Journal of Molecular Structure 1122 (2016) 123–133

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Crystal structures, DFT calculations and Hirshfeld surface analyses of three new cobalt(III) Schiff base complexes derived from meso-1,2-diphenyl-1,2-ethylenediamine

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ARTICLE INFO

Article history:
Received 24 February 2016
Received in revised form
12 May 2016
Accepted 27 May 2016
Available online 30 May 2016

Keywords:
Schiff base
Cobalt(III)
DFT
3D Hirshfeld surfaces
2D fingerprint plots

ABSTRACT

Three new Cobalt(III) Schiff base complexes were synthesized and characterized by spectroscopic methods and x-ray crystallography. The DFT optimized structures of the complexes agreed well with the corresponding x-ray structures. According to the calculated vibrational normal modes, the observed signals in the IR spectra of the complexes were assigned. The experimental UV–Vis spectra of the complexes were also discussed considering the calculated excited states and molecular orbitals. Hirshfeld surface analysis was carried out to study the inter-contact interactions in these complexes. These studies provided comprehensive description of such inter-contact interactions by means of an appealing graphical approach using 3D Hirshfeld surfaces and 2D fingerprint plots derived from the surfaces. It indicated the dominant role of various hydrogen intermolecular interactions such as H···H (above 60%), C···H/H···C (near 15%–20%), O···H/H···O (about 16% or 17% for structures with counter ion ClO_4^-) and H···F (17% for structure with counter ion PF_6^-) contacts into the crystal packing which are discussed in details.

1. Introduction

Schiff bases are considered as privileged ligands in coordination chemistry because of their ease of preparation, enormous structural diversities and great applications of their metal complexes [1]. These ligands have been widely used as chelating ligands and have shown great performance in the fine tuning of the electronic and steric characteristics of their metal complexes [2–5]. There are many applications for transition metal complexes which need such fine tunings including catalysis and biochemical applications. Although huge number of transition metal complexes of Schiff base ligands have been investigated, modern chemists still design Schiff base ligands and their metal complexes for various purposes. In this regard, Schiff base complexes of cobalt(II) and cobalt(III) have attracted great interest. Cobalt(II) complexes of Schiff base ligands are perhaps the first and the most extensively investigated dioxygen carriers [6,7]. Cobalt(III) Schiff base complexes have also been extensively studied for their biological and catalytic activities [8–10]. Cobalt(III) complexes of tetradentate Schiff base ligands usually form octahedral structures with two axial ligands to complete six coordination. Several ligands such as pyridine and its derivatives, imidazoles, morpholine, thiocyanate anion, etc., have been used as axial ligands, and it is shown that these axial ligands also have important contribution on the properties of such cobalt complexes [11,12].

The structural and spectroscopic properties of transition metal complexes could be modeled and studied theoretically by different computational methods. Density Functional theory (DFT) has been extensively used in the prediction of structures, electronic properties, chemical reactions kinetics and mechanism, thermodynamic properties, vibrational, absorption, Raman and NMR spectra of metallic complexes [13–17]. Sayin et al. [17] have investigated the effect of solvent on the geometry of cobalt(II) complex containing tris(2-benzimidazolylmethyl) amine using [B3LYP] functional and

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http://dx.doi.org/10.1016/j.molstruc.2016.05.092

different basis sets. Time dependent DFT (TD-DFT) using [B3LYP] functional has also been employed in order to analyze the electronic excitations of metal complexes [18].

Hirshfeld surface analysis is another computational method which has attracted great interest recently [19]. Such analyses could provide a way to "*the understanding of the intermolecular interactions in the context of crystal packing and the utilization of such understandings in the design of new solids with desired physical and chemical properties*" [20].

In this work, we report the synthesis, spectroscopic and x-ray structural characterization of three new Co(III) Schiff base complexes. DFT calculations were used to study the optimized structure of these complexes as well as their Infrared (IR) and UV–Vis spectra. Hirshfeld surface analysis was also used to investigate intermolecular interactions in the studied crystal structures by the graphical representations based on Hirshfeld surfaces [21] and fingerprint plots [22].

2. Experimental

2.1. Materials and instruments

All chemicals were purchased from commercial sources and were used as received. *Meso*-1,2-diphenyl-1,2-ethylenediamine was synthesized as described elsewhere [23]. Melting points were obtained on a thermoscientific 9100 apparatus. ^{1}HNMR spectra were recorded on a 500 MHz Bruker FT-NMR spectrometer using $CDCl_3$ or DMSO-d_6 as solvent; chemical shifts (δ) are given in ppm. IR spectra were obtained as KBr plates using a Bruker FT-IR instrument. UV–Vis spectra were obtained on a Shimadzu UV-1650 PC spectrophotometer in DMSO solutions. X-ray diffraction data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo/Kα radiation ($\lambda = 0.71073$ Å). Data collections, cell refinements, data reductions and absorption corrections were performed using multi-scan methods with Bruker software [24]. The structures were solved by direct methods using SIR2004 [25]. The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on F^2 using SHELXL [26]. All the hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collections and analyses are reported in Table 1.

2.2. Computational methods

2.2.1. DFT calculations

The stable structures of CoL^{1-3} complexes were determined through [B3LYP] functional. Generally, generalized gradient methods such as [B3LYP] should be expected to give a better description of ground state properties than local spin density approximation [LSDA] [27]. [B3LYP] functional is accepted as a reliable method for the investigation of metal complexes and exploits a combination of [B3] exchange functional [28] and [LYP] correlation functional [29]. We have improved the accuracy of the calculations using [LANL2DZ] basis set along with the corresponding effective core potential (ECP) for Co atom, and [6-31 + G*] for O, N, C, and H atoms. Frequency calculations were also performed on the optimized structures in order to confirm that the structure belong to the local minima on the potential energy surface as well as to analyze the vibrational normal modes of the complexes. Time dependent DFT (TD-DFT), as a reasonable method, was employed in order to predict the electronic excitations of CoL^{1-3} complexes in DMSO solvent introduced in the frame of the Polarizable Continuum Model (PCM) [30]. All calculations were done using the Gaussian03 program [31].

2.2.2. Hirshfeld surface analysis

The Hirshfeld molecular surfaces of the complexes CoL^{1-3} were generated using *CrystalExplorer* 3.1 [32], which accepts the crystal data in CIF format. Bond lengths to hydrogen atoms were set to standard values (C–H/1.083 Å) during calculations. It should be noted that for CoL^2 ($[Co(L)(L')_2]^+[PF_6]^-$), the disorder in counter ion PF_6^- was modeled by running the HS analysis for the $[Co(L)(L')_2]^+$ complex, beside both possible orientations of PF_6^- separately. By comparing two modes, the proportion of interactions showed changes of less than 0.4%; hence, one orientation of PF_6^- was selected and modeled as fully occupied.

For each point on the HS, a pair distance (d_e, d_i) was defined: d_e, the distance from the point to the nearest nucleus external to the surface and d_i, the distance to the nearest nucleus internal to the surface. Moreover, a normalized contact distance ($d_{norm,}$ used to generate HSs in here) based on d_e, d_i and the van der Waals radii of the corresponding atoms ($d_{norm} = \frac{d_i - d_i^{vdw}}{d_i^{vdw}} + \frac{d_e - d_e^{vdw}}{d_e^{vdw}}$) was employed for coding the HS by colors red, blue and white. Red spots exhibit short contacts (with distances shorter than the sum of van der Waals radii), white areas represent contacts with distances equal to the sum of the van der Waals radii, and blue regions are free of any close contacts [30].

The fingerprint plots (FPs) are introduced as the two-dimensional representations of the information provided by the generated HSs. The FPs are plotted on an XY grid formed by (d_e, di) pairs ($X = d_i$ and $Y = d_e$), where the frequency of occurrence of interactions (the number of points with a given (d_e, di) pair) are represented by the different colors blue (low frequency), green (medium) and red (high). Moreover, the complementary regions are visible in the FPs where one molecule act as donor ($d_e > d_i$) and the other as an acceptor ($d_e < d_i$) [22,33]. In Fig. 7 and S3–S4, the quoted regions are introduced by the reciprocal X … H/H … X contacts in which X atom is located inside (for X … H/$d_e < d_i$) or outside (for H … X/$d_e > d_i$) the generated HS as an H-atom acceptor.

2.3. Synthesis of the Schiff base ligand

To a vigorously stirred solution of 5 mmol *meso*-1,2-diphenyl-1,2-ethylenediamine (1.06 g) in 20 mL methanol was added dropwise a solution of 10 mmol acetylacetone (1 mL) in 20 mL methanol. The reaction mixture was refluxed for 4 h and then was left to cool down to room temperature. Slow evaporation of the solvent at room temperature yielded pale yellow precipitate of the target compound after 4 days. The ligand was recrystallized from 1:1 dichloromethane: n-hexane to give pale yellow crystals of the pure target compound. Yield: 1.6 g (85%). M.p. = 184 °C. FT-IR (KBr, cm^{-1}): 3420 ($\nu_{O\text{-}H}$), 1604 ($\nu_{C=N}$), 1286 ($\nu_{C\text{-}O}$). ^{1}HNMR in $CDCl_3$ (δ, ppm): 11.45 (2H, br, O**H**), 7.29–7.05 (10H, m, Ar**H**), 4.94 (2H, s, C**H**Ph), 4.83 (2H, m, **H**C =), 1.99 (6H, d, C**H**$_3$) and 1.66 (6H, d, C**H**$_3$). UV–Vis in DMSO [λ, nm (ε, M^{-1} cm^{-1})]: 216 (127,000), 239 (72,400), 304 (9200), 323 (8600).

2.4. Synthesis of the complexes

The Schiff base complexes were synthesized by the direct reaction between the Schiff base ligand (L), $Co(OAc)_2.4H_2O$ and the axial ligands (L′ = py, 4-Mepy, 1,2-diMeIm) followed by air bubbling to oxidize the metal center. NH_4PF_6 or $NaClO_4$ was added to result the target complexes with the appropriate counter ion which gave the suitable crystals for x-ray crystallography. Scheme 1 shows the schematic representation of the structure of the ligand, the complexes and the synthetic procedure.

2.4.1. Synthesis of $[CoL(py)_2]ClO_4$ (CoL^1)

A solution of 1 mmol of $Co(OAc)_2.4H_2O$ (0.25 g) in 25 mL