pH-Triggered intramolecular electron transfer in asymmetric bis-dioxolene adducts

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The oxidation of the bis-dioxolene 3,3,3′,3′-tetramethyl-5,6,5′,6′-tetrahydroxy-1,1′-spiro-bis(indane) ($CatH_2$–$CatH_2$) in acidic solution yields the *o*-quinone-catecholate (Q–$CatH_2$) as a product. The mixed valence character of the molecule is removed on deprotonation yielding the paramagnetic bis-semiquinonato species due to a formally intramolecular electron transfer. Complexes of formula M(CTH)(SQ–$CatH_2$)(PF_6)$_2$ (M = Cr^{III}, Co^{III}; CTH = tetraazamacrocycle, SQ–$CatH_2$ = semiquinonato form of $CatH_2$–Q) were also prepared. They are six-coordinate, the semiquinonato being coordinated to the metal ion. Evidences are given that intramolecular electron transfer follows deprotonation of the non-coordinated catecholate, yielding the M^{III}(CTH)(Cat–SQ) species, the catecholato being coordinated to the metal ion. The obtained results provide significant examples of systems showing pH-controlled magnetic properties.
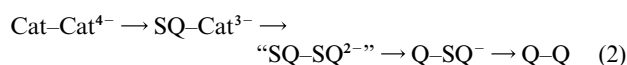
Introduction

The concept of molecular bistability has been often associated with that of the memory effect thus creating some confusion between the two concepts in the chemical literature.[1–16] This is particularly true for works concerning the study of magnetic and optoelectronic properties of materials. The reason for this is clearly the potential application of these systems as functional devices. It is well established that for a memory effect to be present it is required that a molecule may exist in two or more different states for the same values of the external parameters (temperature, pressure, magnetic field, *etc.*) defining the free energy of the system. For a single molecule these requirements have been found to be satisfied *e.g.* in the case of single molecule magnets,[17–19] but in general such a behaviour requires the onset of cooperative effects and then a collection of interacting molecules in the condensed phase. It seems therefore that this point of view holds both at the macroscopic and the mesoscopic levels. However, a more general definition should be adopted when dealing with the bistability of a single molecule: a molecular system should be said to be bistable when a change of one of the parameters defining the state of the system induces a reversible and detectable free energy change to another stable state. Within this framework it is then included the possibility that such a system may undergo the transition between the two states following a chemical reaction. In this case it is necessary to define another important parameter, *i.e.* the molar quantities of the components, as stated by the basic principles of chemical thermodynamics. The example we report in this paper will clarify the importance of this proposition.

It is well known that the oxidation of deprotonated catechol yields *o*-semiquinone and quinone in two steps thus giving rise to a three-membered redox chain

$$Cat^{2-} \longrightarrow SQ^- \longrightarrow Q \qquad (1)$$

In a similar way the oxidation of a deprotonated bis-catecholate tetranegative anion affords four different products thus giving rise to the following redox chain[20–23]

$$Cat\text{–}Cat^{4-} \longrightarrow SQ\text{–}Cat^{3-} \longrightarrow$$
$$\text{``}SQ\text{–}SQ^{2-}\text{''} \longrightarrow Q\text{–}SQ^- \longrightarrow Q\text{–}Q \quad (2)$$

The trinegative and mononegative species of the above redox chain are obviously always paramagnetic radicals ($S = \frac{1}{2}$), which can be considered mixed valence systems and classified, according Robin and Day definition,[24] in three classes. Thus it has been shown that one-electron oxidation of the deprotonated 3,3′,4,4′-tetrahydroxybiphenyl yields the trinegative SQ–Cat which, when acting as bridging ligand towards two metal ions, can be described as a class III mixed valence species.[22] On the other hand we recently showed that a class II character can be attributed to the formally similar species which originates from the *N,N′*-bis(3,5-di-*tert*-butyl-2-hydroxy-phenyl)-1,3-phenylenediamine when coordinated to two manganese(IV) cations.[23] Indeed the different mixed valence character is determined by the extent of the electronic delocalization within the molecule.

A rather different situation may occur when the two dioxolene ligands interact with two different acceptors. In order to show this, 3,3,3′,3′-tetramethyl-5,6,5′,6′-tetrahydroxy-1,1′-spiro-bis(indane) (Cat–$CatH_4$), **1**, has been considered.

Cat-$CatH_4$
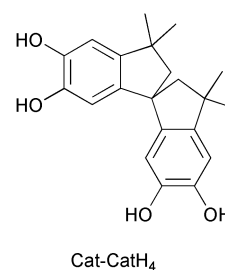
The two-electron oxidation of this molecule in acidic solution yields the quinone-catechol (Q–$CatH_2$) as a dominant product. This molecule contains the two dioxolenes in two different oxidation states, the catecholato form being stabilized by the interactions with proton acceptors, and represents an example of a mixed valence ligand. The existence of this form is due to the nature of the linker which does not allow delocalization between the two dioxolene moieties in contrast to what occurs for the two-electron oxidation product of the above mentioned 3,3′,4,4′-tetrahydroxybiphenyl.

The mixed valence character of the Q–$CatH_2$ molecule is however expected to vanish when the proton acceptors stabilizing the catecholato form are removed. Following this reaction the Q–Cat^{2-} species is expected to be less stable than the SQ–SQ^{2-} bis-semiquinonato one. Thus a pH controlled equilibrium involving a diamagnetic Q–$CatH_2$ species and a paramagnetic

HO—[structure]

Q-CatH$_2$
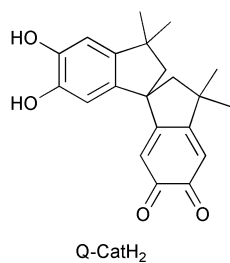
SQ–SQ^{2-} species is expected to occur as a result of a formally intramolecular one-electron transfer induced by an acid–base reaction. Evidence is here presented that this expectation is correct. In addition we show here how the synthesis of this mixed valence dioxolene ligand may allow the preparation of cobalt(III) and chromium(III) complexes of general formula M(CTH)(SQ–CatH$_2$)(PF$_6$)$_2$ (CTH = DL-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) whose charge distribution and magnetic properties are pH dependent.

Experimental

Materials

The M(CTH)Cl$_2$ complexes were prepared following the previously reported procedure.[25,26]

Synthesis of 3,3,3′,3′-tetramethyl-5,6,5′,6′-tetrahydroxy-1,1′-spiro-bis(indane) (Cat–CatH$_4$)

This molecule was synthesised according to literature methods.[27] 5 ml of concentrated HI and 10 ml of acetone were added to a solution of 33 g of catechol in 100 ml of acetic acid. The resulting solution was heated to reflux for 5 h and then cooled at room temperature. A white microcrystalline compound was obtained. It was filtered, washed with cool acetic acid and dichloromethane and then air-dried (yield 60%)

Synthesis of Q–CatH$_2$

An aqueous solution containing 18 mmol of ammonium cerium(IV) nitrate was slowly added were added to a stirred solution of 10 mmol of Cat–CatH$_4$ in 150 ml of acetone. Addition of water induced the precipitation of a brown mycrocrystalline product, which was filtered, washed with water, recrystallised from dichloromethane and then dried under vacuum. This compound was purified by column chromatography on silica gel using dichloromethane–acetone (16 : 1) as eluent. Anal. Found: C, 74.12; H, 6.67. C$_{21}$H$_{22}$O$_4$ requires C, 74.54; H 6.55%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.68 (1H), 6.47 (1H), 6.23 (1H), 5.86 (1H), 2.35 (d, J = 14 Hz, 1H), 2.31 (d, J = 14 Hz, 1H), 2.19 (2H), 1.39 (3H), 1.37 (3H), 1.32 (6H)

Synthesis of M(CTH)(SQ–CatH$_2$)(PF$_6$)$_2$ complexes (M = Cr, Co)

These derivatives were obtained by mixing a methanol solution containining the appropriate M(CTH)Cl$_2$ (1 mmol) with a methanol solution containing the stoichiometric amount of the Q–CatH$_2$ ligand under argon atmosphere. The resulting solution was gently warmed and then an aqueous solution of KPF$_6$ was added thus inducing the separation of solid compounds. They were filtered off and recrystallised from acetone–diethyl ether. Anal. Found: C, 45.81; H, 6,14; N, 5.91. C$_{37}$H$_{58}$CrF$_{12}$N$_4$O$_4$P$_2$ requires: C, 46.04; H, 6.06; N, 5.81%. Found: C, 45.54; H, 6.04; N, 5. 85. C$_{37}$H$_{58}$CoF$_{12}$N$_4$O$_4$P$_2$ requires C, 45.71; H, 6.02; N, 5.77%.

Physical measurements

EPR spectra were recorded on a Varian ESR9 spectrometer. Magnetic field was calibrated by using a small amount of

DPPH radical. Electronic spectra were recorded on a Perkin Elmer Lambda 9 spectrometer. Magnetic measurements were performed with a Cryogenic S600 SQUID magnetometer: data were corrected for magnetism of the sample holder and for the intrisic diamagnetic contribution of the sample by using Pascal's constant.

Results and discussion

The oxidation of 3,3,3′,3′-tetramethyl-5,6,5′,6′-tetrahydroxy-1,1′-spiro-bis(indane) (Cat–CatH$_4$) in acidic solution with cerium(IV) salts in stoichiometric ratio 1 : 2 yields both the *o*-quinone–catechol (Q–CatH$_2$) and the bis *o*-quinone (Q–Q) derivatives as reaction products. Indeed a 2 : 1 ratio of the above products is expected on the basis of statistical considerations. An increase of the yield of the Q–CatH$_2$ is however expected by using a substoichiometric amount of the oxidant. Fractional crystallisation from dichloromethane followed by separation column chromatography allows the isolation of the pure Q–CatH$_2$ product.

The molecule of Q–CatH$_2$ contains the two dioxolene rings in two different oxidation states. However when a solution of this compound in acetonitrile is made alkaline with NMe$_4$OH under inert atmosphere, the colour of the solution turns from brown to blue. The electronic spectra of the acidic and basic solutions (Fig. 1) show that the intensities of quinone transitions decrease upon the addition of the base, whereas new transitions typical of semiquinonate chromophores appear. This spectral behaviour is consistent with the existence of the equilibrium:
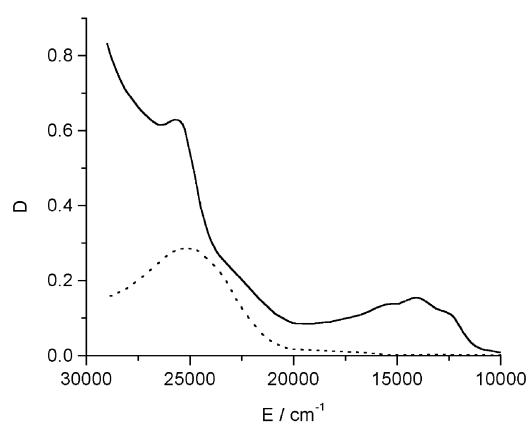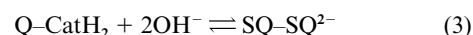
$$Q–CatH_2 + 2OH^- \rightleftharpoons SQ–SQ^{2-} \qquad (3)$$

Fig. 1 Electronic spectra of basic (continuous line) and acidic (dotted line) solutions of Q–CatH$_2$. Assignments are discussed in the text.

Indeed the electronic spectra of Cat–CatH$_4$ shows a transition at 34700 cm^{-1}, whereas a transition at 24800 cm^{-1} is observed in the fully oxidized Q–Q.[28] Both these transitions characterising the catechol and *o*-quinone chromophores are observed in the electronic spectrum of the solution of the Q–CatH$_2$ molecule. When the solution is made alkaline, the observed pattern of bands is typical of a solution containing semiquinonato species. Indeed the transition at 25500 cm^{-1} and the pattern of bands centered at 13800 cm^{-1}, showing a vibronic progression of 1250 cm^{-1}, are well known to characterize the spectra of these radical species.[29,30] The original spectrum was obtained by adding a drop of perchloric acid, thus demonstrating the reversibility of the process.

Definitive support to this hypothesis is given by the room-temperature EPR spectrum of the alkaline solution (Fig. 2) showing a signal centered around g = 2.00 with a hyperfine structure which we attributed to the coupling of each electronic spin with the two protons in the *ortho*-positions. The spectrum
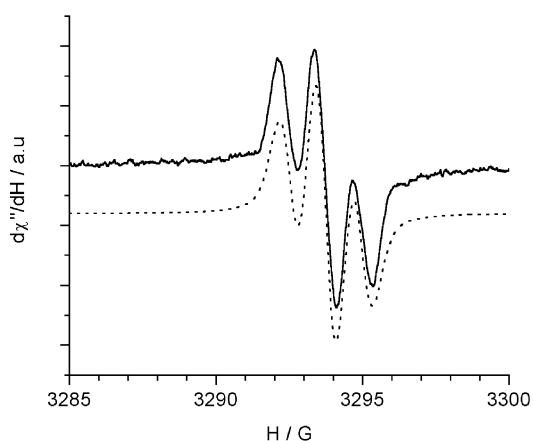
Fig. 2 EPR spectrum of a fluid solution of (SQ–SQ)$^{2-}$ ligand with the best simulated spectrum (dotted line) obtained with parameters reported in the text.

was satisfactorily simulated [31] by using $g = 2.004 \pm 0.001$, $A_{iso}(^1H)$ = 1.2 G and a bandwidth of 0.8 G. The observed value of the coupling with protons, indicating a non-negligible spin delocalization on the dioxolene ring, is in agreement with previous observation on other semiquinone radicals.[32]

The nature of the linker which does not allow spin delocalization between the two moieties is confirmed in the EPR spectrum which does not show any sign of interaction between the two spins on the two radicals, even on cooling. Indeed, at low temperature the hyperfine structure of the spectrum is obviously lost due to freezing of the solution and a single $g = 2.004 \pm 0.001$ line, with a bandwidth of 13 G due to intermolecular dipolar interactions is observed, but no half-field transition was detected. Finally, on the addition of a drop of concentrated acid the mixed valence species Q–CatH$_2$ is reformed and the EPR spectrum accordingly disappears.

The observed result could be anticipated by considering that – as it is well known – simple catecholate CatH$_2$ may coexist with their parent quinone Q both in the solid state and in a diluted state in solution, often yielding donor–acceptor adducts.[33] Furthermore it is also well known that when the catecholate is deprotonated the two species often react yielding semiquinonato as a result of the comproportionation reaction:

$$Cat^{2-} + Q \rightleftharpoons 2SQ^- \qquad (4)$$
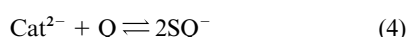
The peculiarity of the present system is then due to the fact that the same molecule contains the two dioxolenes in different oxidation state and therefore the electron transfer reaction may occur by a formally intramolecular mechanism. Since the reactant counterparts are diamagnetic and the product ones paramagnetic, the system is characterised by pH dependent magnetic properties. As expected, the SQ–SQ^{2-} species is characterised by an electronic relaxation time which allows its detection by EPR spectroscopy. This opens the possibility of their application as NMR pH-controlled relaxation probes.[34]

Semiquinonato metal complexes of formula M^{III}(CTH)-(SQ–CatH$_2$)(PF$_6$)$_2$ (M^{III} = Co, Cr) were obtained by oxidative addition of Q–CatH$_2$ with solutions containing stoichiometric amounts of M(CTH)$^{2+}$ cations. The properties of these complexes are strikingly similar to those already observed for the [M(CTH)(SQ)]Y$_2$ (SQ = semiquinonato form of 3,5-di-*tert*-butylcatechol, tetrachlorocatechol, 9,10-dihydroxyphenanthrene) complexes formed by the same acceptors.[25,26,35] Indeed magnetic measurements at room temperature showed that the Co(CTH)(SQ–CatH$_2$)(PF$_6$)$_2$ is characterized by a doublet ground state ($\chi T = 0.38$ emu mol^{-1} K) as expected for a 1 : 1 cobalt(III)–semiquinonato adduct, whereas the chromium derivative is a triplet ground state ($\chi T = 0.99$ emu mol^{-1} K), in agreement with the antiferromagnetic interaction occurring

between the d^3 chromium(III) ion ($S = 3/2$) and a radical *o*-semiquinonato ligand ($S = 1/2$).[24,36] While the electronic spectra of these complexes are fully consistent with this suggestion (see below), their most interesting feature is the strong dependence of their charge distribution on the pH, a behaviour which follows from the properties of the ligand Q–CatH$_2$.

The EPR spectra at room temperature of the cobalt derivative shows the typical pattern arising from the hyperfine interaction of the electron spin of the radical with the $I = 7/2$ nuclear spin of Co, as usually observed in the spectra of cobalt(III)–semiquinonato complexes (Fig. 3). The line–line separation indicate an hyperfine coupling of about 9.5 G in agreement with the degree of spin delocalization from the radical to Co nucleus usually observed in Co–semiquinonato complexes.[25] The peculiar shape of the observed lines is due to the incomplete averaging of the hyperfine interaction caused by the slow tumbling of the molecules compared with the microwave frequency. This phenomenon is common for solution EPR study and can be modelled by assuming a polynomial dependence of the bandwidth on the M_I level involved in the transition: $\Delta H_{pp} = a + bm_I + cm_I^2$.[37] The best simulated spectrum [31] was obtained by using $g = 2.001 \pm 0.001$, $A(^{59}Co) = 9.35$ G and bandwidth parameters $a = 2.7$ G, $b = 0.04$ G, $c = 0.045$ G.

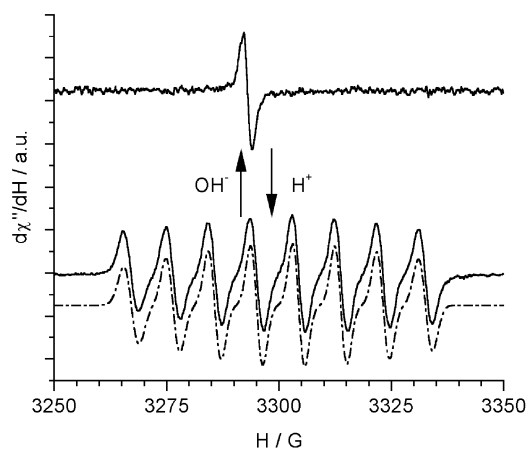**Fig. 3** EPR spectra of a fluid solution of Co(SQ–Cat) (lower) and Co(Cat–Sq) (upper), evidencing the pH-controlled intramolecular electron transfer process. The dashed line is the best simulation for the Co(SQ–Cat) charge distribution obtained with the parameters reported in the text.

Upon the addition of a stoichiometric amount of NMe$_4$OH the hyperfine splitting vanishes and a single signal at $g = 2.0048$ is then observed (Fig. 3, upper) with an isotropic bandwidth of about 2 G. The original splitting is restored by the addition of a drop of concentrated perchloric acid. This behaviour is consistent with the existence of an equilibrium:

$$Co(CTH)(SQ–CatH_2)^{2+} \rightleftharpoons Co(CTH)(Cat–SQ) + 2H^+ \quad (5)$$
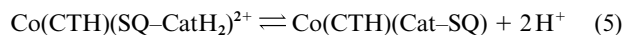
which involves the change of the oxidation number of the coordinated dioxolene upon deprotonation. Thus the delocalization of radical spin on Co nucleus, identified by the hyperfine splitting of EPR spectrum, is observed when the solution is acidic, while it is not when the solution is made basic. This result suggests that in this compound the bis-dioxolene ligand behaves as a class I mixed valence system with no delocalisation between the two dioxolenes.

The electronic spectra of acidic and basic solutions well support this hypothesis. The spectrum of an acetonitrile solution of the complex (Fig. 4, continuous line) shows transitions at 12000, 17700 and 25000 cm^{-1} with shoulders at 19600 and 26100 cm^{-1}. The observed pattern of bands is strikingly similar to that observed for simple Co(CTH)(SQ)$^{2+}$ chromophores.[25] In
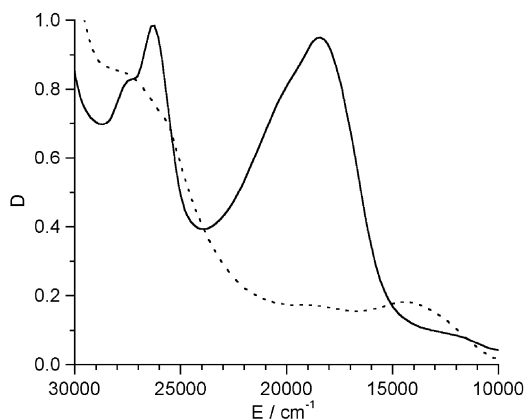
Fig. 4 Electronic spectra of acetonitrile solutions of Co(CTH)(SQ–CatH₂) (continuous line) and Co(CTH)(Cat–SQ) (dotted line) obtained in acidic and basic solutions, respectively. Assignments are discussed in the text.
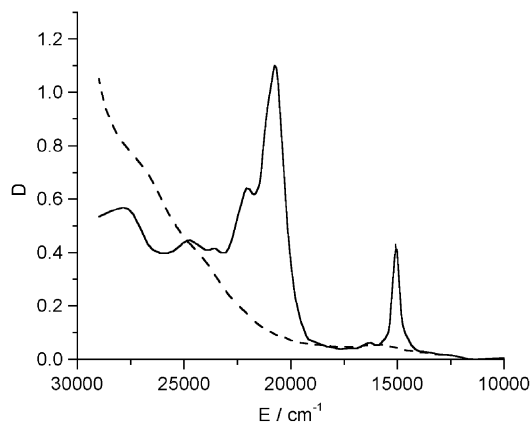

Fig. 5 Electronic spectra of acetonitrile solutions of Cr(CTH)(SQ–CatH₂) (continuous line) and of Cr(CTH)(Cat–SQ) (dashed line) obtained in acid and basic solutions, respectively. Assignments are discussed in the text.

particular, the pattern of bands centered at 12000 cm^{-1} can be attributed to the n$\longrightarrow\pi$* of the coordinated semiquinonate ligand, whereas the transition at 25000 cm^{-1} can be assigned to the first allowed ligand centered π–π* transition. This is a well established assignment for such bands, which are invariably detected in all the 3d-semiquinonato complexes formerly investigated in this Laboratory. In the same way, comparison with the previously investigated cobalt(III)–semiquinonato chromophores helps in assigning the absorption occurring at 17700 cm^{-1} as due to the overlap of the d–d metal transition with a metal-to-ligand charge transfer transition.[25]

When the solution is made alkaline under inert atmosphere, a different electronic spectrum is obtained and bands at 14600, 18400 and 24800 cm^{-1} with a shoulder at 26200 cm^{-1} are observed. This pattern of bands is consistent with the existence of both a cobalt(III)–catecholato chromophore and a non-coordinated semiquinonato ligand. Indeed the strong MLCT transition disappears (Fig. 4, dotted line) and the weak band at 18400 cm^{-1} can be assigned to the metal centered d–d transition. In addition to this transition the cobalt(III)–catecholato chromophores are usually characterised by the presence of two weak LMCT symmetry forbidden (π*$\longrightarrow\sigma$*) transitions in the red and violet regions of the spectrum.[25] These bands are expected to overlap with the above mentioned internal n–π* and π–π* semiquinonate transitions, thus yielding the observed pattern of bands in the expected ranges of the electronic spectrum. As observed for the EPR spectra, the original electronic spectrum is restored upon the addition of a drop of concentrated acid.

A similar behaviour is shown by the chromium derivative. The electronic spectra of acetonitrile solutions of the Cr(CTH)(SQ–CatH₂)(PF₆)₂ show the typical pattern of bands observed for the Cr(tetraaza)(SQ)²⁺ chromophores.[24,36] (Fig. 5) Indeed the features of the band occurring at 14650 cm^{-1} remove any ambiguity about being assigned to the strongly forbidden ^{4}A $\longrightarrow$ ^{2}E transition of the metal ion made allowed due to the antiferromagnetic interaction with the coordinated radical ligand. The assignments of the other transitions follow the DFT investigation recently made by McCusker and coworkers.[38] When the solution is made alkaline under inert atmosphere this pattern of bands disappears and the resulting spectrum is consistent with the presence of the Cr(CTH)(Cat–SQ)²⁺ chromophore, although the overlap of charge transfer bands in the violet and ultraviolet regions does not provide a clear evidence of the nature of the chromophore as previously observed for the cobalt analogue. At any rate we feel that the absorptions at 13000 cm^{-1} (n–π* transitions of the ligand) and at 16000 cm^{-1} (d–d transitions of chromium(III) ion in pseudo-octahedral geometry) can be considered as a sufficient support to our hypothesis.

There is an interesting point concerning the magnetic properties of the two different charge distributions of this complex. According to the class I character of the mixed-valence Cat–SQ species, it can be reasonably expected that in Cr(CTH)-(Cat–SQ)²⁺ the two magnetic centers, *i.e.* the metal ion and the radical ligand, are only weakly interacting. Therefore the magnetic moment at room temperature of the Cr(CTH)(Cat–SQ) complex can be expected to be simply the sum of the two independent contributions of the chromium ion and the radical ligand. The resulting χT is then expected to be of the order of 2.25 emu mol^{-1} K, *i.e.* the sum of the spin-only contributions of 1.875 emu mol^{-1} K for the S = 3/2 metal ion and 0.375 emu mol^{-1} K for the S = 1/2 radical ligand. On the other hand we have shown above that the Cr(CTH)(SQ–CatH₂)²⁺ is a triplet ground state due to the strong antiferromagnetic coupling between the chromium ion and the semiquinonato radical: the change in charge distribution upon deprotonation is then expected to be evidenced by a change of χT from 0.99 emu mol^{-1} K (for the Cr(CTH)(SQ–CatH₂)²⁺ species) to 2.25 emu mol^{-1} K (for the Cr(CTH)(Cat–SQ) species). In this sense the system behaves as a pH-controlled spin crossover system, if we may use a broad definition of spin crossover. Unfortunately the high reactivity towards dioxygen of Cr(CTH)(SQ–CatH₂)-(PF₆)₂ complex once deprotonated does not allow its easy isolation in the solid state. Indeed its alkaline green solution, when exposed to the air, turns yellow in a few seconds and therefore the isolation of the Cr(CTH)(Cat–SQ) species was not attempted.

As discussed above for the CatH₂–Q free ligand, the observed results for the metal complexes are not unexpected. Indeed they are simply due to the different stabilization of the dioxolene ligands upon coordination and protonation and the observed experimental behaviours might easily be anticipated on the basis of the eletrochemical properties of the catecholato ligands in the different chemical situations, *i.e.* protonated or not protonated, coordinated or free ligand. Again we stress that the novelty of the observed results follows the consideration of a system containing two dioxolene ligands whose chemical properties can be controlled in a separate way.

Conclusions

These data show that 3,3,3′,3′-tetramethyl-5,6,5′,6′-tetrahydroxy-1,1′-spiro-bis(indane) undergoes a formally intramolecular electron transfer which is controlled by pH. The existence of the two oxidation states within the Q–CatH₂ molecule can be seen as due to the interaction of one dioxolene moiety with protons, which stabilizes its lower oxidation state. When the protons are removed a redox comproportiation

reaction occurs, the two dioxolenes reaching the same oxidation state. It is important to stress that the above equilibrium involves a reactant and a product with different magnetic properties. In this sense it is then possible to attribute to this compound a formal pH-triggered bistability. We also showed that pH controlled bistability between two charge distributions with different magnetic properties is clearly observed in cobalt(III) and chromium(III) complexes of the ligand.

It is finally worth considering that, until now, chemists have focused mainly their attention on systems whose mixed valence character is determined by metal ions in formally different oxidation states. The few mixed valence bis-bidentate ligands to date investigated have been considered attractive only on the basis of their of electronic delocalization properties and as a consequence class I mixed valence ligands, to our knowledge, have never been considered. The results we obtained show that their chemistry can be rich of interesting perspectives and even have potential application in medical and biological sciences.

Acknowledgements

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