Inorganic Chemistry
Communication
pubs.acs.org/IC

# A Two-Step Valence Tautomeric Transition in a Dinuclear Cobalt Complex

Kerwyn G. Alley,[†] Giordano Poneti,[‡,§] Jade B. Aitken,[⊥,∥,¶] Rosalie K. Hocking,[#] Boujemaa Moubaraki,[#] Keith S. Murray,[#] Brendan F. Abrahams,[†] Hugh H. Harris,[$] Lorenzo Sorace,[‡] and Colette Boskovic*[,†]

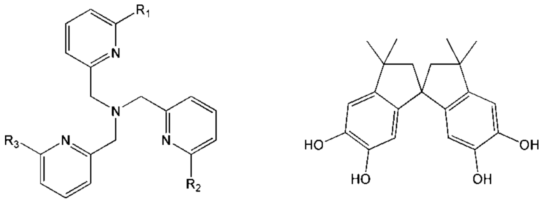
[†]School of Chemistry, The University of Melbourne, Victoria 3010, Australia
[‡]UdR INSTM and Department of Chemistry, University of Florence, Via della Lastruccia 3−13, 50019 Sesto F.no (FI), Italy
[§]Department of Applied Science and Technology, "Guglielmo Marconi" University, Via Plinio 44, 00193 Rome, Italy
[⊥]School of Chemistry, The University of Sydney, New South Wales 2006, Australia
[∥]Australian Synchrotron, Clayton, Victoria 3168, Australia
[¶]Institute of Materials Structure Science, KEK, Tsukuba, Ibaraki 305-0801, Japan
[#]School of Chemistry, Monash University, Clayton, Victoria 3800, Australia
[$]School of Chemistry and Physics, The University of Adelaide, South Australia 5005, Australia

S *Supporting Information*

**ABSTRACT:** A dinuclear cobalt complex with cobalt centers bridged by a bis(dioxolene) ligand exhibits a rare two-step valence tautomeric transition.

Molecules that can be switched between two or more electronic states are of interest for future applications in data storage, display devices, and molecular electronics. One well-known class of switchable molecules are octahedral iron(II) and cobalt(II) complexes that undergo a spin-crossover (SC) between low-spin (LS) and high-spin (HS) states.[1] Molecular switchability can also arise from valence tautomeric (VT) transitions, which involve an intramolecular electron transfer. These have mainly been observed for octahedral cobalt complexes with dioxolene ligands,[2−4] for which the electron transfer from a catecholate (cat) ligand to the LS $\mathrm{Co^{III}}$ ion triggers a spin transition, yielding a HS $\mathrm{Co^{II}}$ ion coordinated to a paramagnetic semiquinonate (SQ) ligand. Both VT and SC transitions are induced by the application of external stimuli including heat, pressure and light or X-ray irradiation.[1−4] Thermal induction of both types of transitions is entropically driven, with the large entropy gain arising from the higher density of vibrational states of the HS $\mathrm{M^{II}}$-containing complex (M = Fe or Co), due to the longer M−O/N bond lengths, and from the higher spin-state degeneracy of this species.

Two-step SC transitions are well established in dinuclear iron(II) complexes and commonly observed as plateaus in the variable-temperature magnetic susceptibility profile.[5] The origin of the steps is often separate LS to HS transitions at each $\mathrm{Fe^{II}}$ center, which can afford a system that exists in three distinct states (LS−LS, LS−HS, and HS−HS). Such three-state systems are potentially important for future applications as three-state switches or molecular ternary memory.[6] In contrast, although VT transitions have been reported for a number of dinuclear cobalt complexes,[7,8] the only report of a two-step VT transition attributable to a dinuclear molecule is for $[\mathrm{Co_2(L)(3{,}5\text{-}DBdiox)_4}]$ (L = 4,6-di-2′-pyridylpyrimidine; 3,5-DBdiox = 3,5-di-*tert*-butylcatechol, or 3,5-di-*tert*-butylsemiquinone).[8] The two-step nature of the VT transition was identified from the variable-temperature near-IR spectra of a thin film, while the powder magnetic susceptibility data did not show steps. In an effort to access two-step VT behavior, we have focused on the tetradeprotonated derivative of 3,3,3′,3′-tetramethyl-1,1′-spirobis(indane-5,5′,6,6′-tetrol) ($\mathrm{spiroH_4}$) as a redox-active bridging ligand, which is potentially accessible in $(\mathrm{spiro^{cat-cat}})^{4-}$, $(\mathrm{spiro^{cat-SQ}})^{3-}$, and $(\mathrm{spiro^{SQ-SQ}})^{2-}$ states.[9] To control the charge distribution across the cobalt dioxolene unit, we followed an approach recently reported by some of us in a study of a family of mononuclear cobalt dioxolene complexes with ancillary ligands derived from tris(2-pyridylmethyl)amine (TPA). This revealed the dependence of the observed redox isomeric form and VT transitions on the ancillary ligand.[10] The sequential addition of methyl groups into the 6 position of the pyridine rings increases the steric hindrance at the cobalt center, thereby modulating its redox properties.



**TPA** ($\mathrm{R_1 = R_2 = R_3 = H}$)
$\mathrm{Me_2TPA}$ ($\mathrm{R_1 = R_2 = Me, R_3 = H}$)
$\mathrm{Me_3TPA}$ ($\mathrm{R_1 = R_2 = R_3 = Me}$)

$\mathrm{spiroH_4}$

Herein we report the synthesis and characterization of three members of a new family of dinuclear cobalt complexes: $[\mathrm{Co_2(spiro)(Me}_n\mathrm{TPA)_2}]^{2+}$, where $n$ = 0 (**1**), 2 (**2**), and 3 (**3**). These are obtained as perchlorate salts in compounds $[\mathrm{Co_2(spiro)(TPA)_2}](\mathrm{ClO_4})_2\cdot 6\mathrm{H_2O}$ (**1a**), $[\mathrm{Co_2(spiro)(Me_2TPA)_2}](\mathrm{ClO_4})_2\cdot 3.5\mathrm{H_2O}$ (**2a**), and $[\mathrm{Co_2(spiro)}$-

**Received:** February 2, 2012
**Published:** March 20, 2012

$(Me_3TPA)_2](ClO_4)_2 \cdot 2H_2O$ (**3a**), which are prepared by the addition of tetradeprotonated spiro$H_4$ to stoichiometric amounts of $Me_n$TPA ($n$ = 0, 2, or 3) and $Co(ClO_4)_2$ in methanol. Analytically pure samples of all three compounds are obtained in yields of greater than 70% and have been characterized by thermogravimetric analysis, magnetic susceptibility, and synchrotron X-ray absorption spectroscopy (XAS).

The formation of single crystals suitable for X-ray diffraction required the use of counteranions other than perchlorate. Single-crystal X-ray diffraction analysis at 130 K reveals that complexes **1** in $[Co_2(spiro)(TPA)_2](PF_6)_2 \cdot 4py$ (**1b**) and **3** in $[Co_2(spiro)(Me_3TPA)_2][CoCl_4] \cdot 7MeOH$ (**3b**) display similar V-shaped molecular structures, with the spiro bridging ligand acting as a hinge between the halves of the molecule (Figures 1 and S1 and Table S1 in the Supporting Information). While the dinuclear complex **3** in **3b** has pseudo-2-fold symmetry, **1** in **1b** is strictly asymmetric, with two chemically distinct cobalt centers. This is readily apparent from inspection of the bond trans to the amine nitrogen of the TPA ligands, which for one cobalt center is occupied by the dioxolene oxygen atom proximal to the spiro carbon and for the other is occupied by the distal oxygen atom. A close inspection of the coordination spheres of the cobalt centers affords Co−O, Co−$N_{amine}$, and Co−$N_{pyridine}$ distances of 1.87−1.88, 1.93−1.94, and 1.91−1.94 Å, respectively, for **1** (Table S2 in the Supporting Information). These distances are consistent with two LS $Co^{III}$ centers. The redox state of dioxolene ligands can often be determined from consideration of the C−O and (O)C−C(O) bond distances.[11] For **1**, the C−O distances are 1.35−1.37 Å and the (O)C−C(O) distances are 1.41−1.42 Å, suggesting that both dioxolene moieties are in the catecholate state. Thus, on the basis of crystallographic data at 130 K, **1** in **1b** is formulated as the LS $Co^{III}$−$(spiro^{cat-cat})$−LS $Co^{III}$ valence tautomer. In contrast, the Co−O/N distances observed for **3** are longer, with Co−O, Co−$N_{amine}$, and Co−$N_{pyridine}$ distances of 1.99−2.10, 2.11, and 2.14−2.25 Å, respectively, consistent with two HS $Co^{II}$ centers. Accordingly, the C−O distances are 1.28−1.29 Å and the (O)C−C(O) distances are 1.47 Å, indicating that both dioxolene moieties are in the semiquinonate state. Complex **3** in compound **3b** is thus formulated as the HS $Co^{II}$−$(spiro^{SQ-SQ})$−HS $Co^{II}$ tautomer at 130 K. Variable-temperature Co K-edge XAS data indicate that the change of anion does not affect the charge distribution in either complex, with temperature-independent spectra obtained between 16 and 300 K for both **1a** and **3a** (Figures 2a and S2 and Table S3 in the Supporting Information). Edge (and preedge) peak energies of 7729.3 (preedge peaks at 7710.5 and 7713.2 eV) and 7725.0 eV (preedge peaks at 7708.8, 7710.3, and 7713.6 eV) are consistent with the assignment of LS $Co^{III}$ and HS $Co^{II}$ for **1** and **3**, respectively.[12]

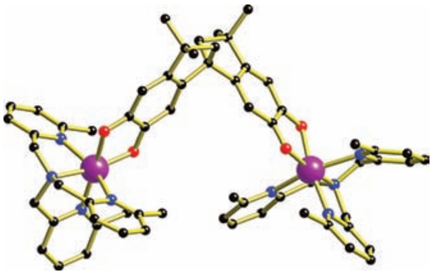


**Figure 1.** Structural representation of complex **3** in **3b**. Color code: Co, purple; O, red; N, blue; C, black.

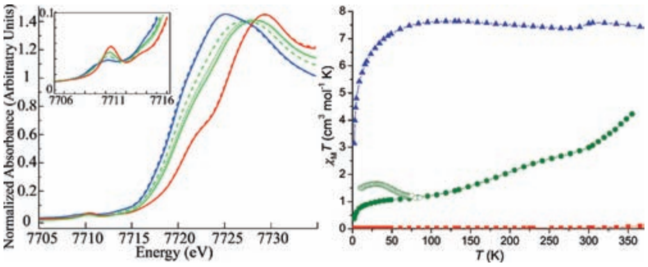


**Figure 2.** Variable-temperature (left) Co K-edge XANES spectra for **1a** (red), **2a** (green), and **3a** (blue) at 16 (solid), 100 (dotted), and 298 K (dashed). (right) $\chi_M T$ data for **1a** (red ■), **2a** (green ●), and **3a** (blue ▲) and photoinduced $\chi_M T$ data for **2a** (green ○).

The $\chi_M T$ vs $T$ data (where $\chi_M$ is the molar magnetic susceptibility per dinuclear unit) for **1a** (Figure 2b) display little variation in the range 2−360 K, from 0.02 to 0.10 cm$^3$ mol$^{-1}$ K, consistent with a diamagnetic LS $Co^{III}$−$(spiro^{cat-cat})$−LS $Co^{III}$ species. The data for **3a** (Figure 2) exhibit an almost constant $\chi_M T$ value of ca. 7.4 cm$^3$ mol$^{-1}$ K between 60 and 360 K, with a gradual decrease in $\chi_M T$ to ca. 3.2 cm$^3$ mol$^{-1}$ K$^{-1}$ at 2 K due to depopulation of the HS $Co^{II}$ energy levels split by spin−orbit coupling. The 360 K $\chi_M T$ value is consistent with two noninteracting semiquinonate radical ligands ($S = {}^1/_2$; $g = 2.0$) and two HS $Co^{II}$ ions ($S = {}^3/_2$; $^4T_{1g}$ state with significant spin−orbit coupling), indicating a HS $Co^{II}$−$(spiro^{SQ-SQ})$−HS $Co^{II}$ species from 2 to 360 K.[13] Thus, the single-crystal X-ray diffraction, powder magnetic susceptibility, and XAS data are all consistent with **1** and **3** possessing temperature-invariant LS $Co^{III}$−$(spiro^{cat-cat})$−LS $Co^{III}$ and HS $Co^{II}$−$(spiro^{SQ-SQ})$−HS $Co^{II}$ electronic states, respectively, between 2 and 360 K.

Despite considerable effort, it has not been possible to grow diffraction-quality crystals of **2**. However, variable-temperature XAS and magnetic measurements have indicated very interesting temperature-dependent behavior for this complex. The magnetic susceptibility data for **2a** (Figures 2b and S3 in the Supporting Information) display a two-step transition between 2 and 355 K, with two distinct regions of change in the ranges 100−300 and 300−355 K. These are assigned to a two-step VT transition for **2**, with both steps incomplete. Upon heating of the sample from 2 K, the onset of the first step of the VT transition is evident at ca. 100 K. Below this temperature, the plateau $\chi_M T$ value of 1.1 cm$^3$ mol$^{-1}$ K in the range 50−100 K indicates a trapped fraction of HS $Co^{II}$-SQ amounting to approximately 15% of the cobalt dioxolene "half-molecules" overall. As the temperature is increased from 100 to 300 K, the first step of the VT transition occurs, with $\chi_M T$ increasing to a value of ca. 3.0 cm$^3$ mol$^{-1}$ K at 300 K, consistent with ca. 40% HS $Co^{II}$-SQ. The $\chi_M T$ profile between 2 and 300 K is obtained reversibly, with no thermal hysteresis (Figure S3 in the Supporting Information). Above 300 K, the $\chi_M T$ curve shows a steeper increase, which is assigned to the beginning of the second step of the VT transition. This step is incomplete at 355 K, with the $\chi_M T$ value of 4.2 cm$^3$ mol$^{-1}$ K indicating a molar fraction of about 60% HS $Co^{II}$-SQ. In contrast to the first step, after heating the sample to 355 K and remeasurement upon cooling, the same profile is not obtained. Thermogravimetric analysis suggests that this is due to an irreversible solvent loss above 300 K, associated with the VT transition (Figure S3 in the Supporting Information). Similar behavior has been found previously for VT cobalt complexes and confirms the solvation dependence of thermal VT transitions.[14]

In the absence of single-crystal X-ray data and due to the incomplete nature of the transition at both low and high temperature, it is impossible to unequivocally explain the two steps in the VT transition of **2a**. Even if a VT process involving only LS $\mathrm{Co^{III}}$−$(\mathrm{spiro^{cat-cat}})$−LS $\mathrm{Co^{III}}$ and HS $\mathrm{Co^{II}}$−$(\mathrm{spiro^{SQ-SQ}})$−HS $\mathrm{Co^{II}}$ charge configurations cannot be ruled out, considerations based on previously reported electrochemical data of Co-spiro complexes suggest as more likely a sequential transition at each half of the dinuclear complex from the low-temperature LS $\mathrm{Co^{III}}$−$(\mathrm{spiro^{cat-cat}})$−LS $\mathrm{Co^{III}}$ tautomer to a mixed HS $\mathrm{Co^{II}}$−$(\mathrm{spiro^{SQ-cat}})$−LS $\mathrm{Co^{III}}$ species and finally to the HS $\mathrm{Co^{II}}$−$(\mathrm{spiro^{SQ-SQ}})$−HS $\mathrm{Co^{II}}$ one.[9] The presence of two steps may be influenced by a very weak electronic coupling of the dioxolene moieties through the spiro center,[9a] with a possible chemical inequivalence of the coordination environments of the two cobalt centers, as in **1b**, also contributing. A detailed study of the solution properties of the three complexes will be reported in due course.

Additional evidence for the VT nature of the low-temperature transition of **2a** comes from variable-temperature Co K-edge XAS data.[12] These exhibit significant temperature dependence in the range 16−298 K, in contrast to the temperature-independent behavior observed for **1a** and **3a**. The XANES and preedge indicate a continuous decrease in the amount of LS $\mathrm{Co^{III}}$ and a concomitant increase in the amount of HS $\mathrm{Co^{II}}$ as the sample is heated from 100 to 298 K, consistent with the first step of the VT transition evident in the magnetic susceptibility data. In the temperature range 100−298 K, the XANES spectra (Figure 2a) show an edge shift from 7728.4 to 7727.2 eV, while ligand-field modeling of the preedge data reveals the expected increase and decrease in the intensity of transitions to $t_{2g}$ and $e_g$ orbitals, respectively (Table S3 in the Supporting Information). Interestingly, the XANES and preedge data below 100 K all show some evidence of additional HS $\mathrm{Co^{II}}$, most prominent at the lowest temperature measured (16 K). This is likely due to a combination of the trapped fraction of HS $\mathrm{Co^{II}}$-SQ observed by magnetic susceptibility and of the product of a VT transition induced by the synchrotron X-ray beam, as reported for other VT cobalt complexes.[4] Unfortunately, instrumental limitations have prevented exploration of the second step of the VT transition of **2a** by XAS measurements above room temperature.

Finally, it proved to be possible to photoinduce a VT transition in **2a**. Photoirradiation at 10 K, with light of wavelengths 534, 658, and 904 nm, results in an increase in $\chi_M T$ from 0.98 to 1.5 $\mathrm{cm^3\ mol^{-1}\ K}$ (Figure 2b), indicative of a partial VT transition from LS $\mathrm{Co^{III}}$−$(\mathrm{spiro^{cat-cat}})$−LS $\mathrm{Co^{III}}$ to HS $\mathrm{Co^{II}}$−$(\mathrm{spiro^{SQ-cat}})$−LS $\mathrm{Co^{III}}$. The percentage of photoconversion for the three wavelengths is in the range 15−20%. Continued measurement of the magnetic susceptibility data shows the thermal curve measured after irradiation collapses back to the nonirradiated curve at ca. 52 K, suggesting the presence of a thermal activation barrier to the relaxation of magnitude similar to those reported in the literature.[3,10,14b,c]

In conclusion, spectroscopic and magnetic measurements reveal that the dinuclear complex $[\mathrm{Co_2(spiro)(Me_2TPA)_2}]^{2+}$ exhibits a rare two-step thermally induced VT transition, which can be partially photoinduced at low temperature. The existence of three different electronic forms of this complex, accessible by two different stimuli, is of interest with respect to future applications as molecular logic gates. The ability to interconvert these states by different stimuli is important for processes such as write−lock−read−unlock−erase cycles.[6]

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental and crystallographic details, crystallographic data (CIF files), Figures S1−S3, and Tables S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: c.boskovic@unimelb.edu.au.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank the Australian and European (ERC-AdG MolNanoM@S) Research Councils for funding. Portions of this research were performed at the XAS beamline at the Australian Synchrotron.

## ■ REFERENCES

(1) Gütlich, P.; Goodwin, H. A. *Top. Curr. Chem.* **2004**, 233−235.

(2) Evangelio, E.; Ruiz-Molina, D. *Eur. J. Inorg. Chem.* **2005**, 2957.

(3) Sato, O.; Cui, A.; Matsuda, R.; Tao, J.; Hayami, S. *Acc. Chem. Res.* **2007**, *40*, 361.

(4) Poneti, G.; Mannini, M.; Sorace, L.; Sainctavit, P.; Arrio, M.-A.; Otero, E.; Cezar, J. C.; Dei, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 1954.

(5) Bousseksou, A.; Molnár, G.; Real, J. A.; Tanaka, K. *Coord. Chem. Rev.* **2007**, *251*, 1822.

(6) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines*; Wiley: Weinheim, Germany, 2003.

(7) (a) Carbonera, C.; Dei, A.; Létard, J.-F.; Sangregorio, C.; Sorace, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3136. (b) Tao, J.; Maruyama, H.; Sato, O. *J. Am. Chem. Soc* **2006**, *128*, 1790. (c) Bin-Salamon, S.; Brewer, S. H.; Depperman, E. C.; Franzen, S.; Kampf, J. W.; Kirk, M. L.; Kumar, R. K.; Lappi, S.; Peariso, K.; Preuss, K. E.; Shultz, D. A. *Inorg. Chem.* **2006**, *45*, 4461.

(8) Hearns, N. G. R.; Korĉok, J. L.; Paquette, M. M.; Preuss, K. E. *Inorg. Chem.* **2006**, *45*, 8817.

(9) (a) Dei, A.; Gatteschi, D.; Sangregorio, C.; Sorace, L. *Acc. Chem. Res.* **2004**, *37*, 827. (b) Affronte, M.; Beni, A.; Dei, A.; Sorace, L. *Dalton Trans.* **2007**, 5253. (c) Dei, A.; Sorace, L. *Dalton Trans.* **2003**, 3382.

(10) Beni, A.; Dei, A.; Laschi, S.; Rizzitano, M.; Sorace, L. *Chem.—Eur. J.* **2008**, *14*, 1804.

(11) Mulyana, Y.; Nafady, A.; Mukherjee, A.; Bircher, R.; Moubaraki, B.; Murray, K. S.; Bond, A. M.; Abrahams, B. F.; Boskovic, C. *Inorg. Chem.* **2009**, *48*, 7765.

(12) Poneti, G.; Mannini, M.; Sorace, L.; Sainctavit, P.; Arrio, M.-A.; Rogalev, A.; Wilhelm, F.; Dei, A. *ChemPhysChem* **2009**, *10*, 2090.

(13) We suggest the small dip in $\chi_M T$ at around 270 K can be assigned to a reversible structural rearrangement of the ligands, which causes a modification in the degree of orbital momentum quenching as per the report in: Juhàsz, G.; Matsuda, R.; Kanegawa, S.; Inoue, K.; Sato, O.; Yoshizawa, K. *J. Am. Chem. Soc.* **2009**, *131*, 4560−.

(14) (a) Evangelio, E.; Rodriguez-Blanco, C.; Coppel, Y.; Hendrickson, D. N.; Sutter, J. P.; Campo, J.; Ruiz-Molina, D. *Solid State Sci.* **2009**, *11*, 793. (b) Mulyana, Y.; Poneti, G.; Moubaraki, B.; Murray, K. S.; Abrahams, B. F.; Sorace, L.; Boskovic, C. *Dalton Trans.* **2010**, *39*, 4757. (c) Dapporto, P.; Dei, A.; Poneti, G.; Sorace, L. *Chem.—Eur. J.* **2008**, *14*, 10915.