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Synthesis and characterization of copper(II) complexes containing tridentate modified amino acid ligands, $[CuL(H_2O)(Pyz)]$ [L = {(3,5-di-*tert*-butyl-2 hydroxybenzyl)amino}acetic acid and *S*(−)2-(3,5-di-*tert*-butyl-2-hydroxy-benzylamino)-3-methyl-butyric acid; Pyz = pyrazole] and their oxidation to a copper(III) coordinated phenoxyl radical

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Abstract

Two new ternary copper complexes, $[CuL^1(H_2O)\ (Pyz)]$ (**1**) [L^1H_2 = {(3,5-di-*tert*–butyl–2-hydroxybenzyl)amino}acetic acid] and $[CuL^2(H_2O)\ (Pyz)]$ (**2**) [L^2H_2 = 2-(3,5-di-*tert*-butyl-2-hydroxy-benzylamino)-3-methyl-butyric acid; Pyz = pyrazole] have been synthesized. The compounds have been characterized by various techniques including IR, UV–visible, circular dichroism (CD) (**2**) and EPR spectroscopy, electrochemical and magnetic susceptibility measurements. The crystal structure of **1** has been determined. The compound crystallizes in the space group $P2_1/a$, with $a = 10.6217(2)$ Å, $b = 10.1645(2)$ Å, $c = 19.4909(5)$ Å, $\beta = 90.7729(9)°$, $V = 2104.13(8)$ Å^3, $Z = 4$. Cyclic voltammetry of the compounds show two reversible oxidative peaks due to metal centered and ligand centered oxidations. The compounds have been oxidized electrochemically and chemically and the oxidized species have been characterized by UV–visible and EPR spectroscopy.

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1. Introduction

Structural and reactivity studies of metals coordinated to sterically protected phenoxide ligands have been the subject matter of numerous research papers in recent years [1–7]. It has been shown that ligands with bulky substituents in *ortho*- and *para*-positions are capable of generating stable metal coordinated phenoxyl radicals [1–7]. Metal coordinated phenoxyl radicals are important due to their involvement in a number of biochemical [8] and catalytic systems [9,10]. For example, in two metalloenzymes, glyoxal oxidase and galactose oxidase, the copper coordinated tyrosyl radical has been shown to be the active species in the catalytic cycles [6]. Similarly, copper coordinated phenoxides have been shown to be capable of aerial oxidation of alcohols, wherein copper coordinated phenoxyl radicals have been shown to be the active species [9,10]. A large number of these reports deal with metal complexes of tripodal N_2O_2 phenolate ligands [6] or N_2O_2 and N_3O donor

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ligands [7]. Also, it may be noted that in most of the reported mononuclear metal complexes all the coordination positions are satisfied by the same ligand and ternary complexes have not been reported. Recently we have reported a tridentate phenolate ligand having N_1O_2 donor sites [11]. We thought to explore the ligation capability of the ligand towards copper. Our aim was to synthesize ternary complexes of copper using the tridentate ligands along with a monodentate co-ligand. Herein we report the synthesis, characterization and structure of the copper complex, $[CuL^1(H_2O)(Pyz)]$ (**1**) [L^1H_2 = {(3,5-di-*tert*-butyl-2–hydroxybenzyl)amino}acetic acid; Pyz = pyrazole]. Also, reported herein is the synthesis and characterization of a new optically active tridentate ligand, *S*(−)2-(3,5-di-*tert*-butyl-2-hydroxy-benzylamino)-3-methyl-butyric acid (L^2H_2), derived form L-valine, and its copper complex, $[CuL^2(H_2O)(Pyz)]$ (**2**).

2. Experimental

2.1. General remarks

All the chemicals used were reagent grade products. The ligand, {(3,5-di-*tert*-butyl-2-hydroxybenzyl)amino}acetic acid (L^1H_2) was prepared by the reported procedure [11]. ^1H NMR spectra were recorded on a Bruker AC 200, 200 MHz NMR spectrometer in $CDCl_3$ solutions at room temperature. EPR spectra were recorded on a Bruker EMX X-band spectrometer. IR spectra were recorded on a Thermo Nicklet Model 870 FT IR spectrometer. The UV–visible spectra were recorded on a Shimadzu UV 600 spectrophotometer. CD spectral measurements were done in methanol using a JASCO CD polarimeter, model J-810. Specific rotations were measured in methanolic solutions of the compound using a JASCO P1020 polarimeter. Cyclic voltammetry experiments were performed using a fully automated CH Instruments electrochemical analyzer (Model 620a) and a three-electrode set-up consisting of a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. All experiments were performed in dry CH_3CN containing tetra-*N*-butylammonium perchlorate (0.2 mol dm^{-3}) as the background electrolyte. The magnetic measurements were done using the Gouy method. The C, H and N contents were estimated using microanalyses on a Perkin Elmer microanalyser, 2400. For the mass spectral measurements a 1:1 methanol/water solution of the compounds was taken and the mass spectra were recorded on a Waters LCT mass spectrometer using the electrospray ionization (ES^- mode) technique.

2.2. Synthesis of the mono sodium salt of S-(−)2-(3,5-di-tert-butyl-2-hydroxy-benzylamino)-3-methyl-butyric acid (L^1H_2)

L-Valine (1.17 g; 10 mmol) was dissolved in an aqueous solution (20 cm^3) of NaOH (0.450 g; 11.25 mmol). To this was added 40% aqueous formaldehyde (8 cm^3; 100 mmol) and the solution was heated for 20 min on a water bath. To the reaction solution was added an ethanolic solution (40 cm^3) of 2,4-di-*tert*-butyl phenol (2.06 g; 10 mmol) dropwise. The reaction mixture was then heated for 5 h on an oil bath at 50 °C. The reaction solution was cooled to room temperature and allowed to stand overnight. The precipitated mono sodium salt of the ligand 2-(3,6-di-*tert*-butyl-2-hydroxy-benzylamino)-3-methyl-butyric acid (L^2H_2) was filtered washed with water and hexane and finally dried in vaccuo. Yield: 3.08 g; 86.5%. *Anal.* Calc. for $C_{20}H_{32}NO_3Na$ (357.46): C, 67.20; H, 9.02; N, 3.92. Found (%): C, 67.18; H, 8.89; N, 3.88. IR (KBr pellet, ν [cm^{-1}]): 3434, 2959, 2361, 1585, 1476, 1226, 1122. UV–visible [λ_{max} (nm) (ε)]: 279 (2205), 227 (3056). ^1H ($CDCl_3$) (ppm): 1.00 (br, m, 6H), 1.26 (s, 9H), 1.45 (s, 9H), 2.21 (br, 1H), 3.35 (d, $J = 4$ Hz), 3.89 (d, $J = 14$ Hz, 1H), 4.36 (d, $J = 14$ Hz 1H), 6.95 (d, $J = 1$ Hz, 1H), 7.30 (d, $J = 1$ Hz, 1H). Mass (significant peak and its assignment): *m*/*z* 334.2212 [$C_{20}H_{32}NO_3^-$, M^-].

2.3. Syntheses of $[CuL^1(H_2O)(Pyz)]$ (1) and $[CuL^2(H_2O)(Pyz)]$ (2)

Compounds **1** and **2** were prepared by a similar procedure and the general procedure is given below. The ligand (1 mmol) was dissolved in methanol (25 cm^3) in a beaker. To this was added solid NaOH (0.08 g; 2 mmol) followed by addition of water (5 cm^3) (Solution A). Pyrazole (1 mmol) was added to a methanolic solution (10 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol) in another beaker (Solution B). To this solution (Solution B) was then added the solution of sodium salt of the ligand (Solution A) and the reaction solution was stirred for an hour. The reaction solution on standing overnight afforded crystalline **1** or **2**. The compound was filtered, washed with water, and finally recrystallized from acetonitrile. Recrystallization of **1** from acetonitrile afforded crystals suitable for X-ray diffraction. Yield: 0.335 g; 76% (**1**), 0.338 g; 70% (**2**). *Anal.* Calc. for $C_{20}H_{31}CuN_3O_4$ (**1**) (441.02): C, 54.47; H, 7.08; N, 9.53. Found: C, 54.40; H, 7.02; N, 9.47%. *Anal.* Calc. for $C_{23}H_{37}CuN_3O_4$ (483.1) **2**: C, 57.18; H, 7.72; N, 8.70. Found: C, 57.08; H, 7.67; N, 8.61%. IR (KBr pellet, ν [cm^{-1}]) (**1**): 3436, 2956, 1631, 1057, 1140, 1111, 939, 758. IR (KBr pellet, ν [cm^{-1}]) (**2**): 3439, 2958, 1629, 1471, 1384, 1087, 1140, 1114, 759. UV–visible [λ_{max} (nm) (ε)] (**1**): 630 (80), 380 (420), 237 (3887), 278 (1890); [λ_{max} (nm) (ε)] (**2**): 635 (145), 431 (463), 245 (3945), 293 (3247).

2.4. X-ray crystallographic study

Suitable crystals of $[CuL^1(H_2O)(DMPZ)]$ (**1**) were grown from a dilute acetonitrile solution at room temperature over a period of 5–6 days. The single crystal data was collected on a Nonius Kappa CCD X-ray diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by the Φ scan and ω-scan methods. The

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