

## Isotopic effects may induce cooperativity in valence tautomeric transition

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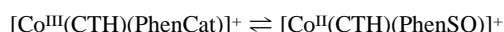
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The replacing of  $\text{CH}_2\text{Cl}_2$  solvent molecules with their deuterated analogues in a Co complex undergoing valence-tautomeric interconversion drastically modifies its magnetic properties giving rise to a thermal hysteresis.

When chemists move to synthesise substances that should be characterised by some peculiar properties, they are usually also today speaking in terms of “building blocks”. The lesson we may learn from the investigation of compounds showing electronic labile ground states, like mixed-valence complexes<sup>1</sup> or compounds undergoing spin crossover<sup>2,3</sup> and valence tautomeric transitions<sup>4–6</sup> is rather illuminating about the limit of this conceptual paradigm. The example we report here provides a significant support to this proposition.

The 1:1 cobalt-dioxolene complexes  $[\text{Co}(\text{CTH})(\text{Phendiox})]\text{PF}_6(x.\text{solvent})$  (CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; Phendiox = semiquinonato (PhenSQ) or catecholato (PhenCat) forms of 9,10-dioxophenanthrene, *x*.solvent =  $\text{H}_2\text{O}$ , 1.5  $\text{CH}_2\text{Cl}_2$ , 0.5  $\text{C}_6\text{H}_5\text{CH}_3$ ) were found to undergo in the solid state to temperature and pressure driven valence tautomeric transition



following to an intramolecular electron transfer process from the ligand to the metal ion.<sup>7</sup> Indeed temperature dependent magnetic susceptibility studies showed that these compounds are diamagnetic at low temperatures, but starting from *ca.* 150 K they become paramagnetic and the  $\chi T$  values increase with increasing temperatures. The transitions can be classified as gradual and no hysteresis effects were detected. Since there is experimental evidence that the complexes of dioxolene ligands can be properly described in terms of localised structures,<sup>4,8–10</sup> these transitions can be described as a change of charge distribution of the  $[\text{Co}(\text{CTH})(\text{Phendiox})]^+$  cation from a  $3d(\pi)^6(\pi^*)^2$  characterising the low-spin cobalt(III)-catecholato complex to the  $3d(\pi)^5(\sigma^*)^2(\pi^*)^1$  of the high-spin cobalt(II)-semiquinonato one.

The crystal structures<sup>‡</sup> of the dichloromethane solvate, **1**, at 295 and 198 K fully supported this hypothesis.<sup>7</sup> As expected the complex was found six-coordinated, the macrocyclic ligand being ligated in a folded configuration and the dioxolene acting as bidentate ligand towards the metal ion. In agreement with magnetic data the observed structural parameters of the complexes were consistent with an equilibrium mixture of the  $[\text{Co}^{\text{III}}(\text{CTH})(\text{PhenCat})]^+$  and  $[\text{Co}^{\text{II}}(\text{CTH})(\text{PhenSQ})]^+$  valence tautomers, the first species being largely the dominant one at 198 K and the latter one predominant at 295 K. No changes in crystal symmetry were detected between the two temperatures. Finally it was found that the dichloromethane molecules were ordered at low temperature and disordered at high temperature. The absence of thermal hysteresis is justified by the stereopacking diagram of this compound, which did not show the existence of strong interactions (*i.e.* hydrogen bonds, stacking interactions, *etc.*) between the neighbouring complexes. These interactions are considered important in any phase transition for inducing cooperativity within the crystal lattice. Therefore it may be suggested that in this compound the valence

tautomeric transition cannot be described as first order phase transition. A similar result was observed for the  $\text{Co}(\text{phen})(\text{DBSQ})(\text{DBCAT})\cdot\text{C}_6\text{H}_5\text{CH}_3$ , which was the first complex found to undergo valence tautomeric equilibrium in the solid state.<sup>11</sup>

We have found that when the dichloromethane molecules are replaced by *d*<sub>2</sub>-dichloromethane the complex shows a significantly different behaviour (Fig. 1). Two different sets of magnetic measurements using long thermalisation times for each point gave the same results within the experimental error. The transition is more abrupt and a significant hysteresis (8 K) is detected. Indeed the transition critical temperatures measured on heating the samples and cooling are  $T_{\uparrow} = 244$  and  $T_{\downarrow} = 236$  K, respectively, which can be compared with the  $T_{\downarrow\uparrow}$  of *ca.* 300 K characterising the previously reported compound. The hysteresis loop can be argued to be larger than the observed one because the transition at 310 K is far to be complete. Unfortunately the presence of relatively volatile dichloromethane molecules makes the compound unstable upon heating, thus not allowing to extend the temperature range of investigation above 310 K. We stress here the fact that the samples of the dichloromethane solvate and of its deuterated analogue were prepared using the same starting compound which was recrystallised by the two different solvents under identical conditions by inducing the solid precipitation as microcrystalline material with the addition of *n*-hexane. Further, both compounds gave the same elemental analysis<sup>§</sup> corresponding to a solvent content of 1.5 molecules.

Three samples of the deuterodichloromethane solvate were independently synthesised and were shown to exhibit the same magnetic behaviour. No change either in weight or in the microanalysis was observed after magnetic measurements. The observed values must be compared with the thermal hysteresis of 5 K observed for the  $\text{Co}(\text{phen})(\text{DBSQ})(\text{DBCAT})\cdot\text{C}_6\text{H}_5\text{CH}_3$ .<sup>11</sup> The large hysteresis, 230 K, observed for the  $\text{Co}(\text{py}_2\text{O})(\text{DBCat})(\text{DBSQ})$  cannot be attributed to lattice effects, but to the peculiar properties of the ancillary  $\text{py}_2\text{O}$  ligand.<sup>12</sup>

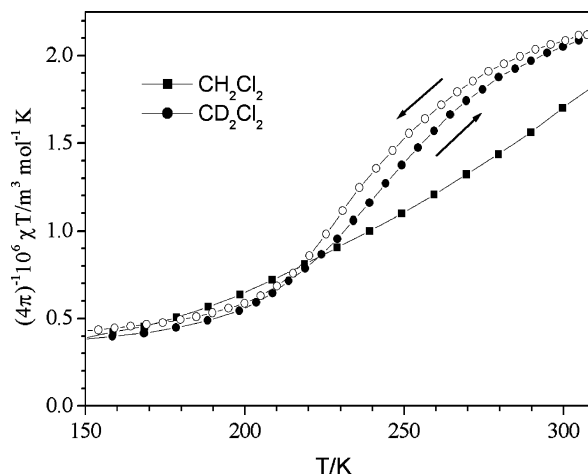


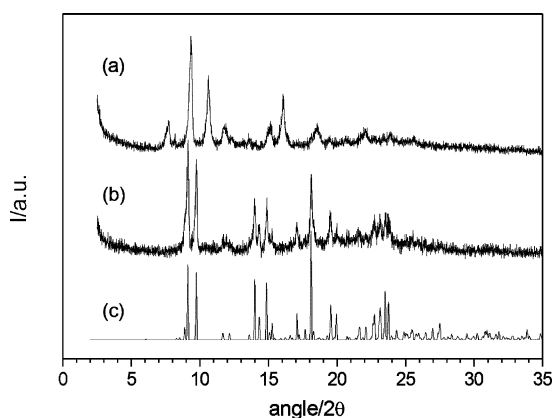
Fig. 1 Temperature dependence of  $\chi T$  for  $[\text{Co}(\text{CTH})(\text{Phendiox})]\text{PF}_6\cdot 1.5\text{CH}_2\text{Cl}_2$  and for the  $\text{CD}_2\text{Cl}_2$  analogue. For the latter, data collected either on heating (full symbols) or on cooling (open symbols) are shown.

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This unexpected anomaly was justified by the X-ray powder analysis of the two complexes. Indeed the diffraction pattern diagrams of the two derivatives were found to be different (Fig. 2). Therefore with the goal of correlating the observed different magnetic properties with the different crystal structures, single crystals of the deuterated solvate were obtained by slow evaporation over two days of deuterodichloromethane-hexane solutions at room temperature. The X-ray diffractometric analysis and magnetic measurements showed that the crystal structure and the magnetic properties of the obtained compound were identical to those of the previously reported undeuterated one. It was therefore suggested that the deuterated solvate gives rise to two crystalline forms, which are in turn characterised by different cooperativity properties. X-Ray powder patterns do not show any change on decreasing temperature down to 150 K. Therefore the transition does not involve a space group change as expected for a first order transition. Therefore, as previously suggested,<sup>11</sup> the transition has a larger order character.

Apparently this polymorphism, which was not detected for the undeuterated solvate, is due to isotopic effects. Polymorphism following isotopic substitution has been recently reported for a system experiencing a strong hydrogen bond<sup>13</sup> but, to our knowledge, has never been observed in molecular systems showing spin transitions. It can be suggested therefore that the energy difference of solvent vibrational modes in the lattice is critical in determining the cooperativity of the whole.

If the above suggestions were true, the observed results would stress again that the failures of the synthetic approach based on the building blocks philosophy are due to its intrinsic reductionist



**Fig. 2** X-Ray powder diffraction patterns of [Co(CTH)(Phendiox)]PF<sub>6</sub>·1.5CD<sub>2</sub>Cl<sub>2</sub>, (a), [Co(CTH)(Phendiox)]PF<sub>6</sub>·1.5CH<sub>2</sub>Cl<sub>2</sub>, (b) and simulated pattern from X-Ray single crystal diffraction data for [Co(CTH)(Phendiox)]PF<sub>6</sub>·1.5CD<sub>2</sub>Cl<sub>2</sub>, (c).

character. Indeed it is not possible to design and understand a system of particles on the basis of the intrinsic electronic properties of the single particles themselves. As a fact the contrary can be partially true, the properties of the particles being often determined by the organisation of the whole system, whose properties are in general different from the sum of those of the components. These differences are not predictable, because we are far from understanding the subtleties of small changes of environmental effects in condensed phase.

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## Notes and references

‡ Crystal data for [Co(CTH)(Phendiox)]PF<sub>6</sub>·1.5CD<sub>2</sub>Cl<sub>2</sub>: CoCl<sub>3</sub>C<sub>31.5</sub>D<sub>3</sub>-PF<sub>6</sub>H<sub>44</sub>N<sub>4</sub>O<sub>2</sub>, *M* = 826.0, monoclinic, space group *C2/c* (no. 15), *a* = 20.303(4), *b* = 12.647(2) *c* = 29.649(10), Å, β = 101.41(2), *U* = 7463(3) Å<sup>3</sup>, *D<sub>c</sub>* = 1.461 g cm<sup>-3</sup>, *Z* = 8, μ(Mo-Kα) = 0.782 mm<sup>-1</sup>, 7222 collected reflections of which 6428 unique reflections (*R*<sub>int</sub> = 0.0435) and 446 parameters. *Goof* = 1.033. Final *R* indexes (*I* > 2σ(*I*)) *R*<sub>1</sub> = 0.0785, *wR*<sub>2</sub> = 0.2148; *R* index (all data) *R*<sub>1</sub> = 0.2067. A chlorine atom of the dichloromethane solvent molecule was found to be disordered over three different sites with occupational factors of 0.50, 0.30 and 0.20. CCDC 227051. See <http://www.rsc.org/suppdata/cc/b3/b313049e/> for crystallographic data in .cif or other electronic format.

§ Elemental analysis found: C 46.04, H 6.01, N 6.83, Co 7.2; calcd.: C 45.75, H 6.09, N 6.77, Co 7.13.

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