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Inorganica Chimica Acta 360 (2007) 3945–3950

Inorganica Chimica Acta

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Optical investigation of spin-crossover in cobalt(II) bis-terpy complexes

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Received 12 December 2006; received in revised form 8 June 2007; accepted 17 June 2007
Available online 28 June 2007

Paper presented in the MAGMANet-ECMM, European Conference on Molecular Magnetism, that took place last October 10–15 in Tomar, Portugal.

Abstract

The spin transition of the $[Co(terpy)_2]^{2+}$ complex (terpy = 2,2′:6′,2″-terpyridine) is analysed based on experimental data from optical spectroscopy and magnetic susceptibility measurements. The single crystal absorption spectrum of $[Co(terpy)_2](ClO_4)_2$ shows an asymmetric absorption band at 14400 cm^{-1} with an intensity typical for a spin-allowed d–d transition and a temperature behaviour typical for a thermal spin transition. The single crystal absorption spectra of suggest that in this compound, the complex is essentially in the high-spin state at all temperatures. However, the increase in intensity observed in the region of the low-spin MLCT transition with increasing temperature implies an unusual partial thermal population of the low-spin state of up to about 10% at room temperature. Finally, high-spin → low-spin relaxation curves following pulsed laser excitation for $[Co(terpy)_2](ClO_4)_2$ dispersed in KBr discs, and as a comparison for the closely related $[Co(4\text{-terpyridone})_2](ClO_4)_2$ spin-crossover compound are given.

Keywords: Spin-crossover; Cobalt(II) bis-terpyridine; Absorption spectra; Magnetic susceptibility; High-spin → low-spin relaxation

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1. Introduction

Spin-crossover solids [1] are molecular compounds of transition metal ions with electronic configurations d^4, d^5, d^6, and d^7, switchable between two states with different optical and magnetic properties: the low-spin (LS) state with maximum number of paired and the high-spin (HS) state with maximum number of unpaired d electrons. The occurrence of a thermal spin transition can be readily understood based on simple thermodynamic considerations [2]: if the zero-point energy difference between the two states is small and such that the low-spin state is the quantum mechanical ground state, an entropy driven transition from the low-spin state at low temperatures to the high-spin state at higher temperatures may be observed. The large majority of known spin-crossover complexes are based on a Fe(II) as central ion, but other transition metal ions also give rise to spin-crossover complexes, such as Co(II), Co(III), Mn(II), Mn(III), Cr(II) or Fe(III). To date, only a few detailed studies discuss the class of Co(II) spin-crossover complexes [3].

The $[Co(terpy)]^{2+}$ complex (terpy = 2,2′:6′,2″-terpyridine) is one of the first and most important cobalt(II) spin-crossover complexes discovered to date [4,5], for which the transition occurs from the ^2E low-spin manifold to the $^4T_1$ high-spin manifold. It has a two tridentate coordination motif. In the low-spin state, the equatorial metal to ligand bond length is 0.17 Å longer than the axial bond length in the low-spin state [6]. This results in a stabilisation of the low-spin state as a consequence of the Jahn–Teller effect [7]. The approximate symmetry of the complex is D_{2d} with an additional Jahn–Teller distortion [7]

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doi:10.1016/j.ica.2007.06.022

resulting in a symmetry lowering to C_{2v}. However, this distortion is small, and for the sake of simplicity will be neglected in the ensuing discussion. The transition to the high-spin state is accompanied by a substantial change in metal–ligand bond lengths: the axial bond length increases by 0.21 Å, the equatorial one by 0.08Å [6]. As a result, the distortion of the coordination octahedron is much less pronounced in the high-spin state.

Previous investigations on $[Co(terpy)]^{2+}$ showed that its spin-crossover behaviour depends crucially on the anion and on solvent content. The anhydrous $[Co(terpy)_2](ClO_4)_2$, for instance, is fully in the low-spin state at low temperatures and shows a transition to the high-spin state with a thermal population ~80% at room temperature [4,5]. The various hydrated forms, on the other hand, show different degrees of partial spin transitions with remnant high-spin fractions at low temperature, or temperature independent populations of the two spin states. In this paper, we present experimental results derived mainly from optical absorption measurements on the $[Co(terpy)]^{2+}$ complex with two different anions, CLO_4^- and PF_6^-, respectively, in the absence of any solvent molecules in the crystal lattices.

2. Experimental

Single crystals of $[Co(terpy)_2](ClO_4)_2$ and $[Co(terpy)_2](PF_6)_2$ were grown from ethanol/acetonitrile solutions according to literature methods [4]. Red, transparent crystals of square pyramidal shape were obtained, which are dichroic in the case of $[Co(terpy)_2](PF_6)_2$. As the presence of water molecules in the unit cell may influence the geometry and the local electronic structure of the title complexes [4,5], the synthesis was performed in water free solvents in order to synthesise the compounds without any lattice water. Elemental analyses confirmed the composition without any lattice solvent molecules. The PF_6^- salts of Co^{2+} and Zn^{2+} are isomorphous and crystallise in the space group $P\bar{4}2_1c$, with the molecular S_4 axis parallel to the crystal c-axis [8].

The $[Co(terpy)_2](ClO_4)_2$ solution for spectroscopic measurements was prepared in a mixture of proprionitrile/butyronitrile (4:5), and corresponding absorption spectra were recorded on a Cary50 spectrometer.

For optical measurements single crystals with a thickness varying from 90 to 140 μm were mounted so as to cover entirely a small aperture in a copper sample holder. For low temperature measurements, the sample holder was inserted into a closed cycle cryostat capable of achieving temperatures down to 10 K, with the sample sitting in 1 bar of He exchange gas for efficient cooling. Complete absorption spectra of crystals, that is, from 6000 to 27 000 cm^{-1}, were recorded on an FT-IR spectrometer (Bruker IFS66/S). The source light was provided either by a tungsten halogen or a xenon lamp, and the signal was measured using a Ge (6000–12 000 cm^{-1}), a Si (9000-21 000 cm^{-1}) or a GaP (18 000–27 500 cm^{-1}) diode detectors.

Relaxation curves were recorded on $[Co(terpy)_2](ClO_4)_2$ dispersed in KBr by monitoring the transient bleaching of the MLCT band of the low-spin species at 505 nm, following pulsed excitation with the second harmonic of a Q-switched Nd:YAG laser at 532 nm, with a repetition rate of 20 Hz. The light provided by a 50 W tungsten halogen lamp was used as probe beam. After passing through the sample, the probe beam was dispersed in a 1/4 m monochromator (Spex 280M), then amplified with a photo-multiplier (R928). Transient absorption curves were recorded using a digital oscilloscope (Tektronix TDS540B).

3. Results and discussion

3.1. The thermal spin transition

The temperature dependence of the solution spectrum of $[Co(terpy)_2](ClO_4)_2$ in proprionitrile/butyronitrile (4:5) at room temperature is presented in Fig. 1a. Absorption max-

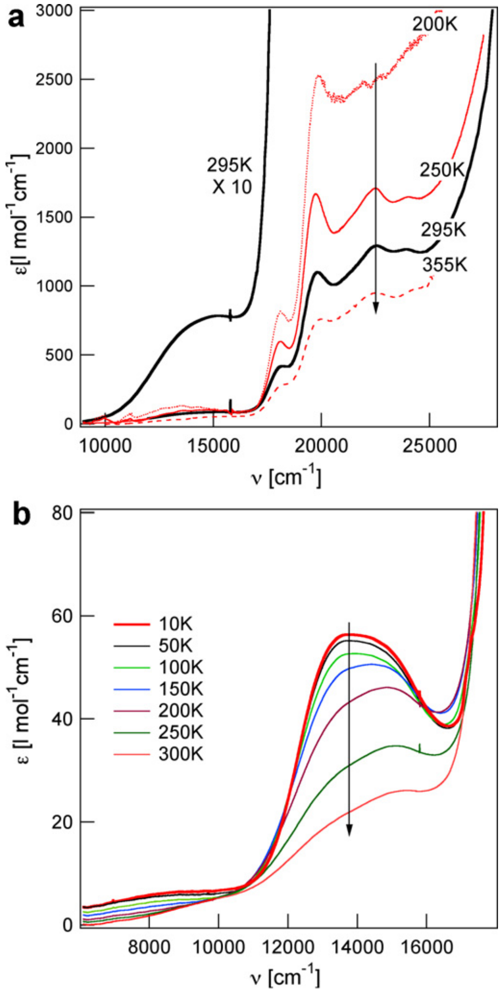

Fig. 1. (a) Temperature dependence of the electronic absorption spectrum for a 10^{-3} M solution of $[Co(terpy)_2](ClO_4)_2$ in proprionitril/butyronitril (4:5). (b) Temperature dependent absorption spectra of single crystals of $[Co(terpy)_2](ClO_4)_2$ between 10 and 300 K.