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Acetate bridged dinuclear Cu(II) complexes with ferrocene based benzimidazol ligands: Synthesis, spectroscopy, electrochemistry, DFT calculations and catecholase activity

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ABSTRACT

Two new benzimidazole ligands, 1-[(E)-ferrocenylmethylidenehydrazino]-2-{5,6-dichloro-2-[(o-chlorophenyl)methyl]-1,3-diaza-1H-inden-1-yl}-1-ethanone (**1**) and 1-[(E)-ferrocenylmethylidenehydrazino]-2-{2-[p-(trifluoromethyl)phenyl]-1,3-diaza-1H-inden-1-yl}-1-ethanone (**2**), and their copper(II) complexes (**1a**, **2a**) have been prepared and characterized by IR, UV–Vis, NMR, TG/DTA and MALDI-TOF mass spectrometry. DFT-based molecular orbital energy calculations and the electrochemical behavior of the compounds have been also studied to explain the redox potentials of the compounds. The catecholase-mimetic activities of the complexes have been investigated by monitoring the formation of 3,5-di-tert-butyl-benzoquinone from 3,5-di-tert-butylcatechol. The catalytic activity of **1a** is slightly lower than that of **2a**, and the correlation between catalytic activity and electrochemical behaviors of the compounds has been established.

1. Introduction

The aerobic degradation of compounds under ambient conditions is of great interest for industrial and synthetic production processes because of economic and environmental benefits [1]. The design and synthesis of functional model complexes for enzyme mimetic activities are therefore important for the development of new and efficient catalysts for electron transport reactions [2–5]. Catechol oxidase is an enzyme containing a dinuclear copper center with a distance of 2.9 Å (in *Lycopus europaeus* [6]) which increases to 4.4 Å in the reduced form, and it catalyzes the aerobic oxidation of catechols to the corresponding o-quinones [7]. This enzyme is known as catecholase. The catecholase mimetic activity of dinuclear copper complexes is well known and extensive catalytic studies have been performed with copper-based model complexes [8–16].

The aim of this study is to synthesize and characterize benzimidazole ligands containing a ferrocenyl unit and to establish a correlation between the catechol oxidase mimetic activity and the electrochemical properties of the compounds. We report the synthesis and characterization of two ferrocene based bezimidazol ligands and their Cu(II) complexes by IR, UV–Vis, NMR, elemental analysis and mass spectroscopy (MS). Quantum chemical calculations have been widely used to study the structural, electronic and spectroscopic properties of different compounds [17,18]. Time-dependent density functional theory (TD-DFT) has led to a new perspective in this area. Therefore, the synthesized molecules have also been studied using density functional theory (DFT) based calculations as a theoretical approach to explain the molecular structure, electronic transitions, redox properties and chemical reactivity of the compounds.

2. Experimental

2.1. General procedures

The syntheses of the ligands were performed under microwave irradiation on a CEM-discover. Ferrocenecarboxaldehyde (Fluka), copper(II) acetate (Merck) and all the solvents were of reagent grade and used without any further purification. 2-{5,6-Dichloro-2-[(o-chlorophenyl)methyl]-1,3-diaza-1H-inden-1-yl}-1-hydrazino-1-ethanone and 1-hydrazino-2-{2-[p-(trifluoromethyl)phenyl]-1,3-diaza-1H-inden-1-yl}-1-ethanone were prepared according to literature methods [19].

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2.2. Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer equipped with an ATR apparatus. Elemental analyses were obtained using a LECO CHNS-932 analyzer at the Middle East Technical University. Heated electrospray ionization (MS-MS H-ESI) and MALDI-TOF mass spectroscopy in a DFB matrix were investigated on a TSQ Quantum Access MAX Triple Stage Quadrupole mass spectrometer at the Central Research Laboratory of RTE University and a Bruker microflex LT at the Gebze Institute of Technology, respectively. ^{1}H and ^{13}C NMR spectra were recorded on an Agilent Technologies 400/54 spectrometer at the Central Research Laboratory of RTE University. UV–Vis spectra were recorded on a Shimadzu 1601 spectrophotometer. Magnetic susceptibility and thermogravimetric data were collected using a Sherwood MK-1 and SII 6300 TG/DTA, respectively. Electrochemical characterizations of all compounds were investigated by cyclic voltammetry on a Gamry 3000 Reference electrochemical analyzer using a platinum disk as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The scan rate was 100 mV s^{-1} and a solution of tetrabutylammoniumperchlorate (TBAP) in CH_2Cl_2 (0.2 M) was employed as the supporting electrolyte.

2.3. Computational details

Density functional calculations, as implemented in GAUSSIAN 09 [20], were used for all the theoretical calculations. The hybrid Becke-3-Lee Yang Parr (B3LYP) density functional theory method [21,22] with the 6-311G++(d, p) basis set [23] for the H, C, N and O atoms and the Los Alamos effective core potentials plus the Double Zeta (LANL2DZ) [24] basis set for the Cu and Fe atoms in the ground state were used for the complete optimizations, without symmetry constraints. Harmonic frequency analyses indicate that the optimized structures of all the compounds are at stationary points corresponding to local minima with real vibrational spectra in the gas phase. Electronic excitations were calculated using the time dependent density functional theory (TD-DFT) formalism [25] with the conductor-like polarizable continuum model (CPCM) [26]. The lowest 150 singlet–singlet transitions of the Cu(II) complexes and 60 singlet–singlet transitions of the ligands were computed in an implicit solvent of dichloromethane. GaussSum [26] was used to calculate the fractional contributions of various groups to each molecular orbital and to describe the UV–Vis bands. GaussView 5.0 [27] was used to visualize the results of the computations.

2.4. Synthesis of the ligands **1** and **2**

The hydrazide ligand, 1-[(E)-ferrocenylmethylidenehydrazino]-2-{2-[p-(trifluoromethyl)phenyl]-1,3-diaza-1H-inden-1-yl}-1-ethanone (**2**), was synthesized following the same procedure as adopted for 1-[(E)-ferrocenylmethylidenehydrazino]-2-{5,6-dichloro-2-[(o-chlorophenyl)methyl]-1,3-diaza-1H-inden-1-yl}-1-ethanone (**1**).

A 10 mL microwave vial was charged with 5 mL of an ethanolic solution of 2-{5,6-dichloro-2-[(o-chlorophenyl)methyl]-1,3-diaza-1H-inden-1-yl}-1-hydrazino-1-ethanone (0.58 g, 1 mmol), ferrocenecarboxaldehyde (0.22 g, 1 mmol) and 1 mL glacial acetic acid. The vial was then capped and subjected to microwave irradiation at 120 °C and 300 W power for a period of 7 min with continuous stirring. The reaction was monitored by TLC with the chloroform mobile phase. After completion of the reaction, the reaction mixture was poured into water, then stirred well, filtered and washed with cold ether.

1. Yield: 0.17 g (33%). Mp: 198 °C (dec.). Color: Golden rod. *Anal.* Calc. for $C_{27}H_{21}Cl_3FeN_4O$ (M = 579): C, 55.94; H, 3.65; N, 9.67; Found: C, 55.81; H, 3.59; N, 9.62%. EI-MS, *m*/*z* (%): 579.410 (100) $[M+H]^+$. FT-IR (cm^{-1}): 3076 *ν*(–NH), 1681 *ν*(C=O), 1607 *ν*(–C=N–), 1509, 1457, 1441 *ν*(Ar-H and Cp-H). ^{1}H NMR *δ* (ppm): 11.52 (s., 1H, –OH); 11.47 (s., 1H, –NH); 8.09 and 7.96 (s., 1H, Fc–HC=N); 7.86 (m., 2H, Ar-H); 7.46 (m., 1H, Ar-H); 7.32 (b.s., 3H, Ar-H); 5.42 and 5.08 (s., 2H, $-CH_2$); 4.76 and 4.64 (s., 2H, $-CH_2$); 4.44 (s., 2H, Cp-H); 4.34 (s., 2H, Cp-H); 4.23 (s., 5H, Cp-H). ^{13}C NMR *δ* (ppm): 167.29, 156.33, 145.730, 142.10, 136.22, 134.41, 133.71, 131.96, 129.66, 129.24, 127.74, 124.38, 120.11, 112.78, 79.17, 70.53, 69.45, 67.93. UV–Vis nm (*ε*, M^{-1} cm^{-1}): 274 (11219), 294 (16345), 443 (430). μ: dia.

2. Yield: 0.39 g (84%). Mp: 217 °C (dec.). Color: Orange. *Anal.* Calc. for $C_{27}H_{21}F_3FeN_4O$ (M = 530): C, 61.15; H, 3.99; N, 10.56; Found: C, 61.12; H, 3.91; N, 10.47 %. EI-MS, *m*/*z* (%): 531,540 (100) $[M+H]^+$. FT-IR (cm^{-1}): 3072 *ν*(–NH), 1682 *ν*(C=O), 1603 *ν*(–C=N–), 1507, 1456, 1427 *ν*(Ar-H and Cp-H). ^{1}H NMR *δ* (ppm): 11.61 (s., 1H, –OH); 11.47 (s., 1H, –NH); 8.03 (d., *J* = 8.4 Hz, 1H, Ar-H); 8.00 (d., *J* = 8.4 Hz, 1H, Ar-H); 7.92 (t., *J* = 8.8 Hz, 1H, Ar-H); 7.86 (s., 1H, HC=N-Fc); 7.74 (d., *J* = 6.8 Hz, 1H, Ar-H); 7.58 (t., *J* = 7.2 Hz, 1H, Ar-H); 7.30 (d., *J* = 6.4 Hz, 1H, Ar-H); 5.44 and 5.02 (s., 2H, CH_2-C=O); 4.62 (s., 2H, Cp-H); 4.40 (s., 2H, Cp-H); 4.20 (s., 5H, Cp-H). ^{13}C NMR *δ* (ppm): 167.82, 162.98, 152.63, 152.52, 149.75, 146.04, 142.83, 137.22, 136.86, 134.73, 130.26, 126.10, 126.06, 123.45, 122.79, 119.78, 111.36, 78.97, 70.58, 69.43, 67.97, 45.88. UV–Vis nm (*ε*, M^{-1} cm^{-1}): 295 (25664), 450 (783). μ: dia.

2.5. Synthesis of the copper(II) complexes, **1a**, **2a**

A hot solution of copper(II) acetate monohydrate (0.20 g, 1 mmol) in 15 mL acetonitrile was added to a hot suspension of the ligand (1 mmol) in 25 mL acetonitrile. The mixture was stirred at 60 °C for 1 h and then filtered to afford a brownish crude product. The resulting solid was recrystallized from CH_2Cl_2 and acetonitrile mixture. The microcrystalline product that formed was filtered and finally dried in a vacuum desiccator over anhydrous $CaCl_2$ (Fig. 1).

1a. Yield: 1.03 g (70%). Mp: 198 °C (dec). *Anal.* Calc. for $C_{58}H_{46}Cl_6Cu_2Fe_2N_8O_6.4H_2O$ (M = 1474.597): C, 47.24; H, 3.69; N, 7.60. Found: C, 48.43; H, 3.63; N, 7.70%. MALDI-TOF MS, *m*/*z* (%): 1494.947 (44 a.u.) $[M+Na]^+$. IR (KBr, cm^{-1}): 1619 *ν*(–C=N), 1538 $\nu_{asym}(COO^-)$, 1456, 1438 *ν*(C=C), 1390 $\nu_{sym}(COO^-)$. UV–Vis (nm, *ε*): 270 (28504), 292 (41859), 299 (39375), 453 (1475). μ_{eff} (B.M.): 1.75. Λ (Ω^{-1} cm^2 mol^{-1}): 2.9.

2a. Yield: 0.83 g (60%). Mp: 203 °C. (dec). *Anal.* Calc. for $C_{58}H_{46}Cu_2F_6Fe_2N_8O_6.4H_2O$ (M = 1375.869): C, 50.63; H, 3.96; N, 8.14. Found: C, 51.36; H, 3.68; N, 8.19%. MALDI-TOF MS, *m*/*z* (%): 1397.791 (136 a.u.) $[M+Na]^+$. IR (KBr, cm^{-1}): 1619 *ν*(–C=N → Cu), 1533 $\nu_{asym}(COO^-)$, 1461, 1448 *ν*(C=C), 1390 $\nu_{sym}(COO^-)$. UV–Vis (nm, *ε*): 295 (31,345), 425 (2018). μ_{eff} (B.M.): 1.39. Λ (Ω^{-1} cm^2 mol^{-1}): 0.0.

3. Results and discussion

3.1. IR spectra

The characteristic N–H, C=O and C=N bands were observed at 3076, 1681 and 1607 cm^{-1} for **1** and 3072, 1682 and 1603 cm^{-1} for **2**, respectively. The sharp peaks in the region between 3072 and 3182 cm^{-1} for the ligands are indicative of hydrogen bonded –NH protons. The absence of *ν*(N–H) and *ν*(C=O) bands in the spectra of both copper(II) complexes indicates that the ligands are transformed into the enol/imine form during complexation and the coordination of the Cu(II) ion with the ligand occurs through