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Unidirectional Charge Transfer in *Di*-cobalt Valence Tautomeric Compound Finely Tuned by Ancillary Ligand

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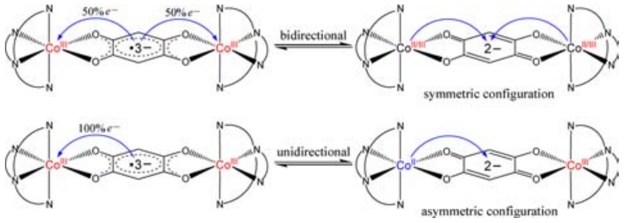
Supporting Information

ABSTRACT: A dinuclear valence tautomeric compound containing a cationic structure with crystallographically distinguishable *hs*-Co^{II} and *ls*-Co^{III} centers undergoes unidirectional charge transfer.

Valence tautomeric (VT) compounds as a spectacular kind of bistable molecule-based material have attracted great attention due to their potential applications in sensors, information storage, and display devices, whose intramolecular charge-transfer behaviors can be easily controlled by external stimuli such as temperature, light, or pressure.[1] Up to now, great efforts in VT systems have been made on mononuclear cobalt compounds with the general formula $[Co(N)_2(Q)_2]$, where Q refers to 3,5- or 3,6-di-*tert*-butylcatecholato or semiquinonato forms,[2] while much less attention has been paid to polynuclear or 1D-3D VT compounds.[3] Recently, two dinuclear cobalt compounds, $[\{Co(tpa)\}_2(dhbq)]\cdot(PF_6)_3$ ($\mathbf{1}\cdot(PF_6)_3$)[4] and $[\{Co(dpqa)\}_2(dhbq)]\cdot(PF_6)_3$ ($\mathbf{2}\cdot(PF_6)_3$)[5] (tpa = tris-(2-pyridylmethyl)amine), dqpa = (di-(2-pyridylmethyl)-N-(quinolin-2-ylmethyl) amine), dhbq = deprotonated 2,5-dihydroxy-1,4-benzoquinone), with similar crystal structures and fascinating VT transitions have been reported by our group, which show the importance of intermolecular interactions on VT transitions modeled by the terminal tetra-N ligands. So it is very interesting to explore new tetra-N ligands to construct dinuclear cobalt compounds that exhibit distinct VT properties.[6]

In $\mathbf{1}^{3+}$ and $\mathbf{2}^{3+}$, the putative configuration, *hs*-Co^{II}–$dhpq^{2-}$–*ls*-Co^{III}, always presents averaged electronic structure, $Co^{II/III}$–$dhpq^{2-}$–$Co^{II/III}$,[5] so the two metal ions are undistinguishable through X-ray diffraction studies. This averaged structure likely means the intramolecular charge transfer takes place equally between either of the two metal ions and dhbq (Scheme 1, top), i.e., bidirectional charge transfer. In terms of charge transfer in dinucelar VT compounds, there is unidirectional charge transfer between one specific metal ion and a redox ligand; thus, asymmetric configuration should also be considered (Scheme 1, bottom). To some extent, unidirectional transfer is more important to the application of bistable materials. Herein, we report a novel VT compound modeled by a new tetra-N ligand that shows crystallographically asymmetric *hs*–*ls* electronic structure, indicating unidirectional charge transfer.

Scheme 1. Bidirectional and Unidirectional Charge Transfer in Dinuclear Cobalt VT Compounds



The title compound $[\{Co(pmea)\}_2(dhbq)]\cdot(BF_4)_3$ ($\mathbf{3}\cdot(BF_4)_3$) and two related ones $[\{Co(pmea)\}_2(dhbq)]\cdot(BF_4)_4$ ($\mathbf{4}\cdot(BF_4)_4$) and $[\{Co(pmap)\}_2(dhbq)]\cdot(PF_6)_3$ ($\mathbf{5}\cdot(PF_6)_3$) (pmea = bis[(2-pyridyl)methyl]-2-(2-pyridyl)ethylamine, pmap = bis[2-(2-pyridyl)ethyl]-(2-pyridyl)methylamine) were synthesized in a way similar to $\mathbf{1}\cdot(PF_6)_3$ (Supporting Information, SI). X-ray crystallographic studies revealed that $\mathbf{3}\cdot(BF_4)_3$ crystallized in the monoclinic space group $P2_1/c$. The asymmetric unit contains a complete +3 cation that has two ancillary polyamine-chelated Co atoms and a bridging dhbq ligand (Figure S1a, SI). Each Co ion is located in a distorted octahedral geometry and is coordinated by two oxygen atoms from dhbq and four nitrogen atoms from pmea, respectively. The dhbq ligand and the substituted six-membered chelating rings of pmea are located in the equatorial plane. In addition, the crystallographically undefined counterions BF_4^- can clearly be detected by IR spectra (1082 cm^{-1}) and elemental analysis (SI). Compounds $\mathbf{4}\cdot(BF_4)_4$ and $\mathbf{5}\cdot(PF_6)_3$ crystallized in the triclinic space group $P\bar{1}$. Each asymmetric unit contains half of the cationic $\mathbf{4}^{4+}$ or $\mathbf{5}^{3+}$ (Figure S1b,c, SI), similar to that previously reported.[4,5a] For $\mathbf{4}\cdot(BF_4)_4$, the cationic structure is $[$*ls*-Co^{III}–$dhpq^{2-}$–*ls*-$Co^{III}]^{4+}$ as a result of full oxidization of $[$*hs*-Co^{II}–$dhpq^{2-}$–*hs*-$Co^{II}]^{2+}$ by $AgNO_3$. In the case of $\mathbf{5}\cdot(PF_6)_3$, two Co ions are partially oxidized to *ls*-Co^{III} state, and therefore the cationic structure is $[Co^{II/III}$–$dhpq^{2-}$–$Co^{II/III}]^{3+}$. Crystal data and selected bond lengths at 173 K are gathered in Tables S1 and S2 of the Supporting Information. The average Co–O and Co–N bond lengths are 1.896 and 1.944 Å for Co1 and 2.080 and 2.092 Å for Co2 in $\mathbf{3}^{3+}$, respectively, while the Co–O and Co–N bond lengths

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are 1.913 and 1.938 Å for the *ls*-Co^{III} ion in $\mathbf{4}^{4+}$ and 2.017 and 2.051 Å for the mixed valence Co$^{II/III}$ ion in $\mathbf{5}^{3+}$, respectively. The Co–O and Co–N bond lengths of Co1 in $\mathbf{3}^{3+}$ are consistent with those in $\mathbf{4}^{4+}$ and other *ls*-Co^{III} mononuclear compounds,[2,7] indicating the low-spin Co^{III} state of Co1 ion, while the values of Co2 are larger than those in $\mathbf{5}^{3+}$ but slightly less than the typical ones in *hs*-Co^{II} mononuclear compounds. The four C–O bond lengths in $\mathbf{3}^{3+}$ range from 1.264(7) to 1.354(7) Å and the intramolecular Co⋯Co distance is 7.712(9) Å, near to the value of $\mathbf{5}\cdot(PF_6)_3$ (7.796(1) Å) and longer than those of $\mathbf{1}\cdot(PF_6)_3$ (7.497(1) Å) and $\mathbf{2}\cdot(PF_6)_3$ (7.521(1) Å).[4,5a] All these data directly prove that the cationic structure of $\mathbf{3}\cdot(BF_4)_3$ is [*hs*-Co^{II}–dhpq^{2-}–*ls*-Co^{III}]$^{3+}$ at temperature above 173 K.

In the solid state, all compounds feature supramolecular three-dimensional structures (Figure S2, SI) that are constructed from alternating layers of cations and counterions. For $\mathbf{4}\cdot(BF_4)_4$ and $\mathbf{5}\cdot(PF_6)_3$ with centrosymmetric cationic structures, the cationic layer is characterized by extended networks with similar C–H⋯π and π⋯π interactions, as shown in Figure S3 of the Supporting Information. While for $\mathbf{3}\cdot(BF_4)_3$, because of the existence of crystallographically distinguished *hs*-Co^{II} and *ls*-Co^{III} centers, the cationic layer can be characterized as an extended network with alternating *hs*-Co^{II} and *ls*-Co^{III} chains (Figure 1), in which Co centers are connected to adjacent ones through $\pi_{py}\cdots\pi_{py}$ interactions. The $\pi_{py}\cdots\pi_{py}$ interactions (4.168 and 4.072 Å) within the *hs*-Co^{II} chains are slightly stronger than those within the *ls*-Co^{III} chains (4.172 Å). Meanwhile, adjacent *hs*-Co^{II} and *ls*-Co^{III} chains are interconnected by various $\pi_{py}\cdots\pi_{py}$ (4.131 and 4.252 Å) and C–H⋯π_{dhbq} (3.664 and 3.680 Å) interactions. These intermolecular interactions may play an important role in favoring the asymmetric unit [*hs*-Co^{II}–dhpq^{2-}–*ls*-Co^{III}]$^{3+}$ and affecting the VT process of $\mathbf{3}\cdot(BF_4)_3$.

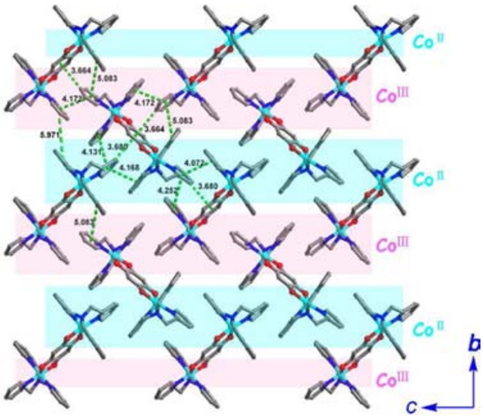

Figure 1. Perspective view of the layer structure of $\mathbf{3}^{3+}$.

The magnetic properties of compounds $\mathbf{3}\cdot(BF_4)_3$ and $\mathbf{5}\cdot(PF_6)_3$ have been investigated over a temperature range of 2–300 K, and their $\chi_M T$ versus T plots are shown in Figure 2. At room temperature and under ambient pressure, the $\chi_M T$ value for $\mathbf{3}\cdot(BF_4)_3$ is 2.37 cm^3 K mol^{-1}, corresponding to a *hs*-Co^{II} ion with unquenched orbital angular momentum as found in other *di*-cobalt VT compounds. Upon cooling, the $\chi_M T$ value gradually decreases and reaches an inclined plateau between 50 and 100 K ($\chi_M T$ is 1.33 cm^3 K mol^{-1} at 50 K). This decrease in the $\chi_M T$ value might be the result of incomplete interconversion from *hs*-Co^{II}–dhbq^{2-}–*ls*-Co^{III} to *ls*-Co^{III}–dhbq$^{\bullet 3-}$–*ls*-Co^{III} or spin transition of the *hs*-Co^{II} ion.[8] To elucidate the true reason responsible for the decrease of $\chi_M T$ values, ESR measurements were carried out between 100 and 300 K (Figure 2, right). The strong signal for $g = 2.001$ at 100 K decreases gradually with increasing temperature, clearly indicating the existence of a dhbq$^{\bullet 3-}$ radical and electron transfer from dhbq$^{\bullet 3-}$ to *ls*-Co^{III}. The radical signal disappears at room temperature in response to the VT conversion. Thus, both variable-temperature magnetic and ESR measurements reveal the occurrence of charge transfer between cobalt centers and electro-active dhbq ligands. Below 50 K, the much more rapid decrease of $\chi_M T$ values (1.04 cm^3 K mol^{-1} at 5 K) may be due to the antiferromagnetic interactions between the dhbq$^{\bullet 3-}$ radical and residual *hs*-Co^{II} ion and/or the zero-field splitting effect of residual *hs*-Co^{II} ion. This VT transition is reversible upon warming. For $\mathbf{5}\cdot(PF_6)_3$, the $\chi_M T$ value at room temperature is 2.52 cm^3 K mol^{-1}, which remains almost unchanged until 150 K (Figure 2, left) and then decreases rapidly to reach a value of 1.58 cm^3 K mol^{-1} at 2 K. This profile indicates that no VT transition occurs throughout whole temperature range, and the decrease of the $\chi_M T$ value can be attributed to the zero-field splitting effect of the *hs*-Co^{II} ion. By comparing $\mathbf{3}\cdot(BF_4)_3$ and $\mathbf{5}\cdot(PF_6)_3$ with $\mathbf{1}\cdot(PF_6)_3$ and $\mathbf{2}\cdot(PF_6)_3$, the critical temperature of VT transition shifts toward a lower temperature range in a sequence of $T_1 > T_2 > T_3 > T_5$ (T_5 is too low to undergo VT transition, Figure S4, SI). The increasing steric hindrance or tension originated from the ancillary tripodal ligands (additional benzene ring or substituted six-membered chelating rings) may be one of the main factors that influences the charge distribution and VT transition in *di*-cobalt compounds, because stronger hindrance or tension tends to stabilize high-spin state.[9]

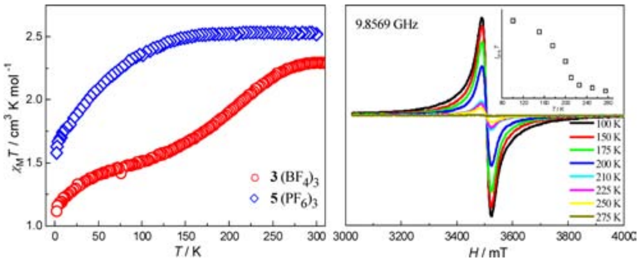

Figure 2. $\chi_M T$ vs T plots of $\mathbf{3}\cdot(BF_4)_3$ and $\mathbf{5}\cdot(PF_6)_3$ (left) and temperature-dependent EPR spectra of $\mathbf{3}\cdot(BF_4)_3$ (right).

The effect of pressure on the VT transition of $\mathbf{3}\cdot(BF_4)_3$ has also been investigated (Figure S5, SI). The transitions under external pressure are more gradual than that under ambient pressure. As external pressure increases, the magnetic curves shift to a higher temperature range. Thus, the transition behavior under external pressure is very similar to those found for $\mathbf{1}\cdot(PF_6)_3$ and $\mathbf{2}\cdot(PF_6)_3$.[5b] According to the putative two-step mechanism of VT transition–spin crossover (SCO) and electron transfer (ET) steps,[5b] the influence of external pressure on the SCO step should move the transition to higher temperature range. At low temperature, applied pressure not only basically blocks the ET step and increases the $\chi_M T$ values but also mainly induces the spin transition from *hs*-Co^{II} to *ls*-Co^{II} state.

In summary, three new *di*-cobalt compounds have been synthesized. $\mathbf{5}\cdot(PF_6)_3$ remains paramagnetic over the whole temperature range, while $\mathbf{3}\cdot(BF_4)_3$ undergoes a gradual and incomplete VT transition that is verified by variable-temperature magnetic and ESR measurements. X-ray crystallographic studies unambiguously reveal that both cations of **4**·$(BF_4)_4$ and **5**·$(PF_6)_3$ have crystallographic centers of symmetry, whereas the cation of **3**·$(BF_4)_3$ lacks a center of symmetry, therefore, giving an asymmetric *di*-cobalt structure. This asymmetric *hs*-Co^{II}–dhbq^{2-}–*ls*-Co^{III} structure exhibits crystallographically distinguishable *hs*-Co^{II} and *ls*-Co^{III} centers and shows unidirectional charge transfer in VT compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, tables, figures, and crystal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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