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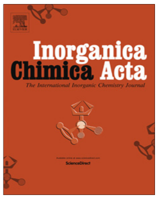

Synthesis, characterization, X-ray structure, spectroscopic and electrochemical studies of copper and zinc complexes with two new polydentate ligands

Seyed Abolfazl Hosseini-Yazdi [a,*], Azadeh Mirzaahmadi [a], Parvin Samadzadeh-Aghdam [a], Ali Akbar Khandar [a], Ghodrat Mahmoudi [a], W. Scott Kassel [b], William G. Dougherty [b]

[a] *Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz 51666-14766, Iran*
[b] *Department of Chemistry, Villanova University, 215 Mendel Science Center, Villanova, PA 19085, USA*

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ABSTRACT

Two new N_2O_5 donor type ligands, 2-{[(2-{2-hydroxy-3-[2-({[(2-hydroxyphenyl)methylidene]amino}methyl)phenoxy]propoxy}benzyl)imino]methyl}phenol (**H_3L1**) and 2-[({2-[2-hydroxy-3-{[(2-hydroxybenzyl)amino]methyl}phenoxy)propoxy]benzyl} amino)methyl]phenol (**H_3L2**) and their metal complexes with Cu(II) and Zn(II) salts were prepared and characterized by NMR, FT-IR, UV–Vis absorption spectroscopy, single crystal X-ray diffraction, CHN elemental analysis and cyclic voltammetry. Complexes were formulated as Cu_2**L1**(CH_3COO) (**1**), Cu_2**L2**(CH_3COO) (**2**), Zn_3**L1**$(CH_3COO)_3$ (**3**), and Zn_2**L2**$(CH_3COO)\cdot 0.5H_2O$ (**4**). Cyclic voltammograms of copper(II) complexes recorded in DMF showed two quasi-reversible reduction peaks related to $(Cu^{II}–Cu^{II}/Cu^{II}–Cu^{I})$ and $(Cu^{II}–Cu^{I}/Cu^{I}–Cu^{I})$ couples and their corresponding oxidation potential peaks. Both Zn(II) complexes display only one irreversible reduction wave which can be attributed to the Zn^{II}/Zn^{0} redox system. The X-ray structure analysis of the trinuclear complex $[Zn_3$**L1**$(CH_3COO)_3]$ shows that Zn(II) centers are coordinated to five atoms. The core of the structure is a triangle of Zn atoms. The Zn centers are bridged with deprotonated alkoxide and phenolate oxygens and two acetate groups. The π–π interactions between phenyl rings of the adjacent molecules in the complex are significant. The centroid–centroid distance is 3.6933(15) Å.

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1. Introduction

Polynuclear transition metal chemistry is an area of modern science which crossing between the sciences of chemistry, biology and physics. Molecular multimetallic compounds have unusual and useful catalytic, optical, biological, photochemical, electronic and magnetic properties [1–11]. Many organic ligands containing N- and O-donor atoms have been systematically studied over recent years, with very successful results in the synthesis of high-nuclearity complexes [12–15,10]. Dicopper(II) complexes with endogenous bridging phenolate ligands are of ongoing interest because of their relevance to copper containing enzymes, tyrosinase and catechol oxidase [16–21]. Most zinc enzymes are classified as hydrolases because they catalyse hydrolysis of such condensed bonds as those in pyrophosphate and esters and in various types of peptides as well [22]. Trinuclear complexes with bridging oxo and carboxylato motifs have received considerable attention due to the isolation and crystallographic characterization of trinuclear active sites of metalloenzymes [23,24]. Cooperativity of metal ions at multinuclear active sites is usually utilized to enhance the catalytic capacity of the model complexes, since the cleavage of the ester bond in the center of enzymes relies on the number of metal ions bound to each substrate [25]. Therefore, one of the synthetic challenges in the research of high nuclearity systems is the design of ligands able to stabilize large nuclearities in order to improve the desired properties. It is interesting to study the coordination behavior of such ligands in the reaction with transition metal ions as well as to study the stoichiometries and geometrical preferences of the resulting species.

In this paper, we describe the preparation of two new N_2O_5 donor type ligands with the ability to accommodate two or more metal ions. Synthesis, characterization, spectroscopic and electrochemical properties of new metal complexes of these ligands were reported. Also the X-ray crystal structure of one of the complexes $[Zn_3$**L1**$(CH_3COO)_3]$ was determined.

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* Corresponding author. Tel.: +98 4113393134; fax: +98 4113340191.
E-mail address: hosseiniyazdi@yahoo.com (S.A. Hosseini-Yazdi).

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2. Experimental

2.1. Materials and general procedures

All reagents and solvents were from Merck or Fluka and were used without further purification but solvents were dried and purified before being used according to the published procedures [26]. 2-[3-(2-Formyl phenoxy)-2-hydroxy propoxy] benzaldehyde (**dialdehyde**) was prepared in a way similar to the reported method using salicylaldehyde and 1,3-dichloro-2-propanol [27]. ^{1}H NMR spectra were collected using Bruker Avance 400 spectrometers. Infrared spectra were obtained on a Bruker Tensor 27 FT-IR spectrometer. Solution UV–Vis spectra were collected using a Shimadzu UV–Vis 1700 spectrometer in DMF. Electrochemical studies were carried out using Autolab PGSTAT 302 ECOCHEMIE. CV measurements were performed using a glassy carbon as working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. The ferrocene/ferrocenium couple (Fc/Fc$^+$; $E_{1/2}$ = 505 mV) was used as a standard but all potentials in the paper are referenced to the Ag/AgCl reference electrode. Solutions containing 10^{-3} M complexes and 0.1 M $LiClO_4$ as supporting electrolyte were deoxygenated by a stream of high purity nitrogen for at least 10 min.

2.2. Synthesis of the ligands

2.2.1. Synthesis of 2-{2-hydroxy-3-[2-(hydroxyliminomethyl)phenoxy]propoxy}benzaldehyde oxime (*dioxime*)

Hydroxylamine hydrochloride (35 mmol, 2.4 g) was dissolved in aqueous NaOH (1.72 g, 50 cm^3 H_2O). The neutralized hydroxylamine solution was added to **dialdehyde** (2 mmol, 1.02 g) in ethanol 96% (100 cm^3) contained in a 250 cm^3 two-necked round-bottomed flask equipped with reflux condensor. The resulting clear solution was refluxed over night. The reaction mixture was cooled to room temperature, poured into hydrochloric acid (2 M, 100 cm^3), and allowed to stand into refrigerator for 1 day. The white precipitate of **dioxime** that formed was filtered off. Then thoroughly washed with water and dried in an oven (40 °C). The white crystalline **dioxime** was used without further purification. Yield: 0.49 g, (75% based on **dialdehyde**). m.p. 170 °C. ^{1}H NMR (DMSO): δ 8.408 (s, 2H, **H**C=NOH), 7.675 (d, 2H, Ar**H**), 7.344 (t, 2H, 2Ar**H**), 7.082 (d, 2H, Ar**H**), 6.956 (t, 2H, Ar**H**), 4.055–4.233 (m, 5H, **H$_2$**C–C**H**(OH)–C**H$_2$**) ppm. Selected FT-IR data (ν/cm^{-1}): 3229 s (OH), 1632 s (C=N), 1597 s, 1490 s, 1454 s (C=C$_{aromatic}$), 1251 s (C–O), 749 s (δ C–H$_{aromatic}$)$_{o.o.p}$.

2.2.2. Synthesis of 1,3-bis[2-(aminomethyl) phenoxy]-2-propanol (*diamine*)

Diamine was prepared by similar procedure to the reported method [28]. **Dioxime** (2.4 mmol, 0.8 g) was dissolved in dry tetrahydrofuran (100 cm^3) under Ar atmosphere in a 250 cm^3 two-necked round-bottomed flask equipped with reflux condensor. The clear solution was cooled to 0 °C in an ice bath, lithium aluminium hydride (13.2 mmol, 0.5 g) was added and the reaction was stirred at 0 °C for 30 min. After which, it was allowed to warm to room temperature. The solution was refluxed for 24 h and then it was allowed to cool to room temperature. Water (7 cm^3) was added, followed by 20% NaOH (7 cm^3) and then more water (7 cm^3) to quench the reaction. The mixture filtered through a sinterglass funnel. After thoroughly washing the lithium salts with dichloromethane (3 × 50 cm^3), the combined filtrates were evaporated and the residue transferred to a separating funnel using dichloromethane (150 cm^3). The organic layer was washed with water (2 × 50 cm^3) and the aquous phase re-extracted with dichloromethane (2 × 50 cm^3). Combined organic layers dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a light brown oil. Yield: 0.44 g (61% based on **dioxime**). ^{1}H NMR as hydrochloride salt (D_2O) δ 7.494 (d, 2H, Ar**H**), 7.410 (d, 2H, Ar**H**), 7.157 (d, 2H, Ar**H**), 7.102 (d, 2H, Ar**H**), 4.604 (m, 1H, C**H**OH), 4.409–4.294 (m, 4H, OC**H**$_2$CH(OH)C**H**$_2$O), 4.230 (d, 4H, ArC**H**$_2$NH$_2$) ppm. Selected FT-IR data (ν/cm^{-1}): 3359 s, 3290, 3175 s (NH$_2$, OH), 3066 w (C–H$_{aromatic}$), 2928 w, 2871w (C–H$_{aliphatic}$), 1593 s, 1490, 1452 (C=C$_{aromatic}$) 1241 s (C–O–C)$_{asym}$, 1038 s (C–O–C)$_{sym}$, 765 s.(δ C–H$_{aromatic}$)$_{o.o.p}$.

2.2.3. Synthesis of 2-{[(2-{2-hydroxy-3-[2-({[(2-hydroxyphenyl) methylidene]amino}methyl)phenoxy]propoxy}benzyl)imino]methyl} phenol (*H$_3$L1*)

Salicylaldehyde (4 mmol, 0.49 g) in dry methanol was added slowly during 1 h to a stirred, hot solution of **diamine** (2 mmol, 0.60 g) dissolved under Ar in dry methanol (70 cm^3) in a 250 cm^3 two-necked round-bottomed flask equipped with reflux condensor and a dropping funnel. The clear yellow mixture was stirred at reflux for 3 h. Evaporation of methanol gave the crystalline product of **H$_3$L1**. Yield: 0.66 g (65%). *Anal.* Calc. for $C_{31}H_{30}N_2O_5$: C, 72.92; H, 5.92; N, 5.49. Found: C, 72.71; H, 5.98; N, 5.34%. ^{1}H NMR ($CDCl_3$): δ 8.346 (s, 2H, ArC**H**N), 7.297–6.765 (m, 16H, Ar**H**), 4.764 (dd, 4H, ArC**H$_2$**), 4.467 (quintet, 1H, C**H**(OH)), 4.193 (d, 4H, ArOC**H$_2$**) ppm. Selected FT-IR data (ν/cm^{-1}): 3448 m (OH), 3064 w (CH$_{aromatic}$), 2923 m (CH$_2$)$_{asym}$, 1638 s (C=N), 1607 s, 1492 s (C=C$_{aromatic}$), 1247 s (C–O–C)$_{asym}$, 1043 s (C–O–C)$_{sym}$, 743 s (δ C–H$_{aromatic}$)$_{o.o.p}$.

2.2.4. Synthesis of 2-[({2-[2-hydroxy-3-{[(2-hydroxybenzyl) amino] methyl} phenoxy) propoxy] benzyl} amino) methyl] phenol (*H$_3$L2*)

Salicylaldehyde (4 mmol, 0.49 g) in dry methanol was added slowly (1 h) to a stirred, hot solution of **diamine** (2 mmol, 0.60 g) was dissolved under Ar in dry methanol (70 cm^3) in a 250 cm^3 two-necked round-bottomed flask equipped with reflux condensor and a dropping funnel. The clear yellow mixture was stirred at reflux for 3 h then was cooled to room temperature, sodium borohydride (10 mmol, 0.38 g) was then added slowly in small portions. After a further 1 h reflux the solvent was evaporated. The resulting oil was transferred to a separating funnel with dichloromethane and water. Then extracted with dichloromethane (3 × 50 cm^3) and the organic layer was washed with water (2 × 50 cm^3). The organic phase was dried with $MgSO_4$. Evaporation of the combined organic layers yielded ligand as a brown oil. Yield: 0.62 g (60%). *Anal.* Calc. for $C_{31}H_{34}N_2O_5$: C, 72.39; H, 6.80; N, 5.33. Found: C, 72.35; H, 6.66; N, 5.44%. ^{1}H NMR as hydrochloride salt (D_2O): δ 7.418 (t, 2H, Ar**H**), 7.272–7.236 (m, 4H, Ar**H**), 7.154 (d, 2H, Ar**H**), 7.006 (t, 2H, Ar**H**), 6.939 (d, 2H, Ar**H**), 6.902–6.867 (m, 4H, Ar**H**), 4.304 (quintet, 1H, C**H**OH), 4.085–4.020 (m, 12H, ArC**H**$_2$, ArOC**H**$_2$) ppm. Selected FT-IR data (ν/cm^{-1}): 3398 m, 3314 m (OH, NH), 3052 w (CH$_{aromatic}$), 2926 w (CH$_2$)$_{asym}$, 2861 w (CH$_2$)$_{sym}$, 1596s, 1489 s, 1456 s (C=C$_{aromatic}$), 1249 s (C–O–C)$_{asym}$, 1039 m (C–O–C)$_{sym}$, 754 s (δ CH$_{aromatic}$)$_{o.o.p}$.

2.3. Synthesis of complexes

2.3.1. Synthesis of Cu$_2$*L1*(CH$_3$COO) (*1*)

An ethanol solution (70 cm^3) of $Cu(CH_3COO)_2 \cdot H_2O$ (2 mmol, 0.40 g) was added dropwise to a hot solution of **H$_3$L1** (0.8 mmol, 0.41 g) dissolved in ethanol too. There was a colour change to green, and reaction mixture was stirred at reflux for 4 h. The mixture stayed at room temperature for 24 h and then green precipitate of complex was formed. Yield: 0.33 g (60% based on **H$_3$L1**). m.p. 180 °C. *Anal.* Calc. for $C_{33}H_{30}Cu_2N_2O_7$: C, 57.14; H, 4.36; N, 4.04. Found: C, 57.45; H, 4.17; N, 4.21%. Selected FT-IR data (ν/cm^{-1}): 3441 m (OH), 3020 w (CH$_{aromatic}$), 2924 s (CH$_2$)$_{asym}$, 2857 m (CH$_2$)$_{sym}$, 1620 s (C=N), 1537 m, 1452 s, 1325 m (C=C$_{aromatic}$, COO$_{acetate}$), 1239 m (C–O–C)$_{asym}$, 1036 m (C–O–C)$_{sym}$, 752 s (δ CH$_{aromatic}$)$_{o.o.p}$.

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