longer (diamine or carboxylate) chains are likely to function as hexadentate ligands with larger metal ions and allow the complexes to attain octahedral angles closer to the ideal with apparently less strain in the M–L bonds by forming (as dominant) less-strained isomers.[10]

The ethylenediaminetetra-3-propionate (4−) ion (edtp), forming four β-alaninate rings, was found to be hexadentate in complexes of Co(III),[11] Cr(III),[11] Ni(II)[12] or Rh(III).[13] Contrary to this, the edtp ligand acts as a pentadentate in the square-pyramidal $[Cu(edtp)]^{2-}$ complex; this dominant geometry was verified crystallographically.[14] However, the hexadentate tetragonal octahedral Cu(II) complexes of some other edta-type ligands that form six-membered rings, such as the favored *trans*(O^6)-Cu(II) isomers of the 1,3-pddadp (1,3-propanediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate (4−) ion) and the Λ-*trans*(O^5)-Cu(II) isomer of the *SS*-edds (2*S*,2*S*′-ethylenediamine-*N*,*N*′-disuccinate (4−) ion), have also been established.[15—17]

With respect to edta complexes,[1—7] the strain in-plane is eased for the hexadentate $[M(1,3\text{-pdta})]^{n-}$ complexes (1,3-pdta = 1,3-propanediaminetetraacetate (4−) ion) containing in-plane six-membered diamine (T) ring, as evidenced in their crystal structures (M = Fe(III),[18] Co(III),[19] Cr(III),[20] Rh(III),[20] Ni(II),[21] V(III)[22] or Cu(II)[23]).

The unsymmetrical ed3ap ligand with hexadentate coordination can yield two geometrical isomers differing in the position of the six-membered ring: *trans*(O^5) (I) and *trans*(O^5O^6) (II) (Fig. 1), both having C_1 molecular symmetry. Only one, the favored less-strained *trans*(O^5) isomer of the $[M(ed3ap)]^-$ complex (M = Co(III)[24] or Cr(III)[25]), was isolated and characterized. The same isomer (*trans*(O^5), Fig. 1) was found to be favored in the complex Mg[Cu(ed3ap)]·8H_2O (**1**) for which X-ray data are reported here. The structural parameters of this complex and the other tetragonal octahedral Cu(II)–edta-type complexes are compared and discussed in relation to their stereochemistry and the structure of the ligand. The electronic absorption spectra of related complexes are also discussed.



I
trans(O^5)

II
trans(O^5O^6)

Fig. 1. Two possible geometrical isomers of the $[Cu(ed3ap)]^{2-}$ complex.

Experimental

Ethylenediamine-*N*-acetic acid dihydrochloride dihydrate (Hedma·2HCl·2H_2O) was prepared by using a previously described procedure.[26] Other commercially obtained reagent-grade chemicals were used without further purification.

Ethylenediamine-*N*,*N*,*N'*-triacetic-*N'*-3-propinic Acid (H_4ed3ap) and Ethylenediamine-*N*-diacetic-*N'*-di-3-propionic Acid (H_4*u*-eddadp) (Condensation Mixture). A mixture containing unsymmetrical edta-type ligands (ed3ap and *u*-eddadp) was prepared by gradual condensation of ethylenediamine-*N*-acetic acid dihydrochloride dihydrate (Hedma·2HCl·2H_2O, 22.70 g, 0.1000 mol) with 3-chloropropionic acid (21.70 g, 0.2000 mol) and then chloroacetic acid (18.90 g, 0.2000 mol) in aqueous NaOH solution by using procedures of Radanović et al.[24a,25a] The obtained mixture contained of several edta-type ligands (edta, **ed3ap**, ***u*-eddadp**, eddadp (ethylenediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate (4−) ion), eda3p (ethylenediamine-*N*-acetate-*N*,*N'*,*N'*-tri-3-propionate (4−) ion) and edtp), and was recently used for preparing complexes *trans*(O^5)-$[M(ed3ap)]^-$ (assigned as **A**) and $[M(u\text{-}eddadp)]^-$ (assigned as **B**) (M = Co(III)[24] or Cr(III)[25]). Other complexes appearing in very small amounts have been directly prepared from the corresponding ligands. The same condensation mixture was used here for preparing copper(II) complexes.

Preparation of the *trans*(O^5) Geometrical Isomer of Magnesium(ethylenediamine-*N*,*N*,*N'*-triacetato-*N'*-3-propionato)-cuprate(II) Octahydrate, Mg[Cu(ed3ap)]·8H_2O (1). The pH of a condensation mixture containing the edta-type ligands was adjusted to 5 by the addition of a HCl solution. To this solution, solid $CuCl_2$·2H_2O (17.050, 0.1000 mol) was then added, and the reaction mixture was stirred at 40 °C for 2 h. The temperature of the mixture was slowly increased to 70 °C; then, after the pH of the blue solution was adjusted to ca. 7 by the gradual addition of $NaHCO_3$, heating (70 °C) with stirring was continued for an additional 2 h. During this process, the volume of the reaction mixture was reduced to ca. 100 ml, and the deposited NaCl was removed by filtration. The obtained filtrate was then desalted by passing it through a G-10 Sephadex column while eluting with distilled water. One third of this eluate was poured into a 5×60 cm column containing Dowex 1-X8 (200—400 mesh) anion-exchange resin in the Cl^- form. The column was then washed with H_2O and eluted with a 0.05 M $MgCl_2$ solution (1 M = 1 mol dm^{-3}) (ca. 0.5 ml min^{-1}). Six bands with 2^- charge appeared on the column. The order of the bands follows the decrease of the six-membered rings incorporated in the complex. The two complexes are those of known structures: a square-pyramidal $[Cu(edtp)]^{2-}$ [14] (the first eluate) and a tetragonal octahedral $[Cu(edta)]^{2-}$ [5] (the sixth eluate). The identification of other complexes formed in very small amounts (the second and third eluate) requires their preparation directly from the corresponding ligands.

The fourth and fifth bands could not be clearly separated, and represent complexes with unsymmetrical ligands: $[Cu(u\text{-}eddadp)]^{2-}$ (**B**) and *trans*(O^5)-$[Cu(ed3ap)]^{2-}$ (**A**). These eluates were collected together, evaporated to 50 ml and desalted. The obtained eluate was reduced to 30 ml and then allowed to stand in a refrigerator for several days. The blue crystals of *trans*(O^5)-Mg[Cu(ed3ap)]·8H_2O (**1** or **A**) were collected by filtration, washed with ethanol and ether, and air-dried (1.5 g). The complex was recrystallized from warm water. Found: C, 24.82; H, 5.49; N, 5.10%. Calcd for *trans*(O^5)-Mg[Cu(ed3ap)]·8H_2O = $MgCuC_{11}H_{30}N_2O_{16}$ (*FW* = 534.21): C, 24.73; H, 5.66; N, 5.24%. Complex **B** could not be purified and isolated, even when various counter ions were used.

Physical Measurements. *trans*(O^5)-Mg[Cu(ed3ap)]·8H_2O (1): A blue crystal having approximate dimensions of 0.60×0.60×0.60 mm, obtained from aqueous solution, was used for data collection. Intensity measurements were made on a Rigaku AFC7S diffractometer using graphite-monochromated Mo*Kα* radiation (λ = 0.71069 Å) at 23 °C.

Crystal data: $MgCuC_{11}H_{30}N_2O_{16}$ (*FW* = 534.21), orthorhombic, space group $Pna2_1$ (No. 33), a = 12.814(5), b = 14.097(4), c = 11.888(5) Å, V = 2147.4(10) $Å^3$, Z = 4, D_c = 1.65 g cm^{-3}, $F(000)$ = 1116.00, $\mu(\mathrm{Mo}K\alpha)$ = 11.27 cm^{-1}.

The cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using setting angles of 25 carefully centered reflections in the range $29.21 < 2\theta < 29.94°$. The structure was solved by the heavy-atom Patterson methods,[27] expanded using Fourier techniques,[28] and refined by least-squares techniques to R = 0.076 (R_w = 0.076) for 2213 reflections ($I > 3.00\sigma(I)$) of 3076 collected in the range of $2\theta < 57.0°$. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms, excluding those of water molecules, were included, but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[29] All calculations were performed using the teXsan[30] crystallographic software package of Molecular Structure Corporation.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 147203.

Lists of the structure factors, the positional parameters, bond lengths and valency angles, anisotropic thermal parameters for non-hydrogen atoms, positional parameters for the hydrogen atoms, and other relevant crystallographic data have been deposited as Document No. 73054 at the Office of the Editor of Bull. Chem. Soc. Jpn.

The electronic absorption spectra were recorded on a Varian Cary 17D spectrophotometer. For these measurements, about 7×10^{-3} M aqueous solutions were used. The electronic reflectance spectra were run on a Varian Cary 2300 spectrophotometer.

Elemental microanalyses for carbon, hydrogen, and nitrogen were performed by the Microanalytical Laboratory, Faculty of Chemistry, University of Belgrade.

Results and Discussion

Description of the Crystal Structure of *trans*(O^5)-Mg[Cu(ed3ap)]·8H_2O (1). An ORTEP drawing of the complex anion, $[Cu(ed3ap)]^{2-}$, is shown in Fig. 2, where the numbering scheme adopted for the respective atoms is also given.

The structural unit consists of $[Cu(ed3ap)]^{2-}$ and [Mg-

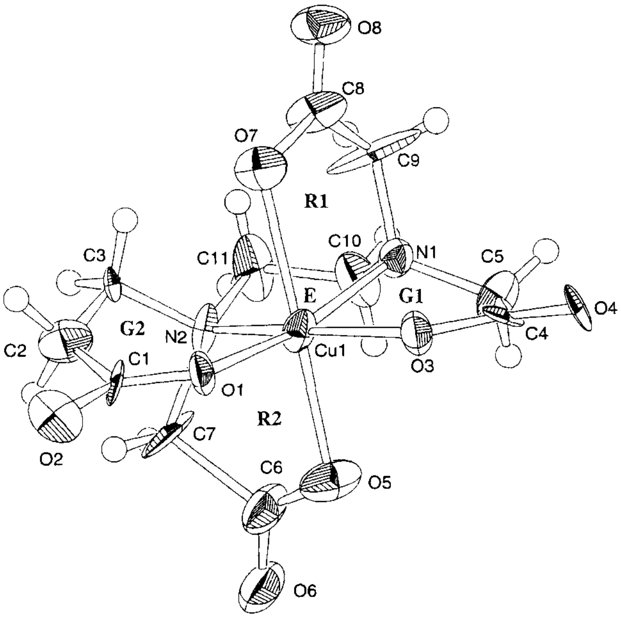


Fig. 2. Molecular structure (ORTEP) of the *trans*(O^5)-$[Cu(ed3ap)]^{2-}$ in *trans*(O^5)-Mg[Cu(ed3ap)]·$8H_2O$.

$(H_2O)_6]^{2+}$ octahedra and two water-solvent molecules. The complex anion of **1** (Fig. 2) represents a *trans*(O^5) isomer with the two glycinate (R1 and R2) rings in the *trans* position and the two (G) rings (glycinate G1 and β-alaninate G2) coordinated in the equatorial plane. The conformations of the chelate rings were found to be: a *twist* for the diamine (*E*) ring (λ for the enantiomorph presented in Fig. 2 having Δ configuration); the *envelope* (or *twist*) for the glycinate rings (R1 relatively flat and R2 and G1 with a significant deviation, unusually large for the R2 ring); and distorted *skew-boat* (*half-chair* (δ)) for the G2 β-alaninate ring with an unusually large deviation.

The four coplanar bonds of the complex anion are nearly equivalent in length, as in the cases for other edta-type Cu(II) complexes.[5a—d,9,15—17,23] However, the two tetragonal bonds for complex (1) (Cu–O(5), 2.26(1); Cu–O(7), 2.34(1) Å) are different one from another, suggesting its distortion toward a square-based pyramidal configuration. The two glycinate (R) rings (*trans*(O^5) coordination) restrict the extent of the distortion[31] for this complex having tetragonality ($T = 0.859$, taken for oxygen ligands) higher than that usually expected for tetragonal octahedral complexes (0.80±0.02).[32,33] The *cis* angles at the Cu(II) ion range from 77.7(4)° to 98.0(2)° and the *trans* ones are: N(1)–Cu–O(1), 167.9(4)°; N(2)–Cu–O(3), 164.0(4)°; and O(5)–Cu–O(7), 171.6(3)°. With respect to edta–Cu(II) complexes,[5] the presence of the β-alaninate (G2) ring in complex **1** (Fig. 2) causes changes in the equatorial valency angles. The O–Cu–O of **1** (98.0(2)°) is larger than the 90° expected for a regular octahedron, but much less with respect to those of hexadentate edta–Cu(II) complexes (av 106.7(2.7)°).[5] Other equatorial valency angles (N–Cu–N and N–Cu–O) in these structures are not very much different. Both axially coordinated acetate groups show a delocalization of electrons within the carboxylate group, while the carbon–oxygen distances of the G1 and G2 rings differ in length, indicating localization of the π-electron pair at the bonds: C(4)–O(4) = 1.17(1) Å (carbon-non-coordinated oxygen for G1) and C(1)–O(1) = 1.21(1) Å (carbon-coordinated oxygen for G2).

The $[Cu(ed3ap)]^{2-}$ and $[Mg(H_2O)_6]^{2+}$ octahedra form discrete units. The presence of thirty two water molecules and the same number of carboxylate oxygens in the unit cell makes the system of hydrogen bonds very complicated. Some of them involving the water molecules from magnesium coordination sphere are very strong [O(9)···O(8), 2.64(2); O(11)···O(6), 2.65(1); O(14)···O(5), 2.65(1) Å (i = $x,y,z+1$)].

Structural Parameters Correlating Stereochemistry of Tetragonal Octahedral Cu(II)–edta-type Complexes. Tetragonal octahedral Cu(II)–edta-type complexes of known structures are listed in Table 1 (complexes **1**—**9**) for which copper-ligand bond-length data are given. The observed individual values, R_S and R_L, for the listed complexes correlate well the local molecular stereochemistry of the Cu(II) ion.[32,33] The extent of distortion of these complexes is restricted by chelation of the multidentate edta-type ligand,

Table 1. Copper-Ligand Bond-Length Data for Tetragonal Octahedral Cu(II)–edta-Type Complexes Involving Mixed (Nitrogen–Oxygen) Donor Atoms

Complex		R_S	R_L	T	Asymmetry in tetragonal bonds (ΔÅ)	Ref.
trans(O^6)-[Cu($H_2$1,3-pddadp)]·$1.5H_2O$	(**2**)	1.954	2.448	0.798	0.014	15)
trans(O^6)-Na_2[Cu(1,3-pddadp)]·$NaNO_3$·$2H_2O$	(**3**)	1.953	2.445	0.799	0.000	16)
trans(O^5)-Mg[Cu(*SS*-edds)]·$7H_2O$	(**4**)	1.984	2.425	0.818	0.242	17)
$[Cu(en)_2(H_2O)_2][Cu_2(edta)_2Cu(en)_2]$·$10H_2O$	(**5**)	1.959	2.337	0.838	0.028	5c)
K_2[Cu(edta)]·$3H_2O$	(**6**)	1.978	2.302	0.859	0.157	5b)
trans(O^5)-Mg[Cu(ed3ap)]·$8H_2O$	(**1**)	1.975	2.30	0.859	0.080	This work
Mg[Cu(1,3-pdta)]·$8H_2O$	(**7**)	1.974	2.272	0.868	0.000	23)
$[Mn(H_2O)_4]$[Cu(edta)]·$2H_2O$	(**8**)	1.991	2.252	0.884	0.074	5a)
$[Cu(H_2edta)(H_2O)]$[a]	(**9**)	2.066	2.291	0.902	0.176	9)

a) Ligand acting as a pentadentate, (the tetragonality is taken as the comparison of the Cu–N lengths). Other complexes listed are hexadentates, for which the tetragonality given is taken as the comparison of the Cu–O lengths.

and depends on its structure as well as the geometry of the complex. The parameter (*T*) for the listed complexes increases in the order: **2** ≤ **3** < **4** < **5** < **6** ≤ **1** < **7** < **8** < **9** (Table 1). We observe that the tetragonality (*T*) (given for oxygen ligands) increases (but not exactly) with decreasing the number of six-membered rings incorporated in the complex (complexes **2**—**4**, **1**, **7**, and **8**). The variation in the tetragonalities of edta complexes **5**, **6**, and **8** depends on the packing in their structures and the interaction of the axially coordinated carboxylate group involved in the covalent bond with the counter ion. Complexes **2**[15] and **3**[16] (*trans*(O^6) coordination) are much more elongated ($T \approx 0.80$ is the same as that observed for tetragonal octahedral complexes involving monodentate ligands).[31—33] Other complexes considered (**1** and **4**—**9**, *trans*(O^5) coordination) have higher *T* values of 0.818—0.884 (for oxygen ligands) and of 0.902 for **9**[9] (for nitrogen ligands), as was observed for elongated rhombic octahedral complexes.[32] Strictly speaking, the stereochemistry of the copper(II) ion present (Table 1) varies from an elongated tetragonal octahedral (complexes **3** and **7**), through an elongated rhombic octahedral (complex **2**) to (in approximation) the square-based pyramidal configuration (complexes **1**, **4**—**6**, **8**, and **9**).

The total deviation of the octahedral angles [$\Sigma\Delta(O_h)$] sums ca. 44° for *trans*(O^6) complexes (**2** and **3**),[16] 64° for **7**,[21,23] 67° for *trans*(O^5)-ed3ap (**1**), and ca. 84° for edta complexes (**6** and **8**).[16] Among these Cu(II) complexes, the studied complex (**1**) shows unexpected large deviations for some bond-angle chelate rings. The bond-angle chelate-ring sums for the five-membered rings are less than the ideal sum and of −1° (for R1), −11° (for R2), and of −12° (for the G1 and E rings). The unusual large total deviation observed for the R2 ring (−11°) is not common for the axially coordinated glycinates in the M–edta-type complexes. The extremely larger deviation is positive for the six-membered (*β*-alaninate) G2 ring and of 42°. The total deviation about the chelating nitrogen atoms in complex **1** sums to roughly 37° (for N1) and 29° (for N2) and is much greater than that measured for complexes (**2**, **3**, **6**, **8**),[16] and **7**.[21] This complex (**1**) shows small deviations for the Cu–O–C(R1,R2) bond angles (+2° for R1 and +0.5° for R2) expected for elongated tetragonal octahedral Cu(II)–edta-type complexes.[16,21]

Electronic Absorption Spectra and Stereochemistry of Complexes. The ligand field absorption spectra are considered for the complex studied (**1**), having 6-5-5 combination of the ring members in the G-plane and, for comparison, for complexes **2**, **3**, and **7** (having the same 5-6-5 combination of the ring members in the G-plane) of known structures and spectral characteristics[16,23] (Table 2, Fig. 3). The parameter (*T*) describing stereochemistry of individual complexes is also given in Table 2. All blue complexes (complex **1** with C_1 molecular symmetry and complexes **2**,[15] **3**,[16] and **7**,[23] having C_2 molecular symmetry) exhibit single unsymmetrical bands in the expected region[32,34] (Fig. 3). The absorption maxima of complexes correspond to the energy gaps of ${}^2A_{1g}$, ${}^2B_{2g}$, ${}^2E_g \leftarrow {}^2B_{1g}$ state, (the electronic transitions of $d_{x^2-y^2} \leftarrow d_{z^2}$, d_{xy}, d_{xz}, d_{yz}, respectively). The reflectance spectra of these cpmplexes (Table 2), with respect to data taken from solution, are only slightly changed retaining nearly the same shape and position of the band maxima indicating that the geometry of complexes is the same in both, solution and solid state.

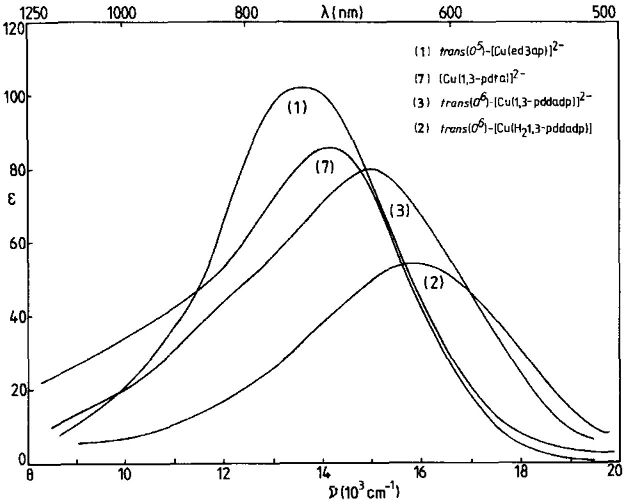


Fig. 3. Electronic absorption spectra of: (**1**) *trans*(O^5)-[Cu(ed3ap)]$^{2-}$ (**7**) [Cu(1,3-pdta)]$^{2-}$ (**3**) *trans*(O^6)-[Cu(1,3-pddadp)]$^{2-}$ and (**2**) *trans*(O^6)-[Cu($H_2$1,3-pddadp)].

The energy of absorption maxima for these tetragonal octahedral complexes decreases in the order: **2** > **3** > **7** > **1** with decreasing ligand field strength (LFS) in the G-plane. Although the parameter (*T*) of complexes (Table 2) increases as the enrgy of absorption maxima decreases, this correlation is not observed to be the linear. The absorption maxima of complexes **2** and **3** (*trans*(O^6) coordination) are separated by 1000 cm^{-1}, but their values of *T* are practically the same ($T \approx 0.80$). The difference in vibrational properties of complexes **2** and **3** arises from the difference in their crystal structures[15,16] (the 1,3-pddadp framework is more rigid for **3**, with covalent bonds only,than for **2**, having hydrogen

Table 2. Absorption Data (Solution or Solid State) for Hexadentate Cu(II)–edta-Type Complexes

Complex		ν $10^3 \times \mathrm{cm}^{-1}$	ϵ	T	Ref
trans(O^5)-[Cu(ed3ap)]$^{2-}$	(**1**)	13.64 (ca. 13.54)[a)]	102	0.859	This work
[Cu(1,3-pdta)]$^{2-}$	(**7**)	14.16 (ca. 14.17)[a)]	86	0.868	23)
trans(O^6)-[Cu(1,3-pddadp)]$^{2-}$	(**3**)	14.97 (ca. 14.97)[a)]	80	0.799	16)
trans(O^6)-[Cu($H_2$1,3-pddadp)]	(**2**)	15.97 (ca. 15.97)[a)]	54	0.798	15)

a) Data for reflectance spectra.

bonds). The increase in the LFS in the G-plane (resulting from strengthening the bonds) is reflected in vibrational properties of the system **2**, namely in the valence vibrations of Cu–L.[16]

The position of band maxima for **2**, **3**, and **7** (with the same 5-6-5 combination of the ring members in the G-plane) was found to be expected.[16,23] In the octahedral complex (**7**) (*trans*(O^5) coordination), with respect to complexes **2** and **3** (*trans*(O^6) coordination), because the stronger axial interaction rises the energy of d_{z^2} orbital and the energy of the $d_{x^2-y^2}$ orbital would therefore be lowered. The lowering of the energy of the d–d transitions for **7** was expected and was found[23] (Table 2). With respect to **7**, the complex **1** shows absorption at lower energy (maximum at 13643 cm^{-1}), for which was found to have nearly the same position as that observed for the $[\mathrm{Cu(edta)}]^{2-}$ complex (maximum at 13700 cm^{-1}).[35a] This suggest that both of these complexes with *trans*(O^5) coordination and different (6-5-5 and 5-5-5) combinatin of the ring members in-plane, have the same LFS in the G-plane. The chelate rings in the G-plane of **1** would tend to be pulled away from the Cu(II) ion due to the strain in the framework as was observed for the in-plane acetates of $[\mathrm{Cu(edta)}]^{2-}$.[35b] Consequently, the energy of the $d_{x^2-y^2}$ orbital for **1** would be lowered and lower energy of d–d transitions for **1** than for **7** would be expected and is found (Table 2).

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