Poster Presentations

[MS24-P35] Towards Controlling the Valance Tautomer Interconversion Character by Solvation.
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Valence tautomers[1] are bi-stable functional molecular materials in which it is observed charge transference between redox active ligands and a metallic center followed by the change of spin of the metal[2], induced by external stimuli such as illumination[3] and/or changes in temperature and pressure[4].

Valence tautomerism (VT) interconversion is essentially entropically driven, associated with remarkable variations in optical and/or magnetic properties, and can be modulated with slight chemical changes. Typical examples of VT compounds are coordination compounds of Co and o-dioxolenes ligands[5].

Crystals of complex [CoIII(SQ)(Cat)
(4-NO2-py)2] (I), where py= pyridine, Cat = 3,5-di-t-butylcatecholate and SQ=3,5-di-t-butylsemiquinonate, were first studied with respect to low spin (LS) to high spin (HS) thermo and photoinduced conversion. It was reported that I become HS–CoIII at temperatures below 110 K with non cooperative LS–CoIII n↔ HS–CoII tautomeric interconversion[6]. Crystals of CoIII(SQ)(Cat)(4-NO2-py)2]/Toluene (II) and CoIII(SQ)(Cat)(4-NO2-py)2]/Benzene (III) have been prepared to investigate further the solvation effects on the interconversion properties. It has been found that solvated crystals undergo to LS–CoIII n↔ HS–CoII interconversion at temperatures below 140 K for II and below 110 K for III. The tautomeric interconversion in I and in II has a non cooperative character whereas for III it is highly cooperative. The remarkable common structural features in the three dimensional packing of compounds I, II and III are the Car–H…Oi_diox and Car–H…ONOi hydrogen bonds between inlayer i symmetry related [CoIII(SQ)(Cat)
(4-NO2-py)2] molecules with distances values summarized below.

Distances at ca. 100 K (Å)

<table>
<thead>
<tr>
<th></th>
<th>I[6]</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H...Odiox</td>
<td>3.24</td>
<td>3.33(2)</td>
<td>3.131(7)</td>
</tr>
<tr>
<td>C–H...ONO</td>
<td>3.32</td>
<td>3.34(2)</td>
<td>3.287(7)</td>
</tr>
<tr>
<td>1CoIII–CoIII</td>
<td>7.283</td>
<td>7.333(1)</td>
<td>6.9491(8)</td>
</tr>
<tr>
<td>2CoIII–CoIII</td>
<td>11.788</td>
<td>11.757(1)</td>
<td>12.331(2)</td>
</tr>
<tr>
<td>3CoIII–CoIII</td>
<td>11.718</td>
<td>14.944(2)</td>
<td>15.357(3)</td>
</tr>
</tbody>
</table>

1, 2 and 3 indicate distances between cobalt atoms in molecules linked by C–H...Odiox C–H...ONO and out of layers respectively.

When compared with I, the inclusion of the toluene in the lattice of II does not affect the symmetry of the crystal structure (I and II are described by P21/c space group, Z=4), but increases the separation between the layers of [CoIII(SQ)(Cat)(4-NO2-py)2] molecules in ca. 30%, weakening the t-butyl interactions, as also observed in [CoIII(SQ)(Cat)
(4-CN-py)2] compound[7].

Benzene solvated crystals III are described by P1 space group, Z=2, and at 100 K. When compared with I and II, benzene solvated crystals present the shortest Car–H…Odiox and similar Car–H…ONO hydrogen bonds lengths. They also present the shortest CoIII–CoIII distances between inlayer molecules linked by Car–H…Odiox and the longest CoIII–CoIIIdistances between
Thus, as already pointed out before[6], VT in [Co\textsuperscript{III}(SQ)(Cat)(4-NO\textsubscript{2}-py)\textsubscript{2}] seems to be due to the intermolecular interactions between inlayer molecules, however the interconversion cooperativity seems to be related with the strength of the Car–H…O\textsubscript{diox} interaction and with the correspondent Co–Coi separation.

Thus solvation play a key role in the definition of the VT interconversion nature.

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