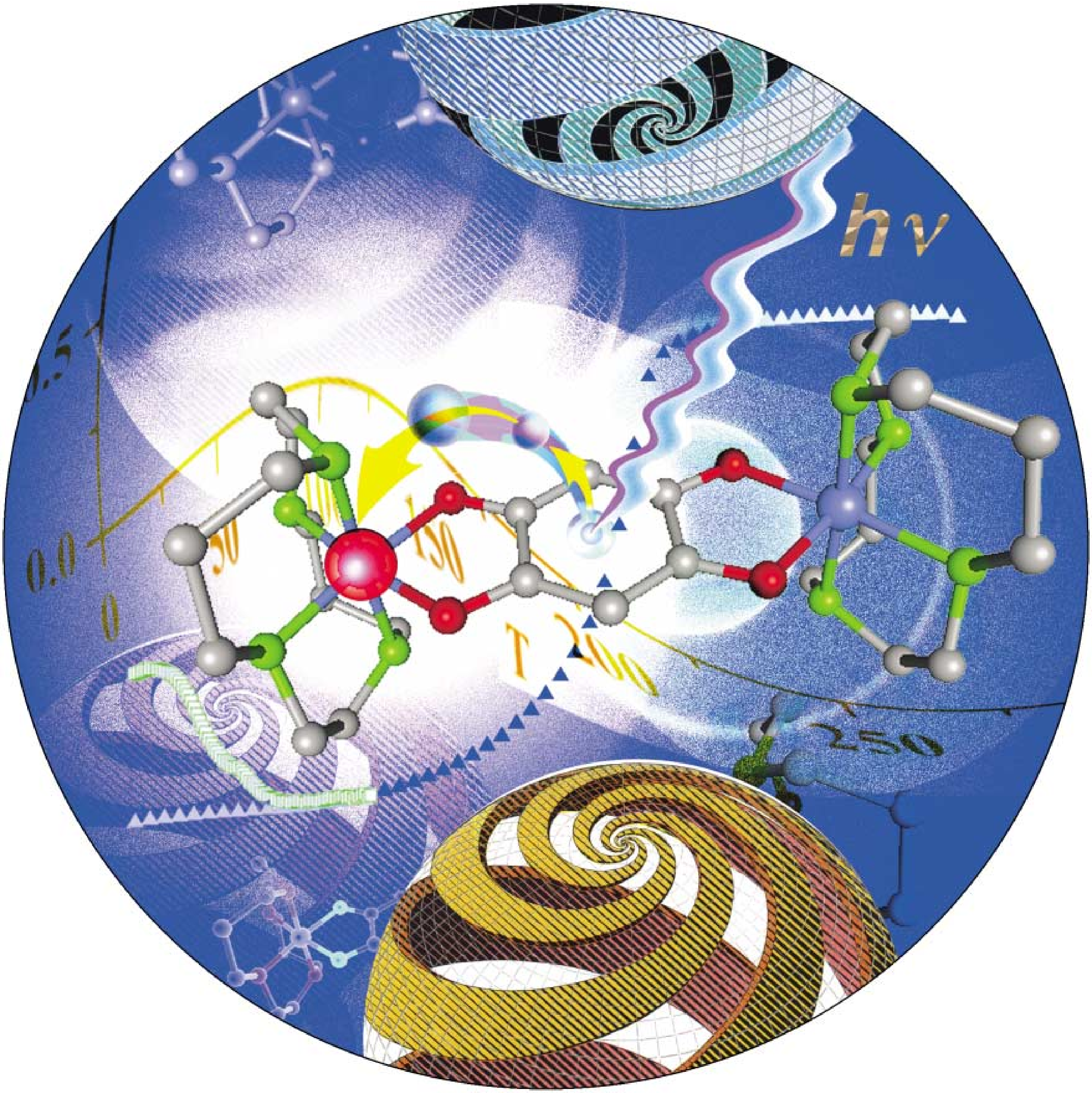
Zuschriften



Das Abstimmen der elektronischen Eigenschaften eines zweikernigen Cobalt-Polyoxolen-Komplexes lieferte ein photoschaltbares System, das eine Entropie-gesteuerte Valenztautomerisierung eingeht. Weitere Informationen dazu finden Sie in der Zuschrift von A. Dei, J.-F. Létard et al. auf den folgenden Seiten.

DOI: 10.1002/ange.200453944

Electron Transfer

Thermally and Light-Induced Valence Tautomeric Transition in a Dinuclear Cobalt–Tetraoxolene Complex**

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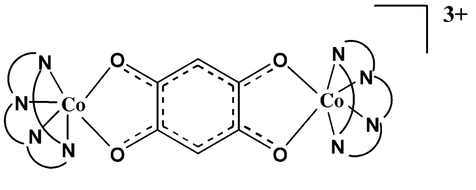
The design of optically switchable molecules is one of the main challenges in modern materials chemistry because such compounds have potential applications in the development of new electronic devices. Particular attention has been devoted to molecules exhibiting electronic bistability, that is, the property to exist in two different electronic states depending on the external parameters.[1] Among the different classes of bistable molecules investigated to date, there is no doubt that those showing electronic states with different magnetic properties are the most attractive. These include spin-crossover metal complexes and cobalt–dioxolene complexes that undergo valence tautomerism.[2,3] Photoinduced spin-state interconversion in spin-crossover iron(II) complexes has been described.[4] Transient interconversions were also observed at room temperature for valence tautomeric complexes,[5] but recently it was found that a low-spin cobalt(III) complex of the general formula [ls-Co^{III}(N–N)(cat)(sq)] (N–N is a diimine ligand, cat and sq represent the catecholato and semiquinonato forms of 3,5-di-*tert*-butylcatechol) undergoes transition to the high-spin isomer [hs-Co^{II}(N–N)$(sq)_2$] after illumination at low temperature.[6,7] We have recently observed that the same phenomenon occurs for the 1:1 cobalt–macrocycle dioxolene adduct [Co^{III}(cth)(phencat)]$(PF_6)\cdot H_2O$ (cth = (*dl*)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, phencat = catecholato form of 9,10-phenanthrenequinone).[8] However, although several transition-metal complexes exhibit spin crossover or valence tautomerism, only the aforementioned metal complexes afford photoswitchable derivatives. It seems reasonable to believe that this is related to the large changes in the acceptor–donor bond lengths (0.15–0.20 Å) associated with the transitions. This is particularly disappointing because the number of molecular systems of potential interest is strongly limited.

With the aim of preparing a new family of cobalt–dioxolene systems that undergo valence tautomerism, we have synthesized [{Co(cth)}$_2$(dhbq)]$(PF_6)_2$ (**1**, dhbq = deprotonated 2,5-dihydroxy-1,4-benzoquinone). This complex—as the previously reported Mn, Cr, Fe, and Ni analogues[9]—is postulated to contain two six-coordinate high-spin cobalt(II) ions bridged by the dinegative tetraoxolene ligand. One-electron oxidation of this compound with a stoichiometric amount of $AgPF_6$ in acetone affords [{Co(cth)}$_2$(dhbq)]$(PF_6)_3$ (**2**, Scheme 1). This complex can be reasonably formulated as containing 1) two cobalt(II) ions bridged by the mononegative tetraoxolene ligand if a ligand-centered oxidation takes place, 2) a mixed-valence cobalt(III)–cobalt(II) couple bridged by the dinegative tetraoxolene if a metal-centered oxidation occurs, or 3) two cobalt(III) ions bridged by the trinegative radical tetraoxolene. In the last case, the oxidation involves both the metal ions and reduction of the ligand occurs as well, as found for the iron analogue.[9]



Scheme 1. Schematic view of the cationic part of complex **2**.

The electronic (see below) and infrared spectra (see the Experimental Section) of **2** at room temperature strongly support the formulation of the compound as a mixed-valence Co^{II}–Co^{III} derivative (hypothesis 2). The temperature-dependent magnetic susceptibility measurements additionally show the existence of a transition between two different species (Figure 1). The $\chi_M T$ product of **2** at low temperature is close to 0.45 $cm^3\,K\,mol^{-1}$, in agreement with a species with a doublet ground state, while the limiting value reached in the

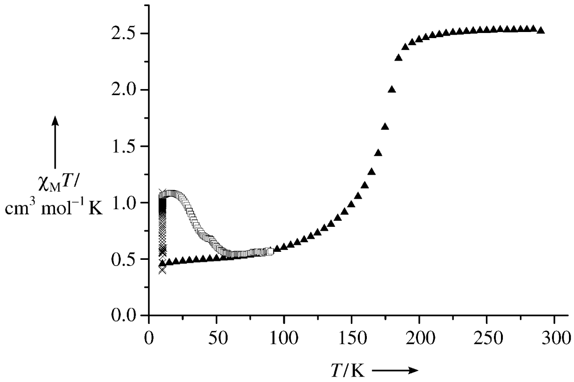


Figure 1. Plot of the $\chi_M T$ product as a function of temperature T for complex **2** measured before (▲) and after (□) irradiation at 647 nm. The crosses (×) indicate the increase of the $\chi_M T$ product with time upon irradiation of the sample. The bump at 45 K on the irradiation curve is a result of a small amount of oxygen.

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[**] The authors would like to acknowledge the CNRS, the Aquitain region, the COST program (D14-WG 0011-01), the CNRS/DFG bilateral project, and the FIRB project of MIUR for funding. We are grateful to Paolo Parri for creating the frontispiece.

DOI: 10.1002/ange.200453944

high-temperature region (2.53 $cm^3 K mol^{-1}$) is consistent with the presence of a $S = 3/2$ paramagnetic species.

Therefore, both hypotheses, a spin-crossover transition involving the cobalt(II) ion and a valence tautomeric interconversion involving the [ls-Co^{III}-($dhbq^{3-}$)-ls-Co^{III}] and the [hs-Co^{II}-($dhbq^{2-}$)-ls-Co^{III}] species, are valid. However, the EPR spectrum recorded at 4 K is unambiguous. The strong signal at $g = 2.00$ (Figure 2) proves the existence of a radical ligand and rules out a [ls-Co^{II}-($dhbq^{2-}$)-ls-Co^{III}]$\rightleftharpoons$[hs-Co^{II}-($dhbq^{2-}$)-ls-Co^{III}] spin-crossover equilibrium. A weak signal at $g = 4.3$ indicates the presence of a small amount (less than 10%) of cobalt(II) ions,[10] which can account for the deviation of the $\chi_M T$ product from the expected value of 0.375 $cm^3 K mol^{-1}$. The progressive disappearance of the radical species above 100 K is evidenced by the investigation of the temperature dependence of the signal at $g = 2.00$ (inset of Figure 2). Indeed if the amount of radical were unchanged at different temperatures, the value of $I_{EPR}T$, which is proportional to the $\chi_M T$ value of the radical moiety, should remain constant. The temperature-induced transition of **2** can be then reasonably attributed to a valence tautomeric interconversion involving an intramolecular one-electron transfer between the tetraoxolene ligand and the low-spin cobalt(III) acceptor with a spontaneous change in spin state from ls-Co^{III} ($S = 0$) to hs-Co^{II} ($S = 3/2$) and the concomitant transformation of the ligand from a paramagnetic ($S = 1/2$) to a diamagnetic ($S = 0$) species. This transition, which occurs around 175 K (Figure 1), can be classified as gradual, in analogy with the definition currently used for spin-crossover complexes;[2] no thermal hysteresis was observed.

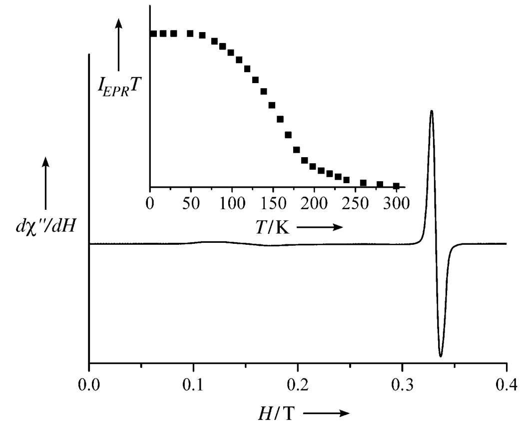

Figure 2. The X-band (9.24 GHz) EPR spectrum of **2** recorded at 4 K. Inset: Plot of the temperature dependence of the product of the intensity of the radical signal, calculated as the area under the curve, with temperature ($I_{EPR}T$).

As a further step we analyzed the effect of light on the magnetic properties of **2**. At 10 K, the sample was initially in the [ls-Co^{III}-($dhbq^{3-}$)-ls-Co^{III}] state. Upon irradiation with light (647.1–676.4 nm),[11] the magnetic moment increased immediately, and the limiting value of $\chi_M T$ measured after a long period of irradiation was almost 1.2 $cm^3 K mol^{-1}$. The light was then switched off and the temperature was increased at 0.3 $K min^{-1}$. The $\chi_M T$ value decreased smoothly and around 60 K the signal recovered the initial value obtained before irradiation. This result shows that the light-induced phenomenon is perfectly reversible. Experiments to increase the level of photoexcitation by increasing the irradiation time or power (up to 30 $mW cm^{-2}$) or changing the wavelength (488.0–514.5 nm, 752.5–799.3 nm) were unsuccessful.

The highest photoinduced rate of population corresponds to 43% if we consider that the [ls-Co^{III}-($dhbq^{3-}$)-ls-Co^{III}]→[hs-Co^{II}-($dhbq^{2-}$)-ls-Co^{III}] process occurs. There are many different explanations for the magnitude of the $\chi_M T$ product under irradiation with light. One of them concerns the strong opacity of the sample (dark purple), which might prevent the penetration of light in the bulk phase; this has been reported for some iron(II) spin-crossover complexes.[7] In this context, the properties of **2** were investigated with a home-built set-up that allows collection of the reflectivity spectra between 400 and 850 nm at a given temperature as well as monitoring of the temperature dependence of the signal at a selected wavelength (±5 nm). Figure 3 displays two selected absorption spectra collected at room temperature and at 80 K. This confirms there is a clear modification of the absorption spectra accompanying the thermally induced valence tautomeric interconversion. The inset of Figure 3 shows the change of the reflectivity signal as a function of temperature at 617 ± 5 nm. The gradual thermally induced valence tautomeric process is clearly observed and the shape of the curve perfectly follows the magnetic data shown in Figure 1. Most remarkably, an almost quantitative photoinduced interconversion occurs at low temperature at the surface. The magnitude of the reflectivity signal recorded at 10 K is in fact close to that recorded at room temperature.

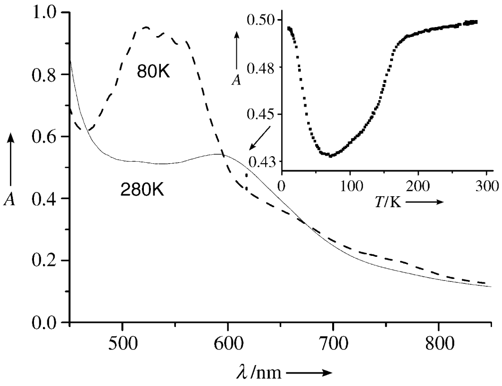

Figure 3. Diffusive absorption spectra of **2** recorded at room temperature and at 80 K. Inset: Plot of the reflectivity at 617 ± 5 nm as a function of temperature (see text for details). The absorbance *A* is given in arbitrary units.

In conclusion, we have prepared a new dinuclear [$\{Co(cth)\}_2(dhbq)](PF_6)_3$ complex that undergoes a tautomeric transition. A gradual thermal transition occurs at around 175 K and quantitative photoconversion was observed at the surface by using a reflectivity technique. In the bulk sample, the level of photoexcitation, as a result of the strong opacity of the sample, is estimated at around 40%. Further work is now in progress to fully characterize the relaxation kinetics as well as the thermodynamic parameters.

In addition to the novelty of the system undergoing valence-tautomeric transition, these results offer an interesting perspective. Indeed, the role of the tripositive metal ion in the above-discussed compound is magnetically ancillary, since its function is that of tuning the redox potential of the bridging ligand. However, the same effect can be, in principle, obtained by substituting the cobalt(II) metal ion with another tripositive paramagnetic metal ion, thus offering the possibility of obtaining valence-tautomeric complexes with different electronic ground states.

Experimental Section

1: A solution of [Co(cth)Cl_2] (2 mmol) in methanol (40 mL) was mixed with an alkaline solution of 2,5-di-hydroxy-1,4-benzoquinone (1 mmol) in methanol (30 mL) under argon. The resulting solution was heated at reflux and then mixed with an aqueous solution of KPF_6. Brown crystals of **1** precipitated.

2: A solution of **1** (0.5 mmol) in acetone (50 ml) was mixed with a solution of $AgNO_3$ (0.5 mmol) in acetone/water (1/1, 30 mL). The resulting suspension was stirred at room temperature for 0.5 h, the silver metal was removed by filtration, and an aqueous solution of KPF_6 was added. Brown-violet microcrystals of **2** unsuitable for X-ray data collection were obtained. Elemental analysis calcd (%) for $C_{38}Co_2H_{74}N_8O_4P_3F_{18}$: C 36.23, H 5.92, N 8.89; found: C 35.84, H 5.99, N 8.65.

The IR spectra of **1** and **2** were very similar to those of the previously reported Mn and Ni analogues.[9] The magnetic susceptibility measurements were carried out on a solid sample with a MPMS-55 Quantum Design SQUID magnetometer operating at $H=2$ T in the 2–300 K temperature range. Irradiation was achieved with a Krypton laser connected through an optical fiber to the SQUID magnetometer. The power on the sample was adjusted to 5 mWcm^{-2}. Bulk attenuation of light intensity was limited as much as possible by preparation of a thin layer of the compound. The weight of the thin layer was determined by comparing the thermal valence tautomeric transition curve with the curve recorded for a heavier sample of the same compound.[11] The reflectivity spectra were recorded on a solid sample with a home-made set-up with a CVI spectrometer. The EPR spectra of polycrystalline powder samples were recorded on a Bruker E5000 spectrometer equipped with an ^{4}He continuous flow cryostat for varying the temperature.

Received: February 5, 2004 [Z53944]

Keywords: cobalt · electron transfer · magnetic properties · photochemistry · tautomerism

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