Synthesis, structural characterization and spectroscopic properties of cobalt complexes with the 2,6-bis(8′-quinolinyl)pyridine ligand

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ABSTRACT

Coordination of the 2,6-bis(8′-quinolinyl)pyridine (**bqp**) ligand to a cobalt (Co) core and its influence to electron spin and configuration on the structures and properties of the resulting complexes has been investigated. The homoleptic complexes Co(*mer*-bqp-$\kappa^3 N,N',N''$)]$^{2+}$ (**1**) and [Co(*mer*-bqp-$\kappa^3 N,N',N''$)]$^{3+}$ (**2**) were prepared and characterized. X-ray structure determinations of complexes **1** and **2** revealed twisted, near-octahedral arrangements relative to the cobalt center. The magnetic data for **1** is typical of those for distorted octahedral (i.e., D_{4h} symmetry) high-spin d^7 species despite the near-ideal octahedral coordination of the **bqp** ligand around the Co(II) core. Electronic spectra for **1** and **2** have been investigated and assigned. Both complexes exhibit intense π–π^* **bqp** ligand centered transitions in the UV region and low intensity mixed charge transfer transitions in the visible region. Neither complex strongly absorbs in visible spectral region. The electrochemistry of these compounds has been studied and compared to that of similar cobalt terpyridine compounds. A metal-centered Co$^{2+/3+}$ redox wave and ligand-based reduction processes were observed for **1** and **2** in acetonitrile. The metal-centered redox potentials were reversible with potentials more positive than comparable cobalt-terpyridine complexes. Density functional theory (DFT) calculations of the electronic and ground state properties are in good agreement with the experimental data.

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1. Introduction

Multi-dentate polypyridyl ligands, such as 2,2′:6′,2″-terpyridine (tpy), 2,2′-bipyridine (bpy), and 1,10-phenanthroline (phen), are attractive ligands for constructing various catalytic, photo- and redox-active structures [1]. Among these, tridentate terpyridine derivatives are particularly unique from the viewpoint of synthetic and structural coordination chemistry [2]. Synthetic modification of the 4′-site on the tpy ligand is attractive as it does not result in isomeric complexes due to the existence of a twofold axis of symmetry in the tpy-$\kappa^3 N,N',N''$ chelate [1c]. This leads to the formation of well-defined structures where directionality is desirable, such as surface attachment and polymerization applications [1c,2e,3]. Because of their planar nature, terpyridine derivatives coordinate almost exclusively as meridional tridentate ligands, and structural changes are restricted when the oxidation state of the center changes [1c]. In this context, bis(terpyridine) metal complexes of the type [M(tpy)$_2$]X$_2$ (tpy = 2,2′:6′,2″-terpyridine; X$^-$ is, commonly, Cl$^-$, ClO$_4^-$, or PF$_6^-$) have been widely investigated due to their inert character and catalytic activity applied to the fields of light-into-energy conversion [4] and artificial photosynthesis [5]. Recently, materials have even been developed based on bis(terpyridine) cobalt(II) spin crossover systems [6].

We have initiated a program to use the 2,6-bis(8′-quinolinyl)pyridine (**bqp**) ligand to produce six-membered chelate rings instead of the traditional five-membered metallocycle formed in [M(tpy)$_2$]X$_2$ complexes. The result of this design is to optimize the N–M–N intraligand and bite angles towards idealized octahedral values of 90° and 180°, respectively, and, thereby, strengthening the ligand field [7]. This strategic design, for example, has previously led to improved quantum yields and prolonged excited state triplet lifetimes for the [Ru(tpy)$_2$]$^{2+}$ complex. Johansson and co-workers showed that when coordinated to a Ru^{II} center, the **bqp** ligand's bite angles were increased and its steric strain reduced, compared to normal terpyridines [7c,8]. As a result, the Ru^{II} bistridentate **bqp** complex exhibits significantly increased lifetimes due to a stronger ligand field and a lower rate of population to the ^{3}MC state [2d,7c].

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Here, we describe the synthesis, structural, spin state and electronic properties of two homoleptic bis(2,6-bis(8'-quinolinyl)pyridine) cobalt complexes Co(mer-bqp-κ^3N,N',N'')$_2$]$^{2+}$ (**1**) and Co(mer-bqp-κ^3N,N',N'')$_2$]$^{3+}$ (**2**) which differ only in the oxidation state of the central metal. Spectroscopic, magnetic and electrochemical properties of the compounds are obtained, and crystal structures of them, are discussed. Coordination of the **bqp** ligand was expected to change the ligand bite angles to near-ideal octahedral symmetries as well as the stability, flexibility, electronic and redox behavior of the resulting complexes. These features of ligand coordination can potentially play a role in the stabilization (or destabilization) of particular spin states, electronic states, or redox states in the resulting complexes, providing valuable information for further developments, in particular for the design of ligands capable of generating mixed-spin states, mixed-valent multinuclear compounds or redox mediators in dye-sensitized solar cells.

2. Experimental

2.1. General remarks

Cobalt(II) acetate tetrahydrate, Co(CH$_3$COO)$_2$·4H$_2$O, ammonium hexafluorophosphate (NH$_4$PF$_6$) and bromine (Br$_2$) were purchased from Aldrich and used without further purification. The 2,6-bis(8'-quinolinyl)pyridine (**bqp**) ligand was prepared in accordance to a previous literature report [8].

All solvents for synthesis were of reagent grade and used as received, unless otherwise specified. Anhydrous methanol (CH$_3$OH) and acetonitrile (CH$_3$CN) were distilled from Na/benzophenone [9]. For UV–Vis spectroscopy and electrochemical studies HPLC grade or reagent grade solvents were used. The reagent grade acetonitrile was first dried over silica gel for a minimum of 24 h. The silica gel was then filtered off and the acetonitrile was distilled over anhydrous calcium hydride [9].

2.2. Physical measurements

UV/vis spectra were recorded using a Cary 50 UV–Vis spectrophotometer with a xenon flashlamp. Room temperature emission spectra were measured on a Cary Eclipse fluorescence spectrophotometer. Low temperature excitation and emission spectra were obtained with a Photon Technologies International QuantaMaster Model C-60 spectrometer equipped with a xenon flash lamp and digital emission photon multiplier tube using a band pathway of 5 nm for excitation and 2 nm for emission. Voltammetry of the complexes was measured using acetonitrile as the solvent and tetra-n-butylammonium hexafluorophosphate (TBAH, 0.1 M) as the supporting electrolyte. The electrolyte was recrystallized in absolute ethanol and dried under vacuum in a desiccator for a minimum of 24 h prior to use [10]. Cyclic voltammograms were recorded using a PINE WaveNow potentiostatic analyzer in a three-electrode configuration. A glassy-carbon disk working electrode (3 mm diameter), a non-aqueous Ag$^+$/AgCl wire quasi-reference electrode, and a Pt disk counter electrode were used for all measurements. Recorded potentials were referenced using the ferrocene/ferrocenium couple (vs. SCE) as an internal standard usually added at the conclusion of the experiment [11]. ^{1}H and ^{13}C NMR spectra were measured with a Bruker AVANCE 500 high-field superconducting NMR spectrometer. Electrospray ionization (ESI) mass spectra were obtained with an Agilent Time-of-Flight MS G1969A Series 6200 in positive ionization mode using 1 ppm of the complexes in a 50% acetonitrile/water (LC/MS) with 10 μM of acetic acid (ionization agent). Magnetic susceptibility measurements in the solid state were carried out on a Johnson Matthey

Mark 1 magnetic susceptibility balance. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

2.3. Computational methods

DFT calculations were carried out by using Gaussian 09, revision A.02 [12]. For Gaussian calculations, Becke's three-parameter hybrid functional with the LYP correlation functional (B3LYP) [13] was used with the Los Alamos effective core potential LANL2DZ [14] basis set. Full geometry optimizations were performed using the B3LYP functional [13]. A double-ζ'' quality basis set consisting of Hay and Wadt's effective core potentials (LANL2DZ) [14] was employed for the Co(II and III) metal ions, and a 6-31G* basis set [15] was employed for the rest of the atoms. The relativistic effective core potential (ECP) replaced the inner core electrons of the Co(II and III) metal ions, leaving only the outer core valence electrons ($4s^24p^63d^7$ and $4s^24p^63d^6$ for Co(II) and Co(III), respectively). A vibrational frequency analysis was carried out in order to confirm the minimum-energy geometries. Molecular orbital (MO) diagrams were constructed for the fully optimized geometries in Gaussian. The Franck–Condon vertical excitation energies and oscillator strengths were obtained with time-dependent DFT (TD-DFT) [16] as implemented in Gaussian. The acetonitrile solvent influence was treated using conductor-like polarizable continuum model (CPCM) [17], as implemented in Gaussian.

2.4. Synthesis of the compounds

2.4.1. Synthesis of [Co(mer-bqp-κ^3N,N',N'')$_2$](PF$_6$)$_2$
2,6-Bis(8'-quinolinyl)pyridine (0.05 g, 1.5×10^{-4} mol) was added to an anhydrous methanol solution (30 mL) containing cobalt(II) acetate tetrahydrate (0.018 g, 7.2×10^{-5} mol). Once addition was complete, the reaction was stirred at room temperature for 2 h. Once stirring was complete, an excess of ammonium hexafluorophosphate (1.0 g, 6.1×10^{-3} mol) was added and immediate precipitation was observed. This was followed by the addition of water (distilled, 20 mL). The resulting brown precipitate was filtered, washed with cold water (3 × 10 mL) and diethyl ether (3 × 10 mL), and dried under vacuum. Yield: 93%. *Anal.* Calc. for C$_{46}$H$_{30}$CoF$_{12}$N$_6$P$_2$: C, 54.29; H, 3.17; N, 8.26. Found: C, 53.86; H, 3.15; N, 8.25%. Electronic absorption (CH$_3$CN), λ_{max}, nm (ε, M^{-1} cm^{-1}): 203 (102374, sh.), 225 (85775), 282 (21152), 306 (19929), 315 (19521), 360 (5522), 460 (1076, br.). ESI MS: $^m/_z$ 363 (parent peak, [M], where M is [Co(mer-bqp-κ^3N,N',N'')$_2^{2+}$]).

2.4.2. Synthesis of [Co(mer-bqp-κ^3N,N',N'')$_2$](Br$_3$)$_3$
Bromine (0.100 g, 1.25×10^{-3} mol) was added to a stirred solution of [Co(mer-bqp-κ^3N)$_2$](PF$_6$)$_2$ (0.068 g, 6.71×10^{-5} mol) and acetonitrile (20 mL). Once the addition was complete, the reaction was stirred at room temperature for 5 h. The resulting solution was evaporated to dryness under reduced pressure. The resulting dark orange solid was collected, washed with water (3 × 10 mL), and dried under vacuum. The yield was quantitative. ^{1}H NMR (CD$_3$CN-d_3): δ 8.50 (dd, J = 8.0 Hz, 2H), 8.45 (t, J = 8.0 Hz, 1H), 8.08 (m, 4H), 8.03 (dd, J = 4.6 Hz, 2H), 7.92 (dd, J = 4.1 Hz, 2H), 7.68 (t, J = 8.0 Hz, 2H), 7.42 (dd, J = 8.1 Hz, 2H). ^{13}C NMR (CD$_3$CN-d_6): δ 162.1, 154.5, 143.9, 143.3, 142.5, 133.2, 132.8, 129.7, 128.2, 128.0, 126.8, 124.1. *Anal.* Calc. for C$_{46}$H$_{30}$CoBr$_9$N$_6$: C, 43.11; H, 2.21; N, 11.17. Found: C, 42.59; H, 2.18; N, 11.09%. Electronic absorption (CH$_3$CN), λ_{max}, nm (ε, M^{-1} cm^{-1}): 208 (138612), 218 (131456, sh.), 266 (67709), 330 (28168, sh.), 357 (31095), 380 (19101, sh.), 461 (506, br.), 626 (0.1, br.). ESI MS: $^m/_z$ 242 (parent peak, [M], where M is [Co(mer-bqp-κ^3N,N',N'')$_2$]$^{3+}$). Note: prior to electrochemical studies an excess of ammonium hexafluorophosphate (1.0 g, 6.1×10^{-3} mol) was added and immediate precipitation was observed. This was followed by the addition of water