Coordination of expanded terpyridine ligands to cobalt

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ABSTRACT

The tridentate expanded terpyridine-like ligand N,N′-dimethyl-N,N′-dipyridin-2-yl-pyridin-2,6-diamine (ddpd) and $[Co(H_2O)_6](BF_4)_2$ give the high-spin complex mer-$[Co(ddpd)_2](BF_4)_2$ with a tetragonally compressed CoN_6 coordination geometry according to X-ray diffraction and SQUID measurements. UV–Vis–NIR spectra indicate a large ligand field splitting close to the high-spin/low-spin crossover point. Oxidation of the Co^{II} complex to Co^{III} is achieved with silver triflate. The self exchange between high-spin Co^{II} and low-spin Co^{III} is slow on the NMR time scale.

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1. Introduction

Oligopyridine metal complexes are widely used in supramolecular chemistry [1,2], for spin-crossover systems [3–7] and as chromophores for light-harvesting applications especially in dye-sensizited solar cells [8,9]. Cobalt(II) complexes of 2, 2′-bipyridine (bpy) and 2,2′;6′,2″-terpyridine (tpy) are known for more than 45 years and much work has been devoted to elucidating their structural coordination chemistry, optical spectra, magnetic data and spin states [10–17]. Recently, even materials have been developed based on bis(terpyridine) cobalt(II) spin crossover systems [18–24].

We have initiated a program to use expanded tpy ligands (N,N′-dimethyl-N,N′-dipyridin-2-yl-pyridin-2,6-diamine, ddpd) giving six-membered chelate rings instead of five-membered ones and thus optimizing the N–M–N angles towards idealized octahedral values (90°, 180°) [25,26]. This ligand-field design has led to improved quantum yields and to prolonged lifetimes of the excited ^{3}MLCT state for ruthenium(II) complexes due to the strong ligand-field imposed by the expanded ligand (Scheme 1) [25]. In copper(II) complexes both the ligand-field splitting Δ_o as well as the Jahn–Teller splitting $4\delta_1$ of mer-$[Cu(ddpd)_2]^{2+}$ is larger as compared to $[Cu(tpy)_2]^{2+}$ with smaller chelate rings (Scheme 1) [26]. Similar to $[Cu(tpy)_2]^{2+}$ the homoleptic complex mer-$[Cu(ddpd)_2]^{2+}$ engages in a dynamic Jahn–Teller distortion, albeit the temperature of the freezing-point is higher [26].

Here, we describe the properties of the homoleptic bis(ddpd) cobalt(II) complex mer-$[Co(ddpd)_2](BF_4)_2$ (**1**) (Scheme 1) with respect to structure, ligand field strength, spin state and redox properties and in comparison to "contracted" $[Co(tpy)_2](X)_2$ complexes.

2. Materials and methods

All reagents were used as received from commercial suppliers (ABCR, Acros, Sigma–Aldrich). The ddpd ligand was prepared according to the literature procedure [25]. IR spectra were recorded with a BioRad Excalibur FTS 3100 spectrometer as CsI disks. (vs) = very strong, (s) = strong, (m) = medium, (w) = weak. Electrochemical experiments were carried out on a BioLogic SP-50 voltammetric analyzer using a glassy carbon working electrode, a platinum wire as counter electrode and a 0.01 m $Ag/AgNO_3$ electrode as reference electrode. The measurements were carried out at a scan rate of 100 mV s^{-1} for cyclic voltammetry experiments using 0.1 M $(nBu_4N)(PF_6)$ as supporting electrolyte in CH_3CN. Potentials are given relative to the ferrocene/ferrocenium couple ($E_{½} = 85 \pm 5$ mV under the experimental conditions). UV–Vis–NIR spectra were recorded on a Varian Cary 5000 spectrometer using 1.0 cm cells (Hellma, Suprasil). ESI mass spectra were recorded on a Micromass Q-TOF-Ultima spectrometer. Melting points were determined using a Gallenkamp capillary melting point apparatus MFB 595 010 and were not corrected. Variable-temperature magnetic susceptibility measurements were carried out with a Quantum Design MPMS-XL7 SQUID magnetometer in the temperature range 2–300 K under an applied magnetic field of 1 T. Experimental susceptibility data were corrected the underlying diamagnetism using Pascal's constants. The temperature dependent magnetic contribution of the holder was experimentally determined and subtracted from the measured susceptibility data. Elemental analyses were performed by the microanalytical laboratory of the chemical institutes of the University of Mainz.

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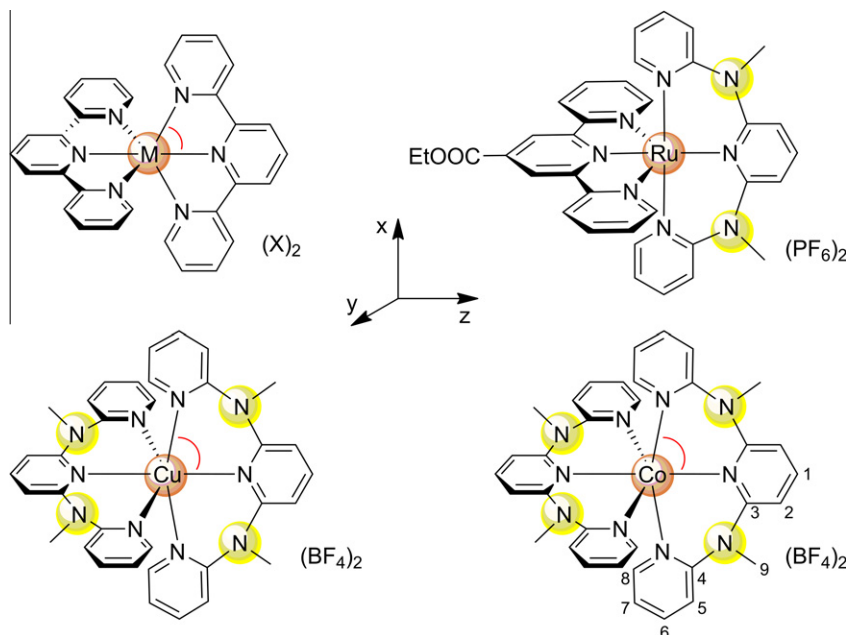
Scheme 1. Bis(tpy) metal complexes, heteroleptic tpy/ddpd-ruthenium(II) complex [25], *mer*-bis(ddpd) copper(II) [26] and *mer*-bis(ddpd) cobalt(II) complex, including atom numbering for NMR assignments.

2.1. Crystal structure determination

Intensity data were collected with a STOE IPDS 2T diffractometer using Mo Kα radiation (λ = 0.71073 Å) and corrected for absorption and other effects. The diffraction frames were integrated using the SAINT package, and most were corrected for absorption with MULABS [27,28]. The structure was solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXTL software package [29,30]. All nonhydrogen atoms were refined anisotropically, while the positions of all hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent carbon atoms with fixed isotropic thermal parameters.

$C_{38}H_{40}B_2CoF_8N_{12}$ (897.37); T = 193(2) K; 0.12 × 0.10 × 0.06 mm; orthorhombic, Fddd (No. 70); a = 14.1890(10) Å; b = 21.426(2) Å; c = 25.844(2) Å; V = 7856.9(11) Å^3; Z = 8; density = 1.517 mg m^{-3}; absorption coefficient 0.523 mm^{-1}; $F(0\,0\,0)$ = 3688; theta range for data collection 3.15–28.48°; limiting indices $-18 \leqslant h \leqslant 16$, $-28 \leqslant k \leqslant 28$, $-34 \leqslant l \leqslant 34$; reflections collected/unique = 21107/2481 [R_{int} = 0.0867]; completeness to theta = 28.47 = 99.5%; absorption correction: semi-empirical from equivalents; maximum and minimum transmission = 0.9693 and 0.9399; data/restraints/parameters = 2481/3/169; goodness-of-fit on F^2 = 1.059; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0479, wR_2 = 0.1125; R indices (all data): R_1 = 0.0704, wR_2 = 0.1238; largest difference in peak and hole: 0.320 and -0.402 e Å^{-3}.

2.2. Density functional theory calculations

DFT calculations were carried out with the GAUSSIAN 09/DFT [31] series of programs. The B3LYP formulation of DFT was used by employing the LANL2DZ basis set [31]. No symmetry constraints were imposed on the molecules. The presence of energetic minima was checked by analytical frequency calculations.

3. Experimental

Synthesis of 1: Cobalt(II) bis(tetrafluoroborate) hexahydrate (115 mg, 0.335 mmol) was dissolved in ethanol (6 ml) and added

to a solution of *N,N′*-dimethyl-*N,N′*-dipyridin-2-yl-pyridin-2,6-diamine (215 mg, 0.738 mmol) in ethanol (8 ml). A yellow suspension formed immediately. After stirring at room temperature for 2 h diethyl ether (40 ml) was added and the yellow precipitate was collected by filtration. The yellow product was washed with diethyl ether (25 ml) and dried under reduced pressure. Crystals for X-ray diffraction were obtained from acetonitrile. Yield 275 mg (0.299 mmol, 89%). Elemental *Anal.* Calc. for $C_{34}H_{34}B_2CoF_8N_{10}$ (815.25)·1.5H$_2$O: C, 48.48; H, 4.43; N, 16.63. Found: C, 48.62; H, 4.07; N, 16.75%. M.p. > 633 °C (decomp.). IR (CsI) $\tilde{\nu}$ = 3454 (br m, crystal water), 3072 (w, CH$_{py}$), 2923 (w, CH$_3$), 2829 (w, CH$_3$), 1595 (s), 1490 (s), 1448 (s), 1437 (vs), 1367(s), 1340 (s), 1311 (w), 1276 (w), 1234 (s), 1169 (s), 1132 (s), 1095 (s), 1057 (vs), 1032 (sh, BF), 949 (w), 868 (w), 784 (s), 615 (w), 584 (w), 521 (w), 432 (w) cm^{-1}. MS (ESI$^+$): m/z (%) = 320.60 (24) [M−(BF$_4$)$_2$]$^{2+}$, 369.09 (100) [M−ddpd−(BF$_4$)$_2$+F]$^+$. ^{1}H NMR (CD$_3$CN, 400 MHz): δ = 74.0 (s, 2 H, H^2), 68.1 (s, 2 H, H^5), 34.8 (br s, 2 H, H^8), 33.9 (s, 2 H, H^7), 22.1 (s, 6 H, H^9), 21.6 (s, 1 H, H^1), 2.8 (s, 2 H, H^6) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN, 100 MHz): δ = 602.1 (s, C^2), 517.8 (s, C^5), 445.2 (s, C^7), 208.0 (s, C^1), 164.1 (s, C^6), 33.0 (s, C^3), 25.5 (s, C^9), -47.9 (s, C^4), -215.9 (br. s, C^8) ppm.

4. Results and discussion

The target complex **1** *mer*-[Co(ddpd)$_2$](BF$_4$)$_2$ is prepared in good yields as yellow powder by ligand displacement in [Co(H$_2$O)$_6$](BF$_4$)$_2$ with two equivalents of the ddpd ligand. ESI mass spectra indicate the correct formation of the bis(ddpd) complex. The tetrafluoroborate counter ions of **1** give rise to an absorption in the infrared spectrum at $\tilde{\nu}$ = 1032 cm^{-1} (BF stretch). Elemental analysis and the IR spectrum indicate the presence of crystal water (**1**·1.5H$_2$O). Single crystals suitable for crystal structure determination were obtained by recrystallization from acetonitrile. The cobalt complex **1** crystallizes with two acetonitrile molecules *mer*-[Co(ddpd)$_2$](BF$_4$)$_2$·2CH$_3$CN in the orthorhombic space group Fddd. The packing of cobalt and boron corresponds to the TiSi$_2$ (C54) structure (Supplementary Information).

As typically found in meridional pseudo-octahedral complexes several intermolecular offset-face-to-face (*off*) and edge-to-face