# The effects of pressure on valence tautomeric transitions of dinuclear cobalt complexes

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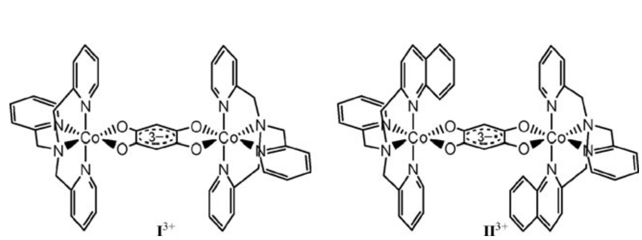
**The effects of pressure on valence trautomeric transition behavior of two complexes, [{Co(tpa)}$_2$(dhbq)]·(PF$_6$)$_3$ (I·(PF$_6$)$_3$) and [{Co(dpqa)}$_2$(dhbq)]·(PF$_6$)$_3$ (II·(PF$_6$)$_3$) (tpa = tris(2-pyridylmethyl)-amine, dpqa = di(2-pyridylmethyl)-*N*-(quinolin-2-ylmethyl)-amine and dhbq = deprotonated 2,5-dihydroxy-1,4-benzoquinone), in the light of changes of magnetic susceptibilities were investigated; the results show that external pressure makes the SC + ET transition process of the two complexes into a general SC process only.**

Molecule-based magnetic materials with bistable electronic states that can be controlled by external parameters have been attracting great attention because of their potential applications.[1–3] Among such materials, spin crossover (SC)[4,5] and valence tautomeric (VT)[6–9] complexes are the most important series that have been extensively studied, as both of them can be stable at different electronic states under certain conditions, and the interconversion between these electronic states are usually able to be affected by physical stimuli such as heat, light or pressure.[10]

In iron(II) SC complexes, the reversible spin transition is ascribed to an intra-ionic transformation between high-spin (*hs*) and low-spin (*ls*) states, $(t_{2g})^4(e_g)^2 \leftrightarrow (t_{2g})^6(e_g)^0$, accompanied with a change of metal–ligand bond lengths of up to 0.2 Å,[11,12] which causes the molecular size in the *hs* state to be larger than that in *ls* one by 3–5%. It is now well accepted that the spin transition is sensitive to pressure, plenty of experiments have revealed that *ls* state is generally stabilized under external pressure and the critical temperature will shift to higher temperature region when higher pressure is applied. The reason is that additional pressure will increase the zero-point energy difference $\Delta E^0$ and decrease the activation energy $\Delta W^0$, thus favoring the *ls* state.[13]

VT can be viewed as a special kind of SC except that the VT complex contains an electroactive ligand. The interconversion between VT isomers comprises intramolecular electron transfer (ET) between metal ion and electroactive ligand as well as spin transition of the metal ion (SC + ET). For cobalt VT complexes, the metal–ligand bond lengths and molecular size vary when the conversion of *hs*-Co$^{II}$ $\leftrightarrow$ *ls*-Co$^{II}$ $\leftrightarrow$ *ls*-Co$^{III}$ occurs, which is thus expected to be pressure-sensitive and favors the *ls*-Co$^{II}$ or *ls*-Co$^{III}$ state as SC complexes do under pressure. Moreover, to some extent the intramolecular electron transfer (ET) between cobalt and the electroactive ligand may also be affected by pressure, which is presumably in favor of the cobalt high-spin state. These make the effects of pressure on VT complexes be not as clear as those on SC ones. To the best of our knowledge, only two examples have been reported that external pressure could affect the VT interconversion,[14,15] in which increasing pressure could enlarge enthalpic energy separation between valence tautomeric isomers, and at high-enough pressure the population of *ls*-Co$^{III}$ form would increase most since the sign of $\Delta G$ is changed at a critical pressure $P_c$. Recently, we have reported two dinuclear cobalt complexes, [{Co(tpa)}$_2$(dhbq)]·(PF$_6$)$_3$ (**I**·(PF$_6$)$_3$)[16] and [{Co(dpqa)}$_2$(dhbq)]·(PF$_6$)$_3$ (**II**·(PF$_6$)$_3$),[17] that showed intriguing VT transition behavior. Now, their magnetic susceptibilities under variable external pressure have been measured, the results revealed that the application of external pressure could influence the SC step as the pressure effects on other SC complexes do, and more important observation is that pressure could make the ET step vanish by enlarging the enthalpic separation $\Delta H$ between valence tautomeric isomers and stabilize the *ls*-Co$^{II}$ state at low temperature. Moreover, the intermolecular interactions and ligand-field strength enhanced by pressure can form *hs*–*ls* Co(II) pairs that make the transition become more general.

The crystal structures of the two complexes, which have been reported elsewhere, show both of them to be composed of herringbone-like arranged dinuclear cationic (Scheme 1) layers that are separated by PF$_6^-$ anions.[16,17] The magnetic properties of as-synthesized **I**·(PF$_6$)$_3$ and **II**·(PF$_6$)$_3$ samples† have been measured under normal pressure (1 bar) in the temperature range of 2–300 K and are shown in Fig. 1, and match the published data.[16,17] Complex **I**·(PF$_6$)$_3$ exhibited an abrupt VT transition and hysteresis around room temperature, while **II**·(PF$_6$)$_3$ showed a gradual VT transition from 300 to 100 K and a small hysteresis around 170 K, showing the



**Scheme 1** The cationic structures of **I**$^{3+}$ and **II**$^{3+}$.

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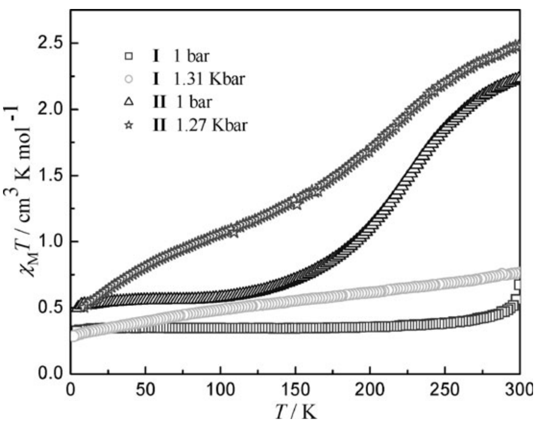


**Fig. 1** $\chi_M T$ *vs.* $T$ plots of $\mathbf{I}\cdot(PF_6)_3$ and $\mathbf{II}\cdot(PF_6)_3$ under external pressure in the temperature region of 2–300 K. Normal atmosphere pressure was assumed to be 1 bar.

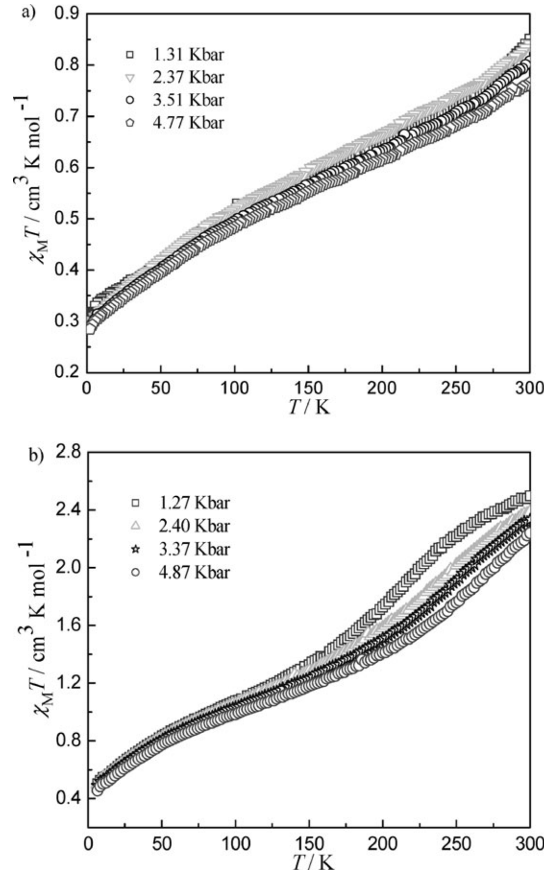


**Fig. 2** $\chi_M T$ *vs.* $T$plots of $\mathbf{I}\cdot(PF_6)_3$ (a) and $\mathbf{II}\cdot(PF_6)_3$ (b) under various pressure in the temperature range of 2–300 K.

inter-isomeric conversion of *ls*-Co$^{III}$–dhbq$^{\bullet 3-}$–*ls*-Co$^{III}$ ↔ *ls*-Co$^{III}$–dhbq$^{2-}$–*hs*-Co$^{II}$. By comparison of the structural features of the two complexes, a conclusion may be drawn that longer Co–N distances[13,16–18] and stronger π···π interactions in $\mathbf{II}\cdot(PF_6)_3$ should play important roles in favoring the *hs*-Co$^{II}$ state and shifting the VT interconversion to a lower temperature range.

Because the two complexes have similar structures but different VT behavior, they are then expected to show different pressure effects on the VT behavior. When a minimal external pressure was applied on complexes $\mathbf{I}\cdot(PF_6)_3$ and $\mathbf{II}\cdot(PF_6)_3$, respectively, interesting phenomena that were not reported previously were observed (as shown in Fig. 1). In a previously reported VT complex, additional external pressure reduced the $\chi_M T$ values and thus indicated that pressure could stabilize the *ls*-Co$^{III}$ species and shift the VT interconversion to higher temperature range.[15] However, in the cases of complexes $\mathbf{I}\cdot(PF_6)_3$ and $\mathbf{II}\cdot(PF_6)_3$, the $\chi_M T$ values increased under external pressure, which along with the tendency of the curves indicated that the transition of *ls*-Co$^{III}$–dhbq$^{\bullet 3-}$–*ls*-Co$^{III}$ ↔ *ls*-Co$^{III}$–dhbq$^{2-}$–*hs*-Co$^{II}$ could still take place even under external pressure, besides which the transition temperature moved to lower temperature regions, implying that external pressure will favor the existence of *hs*-Co$^{II}$ and/or *ls*-Co$^{II}$ species. Moreover, no hysteresis under pressure was observed in the whole temperature region. When the applied pressure on the two VT complexes was increased, the $\chi_M T$ values in the high temperature ranges gradually decreased and the curves clearly shifted to the higher temperature region (as shown in Fig. 2). However, in the low temperature regions, such as below 100 K for both $\mathbf{I}\cdot(PF_6)_3$ and $\mathbf{II}\cdot(PF_6)_3$, the $\chi_M T$ values hardly changed. After the external pressure was removed, the $\chi_M T$ values could recover to the initial ones.

In order to elucidate these different and interesting phenomena, some questions arising in these results must be answered: why do the $\chi_M T$ values became larger once external pressure was applied and the VT interconversion move to lower temperature regions? How does increasing pressure cause the transition to move to higher temperature range?

Indeed, the mechanism of how pressure affects VT interconversion is not yet clear, because the mechanism of VT interconversion itself is still under debate. Generally, a VT transition could be regarded as a two-step or a one-step interconversion.[19] In the two-step process, when temperature decreased, a spin-transition from *hs*-Co$^{II}$ to *ls*-Co$^{II}$ state initially took place, and then the intramolecular electron transfer from the metal ion to ligand occurred. Here, we only consider the dicobalt VT transition to be a two-step mechanism described in eqn (1). During the SC step (eqn (1a)), the transition from *ls*-Co$^{III}$–dhbq$^{2-}$–*hs*-Co$^{II}$ to *ls*-Co$^{III}$–dhbq$^{2-}$–*ls*-Co$^{II}$ state will lead to a volume shrinkage, thus it is desirable in that external pressure will favor the small-volume state and higher pressure will make the transition temperature move to a higher temperature range, as shown in Fig. 2, which is in accordance with the typical effect of pressure on SC complexes.[20–22] In Fig. 2(a), due to incomplete interconversion below room temperature, the tendency of the SC transition can just be seen to slightly shift to higher temperature range.

$$\text{SC step: } ls\text{-Co}^{III}\text{–dhbq}^{2-}\text{–}hs\text{-Co}^{II} \leftrightarrow ls\text{-Co}^{III}\text{–dhbq}^{2-}\text{–}ls\text{-Co}^{II} \quad (1a)$$

$$\text{ET step: } ls\text{-Co}^{III}\text{–dhbq}^{2-}\text{–}ls\text{-Co}^{II} \leftrightarrow ls\text{-Co}^{III\text{-}ls}\text{–dhbq}^{\bullet 3-}\text{–}ls\text{-Co}^{III} \quad (1b)$$

$$\Delta G = \Delta G_{ls\text{-Co(III)}} - \Delta G_{ls\text{-Co(II)}} = \Delta H - T\Delta S \quad (2)$$

During the ET step (eqn (1b)), the energy change is primarily enthalpy driven and the entropy increases with the increasing in spin multiplicity.[23,24] As shown in eqn (2), $\Delta H$ will become larger under increasing pressure, which indicates that the electron transfer process might be influenced by pressure.[13] When the VT transition took place, the Gibbs free energy $\Delta G$ of the eqn (2) was negative, in which the enthalpic separation $\Delta H$ between valence tautomeric isomers could be enlarged by increasing pressure but was not large enough to change the sign of $\Delta G$. So the absolute value of Gibbs free energy $\Delta G$ decreased according to eqn (2), and the equilibrium constant $K$ would become smaller so that the population of *ls*-$Co^{III}$ state resulting from the electron transfer from *ls*-$Co^{II}$ to the bridging dhbq ligand became lower than that under normal pressure, which indicates that the *ls*-$Co^{III}$–$dhbq^{2-}$–*ls*-$Co^{II}$ state would be more stable than the *ls*-$Co^{III}$–$dhbq^{\bullet 3-}$–*ls*-$Co^{III}$ state when pressure is applied. Based upon these results, we can partly conclude that once pressure is applied the electron transfer from *ls*-$Co^{III}$–$dhbq^{2-}$–*ls*-$Co^{II}$ to *ls*-$Co^{III}$–$dhbq^{\bullet 3-}$–*ls*-$Co^{III}$ is prevented, thus the low-temperature $\chi_M T$ values under any pressure can be ascribed to *ls*-$Co^{II}$, but not the $dhbq^{\bullet 3-}$ free radical. Then the SC + ET process in complexes **I**·$(PF_6)_3$ and **II**·$(PF_6)_3$ becomes an SC process only, so they behave as SC complexes under various pressure.

Besides, pressure can also change ligand-field strength as well as intermolecular interactions and thus give rise to interesting electronic states. In dinuclear Fe(II) SC systems for example, the application of pressure could cause strong ligand-field strength at the iron(II) centers, which along with the competition between short-range and long-range intermolecular interactions, led to the existence of *hs*–*ls* pairs.[25] In complexes **I**·$(PF_6)_3$ and **II**·$(PF_6)_3$, ligand fields and intermolecular interactions in the modes of $\pi_{py}\cdots\pi_{py}$, $\pi_{py}\cdots\pi_{benzene}$ and C–H$\cdots\pi_{dhbq}$ may also be influenced by external pressure, which may lead to the formation of *hs*–*ls* Co(II) pairs as found in the dinuclear Fe(II) SC complexes. In this case, the $\chi_M T$ value especially in the low temperature range must be a little larger than that of *ls*-$Co^{II}$ due to a certain *hs*-$Co^{II}$ proportion and the transition of *ls*-$Co^{III}$–$dhbq^{2-}$–*hs*-$Co^{II}$ $\leftrightarrow$ *ls*-$Co^{III}$–$dhbq^{2-}$–*ls*-$Co^{II}$ should be more general. As shown in Fig. 2, the $\chi_M T$ values under pressure are indeed higher than those without pressure and the transitions in whole temperature range become more general.

In conclusion, the effects of pressure on two dinuclear VT complexes and the possible mechanism of how pressure affects the VT transitions have been investigated. We found that the $\chi_M T$ values of **I**·$(PF_6)_3$ and **II**·$(PF_6)_3$ under external pressure were larger than those without additional pressure, and the $\chi_M T$ *vs.* $T$ plots clearly shifted to the higher temperature region upon increasing pressure. The results are very interesting and contrary to those reported for pressure-induced VT conversion. The reasons are that in the two-step VT interconversion mechanism, application of pressure can influence the SC step as the pressure effects on other SC complexes do, and more important is that pressure could make the ET step vanish by enlarging the enthalpic separation $\Delta H$ between valence tautomeric isomers and stabilize the *ls*-$Co^{II}$ state at low temperature. Moreover, the intermolecular interactions and ligand-field strength enhanced by pressure can form *hs*–*ls* Co(II) pairs that make the transition become more general. In effect, external pressure makes the SC + ET transition process of complexes **I**·$(PF_6)_3$ and **II**·$(PF_6)_3$ become the general SC process only. Our investigations have proved that the VT transitions can be efficiently modified by external pressure, which would give some inspiration to the search of switchable molecule-based materials.

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## Notes and references

† The two complexes were synthesized according to the published methods.[16,17] Magnetic measurements were performed with sweeping mode at a rate of 1 K $min^{-1}$ in the temperature range of 2–300 K under a magnetic field of 5000 Oe on Quantum Design MPMS XL-7 magnetometer. EasyLab Mcell 10 hydrostatic pressure cell for Quantum Design MPMS measurement platform was utilized to bring pressure on the samples.[26] The background of the Mcell 10 was measured under the same magnetic field. A superconducting Sn wire is placed inside the pressure cell with the samples, the value of the superconducting transition temperature, $T_c$ [$P$], enables the estimate of the *in situ* pressure from the pressure calibration $T$–$P$ curve.[26]


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