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New symmetrical dinucleating ligand based assembly of bridged dicopper(II) and dizinc(II) centers: Synthesis, structure, spectroscopy, magnetic properties and glycoside hydrolysis

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ABSTRACT

Two dinuclear copper(II) complexes $[Li(H_2O)_3(CH_3OH)]_4[Cu_2Br_4][Cu_2(cpdp)(\mu\text{-}O_2CCH_3)]_4(OH)_2$ (**1**), $[Cu(H_2O)_4][Cu_2(cpdp)(\mu\text{-}O_2CC_6H_5)]_2Cl_2\cdot 5H_2O$ (**2**), and a dinuclear zinc(II) complex $[Zn_2(cpdp)(\mu\text{-}O_2CCH_3)]$ (**3**) have been synthesized using pyridine and benzoate functionality based new symmetrical dinucleating ligand, *N*,*N*′-Bis[2-carboxybenzomethyl]-*N*,*N*′-Bis[2-pyridylmethyl]-1,3-diaminopropan-2-ol (H_3cpdp). Complexes **1**, **2** and **3** have been synthesized by carrying out reaction of the ligand H_3cpdp with stoichiometric amounts of $[Cu_2(O_2CCH_3)_4(H_2O)_2]$, $CuCl_2\cdot 2H_2O/C_6H_5COONa$, and $Zn(CH_3COO)_2\cdot 2H_2O$, respectively, in methanol in the presence of NaOH at ambient temperature. Characterizations of the complexes have been done using various analytical techniques including single crystal X-ray structure determination. The X-ray crystal structure analyses reveal that the copper(II) ions in complexes **1** and **2** are in a distorted square pyramidal geometry with Cu—Cu separation of 3.455(8) Å and 3.492(1) Å, respectively. The DFT optimized structure of complex **3** indicates that two zinc(II) ions are in a distorted square pyramidal geometry with Zn—Zn separation of 3.492(8) Å. UV–Vis and mass spectrometric analyses of the complexes confirm their dimeric nature in solution. Furthermore, ^1H and ^{13}C NMR spectroscopic investigations authenticate the integrity of complex **3** in solution. Variable-temperature (2–300 K) magnetic susceptibility measurements show the presence of antiferromagnetic interactions between the copper centers, with $J = -26.0\ cm^{-1}$ and $-23.9\ cm^{-1}$ ($\hat{H} = -2JS_1S_2$) in complexes **1** and **2**, respectively. In addition, glycosidase-like activity of the complexes has been investigated in aqueous solution at pH ~ 10.5 by UV–Vis spectrophotometric technique using *p*-nitrophenyl-α-D-glucopyranoside (**4**) and *p*-nitrophenyl-β-D-glucopyranoside (**5**) as model substrates.

1. Introduction

Dinuclear metal complexes with two metal ions in close proximity have received a great deal of attention considering their new reactivity patterns, different physical and magnetic properties [1–7]. In this context, considerable efforts have been directed toward the synthesis and characterization of dinuclear copper(II) complexes due to their presence in hemocyanin, tyrosinase, laccase, and ascorbate oxidase [8–11]. The μ-alkoxo-μ-X (X = carboxylate, pyrazolate, azide and nitrite) hetero-bridged dinuclear copper(II) complexes can be considered as special class of exchange-coupled systems where the magnetic properties are more dependent on the second bridging ligand (X). They are antiferromagnetic to weakly ferromagnetic for X = carboxylate, weakly to strongly antiferromagnetic for X = pyrazolate, strongly antiferromagnetic for X = azide, and moderately antiferromagnetic for X = nitrite [12,13]. The literature study reveals that most of the μ-alkoxo-μ-X bridged dinuclear copper(II) systems are antiferromagnetically coupled, whereas ferromagnetic interaction is observed only in few μ-alkoxo-μ-carboxylato bridged complexes [14].

Zinc(II) ion is essentially important in several biological processes. Examples of enzymes that incorporate two zinc centers include metallo-β-lactamases [15], aminopeptidases [16] and alkaline phosphatases [17]. In these enzymes, two zinc(II) ions are

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connected to each other involving carboxylate functionality of amino acid residue and sometime solvent molecule (H_2O or OH^-) with Zn—Zn separation ranging from 3.0 to 3.5 Å [18–22]. The catalytic activity of these zinc containing enzymes is mainly dependent on the bridging groups that hold the two zinc(II) ions at a suitable distance giving a fundamental contribution to the substrate orientation and activation.

So, the model studies with simple dinuclear copper(II) and zinc (II) complexes are becoming more important in understanding the biological functions of dimetallic cores [23–25]. Generally, in a dimetallic system, one metal ion is responsible for substrate binding while the other delivers the activated solvent as nucleophile for hydrolysis. The dinuclear copper(II) and zinc(II) complexes, with either one loosely bound apical exogeneous ligand or coordinatively unsaturated position, have the potential for binding of biologically important sugar substrates [1,26–28]. In this regard, the synthetic metallohydrolases catalyzing glycosidic bond cleavage are useful for promoting biomimetic transformations of carbohydrates. Recently, Striegler and co-workers [29–32] have contributed enormously to the field of supramolecular glycosidase mimics. In this paper, we report the synthesis, structure, spectral characterization, magnetic properties and glycosidase-like activity of dinuclear copper(II) and zinc(II) complexes of a new symmetrical dinucleating ligand, H_3cpdp.

2. Experimental

2.1. Materials and methods

2-Carboxybenzaldehyde, 2-picolylchloride hydrochloride, 1,3-diamino-2-propanol, *p*-nitrophenyl-α-D-glucopyranoside, *p*-nitrophenyl-β-D-glucopyranoside and lithium hydroxide were purchased from Sigma–Aldrich Chemie GmbH, Germany. Copper (II) acetate monohydrate, copper(II) chloride dihydrate, zinc(II) acetate dihydrate and sodium benzoate were purchased from Merck, India. CAPS buffer was purchased from SRL, India. All other chemicals and solvents were reagent grade materials and were used as received without further purification. Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 CHNS/O Series II elemental analyzer. FTIR spectra were obtained on a Perkin–Elmer L120-000A spectrometer (200–4000 cm^{-1}). UV–Vis spectra were recorded using a Shimadzu UV 1800 (190–1100 nm; 1 cm quartz cell) spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a Bruker AC 400 NMR spectrometer. The ESI mass spectra were recorded using a Micromass Q-Tof Micro™ (Waters) mass spectrometer. The potentiometric titration of the ligand was carried out using a Mettler Toledo Seven Compact S220 digital Ion/pH meter in aqueous solution. Thermogravimetric (TG) analysis of the ligand was performed on a NETZSCH STA 449F3 thermal analyzer. The variable temperature magnetic susceptibility data were collected in the temperature range of 2–300 K under an applied field of 1 Tesla on powdered microcrystalline sample with a SQUID magnetometer (MPMS-7, Quantum Design). Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants [33]. The temperature dependent magnetic contribution of the holder was experimentally determined and subtracted from the measured susceptibility data. The program phi1.9 [34] was used for spin Hamiltonian simulations of the data.

2.2. Synthesis of N,N′-Bis[2-carboxybenzomethyl]-N,N′-Bis[2-pyridylmethyl]-1,3-diaminopropan-2-ol (***H_3cdp***)

A solution of 2-carboxybenzaldehyde (4.643 g, 30.00 mmol) and NaOH (1.200 g, 30.00 mmol) in 100 ml methanol was added to 1,3-diamino-propan-2-ol (1.424 g, 15.00 mmol) in 20 ml methanol. The yellowish mixture obtained was heated to 60 °C while stirring for ~4 h. Then the reaction product was cooled in an ice-bath. Excess $NaBH_4$ (1.500 g, 39.50 mmol) was added in portions to the cold solution while stirring. The yellow color was slightly discharged. After 30 min 2 ml conc. HCl was added drop wise to destroy the excess $NaBH_4$. Acidification of the solution to pH ~ 5 by further addition of conc. HCl resulted in the precipitation of white crystalline solid. The white solid was filtered out from mother liquor and washed with water and methanol, and dried at ~80 °C. Yield: 4.95 g (87%). The compound was crystallized from methanol–water solution (1:1; v/v). The product was confirmed by the elemental analysis as **$H_3cdp{\cdot}H_2O$**. *Anal.* Calc. for $C_{19}H_{22}N_2O_5{\cdot}H_2O$: C, 60.63%; H, 6.43%; N, 7.44%. Found: C, 60.25%; H, 6.28%; N, 7.33%. ^1H NMR for sodium salt of the compound (400 MHz, D_2O, 25 °C, δ): 7.46–7.32 (m, 8H), 3.92–3.80 (m, 1H), 2.63 (q, 4H), 2.55 (q, 4H).

2-Picolylchloride hydrochloride (1.640 g, 10.00 mmol) was added in portions to a solution of *N*,*N*′-Bis(2-carboxybenzomethyl)-1,3-diaminopropan-2-ol, **H_3cdp** (1.790 g, 5.00 mmol) and LiOH (0.800 g, 20.00 mmol) in 25 ml of water while stirring. More LiOH (0.400 g, 10.00 mmol) was added to maintain the pH ~ 11 and the reaction mixture was stirred at room temperature for ~28 h. The resulting solution was cooled in an ice bath and acidified with conc. HBr to pH ~ 5. The solution was rotary evaporated under reduced pressure to give a reddish brown gummy product. Then it was extracted in dry methanol and the methanol extract was rotary evaporated to isolate a pure reddish brown gummy product. The product was dried in vacuum over P_4O_{10} and obtained as brown waxy material. The product was confirmed by the elemental and thermogravimetric analyses as **$H_3cpdp{\cdot}LiCl{\cdot}3LiBr{\cdot}14H_2O$**. Yield: 4.018 g (77%). *Anal.* Calc. for $C_{31}H_{32}N_4O_5{\cdot}LiCl{\cdot}3LiBr{\cdot}14H_2O$: C, 33.98%; H, 5.51%; N, 5.11%; Cl, 3.24%; Br, 21.88%. Found: C, 33.88%; H, 5.54%; N, 5.27%; Cl, 2.91%; Br, 21.49%. FTIR (cm^{-1}): ν = 3389(b), 2084(b), 1634(s), 1567(vs), 1441(s), 1399(s), 1298(s), 1154(s), 1094(s), 972(s), 761 (s). ^1H NMR (400 MHz, D_2O, room temperature, δ): 8.47 (d, 2H), 7.81 (t, 2H), 7.64 (d, 2H), 7.39–7.51 (m, 8H), 7.27 (d, 2H), 4.47 (d, 8H), 4.01–4.20 (m, 1H), 3.38 (d, 2H), 3.13 (t, 2H). ^{13}C NMR (400 MHz, D_2O, room temperature, δ): 174.65, 149.32, 148.91, 143.99, 141.31, 138.87, 137.23, 133.20, 130.88, 130.44, 125.01, 124.68, 60.47, 60.25, 57.50, 57.11. Mass spectrum (ESI): *m*/*z* 565 (100%) ($M^+ = \{H_3cpdp{\cdot}H_2O + Li\}^+$), 559 (81%) ($M^+ = \{H_3cpdp{\cdot}H_2O + H\}^+$). TGA analysis: loss of H_2O {136 °C–273 °C: 23.00% (Calculated); 23.35% (Found)}; loss of CO_2 {290 °C–367 °C: 8.03% (Calculated); 8.39% (Found)}.

2.3. Synthesis of $[Li(H_2O)_3(CH_3OH)]_4[Cu_2Br_4][Cu_2(cpdp)(\mu\text{-}O_2CCH_3)]_4(OH)_2$ (***1***)

A methanol solution (10 ml) of $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ (0.184 g, 0.462 mmol) was slowly added to a magnetically stirred methanol solution (15 ml) of ligand H_3cpdp (0.506 g, 0.462 mmol) and NaOH (0.055 g, 1.386 mmol) at ambient temperature during a period of 10 min. The reaction mixture was stirred for 1 h resulting in a green solution. The solution was filtered to discard any insoluble precipitate. The X-ray quality green block shaped single crystals were obtained by slow ether diffusion into the clear filtrate diluted by water after 3–4 days. Yield: 0.301 g (70%). *Anal.* Calc. for $C_{136}H_{170}N_{16}O_{46}Br_4Li_4Cu_{10}$: C, 43.59; H, 4.57; N, 5.98; Br, 8.53; Cu, 16.96. Found: C, 43.47; H, 4.65; N, 5.89; Br, 8.86; Cu, 16.81. FTIR (cm^{-1}): ν = 3400(b), 1615(s), 1586(s), 1562(s), 1483(s), 1448(s), 1385(s), 1105(s), 1052(s), 872(s), 760(s), 666(s), 614(s). UV–Vis spectra (H_2O): λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 678 (146), 261 (4229). Mass spectrum (ESI): *m*/*z* 663 (100%) ($M^+ = \{[Cu_2(cpdp)]\}^+$), 745 (80%) ($M^+ = \{[Cu_2(cpdp)(O_2CCH_3)] + Na\}^+$).