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Synthesis, characterization and structure of a new zinc(II) complex containing the hexadentate *N*,*N′*,*N*,*N′*-bis[(2-hydroxy-3,5-di-*tert*-butylbenzyl)(2-pyridylmethyl)]-ethylenediamine ligand: Generation of phenoxyl radical species

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Abstract

This work summarizes the results of our studies on the structural, spectral and redox properties of a mononuclear zinc(II) complex with the new H_2L ligand (H_2L = *N*,*N′*,*N*,*N′*-bis[(2-hydroxy-3,5-di-*tert*-butylbenzyl)(2-pyridylmethyl)]-ethylene diamine). The crystal structure of the complex $[Zn^{II}(HL)] \cdot ClO_4$ (**1**) was determined by X-ray crystallographic analysis. The structure of this complex consists of a discrete mononuclear cation $[Zn^{II}(HL)]^+$, in a strongly distorted geometry with a slight tendency toward a distorted square pyramidal geometry, as reflected by the structural index parameter τ of 0.44. The zinc(II) cation is coordinated to one oxygen and four nitrogen atoms: the pyridine nitrogen atoms (N22 and N32), tertiary amine nitrogen atoms (N1 and N4) and phenolate oxygen atom (O10). ^1H and ^{13}C NMR spectral data show a rigid solution structure for **1** in agreement with X-ray structure. Potentiometric studies of complex **1** were also performed and revealed three titratable protons which are attributed to the protonation/deprotonation of two phenol groups ($p[K]_{a1} = 4.04$ and $p[K]_{a3} = 11.34$) and dissociation of a metal-bound water molecule ($p[K]_{a2} = 7.8$). The phenolate groups in complex **1** are suitably protected by bulky substituents (*tert*-butyl) in the *ortho*- and *para*-positions, which through electrochemical oxidation generate a one-electron oxidized phenoxyl species in solution. This radical species was characterized by UV–Vis, EPR and electrochemical studies. The Zn(II)-phenoxyl radical species is of bioinorganic relevance, since its spectroscopic, redox and reactivity properties can be used to establish the role of phenoxyl radicals in biological and catalytical systems.

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Keywords: Zinc(II) complex; Phenoxyl radical; Crystal structure; Physicochemical properties

1. Introduction

Phenoxyl radicals have been of recent interest due to their involvement in a range of bioinorganic and catalytical systems [1]. Transition-metal ions bound to a tyrosine radical have also been proven to enhance the radical stability as well as to control the reactivity of the phenoxyl radical species [2]. Model complexes of this kind are important because they allow the determination of the spectroscopy features of coordinated vs. uncoordinated phenoxyl radicals and aid an understanding of their chemical reactivity [1d,2].

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The coordination chemistry of phenoxyl radicals bound to transition metal ions is well developed despite the fact that there are some intriguing questions remaining related to their electronic structure [3]. Recent model studies using Zn(II)-phenoxyl radical complexes have provided an insight into the redox behavior and spectroscopic properties of this species [4]. Zinc(II) complexes were used for a variety of reasons: zinc(II) is redox-innocent over a wide potential range; thus, all observable redox processes of its complexes must be ligand centered. Secondly, if phenoxyl radical species are generated, they are paramagnetic ($S = 1/2$) and are, therefore, ideally suited for EPR spectroscopic characterization. In addition, the electronic spectra of such species are unperturbed by d–d transitions [4d].

In this work, we present the synthesis of a new H_2L ligand, which contains two phenolate pendant arms. The phenolate groups in H_2L are suitably protected by bulky substituents (*tert*-butyl) in the *ortho*- and *para*-positions, which enable the ligand to form stable phenoxyl radical complexes. Thus, we have synthesized a new mononuclear complex with Zn^{II}, which through electrochemical oxidation generates a one-electron oxidized phenoxyl species in solution. This radical species was characterized by UV–Vis, EPR and electrochemical studies. The crystal structure of complex **1** was determined by X-ray crystallographic analysis. The structure of this complex consists of a discrete mononuclear cation $[Zn^{II}(HL)]^+$, in a strongly distorted square pyramidal geometry. Potentiometric and NMR studies of complex **1** were also performed in this work.

2. Experimental

2.1. Abbreviations

H_2L: *N*,*N*′,*N*,*N*′-bis[(2-hydroxy-3,5-di-*tert*-butylbenzyl)(2-pyridylmethyl)]-ethylenediamine, $[TBA]PF_6$: tetra-*n*-butylammonium hexafluorophosphate.

2.2. Materials and general methods

All reagents and solvents for syntheses and analyses were of analytical and/or spectroscopic grade and used without further purification. Only 3,5-di-*tert*-butyl-2-hydroxybenzyl chloride was synthesized following modification of a method described in the literature [4d].

For the electrochemical and spectroscopic studies, high-purity solvents were used as received from Merck. High-purity argon was used to deoxygenate the solution. Elemental analyses were performed with a Perkin–Elmer 2400 instrument. The NMR spectra were obtained on a Bruker-FT 200 MHz (^1H, ^{13}C, ^1H–^1H COSY, ^{13}C DEPT 135) in $CDCl_3$ (H_2L) and CD_3CN (complex **1**), at 25 °C. Chemical shifts were referenced to tetramethylsilane (TMS). Infrared spectra (KBr pellets) were obtained with an FT-IR Perkin–Elmer Model 2000 spectrometer. The electronic spectrum of the phenoxyl radical complex was recorded on a Varian Cary 50Bio spectrophotometer. First derivative EPR spectroscopy of "powdered" and solution samples was carried out with a Bruker ESP 300E X-band spectrometer. Square-wave and cyclic voltammograms were obtained and coulometric experiments were performed with a Princeton Applied Research (PARC) model 273 potentiostat/galvanostat using dichloromethane solutions containing 0.1 mol dm^{-3} $[TBA][PF_6]$ as the supporting electrolyte (argon atmosphere, at room temperature and at −60 °C) in a conventional electrochemical cell. A glassy carbon working electrode and a platinum wire counter electrode were used. Potentials were referenced to the Ag/Ag^+ electrode constructed in our laboratory. The Fc^+/Fc couple of ferrocene ($E^0 = 400$ mV vs. NHE) was used as an internal standard [5] to monitor the reference electrode and was observed at +385 mV versus Ag/Ag^+.

The potentiometric studies were carried out with a Corning pH/ion analyzer, model 350, fitted with blue-glass and calomel reference electrodes calibrated to read $-\log [H^+]$ directly, designated as pH. Bidistilled water in the presence of $KMnO_4$ was used to prepare the water/ethanol (30:70 v/v) solutions. The electrode was calibrated using the data obtained from a potentiometric titration of a known volume of a standard 0.0100 mol dm^{-3} HCl solution with a standard 0.100 mol dm^{-3} KOH solution. The ionic strength of the HCl solution was maintained at 0.100 mol dm^{-3} by addition of KCl. The measurements were carried out in a thermostated cell containing a complex solution (0.05 mol/50 mL water/ethanol solution) with ionic strength adjusted to 0.100 mol dm^{-3} by addition of KCl, at 25.00 ± 0.05 °C. The experiments were performed under an argon flow (cleaned twice by a 0.100 mol dm^{-3} KOH solution) to eliminate the presence of atmospheric CO_2. The samples were titrated by addition of fixed volumes of a standard CO_2-free KOH solution (0.100 mol dm^{-3}). Computations were carried out with the BEST7 program, and species diagrams were obtained with SPE and SPEPLOT programs [6].

2.3. Synthesis

H_2L. This compound was obtained according to the reaction route given in Scheme 1, by the reaction between ethylenediamine and 2-pyridinecarboxaldehyde followed by reduction with $NaBH_4$ and addition of 3,5-di-*tert*-butyl-2-hydroxybenzyl chloride. Yield: 75% based on the amine BPEN (m.p. 134–135 °C). The NMR spectra (^1H, ^{13}C, ^1H–^1H COSY, ^{13}C DEPT 135) and assignments are described in Section 3.

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