Molecular Switches

Modulation of Magnetic Properties at Room Temperature: Coordination-Induced Valence Tautomerism in a Cobalt Dioxolene Complex

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Abstract: The valence-tautomeric six-coordinate complex $[Co(tbdiox)_2(4-papy)_2]$ (1; $tbdiox = redox-active 3,5-di-tert-butyl-o-dioxolene, 4-papy = 4-phenylazopyridine) was synthesized and its electronic structure examined. Whereas 1 shows regular thermally driven valence tautomerism in the solid state, it partially dissociates in solution to form the five-coordinate species <math>[Co(tbdiox)_2(4-papy)]$ (2) and free 4-papy. Species 1 and 2 exhibit different electronic structures—low-spin (Is) Co^{III} and high-spin (hs) Co^{III}, respective-ly—in solution at room temperature and therefore different magnetic properties. Since 1 and 2 are in an equilibrium that is 4-papy-dependent, the magnetic moment of the solu-

tion species can be tuned by means of the ligand content. Thus, the concept of coordination-induced valence tautomerism (CIVT) has been introduced. The electronic structures of **1** and **2** as well as their CIVT were elucidated by X-ray crystallography, electrochemistry, titration experiments, and all variable-temperature SQUID susceptometry, NMR, EPR, and electronic absorption spectroscopy. The experimental findings are strongly supported by broken-symmetry DFT calculations. The magnetic exchange interactions in different types of valence-tautomeric cobalt complexes were explored computationally.

Introduction

Molecular bistability is a fundamental concept in molecular materials research that is defined as the ability of a molecular system to exist in two different electronic states within a certain range of external perturbation.^[1] Valence-tautomeric (VT) metal complexes are among the most well-known examples of molecular bistability.^[2-7] The judicious combination of a redoxactive metal ion and redox-active ligand with close redox potentials in a VT complex affords reversible intramolecular electron transfer giving rise to two distinctly different electronic states (redox isomers). The switching between electronic states in a VT system can be triggered by temperature change, applied pressure, external magnetic field, or light irradiation.[8-10] Since electronic states of VT complexes differ significantly in magnetic properties, color, refractive index, dielectric constant, and other physicochemical properties, this class of compounds has been suggested for applications as molecular switches, sensors, and memory devices.^[11]

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Cobalt dioxolenes are likely the most interesting members of the VT family, because intramolecular one-electron transfer in these species is accompanied by a low-spin⇔high-spin transition at the cobalt center [Eq. (1)]:

$$\mathsf{Is-Co}^{\mathsf{III}}(\mathsf{Cat})(\mathsf{SQ}) \rightleftharpoons \mathsf{hs-Co}^{\mathsf{II}}(\mathsf{SQ})_2 \tag{1}$$

where Cat is a catecholate(2-) ligand, that is, a fully reduced diamagnetic form of dioxolene, and SQ is a benzosemiquinone(1-) ligand, that is, a π -radical form of dioxolene. The presence of one ligand-based spin in the Is-Co^{III} state ($S_{Co} = 0$, $S_{\rm R} = 1/2$), and the existence of three weakly coupled paramagnetic centers in the hs-Co^{II} state ($S_{Co} = 3/2$, $S_{R1} = 1/2$, $S_{R2} = 1/2$) results in drastic changes of magnetic properties associated with the VT transition. Archetypal complexes with the general formula [Co(dioxolene)₂(NN)] (NN is an N-donor chelating ligand) have dominated this research field for a long time.^[2-6] More recently, other types of VT Co dioxolene complexes have been synthesized including [Co(dioxolene)₂L₂] species (L is a monodentate N-donor ligand).[12-16] Despite their obvious similarity, the latter species adopt a trans orientation of N donors, in contrast to the archetypes, which are restricted to a cis configuration. This geometric diversity causes different orientations of ligand-based magnetic orbitals in cis-[Co(dioxolene)₂(NN)] and trans-[Co(dioxolene)₂L₂] species that may yield distinct electronic properties. In contrast to cis-[Co(dioxolene)₂(NN)] species, which are well investigated both in the solid state and in solution, thorough studies of VT inter-



conversion in *trans*-[Co(dioxolene)₂L₂] complexes are almost exclusively restricted to the solid state.^[12-15]

Pursuing the development of VT species that are photoswitchable at room temperature,^[17] we synthesized and structurally characterized *trans*-[Co(tbdiox)₂(4-papy)₂] (1) featuring two redox-active 3,5-di-*tert*-butyl-o-dioxolene (tbdiox) and two axial 4-phenylazopyridine (4-papy) ligands (Scheme 1). The properties of **1** in the solid state and in solution were investi-



Crystal structure

Recrystallization of **1** from acetonitrile afforded prism-shaped crystals suitable for X-ray structure determination. Data collected at 120 K showed an unsolvated, slightly distorted octahedral complex with C_i symmetry in the triclinic space group $P\overline{1}$. The cobalt ion, located at the crystallographic inversion center, is coordinated by two equatorial bidentate *o*-dioxolene and two axial monodentate 4-papy ligands (Figure 1). Both 4-papy



Scheme 1. Bis(o-dioxolene) cobalt complexes of this work.

gated by X-ray crystallography, electrochemistry, and all variable-temperature SQUID susceptometry, NMR, EPR, and electronic absorption spectroscopy. We found that, due to the lability of 4-papy ligands, the electronic state of **1** and thus associated magnetic properties can be changed in a controlled manner by coordination/dissociation of 4-papy ligands in solution at room temperature. This is in strong contrast to the classical *cis*-[Co(dioxolene)₂(NN)] complexes, which do not dissociate under similar conditions. The observed coordination-induced valence tautomerism (CIVT) in **1** is analogous to the recently reported coordination-induced spin crossover (CISCO).^[18] Our experimental results are supported by broken-symmetry DFT calculations that reveal differing electronic structures and magnetic interactions in *cis* and *trans* VT Co dioxolene species.

Results

Synthesis

Complex 1 was prepared under an inert atmosphere by following a modified recipe for VT bis(o-dioxolene) cobalt complexes.^[2,19] Addition of 4-papy to the cobalt tetramer [{Co-(tbdiox)₂)₄] in toluene afforded dark green 1 in good yield. The product is paramagnetic in both solution and the solid state, as confirmed by NMR spectroscopy and SQUID susceptometry, respectively (see below).

Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

ligands are slightly bent and twisted. Instead of the ideal 90°, the O1-Co1-N1 and O2-Co1-N1 angles are 88.2 and 89.9°, respectively, and the aromatic rings of 4-papy form a dihedral angle of 7.1° .

Since the structural features of bis(o-dioxolene)cobalt complexes are diagnostic of the electron distribution in the system,^[3] the oxidation states of o-dioxolene ligands and the metal center can be assigned on the basis of bond-length analysis. The Co-N (1.89(1) Å) and Co-O (1.886(2) Å) bond lengths in 1 determined at 120 K resemble those in analogous Is-[Co^{III}(SQ)(Cat)L₂] complexes reported in the range 1.932-1.964 Å and 1.888–1.898 Å, respectively (L2: two monodentate pyridyl-derived ligands or a bidentate ligand, see Table S6 in the Supporting Information).^[15, 20, 21] In contrast, the Co-N and Co–O bond lengths in hs-[Co^{II}(SQ)₂L₂] isomers are significantly longer, in the ranges of 2.118-2.161 and 2.010-2.057 Å, respectively.^[15, 20, 21] Therefore, 1 must contain a Is-Co^{III} ion in the solid state at 120 K. Consequently, the neutrality of 1 requires the presence of a charge of 3- distributed over two o-dioxolene ligands. Note, that disorder of one 4-papy ligand in the crystalline state introduced some inaccuracy in the Co-N distance.

Generally, intraligand C–O and C–C bond lengths are sensitive to the oxidation state of *o*-dioxolene ligands and thus indicative of the electronic structure of the complex.^[3] At 120 K **1** exhibits C–O distances of 1.327(2) and 1.324(3) Å (Table S6 in the Supporting Information) that are between the typical values found for Cat dianions (1.35 Å) and SQ monoanions

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(1.29 Å).^[3] The same is true for the (O)C-C(O) distance of 1.433(2) Å in 1 when compared with typical values for Cat (1.40 Å) and SQ (1.44 Å).^[3] Both o-dioxolene ligands in 1 show quinoid-type distortion with alternating long-short C-C bonds.^[22] However the quinoid-type distortion in 1 is less pronounced than is usually found for the SQ form of the ligand. Thus, the intraligand bond lengths of o-dioxolenes point to a ligand mixed-valent Is-[Co^{III}(Cat)(SQ)] electronic structure for 1. This is further confirmed by comparison of C-O bond lengths in 1 (1.327(2) and 1.324(3) Å) with the respective distances in reported Is-Co^{III}(Cat)(SQ) (1.320-1.338 Å) and hs-Co^{II}(SQ)₂ (1.291–1.306 Å) isomers (Table S6 in the Supporting Information).^[15,20] Because the cobalt ion is located on the crystallographically imposed inversion center, we cannot distinguish a ligand mixed-valent delocalized ls-Co^{III}(Cat)(SQ)↔ls-Co^{III}(SQ)(Cat) electronic structure from positional disorder in the localized Is-Co^{III}(Cat)(SQ) form.^[14,20] Nonetheless, the electronic structure of 1 at 120 K in the solid state is unambiguously assigned as $ls-[Co^{III}(Cat)(SQ)(4-papy)_2]$.

Magnetochemisty

Magnetic properties of **1** in the solid state were probed by SQUID susceptometry. The effective magnetic moment μ_{eff} of 1.75 μ_{B} is invariant in the temperature range 8–220 K (Figure 2). This is consistent with a spin-doublet S = 1/2 state



Figure 2. Temperature dependence of the effective magnetic moment μ_{eff} of a microcrystalline sample of 1 at external magnetic field of 1 T. van't Hoff fit parameters: $\Delta H = 39.4(3) \text{ kJ mol}^{-1}$, $\Delta S = 99.4(9) \text{ J mol}^{-1} \text{ K}^{-1}$, low- and high-temperature magnetic moments: $\mu_{eff}^{\text{eff}} = 1.760(1) \mu_{\text{B}}$ and $\mu_{eff}^{\text{Hf}} = 5.0 \mu_{\text{B}}$ (fixed).

with the major spin density located at the ligands due to a ls-Co^{III}(Cat)(SQ) electronic structure in the given temperature range. Slight decrease of μ_{eff} at temperatures below 8 K are ascribed to weak intermolecular antiferromagnetic interactions or a saturation effect. Magnetic data in the temperature range 2–220 K can be readily fitted for an S = 1/2 spin system yielding g = 2.075 and a Weiss constant $\Theta = -0.02$ K (Figure S1 in the Supporting Information). More importantly, at temperatures above 220 K, μ_{eff} increases rapidly and reaches a value of 2.87 μ_{B} at 360 K. This behavior was reproduced with several independent samples. The increase in μ_{effr} which is the hallmark of a thermally induced Is-Co^{III}(Cat)(SQ) \rightarrow hs-Co^{III}(SQ)₂ transition

in VT Co complexes, points to the population of electronic states with S > 1/2 at elevated temperatures.^[5]

Assuming that at higher temperatures μ_{eff} approaches a plateau at about 5.0 $\mu_{\rm B}$, which is a typical value for the hs-Co^{II}(SQ)₂ state of related VT Co complexes,^[14] the data were fitted by using the van't Hoff equation (Figure 2). Our best fit yielded an enthalpy change $\Delta H = 39.4(3) \text{ kJ mol}^{-1}$ and an entropy change $\Delta S = 99.4(9) \text{ Jmol}^{-1} \text{K}^{-1}$ associated with the observed conversion in 1. These values approach typical values for thermodynamic parameters observed for VT Co complexes in the solid state ($\Delta H = 14-38 \text{ kJ mol}^{-1}$ and $\Delta S = 48-$ 98 J mol⁻¹ K⁻¹).^[23,24] The relatively large value of Δ S for 1 could be due to two axial pyridyl ligands as opposed to one bidentate NN ligand in classical VT Co species. The transition temperature, for which there are equal amounts of Is-Co^{III}(Cat)(SQ) and hs-Co^{II}(SQ)₂ species, can be easily calculated as $T_{1/2}$ = $\Delta H/\Delta S =$ 396(7) K. Variations in the maximum value of $\mu_{\rm eff}$ which was fixed in the fitting procedure ($\mu_{\rm eff}^{\rm HT}\!=\!5.0\,\mu_{\rm B}$), do not significantly change the thermodynamic parameters (Figures S2 and S3 in the Supporting Information). Consequently, given the μ_{eff} value, which is consistent with a ls-Co^{III}(Cat)(SQ) state at low temperatures, and thermodynamic parameters for the transition at temperatures above 220 K, it is clear that a thermally induced Is-Co^{III}(Cat)(SQ)→hs-Co^{II}(SQ)₂ process is operative.

The magnetic properties of **1** in solution were probed by NMR spectroscopy using the Evans method. At T=293 K, μ_{eff} obtained in toluene solution was 3.86 μ_{B} (Figure 3). This value is much larger than that of about 1.7 μ_{B} expected for a pure ls-



Figure 3. Temperature dependent effective magnetic moment μ_{eff} of "1" in toluene solution determined by the Evans NMR method (toluene/ [D₈]toluene/TMS = 10:1:1). van't Hoff fit parameters: ΔH = 73(5) kJ mol⁻¹, ΔS = 265(17) J mol⁻¹ K⁻¹; low- and high-temperature magnetic moments: μ_{eff}^{IT} = 2.73 $\mu_{\rm B}$ (fixed) and μ_{eff}^{IT} = 4.00(3) $\mu_{\rm B}$.

Co^{III}(Cat)(SQ) state, but smaller than that of 4.34 $\mu_{\rm B}$ reported for a pure hs-Co^{II}(SQ)₂ state in solution.^[25] Hence, the existence of both redox isomers in solution at room temperature (RT) is inferred. Such an equilibrium must be affected by temperature: the Is-Co^{III}(Cat)(SQ) isomer is stabilized at low temperatures, whereas the hs-Co^{III}(SQ)₂ species is preferred at higher temperature due to a positive entropic term.^[5] Indeed, $\mu_{\rm eff}$ decreases to 2.73 $\mu_{\rm B}$ at T=233 K and remains nearly constant down to T= 193 K. On warming, $\mu_{\rm eff}$ increases, reaching 3.98 $\mu_{\rm B}$ at T=318 K.



Whereas a plateau with a constant μ_{eff} is presumably not reached at high temperatures, a low-temperature plateau seems to be attained (Figure 3). In contrast to the low-temperature plateau at $\mu_{\rm eff} = 1.75 \,\mu_{\rm B}$ observed in the solid state, the low-temperature plateau at $\mu_{eff} = 2.73 \,\mu_{B}$ in solution cannot be attributed solely to the presence of Is-Co^{III}(Cat)(SQ). We suggest that the solution contains an additional paramagnetic species with a spin state S > 1/2. The unknown species may arise from partial decomposition of 1 in solution due to reaction with traces of oxygen or small amounts of impurities in solvents. Indeed, whereas the low-temperature plateau was observed at very similar μ_{eff} values for different solid samples, a significant variation in the position of the low-temperature plateau was observed for different solution samples. The presence of small amounts of additional species with S > 1/2 is expected to increase the low-temperature value of $\mu_{\rm eff}$ significantly. For instance, the amount of an impurity with $\mu_{\rm eff}$ = 5 $\mu_{\rm B}$ and similar molecular mass to 1 can be estimated at 20%. All attempts to prevent the formation of such species in solution were unsuccessful.

Similar to the solid state, the temperature-dependent magnetic data of **1** in solution were fitted by using the van't Hoff equation (Figure 3). Generally, thermodynamic parameters $(\Delta H = 73(5) \text{ kJ mol}^{-1}, \Delta S = 265(17) \text{ J mol}^{-1} \text{ K}^{-1})$ are larger in solution than the solid state.^[23,25,26] However, the obtained values are significantly larger than expected for a thermally induced transition in VT Co complexes in solution ($\Delta H = 21-38 \text{ kJ mol}^{-1}$, $\Delta S = 60-133 \text{ J mol}^{-1} \text{ K}^{-1}$).^[25] Unlike the solid state, the temperature dependence of μ_{eff} for **1** in solution cannot be ascribed exclusively to the equilibrium between the two redox isomers ls-Co^{III}(Cat)(SQ) \leftrightarrow hs-Co^{III}(SQ)₂. The large values of ΔH and ΔS in solution may be the result of ligand dissociation (see below).^[27]

EPR spectroscopy

An X-band EPR spectrum recorded on a CH₂Cl₂ solution of **1** at RT exhibited an eight-line pattern arising from coupling of the electron spin of an S = 1/2 species with the I = 7/2 nuclear spin of the 100% abundant ⁵⁹Co isotope (Figure S4 in the Supporting Information). Simulation gave $g_{iso} = 2.0038$ and $A_{iso} = 10.5 \times 10^{-4}$ cm⁻¹. These parameters are synonymous with a ligand-based radical Is-Co^{III}(Cat)(SQ) species.^[4,28,29] The small hyperfine splitting is due to spin density transferred from the ligands to the metal through covalency and/or spin-polarization effects. Cooling to 200 K only served to narrow the spectral lines; the simulation parameters remained unchanged (Figure S6 in the Supporting Information).

Frozen-glass spectra recorded in CH₂Cl₂/toluene solution over the temperature range 10–120 K were invariant (Figure S7 in the Supporting Information). Spectral simulation at 90 K was achieved for g = (1.995, 2.002, 2.010) and a hyperfine interaction $A({}^{59}Co) = (3.0, 22.2, 6.0) \times 10^{-4} \text{ cm}^{-1}$ (Figure 4). The observed signal was unambiguously assigned to a ligand-based radical Is-Co^{III}(Cat)(SQ) species, as previously reported.^[29] Importantly, on varying both temperature and experimental conditions, no additional signals could be detected in the X-band. Although we were only able to detect the Is-Co^{III}(Cat)(SQ) spe-



Figure 4. X-band EPR spectrum of "1" in CH₂Cl₂/toluene solution recorded at 90 K (frequency: 9.7294 GHz; modulation: 0.4 mT; power: 0.15 mW). Fit parameters: g = (1.995, 2.002, 2.010), $A(^{59}$ Co, $I=7/2) = (3.0, 22.2, 6.0) \times 10^{-4}$ cm⁻¹.

cies (S = 1/2) in solution at different temperatures, the presence of cobalt-based radicals cannot be excluded at T > 40 K, as rapid spin relaxation of hs-Co^{II} S = 3/2 paramagnets preclude measurement above 40 K.^[30]

Electronic absorption spectroscopy

The electronic absorption spectrum of **1** recorded in toluene at RT is dominated by an intense band at 309 nm ($\varepsilon = 4.13 \times 10^4 \,\text{M}^{-1} \,\text{cm}^{-1}$), which is accompanied by a shoulder at about 440 nm (Figure S10 in the Supporting Information). These absorptions are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the 4-papy ligand^[31] (see Figure S11 in the Supporting Information for comparison of metal-free 4-papy and **1**) and overlap with the intraligand transitions of dioxolenes.^[32] The relatively weak broad band at about 740 nm ($\varepsilon = 2.1 \times 10^3 \,\text{M}^{-1} \,\text{cm}^{-1}$) and a shoulder at 630 nm are typical for charge-transfer (CT) transitions found in VT bis(*o*-dioxolene)cobalt complexes.^[5,14,33]

An extremely weak and broad absorption band centered at about 2650 nm in the near-infrared (NIR) region (see Figure 8 below) is assigned to an intervalence ligand-to-ligand charge transfer (IVLLCT) transition.^[29,34] This feature is synonymous with a ligand mixed-valent Is-Co^{III}(Cat)(SQ) state.^[5,25] Although the NIR region of the spectrum recorded in solution is blighted by solvent overtones, we can confirm that this band is much weaker than the corresponding feature in VT bis(o-dioxolene) cobalt species with a pure Is-Co^{III}(Cat)(SQ) state. Note that the "CT" character of an IVCT transition generally vanishes in fully delocalized class III mixed-valent species. Thus, the electronic spectrum points to a hs-Co^{II}(SQ)₂ species in solution at RT, with only a minor amount of Is-Co^{III}(Cat)(SQ). Interestingly, a very similar spectrum was reported for a five-coordinate hs- $[Co^{II}(SQ)_{2}L]$ complex^[32] (L is a monodentate pyridine derivative), which additionally suggests (partial) dissociation of one 4-papy ligand from 1 in solution, as was already proposed (see above).

Variable-temperature electronic absorption spectroscopy is a proven method for monitoring thermally driven valence tautomerism.^[5] Therefore, absorption spectra of **1** in toluene were



Figure 5. Temperature dependence of the electronic absorption spectrum of "1" recorded in toluene solution over the temperature range 257–299 K.

collected at different temperatures in the spectral window 345-1020 nm (the available region on the instrument). On cooling to 257 K, the bands at 440 and 740 nm both decreased in intensity, whereby the latter was more affected (Figure 5). With decreasing intensity of the 740 nm band, the shoulder at 630 nm became more prominent at low temperatures, whereas at high temperatures this region is buried beneath the 740 nm peak. The temperature-dependent spectra showed a clean isosbestic point at 402 nm, which indicated an equilibrium between two species. The variable-temperature spectra obtained for 1 in toluene resemble those previously reported^[21,25] and suggest an equilibrium between Is-Co^{III}(Cat)(SQ) and hs-Co^{II}(SQ)₂ in solution. However, direct comparison with reported VT Co systems should be made with care, because monodentate 4-papy ligands are in *trans* positions in 1, as opposed to the more common VT Co complexes with *cis* configuration,^[5,9] and 1 will likely dissociate in solution.

The temperature dependence of the electronic absorption spectrum can be fitted through the van't Hoff equation by monitoring the prominent absorption at 740 nm (Figure 6). The best fit gave $\Delta H = 112(1) \text{ kJ mol}^{-1}$ and $\Delta S = 398(4) \text{ Jmol}^{-1} \text{ K}^{-1}$, which resemble those obtained by NMR spectroscopy (Table 1). Again, the obtained values are too



Figure 6. Temperature dependence of the 740 nm band in the electronic spectrum of "**1**" recorded in toluene solution over the temperature range 257–299 K. van't Hoff fit parameters: $\Delta H = 112(1) \text{ kJ mol}^{-1}$, $\Delta S = 398(4) \text{ J mol}^{-1} \text{ K}^{-1}$; low- and high-temperature molar extinction coeffi-

cients: $\varepsilon^{LT} = 1.45(1) \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$, $\varepsilon^{HT} = 2.1(1) \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$.

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Table 1. Thermodynamic parameters for "1" obtained from variable-temperature experiments.				
Experiment	ΔH [kJ mol ⁻¹]	ΔS [J mol ⁻¹ K ⁻¹]	T _{1/2} [K]	
SQUID (solid) Evans ¹ H NMR (solution) UV/Vis (solution)	39.4(3) 73(5) 112(1)	99.4(9) 265(17) 398(4)	396(7) 275(36) 281(5)	

large for a thermally driven valence tautomerism^[25] and likely result from (partial) dissociation of **1** in solution.^[27] The modest difference between fit parameters in solution is likely due to differing systematic errors in the different methods.

Electrochemistry

To probe the redox properties of the complex, cyclic voltammetry (CV) measurements were performed in CH_2CI_2 at RT. The solution of **1** showed four redox waves with half-wave potentials $E_{1/2} = -1.62$ (D), -1.13 (C), -0.60 (B), and -0.27 V (A) versus Fc^{+/0} (Figure 7). Event A corresponds to an oxidation



Figure 7. Cyclic voltammogram of "1" recorded in CH_2CI_2 solution containing 0.1 \times nBu₄NPF₆ as supporting electrolyte (room temperature, scan rate 25 mV s⁻¹).

process, while B, C, and D are reduction events, as was deduced from the rotating-electrode voltammogram. Although the ratio between the corresponding normalized oxidative and reductive peak currents are near unity, the peak separations ΔE for all four redox couples clearly exceed the ideal value of 58 mV expected for a diffusion-controlled reversible one-electron transfer (Table S1 in the Supporting Information). At higher scan rates, further increases in ΔE for each couple indicated a decrease in reversibility of the observed redox processes (Figure S13 in the Supporting Information). Process D exhibits an approximately fourfold current compared to other waves. This event is assigned to reduction of 4-papy, which was confirmed by independent measurement on 4-papy (Figure S15 in the Supporting Information). The fourfold current of D reflects two-electron reduction of each 4-papy ligand. Processes A, B, and C are assigned to redox events at the bis(o-di-

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oxolene) cobalt core. In view of (partial) dissociation of a 4papy ligand and presence of several redox species in equilibrium, further assignments require detailed investigations that will be reported elsewhere.

Titration with 4-papy

Since several experimental results for **1** suggested (partial) ligand dissociation in solution (see above), the electronic absorption spectrum of **1** was expected to change on addition of 4-papy, which is a relatively weakly coordinating monodentate neutral ligand. Indeed, on addition of 4-papy, the electronic spectrum of **1** was altered significantly (Figure 8). The promi-



Figure 8. Overlay of the electronic spectra of "1" on addition of 13 and about 60 equivalents of 4-papy in toluene at room temperature. Signals marked with asterisk are due to toluene solvent or change of detector.

nent absorption band at 740 nm decreased, whereas an extremely intense broad band in the NIR region appeared at about 2650 nm (Figure 8). An isosbestic point at 1040 nm confirmed an equilibrium between the two species. Since free 4-papy absorbs at $\lambda < 550$ nm, the spectrum of **1** with additional amounts of 4-papy could not be analyzed adequately at $\lambda < 550$ nm. In addition, due to numerous overtone bands of the toluene solvent, the NIR region was only qualitatively scrutinized.

To better determine the position of the intense NIR band, spectra of **1** in the presence and absence of 4-papy were recorded in benzene, which is more transparent in the NIR region. The evolution of the electronic absorption spectrum of **1** on addition of 4-papy in benzene and toluene are very similar (Figure S12 in the Supporting Information). The intense NIR band that appeared at 2715 nm in benzene was unambiguously assigned to the IVLLCT transition, which is a spectroscopic fingerprint for a mixed-valent Is-Co^{III}(Cat)(SQ) species.^[5,25] Although benzene is better suited for monitoring the evolution of the electronic absorption spectrum in the NIR region, toluene was retained for subsequent titration experiments to allow direct comparison with variable-temperature experiments.

Thus, a series of electronic spectra of **1** in presence of different amounts of 4-papy were recorded in toluene at RT in the spectral region 550–1000 nm. As was already mentioned, increasing amounts of 4-papy ligand lead to a decrease of the



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Figure 9. Evolution of the electronic absorption spectrum of "1" in toluene at room temperature on titration with 4-papy.

prominent absorption band at 740 nm (Figure 9). On addition of 33 equivalents of 4-papy, the extinction coefficient at 740 nm approached $1.5 \times 10^3 \, \text{L}\,\text{cm}^{-1}\,\text{mol}^{-1}$ and thereafter remained constant. Concomitantly, the relative intensity of the shoulder around 630 nm increased. Note, that the changes in the electronic spectrum induced by addition of 4-papy are very similar to those observed in the variable-temperature experiment (Figure 5).

The titration data were analyzed further. We can reliably assume that only two cobalt complexes are present in equilibrium in solution: the parent six-coordinate **1** and five-coordinate **2** formed on dissociation of one 4-papy ligand [Eq. (2)]. Our assumption is supported by sharp isosbestic points in both variable-temperature and titration experiments. Moreover, hypothetical four-coordinate species are not stable in solution and were reported to form tetramers.^[35] Hence, if a four-coordinate species were formed in solution, subsequent stepwise formation of tetramers together with the presence of **1** and **2** would give rise to a considerably more elaborate spectral profile than those shown in Figures 5 and 9.

$$\mathbf{2} + 4 \operatorname{-papy} \stackrel{^{n_a}}{\rightleftharpoons} \mathbf{1}$$

Consequently, the decrease in the absorption band at 740 nm during the titration corresponds to the formation of **1**. The intensity of the 740 nm band as a function of 4-papy concentration was successfully modeled by using a nonlinear regression approach with exact solution of the quadratic equation (Figure 10, see Supporting Information for details). The best fit yielded molar extinction coefficients for **1** and **2** of $\varepsilon_1 = 1.34(1) \times 10^3$ and $\varepsilon_2 = 2.60(11) \times 10^3 \text{ Lcm}^{-1} \text{ mol}^{-1}$, respectively, and an association constant $K_a = [\mathbf{1}]/([\mathbf{2}][4-\text{papy}]) = 3(1) \times 10^2 \text{ Lmol}^{-1}$.

Since we expected species **1** and **2** to have different electronic states and thus different magnetic properties, the titration with 4-papy was monitored by the Evans NMR method. With increasing addition of 4-papy to a toluene solution of **1** at RT, the μ_{eff} value gradually decreased from 4.21 μ_{B} (without 4-papy) to 3.17 μ_{B} in a solution containing 33 equivalents of 4-papy (Figure 11). Similarly to the titration monitored by electronic spectroscopy, the magnetic moment remained unchanged despite further additions. Given the assumption that

 $\varepsilon \cdot 10^{-3} / \mathrm{M}^{-1} \mathrm{cm}^{-1}$



Figure 10. Intensity of the 740 nm absorption band in the electronic spectrum of "1" during the titration with 4-papy in toluene. Nonlinear regression fit parameters: $\varepsilon_1 = 1.34(1) \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$, $\varepsilon_2 = 2.60(11) \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$, $K_a = 3(1) \times 10^2 \text{ L mol}^{-1}$ (see Experimental Section for details).



Figure 11. The evolution of the effective magnetic moment μ_{eff} of "1" on titration with 4-papy determined by the Evans NMR method (toluene/ [D_g]toluene/TMS 10:1:1). Nonlinear regression fit parameters: $\mu_{eff} = 2.78(19) \mu_{B}$ (for 1), $\mu_{eff} = 4.5(7) \mu_{B}$ (for 2), and $K_{a} = 5(3) \times 10^{2} \text{ Lmol}^{-1}$ (see Experimental Section).

only two Co species are involved in the equilibrium [Eq. (2)], these data suggest that the magnetic moment of **1** formed in the presence of excess of 4-papy is smaller than that of **2**. The decrease in μ_{eff} as a function of the 4-papy concentration was modeled by using a nonlinear regression approach (see Supporting Information). The best fit yielded μ_{eff} values of 2.78(19) μ_{B} for **1** and 4.5(7) μ_{B} for **2** and an association constant $K_{\text{a}} = 5(3) \times 10^2 \,\text{Lmol}^{-1}$.

We note that 1) the titration experiment monitored by the Evans NMR method (Figure 11) closely resembles the variabletemperature Evans experiment (Figure 3), and 2) the association constants K_a derived from the NMR titration and from the titration monitored by electronic absorption spectroscopy are identical within the error of determination.

Theoretical calculations

Since six-coordinate 1 and five-coordinate 2 coexist in solution (see above), both complexes were studied by theoretical methods at the DFT level. Similar to spin-crossover metal complexes, calculation of relative energies for different electronic states of VT species is rather inaccurate. However, recent theoretical works on VT complexes showed that OPBE^[36] and B3LYP^{*[37]} functionals produce satisfactory results.^[38,39] Therefore, we optimized the geometries of **1** and **2**, as well that of reference complex **3** (Scheme 1) in different electronic states with the OPBE functional and calculated their relative energies. Pertinent states were subsequently analyzed by using the B3LYP functional routinely employed for spin-coupled systems.^[34,40] The magnetic exchange interactions in the hs-Co^{II}(SQ)₂ configuration were investigated by using the broken-symmetry approach.^[41] To facilitate convergence and speed up the calculations all *tert*-butyl groups were replaced by methyl groups.

The agreement between the optimized and the experimental geometry^[21] for **3** in both Is-Co^{III}(Cat)(SQ) (S = 1/2) and hs-Co^{III}(SQ)₂ (S = 5/2) electronic configurations is very good. The increase in metal–ligand bond lengths and the amplification of the quinoid-type distortion was duplicated on going from Is-Co^{III} to hs-Co^{II} (Table S2 in the Supporting Information). Although the conductor-like screening model (COSMO)^[42] was employed in all calculations, the partial localization^[21] of ligand mixed valence in Is-Co^{III} was not reproduced. In our experience this is due to the usage of the OPBE functional, whereas B3LYP and BP86 functionals together with COSMO do reproduce partial localization in related mixed-valent species in our hands.^[43]

The sextet S = 5/2 state is located above the S = 1/2 ground state by 5.2 kcal mol⁻¹ (3.7 kcal mol⁻¹ after zero-point energy (ZPE) correction), which is in agreement with the experimental data for $3^{[21]}$ The magnetic interactions in the hs-Co^{II}(SQ)₂ configuration were analyzed by the broken-symmetry approach. The exchange coupling constant J for the interacting hs-Co^{\parallel} ion (S = 3/2) and two ligand radicals (effective $S_R = 1$) was calculated to be -54 cm^{-1} with the OPBE and -100 cm^{-1} with the B3LYP functional. Although the magnitude of J should be taken with caution,^[44] the calculations nicely reproduce an antiferromagnetic (AF) coupling previously postulated for 3.^[21,45] An elusive S = 3/2 state, which would correspond to an intermediate-spin $Co^{III} S = 1$ ion with one ligand radical or a Is- Co^{II} S = 1/2 ion with two ligand radicals, was calculated as well. Surprisingly, the energy of this S = 3/2 state is very close to that of the S = 5/2 state (Table 2). Spin quartet states have not been observed for this class of compounds experimentally.^[10,29] The overestimated stability of S = 3/2 states in calculations with the OPBE functional was recently identified.^[38] Thus, the important geometrical and electronic features were reproduced in our DFT calculations on 3, allowing us to further use this method to calculate the target six- and five-coordinate complexes.

The optimized structure of the S=1/2 state for 1 matches the experimental geometry for a ls-Co^{III} configuration. With the exception of the Co–N distances, the maximum discrepancies

Table 2. Relative energies E [kcalmol ⁻¹] for different electronic states of 1-3 obtained from spin-unrestricted OPBE-DFT calculations.						
	3	1	2			
S=1/2	0	0	0			
S=3/2 5.7 (3.4) ^[a] 10.4 (10.4) 3.2 (1.						
S=5/2	5.2 (3.7)	7.2 (6.3)	5.9 (3.8)			
[a] Values obtained after ZPE corrections in parentheses.						



between calculated and experimental bond lengths are 0.012 and 0.005 Å for the dioxolene and metal-ligand bonds, respectively (Table S3 in the Supporting Information). The discrepancy between calculated (1.964 Å) and experimental (1.888(14) and 2.04(3) Å) Co-N bond lengths can be traced back to the disorder observed in the X-ray structure. Interestingly, 4-papy ligands are not planar: the six-membered phenyl and pyridyl rings form a dihedral angle of 22.6° in the optimized structure (cf. exptl 7.1°), which is likely due to the interactions between the lone pairs of the azo nitrogen atoms and the β -hydrogen atoms of phenyl and pyridyl rings. Similar to VT Co complexes,[13-15, 20, 46] 1 crystallizes as a trans isomer in which two 3,5-di-tert-butyl-o-dioxolene ligands are related by inversion symmetry. We examined the cis isomer, in which the dioxolene ligands are reflected by a mirror plane.^[47] The energies of the cis and trans isomers were identical within error. Hence, we can assume that possible geometric variations in solution do not influence the equilibrium between 1 and 2. The calculations confirm a ligand-based radical for the S = 1/2 state: the total spin density of +0.96 is equally distributed over both dioxolene moieties with only a minor spin density of +0.04 at the Is-Co^{III} center (Figure S16 in the Supporting Information). The S = 1/2 state is EPR-active (see above); calculated g values match the experimental data (Table 3). The nonzero electron spin density at the cobalt center due to covalency and/or spin polarization is corroborated by the Co hyperfine interactions, with very good agreement between experiment and theory.

Table 3. Calculated EPR parameters for $S = 1/2$ states of 1 and 2. ^[a]			
	1 , S=1/2	2 , S=1/2	
<i>g</i> ₁	1.992 (1.995) ^[b]	1.926	
g ₂	2.002 (2.002)	1.958	
g_3	2.002 (2.010)	1.986	
g_{iso}	2.0016 (2.0038)	1.957	
<i>A</i> ₁ ^[c]	-3.5 (-3.0) ^[d]	+ 9.5	
A ₂	-18.3 (-22.2)	+ 35.2	
A ₃	-5.1 (-6.0)	-62.6	
A _{iso}	-9.0 (-10.5)	-5.8	
[a] Parameters were obtained from the spin-unrestricted ZORA-B3LYP-DFT calculations including COSMO. [b] The experimental values are shown in parentheses. [c] Hyperfine coupling $[10^{-4} \text{ cm}^{-1}]$ with the ⁵⁹ Co nucleus. [d] The sign of the <i>A</i> values was assumed to be negative owing to a domi-			

The sextet S = 5/2 state lies 7.2 kcal mol⁻¹ (6.3 kcal mol⁻¹ after ZPE correction) above the S = 1/2 ground state. Thus, the transition temperature $T_{1/2}$ is expected to be higher for **1** than for **3** ($E_{S=5/2} = 5.2$ kcal mol⁻¹), which is indeed observed experimentally.^[21] The spin sextet hs-Co^{II}(SQ)₂ perfectly reproduces the changes in bond lengths expected to accompany ls-Co^{III} \rightarrow hs-Co^{II} transition in VT complexes. All metal-ligand bond lengths are increased and the quinoid-type distortion is more pronounced in the S = 5/2 state given the two ligand radicals in hs-Co^{III}(SQ)₂ compared to one in ls-Co^{III}(Cat)(SQ) (Table S3 in the Supporting Information). The spin density at the hs-Co^{III} ion in **1** is + 2.77, whereas the net spin density of + 2.23 is equally

distributed between the dioxolenes moieties, which confirms the presence of two ligand-based radicals. The quartet S=3/2 state resides 3.2 kcal mol⁻¹ above the sextet and was not analyzed further.

Magnetic coupling in the hs-Co^{II}(SQ)₂ configuration was investigated by using a broken-symmetry BS(3,2) $M_{\rm S} = 1/2$ solution and corresponding orbital transformation (Figure 12).^[48] Five predominantly Co-based d-type MOs were identified in



Figure 12. Qualitative MO scheme for the BS(3,2) $M_{\rm S}$ = 1/2 state of 1 (hs-Co^{II}(SQ)₂) obtained from spin-unrestricted B3LYP calculations with COSMO; corresponding orbitals are shown. Note that the native coordinate system for octahedral complexes is used for d orbitals, whereas symmetry labels are adapted from the D_{2h} point group to assist comparison with **3**. [a] Heavily mixed metal d orbital.

the valence region. As expected for a high-spin d⁷ ion, two are doubly occupied, while the remaining three are singly occupied metal-based (alpha) magnetic orbitals. Two ligand-based singly occupied MOs, denoted $L_{\pi 1}$ and $L_{\pi 2}$, are complementary beta magnetic orbitals comprising symmetric and antisymmetric combinations of two redox active π^* dioxolene orbitals.^[49] $L_{\pi 1}$ has the appropriate symmetry (b_{2g} in approximate D_{2h} point group) to overlap with one metal-based magnetic orbital, as confirmed by an overlap integral $S_{AB} = 0.20$ ($S_{AB} = 1.0$ for full overlap and $S_{AB} = 0$ for zero overlap between two magnetic orbitals).^[49] This substantial overlap visualizes the major AF interaction between the hs-Co^{II} ion (S=3/2) and two ligand π radicals ($S_{\rm R}$ = 1). Surprisingly, J for this interaction is calculated to be positive $(J = +263 \text{ cm}^{-1} \text{ with OPBE}, +84 \text{ cm}^{-1} \text{ with})$ B3LYP), whereas it was negative for 3 (see above). Thus, the net interaction between the ligand radicals and the cobalt ion in the hs-Co^{II} configuration seems to be ferromagnetic in **1**, in contrast to the general consensus that it is antiferromagnetic in VT bis(o-dioxolene) cobalt species, as described for 3.[21,45]

Geometry optimization of five-coordinate **2** in the S=1/2 state revealed a square-pyramidal geometry. The cobalt ion is located 0.266 Å above the O₄ plane with the dioxolene ligands resting at an angle of 7.3° from each other (Figure S21 in the Supporting Information). All intraquinone and metal–ligand

nant Fermi contribution.



bond lengths of **2** closely resemble those of **1**, except for the Co–N bonds, which are much shorter in **2** (1.886 Å) than in **1** (1.964 Å) due to the *trans* effect in the latter. The EPR parameters calculated with the B3LYP functional for the doublet state of **2** differ significantly from those of **1** and the experimental data (Table 3). Thus, we have no evidence for the existence of a five-coordinate S = 1/2 species in solution.

The S = 5/2 state of **2** lies 5.9 kcal mol⁻¹ (3.8 kcal mol⁻¹ after ZPE correction) above the S = 1/2 state. The sextet state is more stabilized in **2** compared to **1**, as expected from considering the ligand field. Note that the exact energy difference between electronic states in VT Co species is not a reliable quantity, as it is highly functional dependent.^[38] Therefore, the trend in stabilization of the sextet over doublet state on going from **1** to **2** rather than the absolute energy difference between the states is emphasized. The stabilization of the sextet state in **2** is further supported by recent work of Poddel'sky et al., who suggested a hs-Co^{II} configuration for a related five-coordinate [Co(dioxolene)₂L] complex (L is a monodentate imine derivative) in the temperature range 2–300 K.^[32]

The S = 5/2 state of **2** reveals a molecular structure similar to the S = 1/2 state, with the dioxolene ligands canted 15.0° with respect to each other (Figure S22 in the Supporting Information). Although the crystallographic data for **2** are not available, a similar geometry was recently reported for a [Co(dioxolene)₂L] complex (L is a monodentate imine derivative).^[32] All metal-ligand bond lengths are longer and the dioxolene ligands show more pronounced quinoid-type distortion in the sextet state of **2** compared to the doublet state. The spin density of +2.78 reflects the high-spin d⁷ cobalt center, with +2.22 equally distributed between the two ligands indicative of two ligand π radicals and consistent with the hs-Co^{II}(SQ)₂ electronic configuration.

Magnetic coupling in the hs-Co^{II}(SQ)₂ configuration of **2** was analyzed with a BS(3,2) $M_{\rm S}$ = 1 calculation. Identification of two doubly occupied and three singly occupied (alpha) d-type cobalt-based MOs confirmed a high-spin d⁷ electronic configuration for the metal center (Figure 13). Due to the low symmetry of the complex the five metal d orbitals are mixed significantly. Unlike the BS(3,2) state in distorted octahedral 1, the two ligand-based magnetic orbitals $L_{\pi 1}$ and $L_{\pi 2}$ are substantially localized on one dioxolene ligand in square-pyramidal 2. Importantly, both $L_{\pi1}$ and $L_{\pi2}$ in $\boldsymbol{2}$ have the appropriate symmetry to overlap with the corresponding metal-based magnetic orbitals, as confirmed by overlap integrals of $S_{AB} = 0.31$ and 0.19. These substantial overlaps result in a net AF coupling with J calculated at -177 and -162 cm⁻¹ with the OPBE and B3LYP functionals, respectively. Such AF coupling is a common scenario for *cis*-[hs-Co^{II}(SQ)₂L] (L=a bidentate ligand) VT complexes.^[21,45]

The spin quartet state of **2** was calculated as well. With the OPBE functional, the quartet state is located between the S = 1/2 and S = 5/2 states (Table 2). As noted above, spin quartet states have not been observed for this class of compounds.^[10,29] Thus the stability of S = 3/2 state is likely overestimated in our calculations.^[38]



Figure 13. Qualitative MO scheme for a BS(3,2) $M_s = 1/2$ state of **2** (hs-Co^{II}(SQ)₂) obtained from spin-unrestricted B3LYP calculations with COSMO; corresponding orbitals are shown, the *z* axis is aligned with the Co–N vector. [a] Heavily mixed metal d orbital.

Discussion

Coordination-induced valence tautomerism

Six-coordinate 1 shows a regular valence tautomerism Is-Co^{III}- $(Cat)(SQ) \leftrightarrow hs-Co^{II}(SQ)_2$ in the solid state, whereby variable-temperature magnetic susceptibility measurements yield thermodynamic parameters typical for this interconversion (Table 1). Interestingly the properties of 1 become puzzling in solution. Both variable-temperature NMR and electronic absorption spectroscopy reveal changes reminiscent of Is-Co^{III}- $(Cat)(SQ) \leftrightarrow hs-Co^{II}(SQ)_2$ VT equilibrium. However, the too large thermodynamic parameters are not commensurate with a simple VT equilibrium in solution and thus suggest dissociation of 1. Similar observations have recently been made by Hörner, Grohmann, and co-workers, who observed ligand dissociation in spin-crossover metal complexes.^[27] Indeed, Pierpont et al. were the first to report that [Co(dioxolene)₂L₂] (L is a monodentate ligand) species may dissociate, unlike [Co(dioxolene)₂(NN)] (NN is a bidentate ligand).^[33] Although these authors mentioned some variations in electronic absorption spectra of [Co(dioxolene)₂L₂] species induced by changing the solvent, "solution equilibria have not been investigated in detail".[33]

Suspecting (partial) dissociation of **1** leading to five-coordinate **2** and free 4-papy ligand [Eq. (2)], we examined the properties of solutions with excess 4-papy. Two independent titrations with 4-papy were performed by electronic absorption spectroscopy and the Evans NMR method. The changes in the electronic spectrum of "**1**" observed on addition of 4-papy (Figure 9) are strikingly similar to the evolution of the temperature-dependent spectrum on cooling without addition of 4papy (Figure 5). In both cases the prominent absorption band at 740 nm decreased in intensity, whereas the shoulder at 630 nm distinctly developed. Astonishingly, the two electronic



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spectra from these experiments, one at the end of titration (+53 equiv of 4-papy) and the other measured at 257 K seem to be identical (cf. Figures 9 and 5). This provides strong evidence that in both titration and cooling experiments, we observe spectral changes associated with the same process, namely, the coordination of free 4-papy ligand to five-coordinate 2 forming six-coordinate 1 [Eq. (2)]. Since subsequent dissociation to form four-coordinate species can be excluded (see above), titration data were modeled by exclusively considering the equilibrium process [Eq. (2)] to yield $K_a = 3(1) \times 10^2 \, L \, mol^{-1}$ (Figure 10). Consequently, the degree of dissociation α for 1 in the investigated solutions ($c_0 = 5 \times 10^{-4}$ M) at RT is estimated to be 88%. Hence, 2 is the dominant species in solution at RT. On addition of 4-papy to or cooling of the parent solution, the equilibrium [Eq. (2)] is shifted to the right, generating 1. The isosbestic points in the spectra confirm that only two species are involved in equilibrium.

Similarly, the evolution of the effective magnetic moment $\mu_{\rm eff}$ measured by the Evans NMR method during titration (Figure 11) resembles closely the changes observed in the variable-temperature experiment on cooling (Figure 3). Both addition of 4-papy and lowering the temperature decrease the magnetic moment. The titration experiment provided a minimum $\mu_{\rm eff}$ of 2.78(19) $\mu_{\rm B}$ in the presence of a large excess of 4papy, whereas the variable-temperature data revealed a plateau of $\mu_{\rm eff} = 2.73 \,\mu_{\rm B}$ at low temperatures. Astonishingly, these two different experiments converge to an identical magnetic moment. This provides strong evidence that the same process is operative in both experiments. The evolution of $\mu_{\rm eff}$ on titration can successfully be modeled for 1 and 2 in equilibrium [Eq. (2)] to yield $K_a = 5(3) \times 10^2 \text{ Lmol}^{-1}$, very similar to the value obtained by electronic spectroscopy. Thus, according to the Evans NMR method the degree of dissociation α for 1 in solution ($c_0 = 5 \times 10^{-4}$ M) at RT is estimated to be 83%.

Since the parent solution without addition of 4-papy contains about 85% of **2** and 15% of **1** with μ_{eff} = 3.86 μ_{B} (see above), **2** must have a hs-Co^{II}(SQ)₂ electronic configuration with three uncoupled (at RT) paramagnetic centers. The spinonly value for a pure fully uncoupled hs-Co^{II}(SQ)₂ state would be 4.58 $\mu_{\rm B}$. At low temperatures or in the presence of a large excess of 4-papy, 1 is exclusively formed, and must have a smaller magnetic moment. The ultimate low-temperature values of $\mu_{\rm eff} =$ 2.73 $\mu_{\rm B}$ obtained from variable-temperature measurements (Figure 3) and $\mu_{\rm eff} = 2.78(19) \,\mu_{\rm B}$ from the titration experiment (Figure 11) are ascribed to a Is-Co^{III}(Cat)(SQ) S = 1/2 electronic structure for **1**. These values significantly exceed the expected moment of about 1.7 $\mu_{\rm B}$ for an S = 1/2 ligand-based paramagnet. We ascribe the observed deviation to some decomposition of the complex in solution leading to species with S > 1/2. The decomposition product does not interfere with the equilibrium [Eq. (2)], as confirmed by clean isosbestic points in electronic absorption spectra. Note that an S=1 species that would give $\mu_{\rm eff} \! pprox \! 3 \, \mu_{\rm B}$ cannot be constructed for an odd-spin species 1 or 2.

Assuming the presented equilibrium [Eq. (2)], Is-Co^{III}(Cat)(SQ) electronic structure for 1, and hs-Co^{II}(SQ)₂ configuration for 2, we can account for all experimental findings: 1) the evolution

of magnetic moment in variable-temperature and titration experiments, 2) the changes in electronic absorption spectra observed on cooling or on addition of 4-papy, and 3) the assignment of a temperature-independent S = 1/2 signal detected by EPR spectroscopy as arising from **1**. Furthermore, we recorded variable-temperature EPR spectra in the presence of excess 4-papy (ca. 15 equiv). The obtained spectra resemble closely those measured on a pure complex and further confirm our model (Figure S9 in the Supporting Information).

The proposed equilibrium [Eq. (2)] was further supported by TD-DFT calculations. Allowing for the limitations of TD-DFT to calculate electronic spectra for spin-coupled species, we achieved good qualitative agreement between experiment and theory. The calculated spectrum for **2** in the S = 5/2 state shows several intense bands in the visible region due to metalto-ligand charge transfer transitions (Figure S26 in the Supporting Information). In contrast, the S = 1/2 state of 1 reveals weaker transitions in the visible region, whereby the prominent band at 500 nm shows a significant intraligand $n \rightarrow \pi^*$ character of 4-papy (Figure S27 in the Supporting Information). Therefore, the **2** (S = 5/2) \rightarrow **1** (S = 1/2) transition should be accompanied by decreasing absorption in the visible region. This can be best visualized by calculated gradual changes in the electronic absorption spectrum (Figure 14). Indeed, the predicted evolution of the spectrum resembles the experimental variable-temperature (Figure 5) and titration (Figure 9) data. Moreover, a very intense IVLLCT band (exptl: 2650 nm = 3774 cm⁻¹),^[29,34] characteristic of a Is-Co^{III}(Cat)(SQ) state,^[5,25] was qualitatively reproduced in our calculations for the S = 1/2state of **1** (calcd: 1270 nm = 7877 cm⁻¹; Figure S28 in the Supporting Information). No similarly intense NIR bands were observed in the calculated spectrum for the S = 5/2 state of **2**.



Figure 14. Predicted evolution of the electronic absorption spectrum accompanying the [hs-Co^{II}(SQ)₂(4-papy)] (2) \rightarrow [ls-Co^{III}(Cat)(SQ)(4-papy)₂] (1) conversion; spin-unrestricted B3LYP-TD-DFT calculations with COSMO; see Experimental Section for further details.

Although VT interconversion due to coordination of solvent molecules in solution is known,^[50] valence tautomerism induced by coordination/dissociation of ligands in solution is nearly unexplored. In this context, we mention a recent work by Minkin and co-workers, who reported six-coordinate complex ls-[Co^{III}(SQ*)(NO)₂] featuring one redox-active phenoxazine-1-one ligand (Q*; SQ*=one-electron-reduced form of Q*; NO = bidentate ligand).^[51] Although the complex has a ls-Co^{III}(SQ*) electronic structure in the solid state, a neutral ligand Q*



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is believed to detach, leaving a hs-Co^{II} species in solution.^[51] In our case, an auxiliary 4-papy ligand detaches from 1, leaving a hs-Co^{II}(SQ)₂ species with both redox-active ligands intact.

The CIVT reported herein is reminiscent of the CISCO recently reported by Tuczek, Herges, and co-workers,^[18] who demonstrated switching of magnetic properties in Ni^{II} porphyrin complexes through coordination/dissociation of pyridine-derived ligands in axial positions. The accompanying changes in coordination number and geometry resulted in a high-spin (S = 1) \leftrightarrow low-spin (S=0) transition. By careful evaluation of more than 400 NMR spectra, Tuczek, Herges et al. were able to extract binding enthalpies and entropies for the two-step process with great accuracy.^[18] Although a variation of their method is in principle applicable to our VT system, such studies are beyond the scope of this work. Also we comment on a series of papers by Jung et al.,^[46] who synthesized several closely related [Co(o-dioxolene)₂L₂] (L is an N-donor ligand) VT complexes. The properties of these species were investigated both in the solid and in the solution state, and VT interconversion in both phases have been suggested. Due to close similarity with 1, we propose that the complexes of Jung et al. similarly dissociate in solution. However, this possibility was not considered in their work.[46]

Magnetic exchange coupling

Another aspect of this work deals with theoretical investigation of magnetic exchange in VT bis(o-dioxolene) cobalt species. Rheingold, Hendrickson et al. proposed that weak intramolecular antiferromagnetic exchange interactions between a hs-Co^{II} ion (S=3/2) and each ligand π radical (S_R=1/2) are present in cis-[hs-Co^{II}(SQ)₂(NN)] complexes (NN is an N-donor chelating ligand).^[21] This was based on previous observations by Pierpont, Hendrickson et al. on generally weak AF interactions between a hs-Co^{II} ion and SO radicals determined for some related species.^[45] The net weak AF interactions are due to only one cobalt t_{2g} magnetic orbital leading to an AF pathway that is in competition with two cobalt e_a magnetic orbitals responsible for ferromagnetic pathways in pseudo-octahedral hs-Co^{II} complexes.^[45] Indeed our calculations on *cis* species **3** and previous calculations by Noodleman, Hendrickson, and Adams^[29] reproduce net AF exchange interactions between a hs-Co^{II} ion and ligand $\boldsymbol{\pi}$ radicals, although the strength of interactions is likely overestimated. The J value was calculated to be -54 and -100 cm⁻¹ by using OPBE and B3LYP functionals, respectively, in our work, and as -594 cm⁻¹ by Noodleman et al.^[29] Intramolecular magnetic coupling in VT bis(o-dioxolene) cobalt species is too small to be experimentally detected at elevated temperatures at which the hs-Co^{II} ion and two ligand π radicals are uncoupled.

It is intriguing that the net coupling between the hs-Co^{II} ion and the ligand π radicals in 1 is ferromagnetic. To understand such a striking difference between 1 and 3, one must recall that the geometries of these two complexes are different. The two N donors of the chelating phenanthroline ligand occupy *cis* positions in 3, whereas the two N donors of pyridine rings are located at *trans* positions in 1. Consequently, due to restrictions imposed by the bite angles of the chelating ligands, **3** shows a trigonally distorted octahedral geometry (Bailar twist angles $\Theta = 44.6$, 44.5, 39.9°). This distortion results in nonzero spatial overlap between two cobalt e_g magnetic orbitals, which transform into e" in trigonal-prismatic D_{3h} geometry, with a proper combination of ligand π -type magnetic orbitals that transform as e" as well (Figure 15).^[52] Thus, there are two AF pathways in D_{3h} : the main one due to e' magnetic orbitals (t_{2g} in O_{hr} overlap integral $S_{AB} = 0.30$) and an additional pathway due to e" magnetic orbitals (e_g in O_{hr} , $S_{AB} = 0.06$). In this way, the enhanced AF exchange exceeds ferromagnetic exchange and leads to net antiferromagnetic coupling between the hs-Co^{II} and ligand π radicals in **3**.



Figure 15. Qualitative MO scheme for a BS(3,2) $M_{\rm S} = 1/2$ state of **3** (hs-Co^{II}(SQ)₂) obtained from spin-unrestricted B3LYP calculations with COSMO; corresponding orbitals are shown. Note that the native coordinate system for octahedral complexes is used for d orbitals, whereas symmetry labels were adapted from the D_{3h} point group to assist comparison with **1**. [a] Heavily mixed metal d orbital.

In contrast, 1 exhibits a tetragonally distorted octahedral geometry. This renders two metal e_g orbitals, which now transform into a_g and b_{1g} in D_{2h} , strictly orthogonal to the ligand π type magnetic orbitals, which transform as b_{1u} and b_{2q} in D_{2h} (Figure 12).^[49,53] Thus, there is only one AF pathway in D_{2h} : the d_{xz} and $L_{\pi 1}$ magnetic orbitals couple antiferromagnetically $(S_{AB} = 0.20)$, because both transform as b_{2q} . This weakens the AF exchange in 1 compared to 3, which is therefore superseded by ferromagnetic exchange giving rise to net ferromagnetic coupling between the hs-Co^{II} ion and ligand π radicals in **1**. Hence, distinctly different geometries of 1 and 3 result in differing net coupling between a hs-Co^{II} ion and ligand π radicals. Although the experimental data on magnetic coupling between a genuine $^{\scriptscriptstyle[53]}$ hs-Co $^{\scriptscriptstyle \|}$ and two semiquinone π radicals in tetragonally distorted octahedral complexes is not available, it would be interesting to synthesize such spin-coupled species to validate our DFT-based hypothesis on ferromagnetic coupling.

The low symmetry of five-coordinate **2** leads to significant mixing of metal d orbitals, which generates multiple overlaps

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between metal- and ligand-based magnetic orbitals and thus accounts for net AF coupling between the hs-Co^{II} ion and the ligand π radicals in **2** (Figure S25 in the Supporting Information).

Conclusion

The six-coordinate VT complex trans-[Co(tbdiox)₂(4-papy)₂] (1) has been synthesized and crystallographically characterized. In the solid state, 1 shows a regular thermally driven valence tautomerism Is-Co $^{II}(Cat)(SQ) {\leftrightarrow} hs\text{-Co}^{II}(SQ)_2$ with high transition temperature $T_{1/2}$ = 396(7) K (Cat²⁻ = fully reduced form of o-dioxolene, SQ⁻ = π -radical form of *o*-dioxolene). Partial dissociation of 1 in solution yields five-coordinate [Co(tbdiox)₂(4-papy)] 2 and free 4-papy. The electronic configurations of 1 and 2 in solution at room temperature are different. Six-coordinate 1 has a Is-Co^{III}(Cat)(SQ) configuration, whereas the five-coordinate **2** has a hs-Co^{II}(SQ)₂ configuration due to the weaker ligand field. Consequently the magnetic properties of 1 and 2 are different. Since 1, 2, and 4-papy are in equilibrium [Eq. (2)], addition of 4-papy to the solution shifts the equilibrium towards 1 and thus changes the magnetic moment of solution. The observed effect is coined coordination-induced valence tautomerism (CIVT), a mechanism to switch between two electronic states in valence tautomeric metal complexes and thereby the magnetic properties at room temperature.

The experimental findings obtained from X-ray crystallography, electrochemistry, titration experiments, variable-temperature SQUID susceptometry, NMR, EPR, and electronic absorption spectroscopy are confirmed and supported by theoretical calculations. Two different scenarios for magnetic exchange coupling in VT bis(o-dioxolene) cobalt complexes were disclosed by broken-symmetry DFT calculations. The hs-Co^{II} ion (S = 3/2) in *cis*-[hs-Co^{II}(SQ)₂(NN)] is antiferromagnetically coupled with two ligand π radicals ($S_R = 1$), whereas the coupling is ferromagnetic in *trans*-[hs-Co^{II}(SQ)₂L₂] homologues (NN is a bidentate and L is a monodentate ligand). The observed diversity in magnetic exchange is caused by differing spatial overlap between magnetic orbitals due to different geometries of *cis* and *trans* species.

We believe that the CIVT observed at room temperature in solution can be employed for monolayers of VT deposits in the future. The reversible coordination/dissociation of a substrate to a cobalt center could be used, for instance, as a single-molecule sensor with magnetic response. Other VT metal complexes showing CIVT and solution-stable species featuring photoisomerizable ligands are currently under investigation.

Experimental Section

Materials

All starting materials and solvents were utilized as received without further purification unless otherwise noted. Pure anhydrous solvents, required for work under inert gas atmosphere, were gathered from a solid-state solvent purification system (Glass Contour System, Irvine, CA) and stored over activated molecular sieves. The precursor cobalt tetramer was obtained as a benzene solvate [Co-(tbdiox)₂]₄·(C₆H₆)_{2.75} by a synthetic procedure described by Pierpont et al. (tbdiox = 3,5-di-*tert*-butyl-o-dioxolene).^[35] 4-Phenylazopyridine (4-papy) was prepared according to the method described by Brown and Granneman.^[54]

Instrumentation and physical measurements

Elemental analyses were carried out with a EuroVector EA elemental analyzer . Magnetic susceptibility data of solid samples were collected with a Quantum Design MPMS 5XL SQUID magnetometer. Measurements were obtained for a powder restrained within a polycarbonate gel capsule. DC susceptibility data were collected in the temperature range 2–360 K in the applied magnetic field of 1 T. The program JulX was used for the simulation and analysis of magnetic susceptibility data.^[55] All EPR spectra were recorded at the EPSRC National UK EPR Facility and Service at The University of Manchester. X-band fluid-solution spectra were collected with a Bruker EMX Micro spectrometer and frozen-solution data on a Bruker E580 spectrometer. Simulations were performed with the Bruker Xsophe software package.^[56] Electrochemical measurements were performed under nitrogen atmosphere at room temperature by using a standard three-electrode setup with glassy carbon working electrode and platinum rods as counter and reference electrodes. The potentiostat was a µAutolab Type-III. Analyte solutions were prepared in CH₂Cl₂ containing 0.1 M nBu₄NPF₆ as supporting electrolyte. All potentials are referenced to the Fc^{+/0} redox couple, which was measured after adding ferrocene to the analyte solution. NMR spectra were recorded with JEOL JNM-LA 400 FT NMR spectrometer and processed with Delta V4.0 software provided by Jeol Ltd. Magnetic susceptibility data in solution were measured by the Evans NMR method.^[57] The outer tube (standard NMR tube with a PTFE spindle valve) contained the reference solvent mixture C₇H₈/C₇D₈/TMS (10:1:1). The inner tube (capillary tube with 1.5 mm diameter sealed with inert wax) contained the paramagnetic complex in the same solvent mixture. Electronic absorption spectra were recorded with a Shimadzu UV 3600 UV/Vis/NIR spectrophotometer. The samples were prepared under anaerobic conditions and sealed in QS Quartz Suprasil cells (10 mm light path) with PTFE spindle valves. Temperature-dependent electronic absorption spectra were recorded with an Analytik Jena Specord S600 spectrophotometer. The samples were prepared under anaerobic conditions and measurements were conducted inside a glove box by using QS Quartz Suprasil cells (10 mm light path). The solutions were continuously stirred with a magnet bar and the temperature inside the cells was monitored.

Variable-temperature magnetic susceptibility measurements and variable-temperature electronic absorption spectra were fitted by using Equations (4) and (5), respectively, derived from van't Hoff Equation (3). The following quantities were used: enthalpy change ΔH , entropy change ΔS , equilibrium constant K_{eqr} observed effective magnetic moment μ_{eff} high- and low-temperature magnetic moments μ_{eff} (HT) and μ_{eff} (LT), observed absorption A_{obsr} and high- and low-temperature absorptions A(HT) and A(LT).

$$\ln K_{\rm eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{3}$$

$$\mu_{\text{eff}} = \sqrt{\frac{e^{\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right)}\mu_{\text{eff}}^2(\text{HT}) + \mu_{\text{eff}}^2(\text{LT})}{e^{\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right)} + 1}}$$
(4)

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$$A_{\rm obs} = \frac{e^{\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right)} A({\rm HT}) + A({\rm LT})}{e^{\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right)} + 1} \tag{5}$$

Theoretical calculations

The program package ORCA 2.7 revision 0 was used for all calculations.^[58] The geometries of all complexes were fully optimized by a spin-unrestricted DFT method with OPBE functional.^[36] The stability of all solutions was checked by performing frequency calculations; no negative frequencies were observed. The single-point calculations were performed with OPBE and B3LYP functionals.^[59] Triple- ζ basis sets with one set of polarization functions [TZV(P)] were used for all atoms except carbon and hydrogen, for which double- ζ basis sets with one set of polarization functions [SV(P)] were used.^[60] The conductor-like screening model (COSMO) was routinely used for all calculations.^[42] RI and RIJCOSX approximations^[61] combined with appropriate Ahlrichs auxiliary basis sets^[62] were routinely employed to speed up the calculations. The EPR parameters were calculated with B3LYP functional including relativistic effects in the zero-order regular approximation (ZORA),^[63] the "core-prop" [CP(PPP)] basis set for cobalt^[64] and the corresponding TZV-ZORA and SV-ZORA basis sets for the remaining atoms were used.^[65] The exchange coupling constants J were calculated on broken-symmetry^[41] geometries by using Equation (6)^[66] and assuming that the spin Hamiltonian of Equation (7) is valid,

$$J = \frac{E_{\rm BS} - E_{\rm HS}}{\langle \hat{S}^2 \rangle_{\rm HS} - \langle \hat{S}^2 \rangle_{\rm BS}}$$
(6)

$$\hat{H} = -2J\hat{S}_{A}\hat{S}_{B} \tag{7}$$

where $E_{\rm BS}$ is the energy of the broken-symmetry solution, $E_{\rm HS}$ is the energy of the high-spin state, $<\hat{S}^2>_{\rm HS}$ is the expectation value of \hat{S}^2 operator for the high-spin state, $<\hat{S}^2>_{\rm BS}$ is the expectation value of $\hat{S}_{\rm A}$ and $\hat{S}_{\rm A}$ and $\hat{S}_{\rm B}$ are local spin-operators.

TD-DFT calculations were performed with the B3LYP functional. The full width at half-maximum (FWHM) was set to 2000 cm⁻¹ for each transition in calculated UV/Vis/NIR spectra. To calculate the evolution of the electronic spectrum (Figure 14) the calculated spectra of two species were added according to Equation (8), where *a* and *b* are weighting coefficients such that a+b=1, and ε_1 and ε_2 are the extinction coefficients of **1** and **2**, respectively. Molecular orbitals and spin-density maps were visualized with the program Molekel.^[67]

$$\varepsilon = a\varepsilon_1 + b\varepsilon_2 \tag{8}$$

Synthesis of 1

4-Phenylazopyridine (200 mg, 1.12 mmol) dissolved in 10 mL of toluene was added dropwise to $[Co(tbdiox)_2]_4$ -2.75 C₆H₆ (300 mg, 0.14 mmol) dissolved in 50 mL of hot (80 °C) toluene. The reaction mixture was stirred overnight at 80 °C and stored at -35 °C for 3 d, after which a gray-green precipitate of 1 was collected and dried in vacuo (283 mg, 58.3% yield). Elemental analysis calcd (%) for C₅₀H₅₈CON₆O₄: C 69.35, H 6.75, N 9.70; found: C 69.63, H 6.60, N 10.01. Slower precipitation at 4 °C over several weeks gave a crystal-line dark-green toluene hemisolvate 1·0.5 C₇H₈. Elemental analysis

calcd (%) for $C_{53.5}H_{62}CoN_6O_4$: C 70.45, H 6.85, N 9.21; found: C 70.22, H 6.82, N 9.46.

X-ray crystallographic data collection and structure refinement

Suitable crystals were embedded in protective perfluoropolyalkyl ether oil and transferred to the cold nitrogen gas stream of the diffractometer. Intensity data of 1 were collected at 120 K on a Bruker Kappa APEX2 IµS Duo diffractometer equipped with Quazar focusing Montel optics (Mo_{Ka} radiation, $\lambda = 0.71073$ Å). Data were corrected for Lorentzian and polarization effects; semi empirical absorption corrections were applied on the basis of multiple scans by using SADABS.^[68] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 by using SHELXTL NT 6.12.^[69] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in position of optimized geometry, and their isotropic displacement parameters were tied to those of their corresponding carrier atoms by a factor of 1.2 or 1.5. The complex molecule is situated on a crystallographic inversion center and exhibits crystallographically imposed C_i symmetry. The pyridyl ligands are subject to disorder with different orientations of the central azo group. Two alternative orientations were refined and resulted in site occupancies of 66(2)% for N1-N3, C15-C25 and 34(2)% for N1A-N3A, C15A-C25A. Furthermore, one of the independent tBu groups was disordered. Here, also two different orientations were refined to give site occupancies of 60(2)% for C8-C10 and 40(2)% for C8A-C10A. SIMU and ISOR restraints were applied in the refinement of the disorder. The crystallographic data, data collection and structure refinement details are summarized in Table S5 in the Supporting Information. CCDC-984219 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif and are also available as Supporting Information.

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