Dinuclear EGTA-copper(II) chelates with imidazole as auxiliary ligand

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Abstract

By reaction of Cu₂CO₃(OH)₂ and H₄EGTA with or without imidazole, the compounds [Cu₂(EGTA)(H₂O)₂] · 2H₂O (1), [Cu₂(EGTA)(Him)₂] · 4H₂O (2) and [Cu₂(EGTA)(Him)₄] · 4H₂O (3) have been prepared. The EGTA acts in a l²-bridging mode, with each half being tripodal-tetradentate in mer-NO₂ + O(ether, apical) or NO + O(carboxy, apical) + O(ether, apical) conformation for compounds 1 and 2 or 3 and [Cu₂(EGTA)(en)₂] · 4H₂O (4), respectively, as expected from the number of N donor atoms (0 and 1 or 2) supplied by the auxiliary ligands. The Cu–O(ether) bond length increases in the series 1 < 2 < 3 < 4, mainly influenced by the coordination number (5 or 6) of the copper(II) atom, the influence of the Jahn–Teller effect on it, giving from 4 + 1 to 4 + 1 + 1 surroundings, and the number of N atoms (1 to 3) among the four closest donor of the Cu(II) atom.

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The ethylenedi(oxyethylene)nitrilo)tetraacetic acid (H₄EGTA, also named 3,12-bis(carboxymethyl)-6,9-dioxa-3,12-diaza-tetradecanedioic acid) is the free-acid form of a common highly polydentate ligand. Most applications of the octadentate EGTA arise from its good calcium ion binding properties against a poor affinity for magnesium ion. In addition of the crystal structure of H₄EGTA [1] a series of reports concerns the octadentate role of EGTA in metal chelates of the ‘hard acid’ metal ions Ca(II) [2,3], Sr(II) [3], Ba(II) [3], Mn(II) [4], Cd(II) [2,5], La(III) [6], Ce(III) [6], Nd(III) [7], Gd(III) [8], Dy(III) [6], Ho(III) [6], Er(III) [7], Zr(IV) [9] and Hf (IV) [9]. On the other hand, it is also known that EGTA acts as a bridging-dinucleating chelating agent for Mg(II) [3], Cu(II) [4,10,11] or W(IV) [12]. In these dinuclear chelates, each half of µ₂-EGTA acts as NO₂-tridentate for Mg(II) or W(IV) (without metal-O ether coordination bond) or as NO₂ + O(ether) tripodal-tetradentate in [Cu₂(EGTA)(H₂O)₂] · 2H₂O (hereafter compound 1) [4,10] and in the closely related mixed-ligand derivative [(en)Cu(µ₂-EGTA)/Cu(en)] · 4H₂O (compound 4) [11]. The binding of en diamine in 1 to give 4 increases the Cu(II) coordination number (from 4 + 1 to 4 + 1 + 1 *), the Cu–O(ether) bond length (from 2.409 Å [10] to 2.756(3) Å [11]) and the Cu–Cu separation in the dinuclear unit (from 7.052 Å [10] to 7.688 Å [11]). Moreover, in compound 1 each half µ₂-EGTA exhibits a mer-NO₂ + O(ether, apical) conformation, whereas in 4 is NO + O(carboxy, apical) + O(ether, apical). A structural comparison of compounds 1 and 4 strongly suggests the possibilities to add one or two imidazole (Him) ligands per Cu(II) atom of the dinuclear Cu₂EGTA chelate. In order to study that and as a part of our program on mixed-ligand Cu(II) complexes with N-heterocyclic auxiliary ligands [13,14], we report the synthesis, structure and properties of compound 1 [15] and its derivatives [Cu₂(EGTA)(Him)₂] (compound 2) [16] and [Cu₂(EGTA)(Him)₄] · 4H₂O (compound 3) [17], which were obtained by reaction of Cu₂CO₃(OH)₂ and H₄EGTA with or without an appropriate amount of Him in water.

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Our structural data for compound 1 (deposited in the CSD database) agree well with those reported by Dyatlova et al. at 283–303 K [10] or by Anderson and Schauer at 143 K [4]. Coordination bond length and selected angles of the studied crystals of compounds 2 and 3 are reported in the legend of Figs. 1 and 2, respectively. In the polymeric compound 2 [18] both metal ions linked by the same μ2-EGTA exhibit different coordination polyhedra, of type 4 + 1 or 4 + 1 + 1s for Cu1 and Cu2, respectively [the asterisk indicating a weak coordination bond Cu2–O5 (2.858(3) Å) slightly shorter than the sum of the Van der Waals radii of O and Cu atoms (1.50 + 1.40 = 2.90 Å)]. In the crystal, the polymeric arrangement is generated by dinuclear complex units sequentially bridged by carboxylate groups in the syn-anti conformation, by means of a Cu2–O5 bond, running through a twofold screw axis parallel to the a-axis and reinforced by a N–H···O(carboxy) hydrogen bond. Another N–H···O(carboxy) hydrogen bond links polymeric chains building up 2D layers, parallel to the ab plane, which superpose along the c-axis. Any H-bonding interaction contributes to the inter-layer interactions. Interestingly, the dihedral angle defined by the Him plane and the mean plane of the four closest donor atoms for Cu1 and Cu2 are still different (8.34° and 32.80°, respectively). It is also important to note that each half EGTA ligand exhibits a mer-NO2 + O(ether, apical) conformation in compounds 1 (without Him) and 2. The dinuclear complex molecule of compound 3 [18] is centrosymmetric and the Cu(II) exhibits a distorted octahedral coordination of the type 4 + 1 + 1s. Once more, in this case, the longest distance corresponds to the apical Cu–O(ether) bond. Because of the well known affinity between the Him ligand (a borderline base of Pearson) and the Cu(II) (a borderline acid of Pearson), both Him ligands are cis-coordinated to the metal among the four closest donors. They fall nearly perpendicular to each other (dihedral angle 87.08°) and define relevant dihedral angles with the mean plane of the four closest donor atoms (32.85° and 78.34°). Twelve cis-(bis-imidazole)copper(II) structures are deposited in the Cambridge Structural Database (CSD, ver 5.26, August 2005 update) with Him-1/Him-2 dihedral angles ranging from 52.3° [19] and 89.2° [20]. In contrast, trans-Cu(Him)2 structures show nearly coplanar Him ligands (with some exceptions). The cis-coordination of the two Him ligands, as referred, represents that each half EGTA ligand in 3 adopts a forced NO + O(carboxy, apical) + O(ether, apical) coordination, closely similar to that previously reported for compound 4 (with one en ligand instead of two Him ligands) [11]. A comparison of compounds 1 to 4 reveals that the Cu–O(ether) bond distance (Å) increases in the series 1 [2.413(2)] < 2 [2.547(3), average] < 3 [2.609(2)] < 4 [2.756(3)]. Comounds 1 and 2 approach to five-coordinated Cu(II) atoms with CuNO3 + O(ether) (1) or CuN2O2 + O(ether) (2) chromophores (ignoring the very weak coordination bond which polymerize compound 2). On the other hand, compounds 3 and 4 have six-coordinated Cu(II) atoms with CuN2O3 + O(ether) chromophore. The referred series of Cu–O(ether) distance seems influenced by three factors: (1) The coordination number of the metal atom. (2) The distortion of the Jahn–Teller effect on the Cu(II) coordination polyhedra. (3) The basicity of the four closest donors. It is largely assumed that in related coordination...
compounds an increase in the coordination number represents an increase in the ‘averaged metal-donor distance’. In copper(II) complexes, where the distortion of the coordination polyhedron is dominated by the Jahn–Teller effect, we should expect four closest donors (with Cu–O or Cu–N bond of ca. 2 Å) and one or two axial/distal lone pairs. A comparison of 1 and 2 or 3 and 4 revealed that the incoming of one Him instead H2O or two Him instead en represents an enlargement of the Cu–O(ether) bond. Thus, we found that for both five and six-coordinated compounds the Cu–O(ether) distance increases with the number and basicity of the N atoms among the four closest donors of the Cu(II) atom (irrespectively of the averaged metal-donor distance in the plane of the four closest donor atoms). In contrast, a similar trend is not observed for the Cu···Cu separation (Å) between metal atoms chelated by each μ2-EGTA, where the series is 2 [6.994(1)] < 3 [7.054(1)] < 4 [7.266(1)] < 5 [7.688(1)]. Perhaps that is due to extra shortening of the Cu···Cu separation in compound 2 because of its particular 1D polymeric structure.

We can conclude that the aqua equatorial ligand of compound 1 can be replaced by the Him ligand without modify the mer-NO2 + O(ether, apical) conformation of the half μ2-EGTA ligand in compounds 1 and 2. In addition, working with auxiliary ligand in excess, it is possible to bind two Him per Cu(II) atom as in compound 3, in such a way that each half of μ2-EGTA exhibits a NO + O(carboxy, apical) + O(ether, apical) in the Cu(II) coordination polyhedron of compounds 3 and 4. The increasing number and basicity of N atoms among the four closest donors for Cu(II) elongates the weak Cu–O(ether) bond or interaction, but each half of μ2-EGTA retains the tripodal-tetradentate role in all LCu(μ2-EGTA)L complexes of known structure irrespectively of the auxiliary ligand L = H2O, Him (one or two) or en.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis of compounds [Cu2(EGTA)(H2O)]2·2H2O (1), [Cu2(EGTA)-(Him)]2·2H2O (2) and [Cu2(EGTA)-(Him)]2·4H2O (3), have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 292578, 292579 and 297109, respectively. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.05.023.

References

[15] Compound 1. Synthesis: Cu3CO3(OH)2 (2 mmol) and H2EGTA (2 mmol) were reacted in water (100 mL) with controlled heat, stirring and vacuum. The resulting blue solution (A) was filtered and air-dried. Yield: 76.46% (0.88 g). Elemental analysis for Cu4H2Cu2N2O4·3H2O calcld. C, 29.22; H, 4.90; N, 4.87; found: C, 29.15; H, 5.33; N, 4.94%. FT-IR (KBr disk, cm−1): 3345, 3115 and 1626 of (C–O–C). Electronic
Compound 2. Synthesis: to a stirred solution A prepared as in [15], 2 mmol of Him was added. The dark blue solution was filtered and evaporated at r.t. to produce the desired compound in a good yield (90%, 1.15 g). Crystals were grown by evaporation of a concentrated aqueous solution (~5%). Elemental analysis for C_{20}H_{28}Cu_{2}N_{6}O_{10}: calcd. C, 37.56; H, 4.41; N, 13.14%; found: C, 37.78; H, 4.88; N, 13.22%. FT-IR (KBr disk, cm^{-1}): 3162, 1550 and 760 from Him, 1609, 1592 and 1080 from EGTA. Electronic spectrum (cm^{-1}): 15220. ESR: isotopic g = 2.07. Cu = 1.81 BM (r.t.). TGA: pyrolysis of EGTA in three steps (220–450 °C) to give CuO.

Compound 3. Synthesis: to a stirred solution A prepared as in [15], 8.8 mmol (10% in excess) of Him was added. The dark blue solution was filtered and evaporated on a crystallization device. Yield: 79.5%, 1.35 g. Elemental analysis for C_{26}H_{44}Cu_{2}N_{10}O_{14}: calcd. C, 36.83; H, 5.23; N, 16.52; found: C, 37.07; H, 5.84; N, 16.82%. FT-IR (KBr disk, cm^{-1}): 3433 and 1623 from H_{2}O, 3140, 1539 and 755 from Him, 1608, 1586, 1399, 1385, 1100 and 1070 from EGTA. Electronic spectrum (cm^{-1}): 12515. ESR: isotopic g ~ 2.08. \( \mu_{\text{Cu}} = 1.87 \text{ BM (r.t.)} \). TGA: water loss 90–150 °C; calcd. for 4H_{2}O 8.56%, exp. 9.87% and pyrolysis of EGTA (150–480 °C, three steps) to give CuO (calcd. 18.76%, exp. 17.86%).