Review

Switchable cobalt coordination polymers: Spin crossover and valence tautomerism

Olga Drath, Colette Boskovic *

School of Chemistry, University of Melbourne, Victoria 3010, Australia

A B S T R A C T

Electronically labile, or switchable, cobalt coordination polymers exhibit reversible spin crossover (SCO) or valence tautomeric (VT) transitions upon the application of an external stimulus, such as temperature variation. Spin crossover transitions at pseudo-octahedral cobalt(II) centers with an appropriate ligand field involve a heating-induced transition from the low-spin to high-spin electronic configurations. Valence tautomeric transitions are most commonly observed for cobalt-dioxolene systems, which undergo an intramolecular electron transfer and concomitant spin transition at the cobalt center, from low-spin-cobalt(III)-catecholate at low temperature to high-spin-cobalt(II)-semiquinonate upon heating. The VT transition can also be induced by light, while the cobalt(II) SCO transition cannot. Incorporation of these switchable moieties into coordination polymers (CPs) is generally achieved using polytopic nitrogen-donor linking ligands. All but one of the switchable cobalt CPs that have been structurally characterized are 1D chains, most of which exhibit VT transitions rather than SCO. There is a single example of a switchable 2D cobalt CP where VT cobalt-dioxolene moieties are linked by a tetratopic nitrogen-donor bridging ligand. Efforts to confer the VT properties to compounds suitable for applications as materials or in devices have mainly focused on the incorporation of the 1D chain VT CPs into nano- and microparticles, in which the VT transition is generally maintained. Valence tautomeric nanoparticles synthesized from 1D chain CPs have been grafted on to gold surfaces as self-assembled monolayers.

© 2017 Elsevier B.V. All rights reserved.

Contents

1. Introduction

Prussian blue is an early example of a functional coordination polymer (CP), with its use as a pigment dating back to the early 18th century. The structure of Prussian blue involves cyanide ligands that link iron centers into an infinite 3D network [1]. Replacement of the cyanide ligands with larger ditopic organic ligands that can link metal centers into potentially porous frameworks has afforded a substantial field of contemporary chemical endeavor. Many thousands of CPs, or metal–organic-frameworks (MOFs), have now been synthesized and structurally characterized

[2–6]. Research in the field has recently shifted from the original emphasis on generating new structural types to dedicated efforts to optimize the chemical and physical features to develop materials for future applications ranging from sensing, separations, gas storage and heterogeneous catalysis [7–10]. Prussian blue is comprised of both Fe(II) and Fe(III) centers and the intense blue color that gives rise to its use as a pigment is due to an intervalence charge transfer between the mixed-valence iron centers [11]. Thus Prussian blue is also the first example of a synthetic CP with functionality derived from its electronic properties, acting as a forerunner for the interest in CPs with electronic features that can potentially be harnessed in devices and new materials. Electronic properties that have been identified in CPs as relevant for future applications include luminescence, conduction and non-linear optical and magnetic properties, while CPs may also one day find employment in optoelectronic or photonic devices [10,12–14].

A class of CPs that are of interest for their electronic properties are those that undergo spin crossover (SCO). This phenomenon involves a stimulated reversible spin transition, generally at an octahedral metal center with d^4 to d^7 electronic configuration. The best known class of SCO compounds feature the d^6 Fe(II) ion, for which the transition is most commonly induced by heating/cooling. However, other stimuli are also active, notably irradiation with visible light, making use of so-called light-induced excited spin-state trapping (LIESST), which can be reversed through irradiation at a different wavelength via the reverse-LIESST effect [15–17]. Ranging from 1D chains to 2D nets and 3D networks, there are a number examples of CPs that exhibit SCO at Fe(II) centers [18–20]. Of great importance to the field of SCO is pioneering work from Kahn et al. who identified SCO in the 1D polymers [Fe(4-R-1,2,4-triazole)$_3$]$^{2+}$ (R = H, NH$_2$ and CH$_2$CH$_2$OH), which are bistable with substantial hysteresis at room temperature [21]. Another interesting family of SCO CPs are the heterometallic 3D Hofmann networks of general formula {Fe(NLN)[M(CN)$_4$]} (NLN = ditopic N-donor ligand such as pyrazine (pyz) and M = Ni, Pd or Pt), which can exhibit guest-sensitive hysteresis and multi-step SCO transitions that may ultimately find application in gas sensors or stimuli-responsive switching devices [22–29].

After Fe(II), the d^7 Co(II) ion is the next most prevalent ion for SCO [30,31], although the field of SCO of Co(II) systems is far less developed and SCO has been reported for relatively few Co(II) CPs. Instead there are more examples of Co CPs that exhibit the related, but more complicated, phenomenon of valence tautomerism [32–40]. Also predominantly stimulated by temperature variation, valence tautomeric (VT) transitions involve an intramolecular electron transfer between a redox-active metal center and a coordinated ligand that is also redox-active. By far the largest family of VT compounds are cobalt-dioxolene systems, for which SCO accompanies the electron transfer. All cobalt CPs that exhibit VT are based on linked cobalt-dioxolene units. Compounds that exhibit either VT or SCO can be described as electronically labile and they exhibit a number of features in common. For future practical applications it is important that the transitions are reversible and thus the systems are "switchable". If hysteresis accompanies the transition, the system is said to be bistable, which is essentially for applications in display devices or data storage. It is also important that the two forms that are interconverted can be readily distinguished. This is generally true for both SCO and VT compounds based on cobalt, for which the species with the two different electronic states and/or charge distributions, typically have distinctly different structural, optical and magnetic properties. Thus the transitions can be monitored by a variety of physical techniques, including magnetic susceptibility, X-ray diffraction and EPR or electronic spectroscopy. Both SCO and VT transitions can occur in solid and solution states, although the transition characteristics often differ in different media.

There are several motivations for extending switchable SCO or VT systems from discrete metal complexes into 1D, 2D or 3D CPs. First, arranging the switching units into infinite CPs can substantially increase the cooperativity of the transition as it propagates through the CP with a domino-like effect, affording the abrupt transitions and possibly bistability that are important for applications. Second, porous 2D and 3D materials can exhibit host–guest interactions that can tune the characteristics of the electronic transition and give rise to applications related to sensing, separation or heterogeneous catalysis. Third, the combination of SCO or VT units into CPs with other functional units can potentially give rise to multifunctionality. Finally, CPs can in some instances be readily incorporated into materials such as gels, films, fibres, nanoparticles and microspheres [41–43], which may facilitate the exploitation of the VT/SCO properties in devices. The most explored electronically labile, or switchable, CPs are those that feature SCO at Fe(II) and the reader is referred to several reviews of this topic [18–20]. In contrast, the area of cobalt CPs that exhibit SCO and/or VT transitions is yet to be reviewed in a dedicated way and it is the intention of the present work to fill this void.

2. Spin crossover in cobalt compounds

Thermally induced spin crossover in Co(II) compounds generally involves the transfer of an electron from a t_{2g} orbital of a low-spin (LS) pseudo-octahedral Co(II) ion with a ^{2}E ($t_{2g}^6 e_g^1$) ground term to an antibonding e_g^* orbital, affording the ^{4}T$_1$ ($t_{2g}^5 e_g^2$) high-spin (HS) state (Fig. 1). A spin change of $\Delta S = 1$ is associated with this transition from $S = 1/2$ to $S = 3/2$, which is less that the ΔS value of 2 for SCO at Fe(II) (from $S = 0$ to $S = 2$). The ^{4}T$_1$ HS octahedral Co(II) ion has significant first order orbital angular momentum, while the LS Co(II) ion tends to undergo Jahn-Teller distortion.

Spin crossover occurs most commonly for Co(II) complexes with an N$_6$ coordination sphere, which can be realized using combinations of monodentate and chelating N-donor ligands. The most common examples are [Co(N$_3$L)$_2$]$^{2+}$ complexes, where N$_3$L is a tridentate triimine ligand such as terpyridine. There are also examples of [Co(N$_2$L)$_3$]$^{2+}$ SCO complexes, where N$_2$L is a bidentate diimine ligand. For isostructural complexes, the crystal field splitting is larger for Fe(II) than for Co(II), consequently ligand sets that are appropriate to induce SCO in an Fe(II) complex may not give rise to SCO in Co(II). The other property distinguishing Co(II) SCO is the strong Jahn-Teller effect in the LS state, which arises from the singly occupied e_g^* orbital. Quite often, the coordination geometry of a LS-Co(II) ion is markedly distorted from octahedral. The [Co(N$_3$L)$_2$]$^{2+}$ complexes in the LS state consist of two *trans*-disposed shorter axial bonds (ca. 1.9 Å Co—N distances) and four longer equatorial bonds (ca. 2.1 Å Co—N distances). Associated with the increased population of the antibonding e_g^* orbitals, the SCO transition induces an increase in bond lengths, which is observed mainly for the two axial bonds while the equatorial bonds elongate to a very small extent, resulting in a much less distorted octahedral geometry in the HS state. The average difference in the six bond lengths between the LS and HS Co(II) states is around 0.07–0.11 Å versus 0.18–0.20 Å for SCO in Fe(II) complexes [31]. Thermally-induced SCO transitions in Co(II) complexes are entropically driven, with the entropy gain arising from both the higher density of vibrational states of the HS-Co(II) complex (due to the longer Co—N bond lengths) and the higher spin state degeneracy of HS-Co(II) versus LS-Co(II). A consequence of the smaller difference in bond lengths for Co(II) SCO systems, and the resulting weaker intermolecular cooperativity, is that the transitions are generally more gradual than for Fe(II) and are often incomplete,