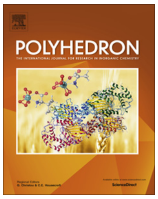
Polyhedron 138 (2017) 31–36

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Synthesis, crystal structure and electronic property of a tetraoxolene bridged dinuclear cobalt(II) complex with bipyridyl blocking ligand

Narayan Ch. Jana [a], Paula Brandão [b], Amrita Saha [c], Anangamohan Panja [a,*]

[a] *Department of Chemistry, Panskura Banamali College, Panskura RS, WB 721152, India*
[b] *Department of Chemistry, CICECO-Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal*
[c] *Department of Chemistry, Jadavpur University, Kolkata 700032, India*

ARTICLE INFO

Article history:
Received 23 June 2017
Accepted 2 September 2017
Available online 9 September 2017

Keywords:
Redox active ligand
2,5-Dihydroxy-1,4-benzoquinonate ligand
Dinuclear cobalt(II) complex
Crystal structures
Cyclic voltammetry

ABSTRACT

The design of molecule-based systems displaying tuneable optical and/or magnetic properties under external perturbations has received a considerable interest because of their potential applications in high-performance molecule-based electronic devices, switches, sensors, and displays. Several valence tautomeric tetraoxolene bridged dinuclear cobalt complexes with tetradentate terminal ligands have been synthesized in this regard, but none was reported with bidentate terminal ligand. In order to increase the scope in this field, a new tetraoxolene bridged dinuclear cobalt(II) complex with three different lattice solvate molecules $[Co_2(bpy)_4(DHBQ^{2-})](BPh_4)_2{\cdot}2CH_3COCH_3$ ($\mathbf{1}(BPh_4)_2{\cdot}2CH_3COCH_3$), $[Co_2(bpy)_4(DHBQ^{2-})]{\cdot}(BPh_4)_2{\cdot}2MeCN$ ($\mathbf{1}(BPh_4)_2{\cdot}2CH_3CN$) and $[Co_2(bpy)_4(DHBQ^{2-})]{\cdot}(BPh_4)_2{\cdot}2DMF$ ($\mathbf{1}(BPh_4)_2{\cdot}2DMF$), where bpy is 2,2-bipyridine and $DHBQ^{2-}$ is deprotonated 2,5-dihydroxy-1,4-benzoquinone, have been reported. Their crystal structures were determined by single-crystal X-ray diffraction study. In the complex cation $[Co_2(bpy)_4(DHBQ^{2-})]^{2+}$, cobalt(II) centers are hexa-coordinated by four nitrogen atoms from two bipyridine ligands and two oxygen atoms from dinegative tetraoxolene ligand which bridges two cobalt(II) ions in a bis-bidentate fashion. An extensive effort has been made to visualize the noncovalent interactions in the solid state. Electrochemical studies were also carried out to realize the electronic flexibility in these systems.

1. Introduction

Research in the field of molecular materials with closely associated different electronic states that can be switched by external stimuli, such as heat, light, electric and magnetic field, have been attracted great deal of attention because of their possible application as molecular electronic switches, displays, and memory storage devices [1–10]. Spin-crossover (SCO) and valence tautomeric (VT) complexes are well known molecular materials that exhibit bistable electronic properties, usually associated with distinguishable magnetic and/or optical properties [10–18]. SCO transition involves the spin reversal between high-spin (HS) and low-spin (LS) states within a metal ion, while VT transition in metal complexes is governed by an intramolecular electron transfer (IET) between a metal center and a redox non-innocent organic ligand. Cobalt complexes have been considered excellent candidates in this regard as they exhibit both SCO and VT transitions [19–22]. Since the first report of valence tautomeric transition well back in 1980s [23], a large number of cobalt-based complexes have been synthesized utilizing redox-active dioxolene ligands and ancillary N-donor ligands, which has led to the development of VT systems and the identification of main factors governing their electronic bistability [13,24,25]. Besides the dioxolene ligand systems, dinuclear cobalt and iron complexes with tetraoxolene ligand, such as chloralinate ion consisting of a delocalized π system, have been shown to exhibit weak anti- and ferro-magnetic coupling and SCO transitions [26–29]. Cobalt complexes derived from 2,5-dihydroxy-1,4-benzoquinonate ($DHBQ^{2-}$) ligand, on the other hand, usually exhibit valence tautomeric transitions [30–34]. A remarkable contribution in this series is the isolation of a dinuclear cobalt complex with bridging $DHBQ^{2-}$ ligand and tris(2-pyridylmethyl) amine (tpa) terminal ligand that displayed thermal- and photo-induced valence tautomeric transition between cobalt center and tetraoxolene ligand associated with a thermal hysteresis loop at room temperature [35], which is one of the foremost criteria for application of these molecular materials in information storage devices. Literature reports reveal that the possibility of switching between the electronic states in these molecules is closely associated with several factors, namely coordination environment of the

---

* Corresponding author.
E-mail address: ampanja@yahoo.co.in (A. Panja).

http://dx.doi.org/10.1016/j.poly.2017.09.002
0277-5387/

metal centers, donor/acceptor abilities of the ancillary ligands, steric hindrance, the solid state packing and intermolecular interactions, coulombic interactions with the counter ions [36–40]. It is worth noting that the progress in this field is so far mainly revolved around tpa type tetradentate tripodal N-donor ancillary ligands for the development of Fe/Co based tetraoxolene bridged dinuclear complexes [26–33,35]. Therefore, the exploration of the coordination chemistry of tetraoxolene-bridged dinuclear cobalt/iron compounds using bidentate N-donor ancillary ligands could be worthy as that would increase the scope in this field. With this aim, in this present endeavor, 2,5-dihydroxy-1,4-benzoquinonate ($DHBQ^{2-}$) has been reacted with cobalt(II) salts in different solvents and in presence of 2,2′-bipyridine (bpy) and tetraphenylborate ions. Successfully, we ended up with isolation of a dinuclear cobalt(II) complex with three different lattice solvents. Herewith, we report the structures and electronic properties of three isomorphic dinuclear cobalt(II) compounds, $[Co_2(bpy)_4(DHBQ^{2-})](BPh_4)_2\cdot 2CH_3COCH_3$ (**1**$(BPh_4)_2\cdot 2CH_3COCH_3$), $[Co_2(bpy)_4(DHBQ^{2-})]\cdot(BPh_4)_2\cdot 2MeCN$ (**1**$(BPh_4)_2\cdot 2CH_3CN$) and $[Co_2(bpy)_4(DHBQ^{2-})]\cdot(BPh_4)_2\cdot 2DMF$ (**1**$(BPh_4)_2\cdot 2DMF$).

2. Experimental

2.1. Materials and physical measurements

2,5-Dihydroxy-1,4-benzoquinone (H_2DHBQ), cobalt nitrate hexahydrate, 2,2′-bipyridine, sodium tetraphenyl borate and triethylamine were of reagent or analytical grade chemicals and purchased from commercial sources and used as received. Solvents were of analytical grade and used without further purification.

Elemental analyses for carbon, hydrogen and nitrogen were performed in a PerkinElmer 240 C elemental analyzer. The infrared spectra in the range of 400–4000 cm^{-1} were recorded on a PerkinElmer Spectrum Two FTIR spectrophotometer with samples prepared as KBr pellets. Cyclic voltammetric experiments were made at room temperature in acetonitrile using tetrabutylammonium perchlorate as a supporting electrolyte on a CH Instrument electrochemical workstation model CHI630E using a conventional three electrodes assembly comprised of platinum working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode.

2.2. Synthesis of $[Co_2(bpy)_4(DHBQ^{2-})](BPh_4)_2\cdot 2CH_3COCH_3$ (**1**$(BPh_4)_2\cdot 2CH_3COCH_3$)

A solution of $Co(NO_3)_2\cdot 6H_2O$ (0.5 mmol) and 2,2′-bypyridine (1.0 mmol) in acetone (20 mL) was added to a solution of H_2dhbq (0.25 mmol) and Et_3N (0.5 mmol) in acetone (10 mL). The resulting solution was stirred at room temperature for 5 min, after which the solution was refluxed for 30 min, and then allowed to cool at room temperature. To the resulting solution sodium tetraphenylborate (1.0 mmol) in 10 mL of acetone was added, and the reaction mixture was allowed to stir for 10 min and it was filtered. Block-like red crystals were obtained by slow evaporation of the resulting solution, which was washed several times with cold acetone/ether and air dried. Yield: 64%. *Anal.* Calc. for $C_{100}H_{86}B_2Co_2N_8O_6$: C, 73.45; H, 5.30; N, 6.85. Found: C, 73.20; H, 5.10; N, 6.80%. FTIR (KBr, cm^{-1}): 3550–3414s, 3055m, 1712s, 1638w, 1618m, 1532s, 1472m, 1442s, 1313m, 1257s, 1221w, 1156m, 1061w, 1022w, 815m, 770m, 735 , 753m, 706m, 613m, 469w.

2.3. Synthesis of $[Co_2(bpy)_4(DHBQ^{2-})]\cdot(BPh_4)_2\cdot 2MeCN$ (**1**$(BPh_4)_2\cdot 2CH_3CN$)

An identical synthetic method as described for compound **1**$(BPh_4)_2\cdot 2CH_3COCH_3$ was applied for the synthesis of **1**$(BPh_4)_2\cdot 2CH_3CN$ using acetonitrile solvent. Color: red. Yield: 0.152 g (80%). *Anal.* Calc. for $C_{98}H_{80}B_2Co_2N_{10}O_4$: C, 73.51; H, 5.04; N, 8.75. Found: C, 73.40; H, 4.95; N, 8.61%. FTIR (KBr, cm^{-1}): 3550–3410s, 3055m, 2252w, 1638m, 1618m, 1533s, 1472m, 1441m, 1393m, 1314m, 1256m, 1157w, 1060m, 1021m, 815m, 766m, 735m, 706m, 613m, 470w.

2.4. Synthesis of $[Co_2(bpy)_4(DHBQ^{2-})]\cdot(BPh_4)_2\cdot 2DMF$ (**1**$(BPh_4)_2\cdot 2DMF$)

Compound **1**$(BPh_4)_2\cdot 2DMF$ was synthesized following very similar method as described for **1**$(BPh_4)_2\cdot 2CH_3COCH_3$ in dimethylformamide solvent. Block-shaped red crystals were separated out from the reaction mixture upon standing at ambient condition after several days. Color: red. Yield: 0.142 g (83%). *Anal.* Calc. for $C_{100}H_{88}B_2Co_2N_{10}O_6$: C, 72.12; H, 5.33; N, 8.41. Found: C, 72.05; H, 5.25; N, 8.30%. FTIR (KBr, cm^{-1}): 3548–3410s, 3237m, 3055m, 1671m, 1638m, 1618m, 1533s, 1473m, 1442m, 1388w, 1314m, 1258m, 1157w, 1061m, 1022m, 818m, 763m, 734m, 706m, 612m 472w.

2.5. X-ray crystallography

X-ray crystallographic data collection for all three solvates of **1**$(BPh_4)_2$ were carried out using a Bruker Kappa Apex-II CCD diffractometer with graphite monochromated Mo Ka radiation (λ = 0.71073 Å), at room temperature. Intensity data were collected in φ and ω directions and were averaged during the refinement cycles. The data sets were integrated with the Bruker Apex-II suite program and the reflection data were then corrected for Lorentz and polarization effects. Finally, absorption effects were corrected by multi-scan absorption correction method implemented on SADABS program [41]. All the structures were solved by the direct methods and all non-hydrogen atoms were refined with independent anisotropic displacement parameters by the full-matrix least squares technique based on F^2 using the SHELXL-2013 [42]. Hydrogen atoms attached to carbon atoms were included in the geometrically idealized positions. Their isotropic thermal displacement parameters were fixed depending upon the parent atoms and then were allowed to ride on their parent atoms. A summary of the crystallographic data and refinement parameters are given in Table 1.

3. Results and discussion

3.1. Syntheses and general characterizations

Compounds of general formula $[Co_2(bpy)_4(DHBQ)](BPh_4)_2\cdot 2X$ (X = solvent) were prepared by the reaction of bidentate bipyridyl ligand with hexaaqua salt of cobalt nitrate in three different solvents and subsequent addition of the dinegative $DHBQ^{2-}$ anion and sodium tetraphenylborate. Block dark red crystals were obtained for all the cases in moderate to high yield. The elemental analyses confirm that compositions of these compounds are eventually identical to those obtained from X-ray diffractions. All these compounds are partly soluble in common alcohols but completely soluble in acetonitrile and dimethylformamide.

The IR spectra of all three solvates of [**1**$(BPh_4)_2$] (Fig. 1) are quite similar to each other and in particular show a very intense band in the range 1530–1535 cm^{-1} to be assigned to carbonyl stretching mode of the bridging $DHBQ^{2-}$ ligand [43]. In addition, a sharp and moderate band appears at 1712 cm^{-1} and 1671 cm^{-1} in **1**$(BPh_4)_2\cdot 2CH_3COCH_3$ and **1**$(BPh_4)_2\cdot 2DMF$, respectively, which are characteristic stretching of carbonyl and amide groups in solvents acetone and DMF, respectively. Moreover, a weak stretching for $-C{\equiv}N$ bond for solvent acetonitrile molecule is appeared at 2252 cm^{-1} in **1**$(BPh_4)_2\cdot 2CH_3CN$.