Towards Controlling the Solid State Valence Tautomer Interconversion Character by Solvation

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ABSTRACT: Crystals of [Co(diox)2(4-NO2-py)2] (I) and [Co(diox)2(4-CN-py)2] (2) where diox are the o-Dioxolene 3,5-di-t-butylsemiquinonate (SQ) and/or 3,5-di-t-butylcatecholate (Cat) ions, 4-NO2-py is 4-nitro-pyridine, 4-CN-py is 4-cyano-pyridine, are among the few known crystals presenting both thermal-induced and photoinduced Δs-[M3+2(SQ)+](Cat2+) ↔ Δs-[M3+2(SQ)+] ⋅ [Co(diox)2(4-NO2-py)2] loose electron tautomerism interconversion (VTI). In 2 the thermal-induced VTI is cooperative, characterizing an abrupt conversion and in 1 it is non-cooperative. In this work, crystals of [Co(diox)2(4-NO2-py)2]·benzene (IBZ), [Co(diox)2(4-NO2-py)2]·toluene (ITL), [Co(diox)2(4-CN-py)2]·benzene (2BZ) and [Co(diox)2(4-CN-py)2]·toluene (2TL) have been prepared and analyzed by single crystal X-ray diffraction in order to investigate how solvation modulates thermal-induced VTI. The saltate crystals, like the nonsolvated ones, present essentially reversible thermal-induced and photoinduced VTI. ITL crystal presents the same monoclinic symmetry and the same intermolecular hydrogen-bonded network of U and both present a non-cooperative thermal-induced VTI. IBZ crystal has triclinic symmetry and present a cooperative and abrupt VTI with a thermal hysteresis of ~30 K. In contrast to 2, thermal-induced VTI in 2BZ and 2TL is non-cooperative despite the fact that 2, 2BZ and 2TL crystals exhibit the same monoclinic symmetry and the same intermolecular hydrogen-bonded network. In 2BZ and 2TL benzene and toluene molecules as well as the t-butyl groups of the o-dioxolene molecules convert gradually from being dynamically disordered at about 300 K to a static disorder state below 150 K. The layer separation distance of interacting [Co(diox)2(4-X-py)2], X=CN and NO2, molecules in all solvate crystals is ~15 Å in the 2, which presents cooperative VTI, it is ~12 Å. An order-disorder component might account to the stabilization of the metastable hs-Co2+ state in 2BZ and in 2TL but no disorder was found in the 1TL crystals. Therefore, the lack of cooperativeness in the thermal-induced VTI in these crystals seems to be due to the large distance between the layers of interacting molecules. Cooperativeness in the VTI of IBZ crystal is likely to be related with the unique molecular bond scheme network that connects neighboring active [Co(diox)2(4-NO2-py)2] molecules through the o-Dioxolene oxygen atoms bonded directly to the Co ion.

Introduction

Functional molecular materials possess at least two distinct states that interconvert when subject to an external stimuli. Their proprieties can be enhanced and/or adjusted through chemical changes and thus it is important to understand the forces driving their formation and organization as well as the mechanisms of interaction between individual active units. The study of functional molecular materials can therefore help in the development of molecular scale electronic devices.12 Valence tautomers3 are electronically labile compounds showing charge transfer between redox active ligands and a metallic center followed by the change of electronic spin of the metal. The electronic states in the valence tautomers are nearly degenerate and this leads to vibronically coupled interactions with an appreciable sensitivity to the environment.4 The valence tautomerism interconversion (VTI) is essentially entropically driven,6 associated with remarkable variations in the optical and magnetic properties and can be modulated with chemical changes. VTI is induced by external stimuli such as irradiation by light6,7 soft8 and hard X-rays9 and by changes such as temperature or pressure.10,11 VTI can be described by the following reaction scheme:

\[ \Delta s\cdot[M^{n+1}L^{m+1}] \leftrightarrow \Delta s\cdot[M^{n+}] \]

where \( \Delta s \) stands for the low spin state, \( \Delta s \) for the high spin state, \( M \) for the metal ion and \( L \) for redox ligands., and in a formal sense, this equation is similar to the one used to describe the spin-crossover equilibrium. The VTI involves a change of the electronic population of the anti-bonding \( e_g \) metal orbitals that affects the length of the metal-ligand bond and the exothermic/endothermic character of the interconversion. At low temperatures, where the free energy changes are largely determined by the enthalpy contributions, the tautomer ground state is characterized by unpopulated anti-bonding \( e_g \) orbitals and thus by short metal-ligand bonds. However, re-
versatile metastable states at very low temperatures can also be induced by light irradiation\textsuperscript{13, 14}. The lifetime of this photoinduced metastable species depend on the free energy barrier of the relaxation process and decay seems to begin as soon as the light stimulus is removed\textsuperscript{15, 16}. Typical examples of valence tautomers are coordination compounds of cobalt, and o-dioxolene ligands and ancillary amine ligands\textsuperscript{5, 17}. In these complexes the o-dioxolene organic moiety binds the metal ion in two different redox states: as a bi-negative catecholate ($\text{Cat}^-$) and a mono-negative radical semiquinonate ($\text{SQ}^-$). The o-dioxolene ligands can have filled or partially filled molecular orbitals that are close in energy to the $\text{Co}$ $d$-orbitals allowing moderated interactions with the metal $d$-orbitals, even though the metallic and free ligand orbitals characters are kept. The extension of this interaction is enough to keep the separation of the metal and ligand orbitals in the order to allow electron transfer between them, followed by changing in the metal multiplicity. Since the frontier orbitals have preferentially metal and ligand based character it is possible to change the charge distribution in the complexes by changing the redox potential of the o-dioxolene derivative ligand and the nature of ancillary ligands. Adams et al\textsuperscript{18} reported the first observation of VTI in solid state for the compound of $[\text{Co(diox)}](\text{phen})$, where diox are the 3,5-di-r-butylsemiquinonate and/or 3,5-di-r-butylcatecholate ions and phen is phenanthroline. In this seminal work, the interconversion characteristics were investigated by correlating the single crystal X-ray structural data at room and low temperatures with the temperature-dependent magnetic moment ($\mu_\text{eff}$) measurements for non-solvate, toluene, methyl cyclohexane and chlorobenzene solvates as well as for toluene desolvated samples. The critical role played by the ordering-disordering process of the solvate toluene molecules in determining the cooperative and abrupt character of the VTI was established. Crystals of $[\text{Co(diox)}](4\text{-NO}_2\text{-py})_2$ (1), $[\text{Co(diox)}](4\text{-CN}\text{-py})_2$ (2) and $[\text{Co(diox)}](4\text{-Br}\text{-py})_2$ (3), were first studied with respect to the thermo and photoinduced VTI (scheme I).\textsuperscript{19, 20} Additionally, Schmidt et al have also noted the influence of solvent in the crystal packing and its role in the interconversion, showing a more gradual interconversion for toluene solvated crystal.\textsuperscript{19}

**Scheme I: VTI $ls$-$[\text{Co}^{2+}(\text{SQ}^-)(\text{Cat}^-)]$$\leftrightarrow$$hs$-$[\text{Co}^{3+}(\text{SQ}^+)]_2$ in $[\text{Co(diox)}](4\text{-X}\text{-py})_2$ complexes; $X$=CN, NO$_2$ and Br

It was reported that VTI in 1 is non-cooperative and takes place over a large temperature range exhibiting pure $ls$-$[\text{Co}^{2+}(\text{SQ}^-)(\text{Cat}^-)]$ state below 110 K whereas in 2 and in 3 VTI is cooperative and abrupt, exhibiting pure $ls$-$[\text{Co}^{3+}(\text{SQ}^+)(\text{Cat}^-)]$ state below 150 K and 100 K, respectively. In this work crystals of $[\text{Co(diox)}](4\text{-NO}_2\text{-py})_2$; benzene ($1BZ$), $[\text{Co(diox)}](4\text{-NO}_2\text{-py})_2$; toluene ($1TL$), $[\text{Co(diox)}](4\text{-CN}\text{-py})_2$; benzene and ($2BZ$), $[\text{Co(diox)}](4\text{-CN}\text{-py})_2$; toluene ($2TL$), (scheme II), have been prepared and analyzed by temperature dependent single crystal X-ray diffraction in order to investigate how solvation modulates thermal-induced VTI properties.

**Scheme II: $[\text{Co(diox)}](4\text{-CN}\text{-py})_2$ and $[\text{Co(diox)}](4\text{-NO}_2\text{-py})_2$ complexes**

**Experimental**

**Complexes synthesis and characterization**

All of the chemicals for syntheses and analysis were of analytical grade and used without further purification. The preparation of $[\text{Co(diox)}](4\text{-NO}_2\text{-py})_2$ and $[\text{Co(diox)}](4\text{-CN}\text{-py})_2$ have been previously reported\textsuperscript{20}. Solvated single crystals samples suitable for X-ray diffraction were grown by slow evaporation in test tube over $N_2$ atmosphere and kept in this condition until the measurements.

**Instrumental details**

X-ray diffraction data collections were performed using Oxford-Diffraction GEMINI diffractometers at home facilities and at the Swiss Norwegian Beam Line, ESRF-France. Measurements were performed during heating and cooling processes with temperatures ranging from 290 K down to 90 K. An Oxford Cryojet device with precision better than $\pm 2$ K was used to control the samples temperatures during the experiments. For data consistency, temperature dependent measurements were always performed using the same sample. Table S1 in the supplementary information (SI) shows the details of the different measurements performed.

**Structure determination by single crystal X-ray diffraction**

For all samples investigated, the X-ray diffraction data integration and scaling of reflections intensities were performed with the CrysAlis suite.\textsuperscript{21} Final unit cell parameters were based on the fitting of all measured reflections positions. Analytical and Semi-Empirical\textsuperscript{22} absorption corrections were performed using CrysAlis suite.\textsuperscript{21} The program XPRED\textsuperscript{24} was used for the space group identification and final data reduction. The structures of all compounds were solved by direct methods using the SIR92\textsuperscript{25} program. For each compound, the positions of all but the hydrogen atoms could be unambiguously assigned on consecutive difference Fourier maps. Refinements were performed using SHELXL2013\textsuperscript{26} based on $F^2$ through full-matrix least square routine. During the refinements disordered $r$-butyl groups and solvate molecules were identified and modeled with split atomic positions. All, except the hydrogen atoms, were refined with anisotropic atomic displacement parameters. The hydrogen atoms in the compounds were added in the
structure in idealized positions and further refined according to the riding model. $^{27}U_{eq}(H) = 1.2U_{eq}(C)$ for aromatic molecules and $U_{eq}(H) = 1.5U_{eq}(C)$ for methyl groups. CCDC 1448193, 1448194, 1448195, 1448196, 1448197, 1448198, 1448310 and 1448311 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

**Structure description**

The single crystal X-ray diffraction data were used to investigate the structural properties of 1BZ, 1TL, 2BZ and 2TL including the geometry of pure 1s-[Co$^{3+}$(SQ$^-$)(Cat$^2$)] and hs-[Co$^{2+}$(SQ$^-$)] states, the solvates position and orientation as well as to follow the changes in the crystalline structure upon heating and cooling. The hs-[Co$^{2+}$(SQ$^-$)]$\leftrightarrow$1s-[Co$^{3+}$(SQ$^-$)(Cat$^2$)] interconversion can be investigated by temperature dependent single crystal X-ray diffraction techniques, since this technique provides very accurate bond-distance measurement with precision much smaller than the distances changes caused by VTI. Usually Co$^{3+}$-L bond lengths are 0.1 to 0.2 Å longer than those observed for Co$^{3+}$-L (L = ligand atom nearby the metal ion). The C-O and C-C bond distances of the redox-active ligands also change according to the SQ$^-$ or Cat$^2$ oxidation state of the ligands. C-O bond lengths are longer than 1.3 Å in the Cat$^2$ whereas the C=O bond lengths in the SQ$^-$ are ~1.30 Å. C–C bond lengths in Cat$^2$ are slightly longer (~0.2 Å) than the ones found in SQ$^-$ due to the higher aromaticity of Cat$^2$. Finally the C–C bond length of the aromatic carbon atoms bonded to the two oxygen atoms binding the Co ion is shorter in the Cat$^2$ than in SQ$^-$.

For 1BZ, 1TL, 2BZ and 2TL sample characteristics, data collection and refinements parameters for representative temperature measurements are indicated in SI Tables S2 and S3.

In the structures of 1BZ, 1TL, 2BZ and 2TL solvate crystals, the Co atoms sit on an inversion center, hence only half of each [Co(diox)(4-NO$_2$-py)$_2$] and [Co(diox)(4-CN-py)$_2$] molecules are crystallographically independent. Since the Co ions in these complexes have an octahedral coordination there are only two Co–O (namely Co-O1, Co-O2) and one Co-N independent refined distances in the structures. Consequently, the mixed valence Cat$^2$/SQ$^-$ delocalization around the Co atoms in the 1s-[Co$^{3+}$(SQ$^-$)(Cat$^2$)] state cannot be investigated by the analysis of the interatomic distances obtained from the X-ray diffraction data. Figure 1 shows the molecular structure and the atomic labeling scheme for the atoms in the asymmetric unit of 1BZ, 1TL, 2BZ and 2TL crystals. In all crystals, pyridine rings coordinate the Co ion in a trans conformation, with the orientation of the pyridine ring defined by the steric hindrance of t-butyl group in the position of the C6 atom and by four intramolecular C$_9$—H O$_{meta}$ hydrogen bonds between the adjacent carbon atoms of the pyridine and one oxygen atom of the dioxolene moiety as listed in SI Tables S4-7. Benzene and toluene solvate molecules are also bonded to the structures through hydrogen bonds between carbon solvent atoms and terminal nitro and cyano groups. π-stacking interactions between pyridine and solvent aromatic rings may contribute to keeping these groups parallel.

**Co(diox)$_2$(4-NO$_2$-py)$_2$**

Non-solvated [Co(diox)$_2$(4-NO$_2$-py)$_2$] (I) and 1TL crystal structures are similar and described by the monoclinic P2$_1$/c

![](image)

Figure 1. Molecular geometry and atomic labeling scheme used in the description of 1BZ (110 K), 1TL (100 K), 2BZ (123 K) and 2TL (123 K) structures. Only atoms of the asymmetric units are labeled. Ellipsoids are drawn at 50% of probability levels. Hydrogen atoms are represented in wireframe style for the sake of clarity.

The X-ray diffraction data analysis shows that thermal-induced VTI in both 1BZ and 1TL crystals are followed by major structural reversible changes. 1TL crystals contract in all directions whereas the 1BZ expands in the a direction and contracts in the b and c directions while the overall unit cell volume is also reduced upon cooling (Figure 2a,b). It was observed during the hs-[Co$^{2+}$(SQ$^-$)]$\leftrightarrow$ls-[Co$^{3+}$(SQ$^-$)(Cat$^2$)]
conversion of both solvates that an isotropic contraction of the Co–L distances of approximately 0.15 Å occurred. The Co–L distances during the cooling change abruptly for 1BZ at ~120 K and smoothly for 1TL over the entire investigated temperature range (Figure 2c,d). The Co–L distances contraction/expansion upon cooling and heating reveal a remarkable hysteresis of ~30 K for 1BZ (Figure 2c). Following the overall unit cell and Co–L distance changes upon cooling and heating process, the solvents molecules, NO₂ and pyridine moieties also change their relative orientation in both the 1BZ and 1TL complexes. In 1BZ solvate benzene molecules interact with NO₂ group keeping their relative orientation unchanged upon cooling and heating. However both the NO₂ group and the solvate benzene molecules change their relative orientation abruptly and reversibly in relation to the pyridine ring plane during the VT (Figure 2e). In 1TL only smooth changes in the orientations of the the NO₂, pyridine and toluene ring planes are observed (Figure 2f).

![Figure 2](image-url)  
Figure 2. Relative changes in the lattice parameters of (a) 1BZ and (b) 1TL crystals upon cooling. Behavior of the interatomic Co–O and Co–N distances in 1BZ (c) and in 1TL (d) computed from the analysis of the temperature dependent X-ray diffraction data. Co–L distance for 1TL was computed after the refinement of a low-resolution data (CuKα) and high-resolution data obtained at the Swiss Norwegian Beam Line at the ESRF (SNBL). Angles between normal vector from solvents, NO₂ and pyridine ring planes in (e) 1TL and (f) 1BZ crystals upon cooling.
The superposition of the non-solvated crystal structure of \( I \) with those of the solvate forms \( ITL \) and \( IBZ \) are shown in Figure 3. The toluene solvate molecule in \( IT \) and the benzene solvate in \( IBZ \) structures increase the separation between the layers of \([Co(diox)_{2}(4-NO_{2}-py)_{2}]\) interacting molecules by ca. 20% when compared with the non-solvated form \( I \). This is reputed to contribute to the weakening of the \( t \)-butyl interactions and to the lack of cooperativity in the VTI in \( I^{19,20} \).

![Figure 3](image)

**Figure 3:** (a) Superposition of the structures of the non-solvated \([Co(diox)_{2}(4-NO_{2}-py)_{2}]\) (orange) and \( ITL \) (black). (b) (a) Superposition of the structures of the non-solvated \([Co(diox)_{2}(4-NO_{2}-py)_{2}]\) (orange) and \( IBZ \) (black). Both, toluene and benzene solvation molecules increase the separation between the layers of interacting \([Co(diox)_{2}(4-NO_{2}-py)_{2}]\) molecules. Unit cell directions are indicated. Hydrogen atoms were omitted for sake of clarity.

In \( I, IBZ \) and in \( ITL \) structures, \([Co(diox)_{2}(4-NO_{2}-py)_{2}]\) in layer molecules are linked by two major hydrogen bonds types: \( C_{ar} - H \cdots O_{diox} \) and \( C_{ar} - H \cdots ONO \), where \( C_{ar} \) are aromatic carbon atoms of the pyridine ring and \( O_{diox} \) stands for an oxygen atoms of the dioxolene group binding the cobalt ion (Figure 4). Four \( C_{ar} - H \cdots O_{diox} \) bonds are observed between \([Co(diox)_{2}(4-NO_{2}-py)_{2}]\) neighbor moieties in both \( IBZ \) and \( ITL \) crystals: the oxygen atom \( O2 \) of the dioxolene acts as acceptor in two while the carbon atom \( C16 \) of pyridine ring acts as a donor in other two H-bonds (Figure 4b,d). As evidenced by the distances shown in Table 1, the shortest and therefore the strongest \( C_{ar} - H \cdots O_{diox} \) bonds between neighbors molecules were found for \( IBZ \) crystals. Thus, solvation seems to affect only the strength but not the number of these H-bonds. \( C_{ar} - H \cdots ONO \) interactions also control the packing of the \( I, IBZ \) and in \( ITL \) structures and solvation does affects the number, but not the strength, of such bonds between neighboring molecules as indicated in Table 1. For the \( IBZ \) solvate crystal four \( C_{ar} - H \cdots ONO \) interactions are observed for each molecule whereas for \( I \) and for \( ITL \) solvate crystal only two of such interactions are observed, as indicated in Figure 4.

![Additional diagrams](image)
Figure 4: View of the crystal packing of the (a) 1BZ and (c) 1TL solvate crystals towards e direction. Interaction between solvent molecules and NO₂ group are also indicated. In-layer (grey shadow) C–H...O_dox and C_ar–H...ONO hydrogen bonds between neighbor molecules shown in (b) and (d) towards a direction are represented in red and black lines respectively. The t-butyl groups of the dioxolene moieties in (b) and (d) are omitted for clarity.

Co(diox)(4-CN-py)₂

Similarly the crystal structure of the non-solvate [Co(diox)(4-CN-py)₂] (2) the 2TL and 2BZ solvate crystal structures are described by the P2₁/c symmetry with Z=2. The VTI hş-[Co⁵⁺(SQ⁻)₂]→hs-[Co⁵⁺(SQ⁻)(Cat⁺)] in both 2TL and 2BZ crystals is followed by an smooth isotropic contraction of the first coordination sphere around the Co ions by approximately 0.15 Å, by the reorientation of the toluene and benzene solvents and by an anisotropic unit cell volume contraction with no change in their crystal symmetry (Figure 5). The 2BZ crystal structure is ordered over the temperature range investigated, whereas in the 2TL crystal structure the solvate molecules and t-butyl groups convert from being dynamic to static disordered below 183 K. The ordering of the toluene influences the behavior of the monoclinic β angle as well as the toluene-pyridine ring normal vector angles as indicated in (Figure 5c,d). Thus, as in 2, 2TL also seems to show an order-disorder component in its VTI.

Figure 5: Relative changes in the lattice parameters of (a) 2BZ and (b) 2TL crystals upon cooling. (c) Behavior of the interatomic Co–O and Co–N distances in 2BZ and in 2TL computed from the analysis of the temperature dependent X-ray diffraction data. (d) Angles between normal vectors from solvents, dioxolene and pyridine molecule planes in 2TL and 2BZ crystals upon cooling.

The superposition of 2 and the 2BZ and 2TL crystal structures are shown in Figure 6. In the solvate crystals, the separation between the layers of [Co(diox)(4-CN-py)₂] interacting molecules increase by ca. 23% when compared with the non-solvated form. [Co(diox)(4-CN-py)₂] in layer molecules are linked by two major hydrogen bonds: C_ar–H...O_dox and C_ar–H...N_cyano. The strength and geometrical properties of these bonds depend little on the solvent and on the temperature (Table 1).
Figure 6: (a) Superposition of the structures of the non-solvated [Co(diox)_{2}(4-CN-py)] (grey) and 2BZ (black) and (b) of [Co(diox)_{2}(4-CN-py)] (orange) and 2TL (black). Both, toluene and benzene solvation molecules increase the separation between the layers of interacting [Co(diox)_{2}(4-CN-py)] molecules. The unit cell directions are indicated. (c) 2BZ (black) and 2TL (orange) superposition towards ε direction. (d) In-layer C_{ar}-H... O_{diox} and C_{ar}-H... N_{py} interactions represented in red and black lines respectively towards a direction. t-butyl groups in (d) were omitted for clarity.

Table 1: Selected distances in (Å) in 1, 1TL, 1BZ, 2, 2TL and 2BZ.

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<th></th>
<th>1BZ</th>
<th>1TL</th>
<th>1BZ</th>
<th>1</th>
<th>1</th>
<th>100 K</th>
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<tr>
<td></td>
<td>110 K</td>
<td>280 K</td>
<td>100 K</td>
<td>250 K</td>
<td>95 K</td>
<td>143 K</td>
</tr>
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<td>C19-H19-O1^iv</td>
<td>2.824(3)</td>
<td>3.051(3)</td>
<td>C19-H19-O1^iv</td>
<td>2.850(3)</td>
<td>3.084(3)</td>
<td>C19-H19-O1^iv</td>
</tr>
<tr>
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<td>6.7872(3)</td>
<td>Co-Co^v</td>
<td>7.3495(2)</td>
<td>7.3742(2)</td>
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<tr>
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<td>12.7759(5)</td>
<td>Co-Co^v</td>
<td>11.7995(2)</td>
<td>2.0695(2)</td>
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<table>
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<tr>
<th></th>
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<td>123 K</td>
<td>273 K</td>
<td>120 K</td>
<td>270 K</td>
<td>95 K</td>
<td>143 K</td>
</tr>
<tr>
<td>Co-Co^v</td>
<td>7.316(5)</td>
<td>7.2956(4)</td>
<td>Co-Co^v</td>
<td>7.387(1)</td>
<td>7.362(1)</td>
<td>Co-Co^v</td>
</tr>
</tbody>
</table>

Bond types: C16-H16-O2/C_{ar}-H...O_{diox}, C18-H18-O3/C_{ar}-H...ONO and C18-H18-N2/C_{ar}-H...N_{py}. C15-H15-O1 and C19-H19-O1^a are intramolecular interactions. C_{ar} is aromatic carbon atom, O_{diox} is a dioxolene oxygen atom and N_{py} is the nitrogen atom from the cyano group. Distances data from non-solvated crystals 1 and 2 were taken from references 19 and 20 respectively. Symmetry operations: i=x-1,y,z; ii=x+1,y-1,z+1; iii=x-1,y,-z+1; iv=x+1,y,z; v=x,y,z; vi=x,-y+1/2,z+1/2; vii=-x,-y+1,-z+1; viii=-x,-y+1/2,-z+1/2; x=-x,-y,-z. * The labeling scheme was adapted to keep relation with the solvated structures.
VTI properties

According to the variable temperature magnetic susceptibility data, \( I \) presents a non-cooperative whereas 2 presents a cooperative \( hs\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\)=)\(\leftrightarrow\)\(ls\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\)=)\(\leftrightarrow\)\(ls\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\))\(_{\text{non}}\)\(_{\text{co}}\) transition.\(^{19}\) VTI in 1BZ, 1TL, 2TL and 2BZ solvate samples were characterized by following the crystallographic parameters and in particular the Co L distance changes in the Co first coordination shell. The interatomic distances obtained from the X-ray diffraction data provided two values for Co–O and one value for Co–N distance in each temperature. Refined distances for Co–L in pure state \( hs\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\)) and \( ls\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\))\(_{\text{co}}\) are in agreement with the values obtained from a survey of about 34 similar structures deposited in CCDC\(^{28}\) (Table 2). Using the refined Co–L distances for a given temperature (\( D_{\text{exp}}^{Co-L} \)), we could compute the Co\(^{2+}\) concentration for a given distance \([hs-Co^{2+}]_L\) by the following equation:

\[
[hs-Co^{2+}]_L = \frac{(D_{\text{exp}}^{Co-L} - D_{Co}^{Co^{2+}})}{(D_{Co^{2+}} - D_{Co^{3+}})}
\]

(1)

Where \( L \) stands for \( O \) and \( N \) atoms, \( D_{Co^{2+}}^{Co-L} \) and \( D_{Co^{3+}}^{Co-L} \) are the values of Co–L distances in \( ls\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\)=) and \( hs\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\))\(_{\text{co}}\) states, respectively. The average concentration \([hs-Co^{2+}]\) value for a given temperature was obtained averaging the values obtained for each Co ion neighbor. Thus,

\[
[hs-Co^{2+}] = \sum_{L} [hs-Co^{2+}]_L \quad L = O, N
\]

(2)

Table 2: Co–O and Co–N interatomic distances.

<table>
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<tr>
<th></th>
<th>( hs)-(Co(^{3+})(SQ(^-))(<em>2))(</em>{\text{co}}) state</th>
<th>( ls)-(Co(^{3+})(SQ(^-))(_2)=) state</th>
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<td><strong>Refinement distances</strong></td>
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<tr>
<td>Co(^{3+})-O</td>
<td>1.886(4) Å</td>
<td>2.052(8) Å</td>
</tr>
<tr>
<td>Co(^{3+})-N</td>
<td>1.958(3) Å</td>
<td>2.184(6) Å</td>
</tr>
<tr>
<td><strong>CCDC survey distances</strong></td>
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<tr>
<td>Co(^{3+})-O</td>
<td>1.86(1) Å</td>
<td>2.04(2) Å</td>
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<tr>
<td>Co(^{3+})-N</td>
<td>1.94(1) Å</td>
<td>2.17(3) Å</td>
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</tbody>
</table>

As already highlighted in Figure 3 and in Figure 6, all the solvate tautomers present distances between interacting layers of \([Co(diox)(4-X-py)_2]\) X=NO\(_2\),CN molecules of ~15 Å, whereas in the non-solvate ones these distances are ~11.6 Å. Since 1BZ and 2 crystals present a cooperative VTI, the layer separation alone does not explain the lack of cooperativity in 1TL, 2TL and 2BZ. Indeed, 1TL, 2TL and 2BZ crystals have the same crystal packing and similar intermolecular interactions as their nonsolvate 1 and 2 relatives, whereas 1BZ present a unique intermolecular network. Therefore, the number and the strength of the intermolecular interactions might also play an important role in the cooperativity. Remarkably, each [Co(diox)]\(_2\)(4-NO\(_2\)-py)\(_2\) molecule in the 1BZ crystal make eight hydrogen bonds with their neighbors, being four of them of the type \( C_o-H-O_{diox} \) involving oxygen atoms directly bounded to the Co ions. Thus the Co atom coordination shell expansion/contraction during the \( hs\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\)=)\(\leftrightarrow\)\(ls\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\))\(_{\text{co}}\) interconversion could be readily transmitted trough neighbor molecules contributing for the cooperativity. It is worth noting that 1BZ crystal present the shortest \( C_o-H-O_{diox} \) hydrogen contact distances and consequently the shortest in layer Co-Co separation, among all investigate solvate crystals (Table 1).

VTI Thermodynamics

Thermodynamic parameters of the tautomeric \( hs\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\)=)\(\leftrightarrow\)\(ls\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\))\(_{\text{co}}\) interconversion can be determined by the smooth change in the angles formed by the solvent and pyridine ring planes. In the opposite way, for the sample with cooperative VTI, 1BZ, the angles formed by solvent and pyridine rings change abruptly. This evidences that the crystal packing hold the abrupt/smooth VTI character observed in the variation of bond length between metal and ligands.

Figure 7: \([hs-Co^{3+}]\) concentration during the interconversion \( hs\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\)=)\(\leftrightarrow\)\(ls\)-(Co\(^{3+}\)(SQ\(^-\))\(_2\))\(_{\text{co}}\). The fittings were performed by least square procedures according with the equilibration equation (4). \( T_{1/2} \) is the temperature in which \([hs-Co^{3+}]\)=[\(ls\)-Co\(^{3+}\)].
obtained from the fitting of the $[hs\cdot Co^{3+}]$ data shown in (Figure 7), using the equilibrium equation below:

$$K_{VT} = \frac{[hs\cdot Co^{3+}]}{[ls\cdot Co^{2+}]} = \exp\left(-\frac{\Delta G}{RT}\right).$$

(3)

Since $[ls\cdot Co^{2+}] = (1 - [hs\cdot Co^{3+}])$ and $\Delta G = \Delta H - T\Delta S$,

$$[hs\cdot Co^{3+}] = 1/[\exp\left(\frac{\Delta H}{RT} - \frac{\Delta S}{R}\right) + 1]$$

(4)

where $\Delta G$ is the Gibbs energy change, $\Delta H$ is the enthalpy change, $\Delta S$ is the entropy change, $T$ is Temperature and $R$ = 8.314 J/Kmol. The values of $\Delta H$ and $\Delta S$ listed in Table 3 were obtained from the least-square fit of $[hs\cdot Co^{3+}]$ data shown in Figure 7. $T_{1/2}$ (the temperature in which $[hs\cdot Co^{3+}]=[ls\cdot Co^{3+}]$) was obtained from the interception between fitted curves and the horizontal line drawn in Figure 7. With the exception of the $\Delta S$ value of the 1BZ, all the remaining values obtained are similar to the ones found in related complexes.290

Table 3 Enthalpy ($\Delta H$) and entropy ($\Delta S$) change during the $hs\cdot[Co^{2+}(SQ')_2] \leftrightarrow ls\cdot[Co^{3+}(SQ')(Cat^2)]$ interconversion.

<table>
<thead>
<tr>
<th></th>
<th>$T_{1/2}$ (K)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1BZ Cooling</td>
<td>145</td>
<td>136(8)</td>
<td>938(57)</td>
</tr>
<tr>
<td>1BZ Heating</td>
<td>165</td>
<td>198(2)</td>
<td>1198(13)</td>
</tr>
<tr>
<td>1TL</td>
<td>207</td>
<td>23(2)</td>
<td>110(11)</td>
</tr>
<tr>
<td>2TL</td>
<td>222</td>
<td>22(1)</td>
<td>99(5)</td>
</tr>
<tr>
<td>2BZ</td>
<td>241</td>
<td>30(2)</td>
<td>126(6)</td>
</tr>
</tbody>
</table>

Conclusion

The structure of the solvate 1BZ crystal is described by the triclinic $P1$ space group symmetry with $Z=1$, 1TL, 2TL and 2BZ solvate crystal structures are described by the $P2_1/c$ symmetry with $Z=2$. 1TL, 2BZ and 2TL show a non-cooperative VTI occurring gradually in a temperature range between 250 K and 180 K. For all these crystals, pure $ls\cdot[Co^{3+}(SQ')(Cat^2)]$ states can only be achieved at temperatures below 150 K. 1BZ crystals present a cooperative interconversion with hysteresis of ~30 K in which $ls\cdot[Co^{3+}(SQ')(Cat^2)]$ pure state is observed below 120 K for cooling and up to 150 K during the heating processes. VTI in all these crystals are characterized by an isotropic change in the $Co-N$ and $Co-O$ distances, an anisotropic change in the unit cell volume, the reorientation of the solvates molecules and pyridine ring planes and by an invariance in the intermolecular hydrogen-bonded lattice. Due to the steric hindrance of the t-

butyl only one oxygen atom of the dioxolene group coordinating the metal ion is involved in intermolecular interactions with $Co-H$ groups. Together all these structure accommodation effects and in particular the strength and the number of direct contacts towards the dioxolene oxygen atoms, seem to account for the VTI properties.

All the solvate tautomers present distances between interacting layers of $[Co(diox)_2(4-X-py)_2]$ X=NO$_2$,CN molecules of ~15 Å, whereas in the non-solvate ones these distances are ~11.6 Å. Remarkably, when compared with 1TL, 2BZ and 2TL crystals as well as with the non solvated 1 and 2 crystals, 1BZ present the shortest and therefore the strongest $Co-H$ $O_{diox}$ hydrogen as well as the shortest $Co-Co$ distances. Cooperativity in the VTI of 1BZ, in contrast to 2 that also presents cooperative VTI, seems to be related with the number and particularly with the strength of the $Co-H$ $O_{diox}$ interaction and with its correspondent $Co-Co$ separation. Thus benzene and toluene solvation of 1 and 2 crystals plays a key role in the definition of the nature of the VTI observed in these compounds, despite the solvates molecules are not directly involved in the intermolecular contact network of the $[Co(diox)_2(4-X-py)_2]$ X=NO$_2$,CN molecules.

ASSOCIATED CONTENT
Crystallographic data (CIF) and pictures about intramolecular and intermolecular interactions. *This material is available free of charge via the Internet at http://pubs.acs.org

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS
VTI – Valence Tautomerism Interconversion. 1BZ=[Co(diox)$_2$(4-NO$_2$-py)$_2$]-benzene, 1TL=[Co(diox)$_2$(4-NO$_2$-py)$_2$]-toluene, 2BZ=[Co(diox)$_2$(4-CN-py)$_2$]-benzene and 2TL=[Co(diox)$_2$(4-CN-py)$_2$]-toluene crystals

REFERENCES
1 O. Kahn, Science, 1998, 279, 44.