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Thermally Induced and Photoinduced Valence Tautomerism in a Two-Dimensional Coordination Polymer

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Herein reported is the first two-dimensional coordination polymer capable of undergoing thermally induced and photoinduced valence tautomeric transitions.

Electronically labile metal complexes possess two or more electronic states energetically accessible upon a change of conditions (temperature, pressure, or application of irradiation)[1] that result in changes in the structural features and physical properties.[2] Interesting mechanical, magnetic, and photophysical properties have been observed, based on which futuristic applications of such materials for the development of miniature molecule-based display devices and data storage elements have been envisioned.[1,3]

Valence tautomers (VTs), capable of reversible interconversion between redox isomers, are such a family of molecules.[4] The studies of valence tautomerism have been concentrated on mononuclear Co complexes of the general formula $[Co(Q)_2(L)]$, wherein Q is a *o*-quinone-based ligand and L is typically a pyridyl-based chelating ligand.[5] The quinone-based ligand undergoes a two-step redox reaction, affording a semiquinonato ($Sq^{\bullet-}$) ligand and a catecholato (Cat^{2-}) ligand upon reduction by one and two electrons, respectively.[5,6] When the energies of the metal and ligand frontier orbitals are comparable, intramolecular electron transfer (LMCT or MLCT) is a likely event.[7] Together with the spin transition of the metal center, interconversion of two redox isomers, low-spin (ls) $[Co^{III}(Sq)(Cat)(L)]$ and high-spin (hs) $[Co^{II}(Sq)_2(L)]$, is achieved.[5,7]

Although most of the progress in the study of VT complexes has been achieved with mononuclear Co complexes, there exist a small number of one-dimensional coordination polymers containing Co complex units with a bridging ditopic ligand such as pyrazine[8] or a bis-bidentate dioxolene ligand.[9] For the former, interesting photomechanical effects upon valence tautomerization have been demonstrated in crystalline form. That similar properties are not found in their mononuclear or dinuclear cognates suggests that the observed properties are a result of the cooperativity unique to the extended systems.[10] For the latter, thermal hysteresis has been found to be induced by the bis-bidentate ligand in VT interconversion processes of the putative polymeric complex structure.[11] These results suggest that interesting properties associated with VT may be achieved with higher-dimensional

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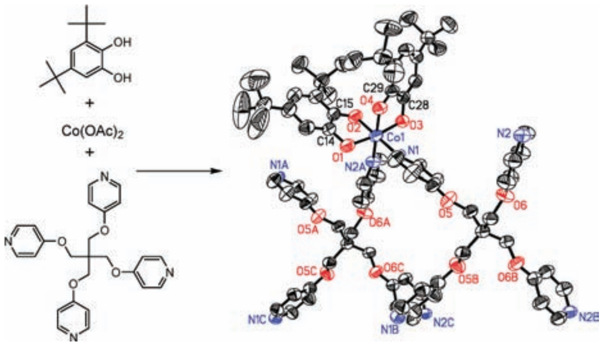

Figure 1. Synthesis and ORTEP drawing of the valence tautomeric unit of **1**. Selected bond distances (Å) at 293 K: Co1−O1 1.894(3), Co1−O2 1.888(3), Co1−O3 1.927(3), Co1−O4 1.894(3), Co1−N1 1.963(4), Co1−N2 1.944(4), O1−C14 1.350(5), O2−C15 1.318(5), O3−C28 1.335(5), O4−C29 1.290(5), C14−C15 1.391(7), C28−C29 1.415(7).

framework structures using $Co(Q)_2$ units as building blocks. It was with this consideration that we set out to synthesize a two-dimensional coordination polymer, reported herein, featuring discrete $Co(Q)_2$ units interlinked by tetrakis(4-pyridyloxymethylene)methane (TPOM), a tetrapyridyl bridging ligand (Figure 1), and to explore any interesting properties arising from its novel structure.

The title compound, formulated as $\{[Co^{III}(3,5\text{-DBcat})(3,5\text{-DBsq})]_2(TPOM)\}\cdot 8H_2O\cdot 2C_2H_5OH$ (**1**; 3,5-DBcat = 3,5-di-*tert*-butylcatecholate and 3,5-DBsq = 3,5-di-*tert*-butylsemiquinone) based on crystallographic analysis, was obtained by layering an ethanol solution containing 3,5-di-*tert*-butyl-1,2-catechol and TPOM onto an aqueous solution of $Co(CH_3COO)_2\cdot 4H_2O$ (Supporting Information, SI). The asymmetric unit of this fascinating coordination polymer and the first example of a two-dimensional VT system, to the best of our knowledge, contains one distinct Co atom, two complete dioxolene ligands, and half of a bridging TPOM ligand (Figure 1). The Co atom is hexacoordinate with its slightly distorted octahedral coordination sphere containing four O atoms from two dioxolene ligands and two cis-disposed pyridyl N atoms of different TPOM ligands. At 293 K, the Co−N bond lengths are 1.944(4) and 1.963(4) Å, while the Co−O bond lengths range from 1.888(3) to 1.927(3) Å. These metric values are comparable to those of previously reported mononuclear ls Co^{III}(Cat)(Sq) complexes.[5-7] The existence of radical $Sq^{\bullet -}$ ligand at room temperature was confirmed by electron spin resonance (ESR) measurement; there is one strong signal at $g = 1.996$ (Figure S1 in the SI). The C−O bond lengths of O1−C14 1.350(5) Å and O2−C15 1.318(5) Å (average 1.334 Å) are slightly longer, as expected, than those of the putative $Sq^{\bullet -}$ ligand [O3−C28 1.335(5) Å and O4−C29 1.290(5) Å (average 1.313 Å)]. This assignment is consistent with the bond lengths of the involved carbon atoms; the C14−C15 and C28−C29 bond lengths are 1.391(7) and 1.415(7) Å, respectively, with the one associated with the $Sq^{\bullet -}$ ligand being slightly longer.[5-7] It should be noted that these metric values are not as distinct as those anticipated from clearly defined Cat^{2-} and $Sq^{\bullet -}$ ligands. This is not surprising because the crystal data set was collected at 293 K (Tables S1 and S2 in theSI) and the VT interconversion of $\{[Co^{III}(3,5\text{-DBcat})(3,5\text{-DBsq})]_2(TPOM)\}$ and $\{[Co^{II}(3,5\text{-DBsq})(3,5\text{-DBsq})]_2(TPOM)\}$ (see below) occurred at near room temperature.

In the structure of **1**, the four pyridyl groups of the inherently flexible TPOM ligand adopt a distorted tetrahedral disposition, each of which coordinates to a different Co atom. As shown in Figure 1, two adjacent coordination sites of each Co atom are occupied by two N atoms from different TPOM ligands. The remaining pyridyl groups on each of these TPOM ligands are utilized in the same fashion. As such, a wavelike structure composed of two layers of Co atoms and a "sandwiched" layer of bridging TPOM ligands is assembled; diamond-shaped pores along the crystallographic *ab* plane can be clearly identified (Figure S2 in the SI and Figure 2). These layers stack along the *c* axis, yielding a rather porous structure, inside which solvent molecules are housed; the identity and number of solvent molecules cannot be identified by single-crystal X-ray analysis. However, thermogravimetric (TGA; Figure S3 in the SI) and elemental analyses suggest that there exist four H_2O and one C_2H_5OH per crystallographically determined asymmetric unit.

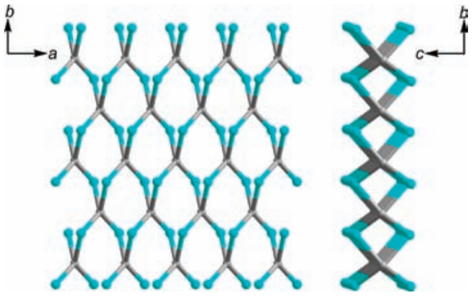

Figure 2. View of the layered structure of complex **1** in a simplified ball-and-stick model.

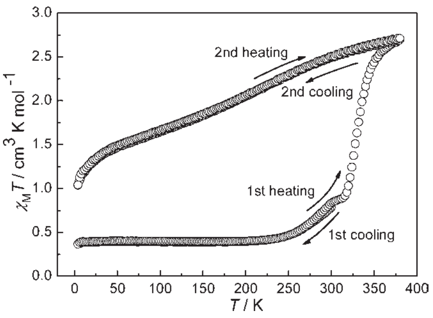

Figure 3. $\chi_M T$ vs T plots of **1**.

The magnetic properties of **1** were studied in two successive cooling/heating cycles in the 5−380 K temperature range. The corresponding plots of $\chi_M T$ versus T are shown in Figure 3. First, the sample was cooled from 300 to 5 K (designated as the first cooling). The $\chi_M T$ value decreases gradually from 0.78 cm^3 K mol^{-1} to a constant value of 0.40 cm^3 K mol^{-1}, typical of an $Sq^{\bullet -}$ radical ($S = {}^1/_2$), between 220 and 5 K. The wide plateau indicates that, below ca. 220 K, the ls $\{[Co^{III}(3,5\text{-DBcat})(3,5\text{-DBsq})]_2(TPOM)\}$ species is dominant, a conclusion consistent with the observed metric values of the C−O and C−C bond distances of interest.[5-7] Upon heating, three distinct stages of $\chi_M T$ change versus T were observed. From 5 to 220 K, the $\chi_M T$ value remains constant at 0.40 cm^3 K mol^{-1}, essentially the reverse of the aforementioned cooling process. From 220 K, the $\chi_M T$ value increases gradually, reaching a value of 0.89 cm^3 K mol^{-1} at 314 K, indicating the occurrence of electron transfer from the Cat^{2-} ligand to the Co^{III} center, resulting in a population of the $Co^{II}-Sq^{\bullet -}-Sq^{\bullet -}$ isomer. The relatively high transition temperature may be a reflection of the cooperativity originating from the polymeric two-dimensional structure.[8,9] The $\chi_M T$ value then rises rapidly, reaching the value of 2.69 cm^3 K mol^{-1} at 380 K, corresponding to a hs Co^{II} ion ($S = {}^3/_2$) with two Sq$^{\bullet -}$ radicals ($S = {}^1/_2$).[5−7]

TGA (Figure S3 in the SI) shows that desolvation of the as-prepared sample of **1** starts at room temperature and continues until its completion at ca. 380 K. The solvent-free structure is, however, stable up to ca. 430 K, above which decomposition occurs. It is reasonable to assume that it is desolvation that causes the abrupt and unsmooth VT transition at ca. 314 K. Because desolvation is completed at the conclusion of heating cycle 1, magnetic studies can be carried out in any further cooling/heating cycle using the solvent-free sample obtained. In fact, a completely different magnetic behavior versus temperature change was observed. Upon cooling, the $\chi_M T$ value decreases gradually from 2.69 cm^3 K mol^{-1} at 380 K to 1.38 cm^3 K mol^{-1} at 30 K, below which an abrupt and rapid $\chi_M T$ decrease occurred, reaching a value of 1.00 cm^3 K mol^{-1} at 5 K. The corresponding heating process gave a $\chi_M T$ versus T curve that is essentially superimposable with the one from the above cooling process. In other words, the solvent-free sample undergoes a reversible VT transition, but without a well-defined transition temperature, thus suggesting an incomplete VT transition. In contrast, during the first cooling/heating cycle, the VT transition is irreversible because of desolvation of the as-prepared sample. To the best of our knowledge, the present work represents the first comparative study of a VT complex between its solvated and solvent-free forms.[12] Although how exactly the solvent molecules influence the VT behavior remains unclear because of the lack of detailed structural information on the solvent-free complex, the "softness" imparted by the solvate molecules trapped in the crystalline lattice is hypothesized to play an important role in affecting the vibrational relaxation of the molecules, and hence the different VT behaviors.[13] Further research along this line is worthwhile and is expected not only to generate insights into the VT properties of such complexes but also to discover useful materials through the systematic introduction of selected solvents to the desolvation samples.

Although most VT complexes display thermally induced interconversion between the redox isomers, valence tautomerism can also be induced by optical irradiation. When compound **1** was irradiated with a blue light (457−473 nm and 150 mW) for 3 h at 5 K, the $\chi_M T$ value increased from 0.40 cm^3 K mol^{-1} to 1.00 cm^3 K mol^{-1} (Figure 4), clearly suggesting charge transfer putatively from Cat^{2-} to ls Co^{III}. The percentage of conversion was found to be about 30%. When the light was switched off and the sample was heated at 1 K min^{-1} to 20 K, the $\chi_M T$ value increased smoothly to 1.05 cm^3 K mol^{-1} because of the zero-field splitting of the hs Co^{II} ion.[14] The metastable state was readily accessible until 35 K, after which the $\chi_M T$ value gradually decreased, and the initial magnetic susceptibility value was restored at 78 K. The observed behavior indicates that the interconversion between {[Co^{III}(3,5-DBcat)(3,5-DBsq)]$_2$(TPOM)} and {[Co^{II}(3,5-DBsq)(3,5-DBsq)]$_2$(TPOM)} is photoswitchable.

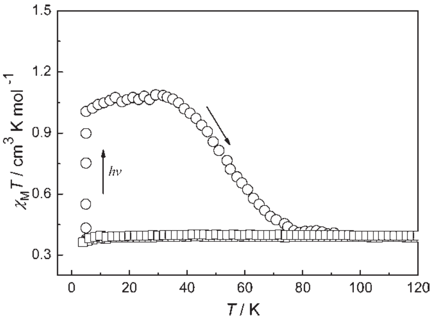

Figure 4. Evolution of $\chi_M T$ of **1** under irradiation at 457−473 nm and 5 K, followed by thermal relaxation of the metastable state from 5 to 90 K.

In summary, we report herein the first example of a two-dimensional coordination polymer that undergoes VT conversion, both thermally and by optical irradiation. The formulation of the compound {[Co^{III}(3,5-DBcat)(3,5-DBsq)]$_2$(TPOM)}, featuring a diamagnetic Co^{III} complex coordinated by two dioxolene ligands in different forms (Cat^{2-} and Sq$^{\bullet -}$), is collectively supported by crystallographic analysis, electron paramagnetic resonance spectroscopic studies, and magnetic measurement. The incorporation of VT complex units into sophisticated framework structures may lead to technologically interesting materials cooperative in their physical properties, although there is little interaction between the Co complex units in the present network structure because a flexible ether moiety is contained in the linker. Together with the large number of mononuclear VT complexes known and the small number of one-dimensional VT coordination polymers, complex **1** and many other higher-dimensional VT framework compounds to be synthesized are expected to contribute to the systematic studies of VT materials.

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Supporting Information Available: Experimental details, tables, TGA, ESR, powder X-ray diffraction, and crystal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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