Quinonoid Metal Complexes: Toward Molecular Switches

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ABSTRACT

The peculiar redox-active character of quinonoid metal complexes makes them extremely appealing to design materials of potential technological interest. We show here how the tuning of the properties of these systems can be pursued by using appropriate molecular synthetic techniques. In particular, we focus our attention on metal polyoxolene complexes exhibiting intramolecular electron transfer processes involving either the ligand and the metal ion or the two dioxolene moieties of a properly designed ligand thus inducing electronic bistability. The transition between the two metastable electronic states can be induced by different external stimuli such as temperature, pressure, light, or pH suggesting the use of these systems for molecular switches.

Introduction

Molecular systems are more and more associated with the development of new classes of functional materials, suffice it to mention organic conductors, molecular materials for optoelectronics, and molecular magnets.[1-3] In some cases, the materials are reaching the market, and there are strong expectations that the materials of this century will be characterized by the diffusion of molecular techniques. The reason for this interest is associated with the possibility of fine-tuning the properties of the materials using molecular synthesis and exploiting "chemical ingenuity" for obtaining new types of physical properties.

Another important point is the possibility of using molecular systems as ideal testing grounds for the observation of sophisticated physical properties. The recent observation of quantum tunneling of the magnetization in single molecule magnets is a clear illustration of this point.[4] In the framework of the design of new classes of materials of possible technological interest, particular attention is devoted to molecules that may show interplay between charge mobility and magnetic properties. In fact, these molecules can be considered as the analogues of spintronic devices and may afford new tools for understanding the mechanism of charge transfer in the presence of magnetic fields.

The possibility of inducing a reversible change in the electronic distribution of a molecular system by varying an appropriate external parameter, T, P, $h\nu$, etc., paves the way for information storage at the molecular level.[3,5-7] The type of application depends on the mechanism by which the interconversion between the two different states occurs.[8] If the transition occurs irreversibly, that is, with a hysteresis curve, the system can be in one state or the other depending on the history of the sample, allowing information storage.[4,9,10]

The above requirements are met in systems characterized by quasi-degenerate ground states such as spin-

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Andrea Dei has been Associate Professor in Inorganic Chemistry at the University of Florence since 1981. His current research interests are focused on synthesis of new metal dioxolene complexes acting as potential building blocks for molecular-based magnetic materials, as electronic bistable molecules, or both.

Dante Gatteschi has been Professor of Inorganic Chemistry at the University of Florence since 1980. His inital research interests have been in the investigation of coordination compounds using several different techniques and in particular EPR spectroscopy. Since the 1980s, he has focused on molecular magnetism where he contributed to the development of metal radical approaches to molecular magnets and of the field of single-molecule magnets, that is, molecules of which the magnetization relaxes slowly at low temperature, behaving as nanomagnets.

Claudio Sangregorio obtained the PhD in Material Science in 1997 at the University of Florence under the supervision of D. Gatteschi. At present, he has a position as researcher in the same institution. His research interests are in the field of nanosized magnetic materials, ranging from metal or metal oxide based nanocomposites to high-spin molecular clusters.

Lorenzo Sorace got his Ph. D. in Chemistry in 2001 at the University of Florence with a thesis on magnetism and magnetic anisotropy of spin clusters under the supervision of D. Gatteschi. He is mainly interested in the use of EPR for the analysis of the properties of molecular magnets.
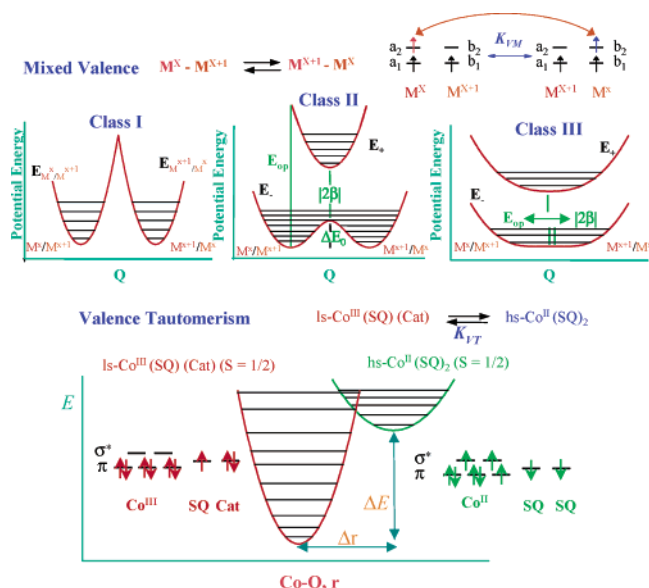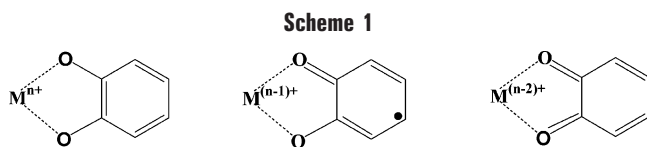
FIGURE 1. Schematic representation of energy diagrams vs reaction coordinates of the three classes of mixed valence systems (top) and of cobalt valence tautomers (bottom).

Scheme 1

crossover,[7,9,10] valence tautomers,[11−13] and mixed valence species.[14,15] All of them can in principle be used as molecular switches.

Traditionally, mixed valence species contain at least two identical metal ions in different oxidation states. Following Robin and Day,[16] they are in turn classified as class I, II, or III according to the degree of electronic delocalization. Valence trapping characterizes class I behavior, whereas in class III derivatives, the two metal ions are undistinguishable as a consequence of complete electronic delocalization. For switching purposes, class II mixed valence systems are the most appropriate. Indeed in these molecules, the electron transfer involving two distinguishable sites may occur following thermal or photochemical activation. A scheme of the three classes is shown in Figure 1 (top) where the electron transfer involves electronic states with the same energy. The same considerations hold when the free energies of these states are different from each other (Figure 1, bottom).

By extension, mixed valence species can be obtained also in systems that contain organic moieties that are stable in different oxidation states. *o*-dioxolenes can bind to metal ions in three different redox states, corresponding to catecholate (Cat), semiquinone (SQ), and quinone (Q), Scheme 1. The low covalent character of their bond to the metal ion in general gives rise to a well-defined charge distribution.[17] In fact, the metal dioxolene complex can often unambiguously be described—on the basis of its structural, magnetic, and spectroscopic features—as one of the isomeric species $[M^{n+}-Cat^{2-}]^{(n-2)+}$, $[M^{(n-1)+}-SQ^{-}]^{(n-2)+}$, or $[M^{(n-2)+}-Q]^{(n-2)+}$. If at least two

quinonoid moieties are present in one complex, mixed valence species based on organic moieties can be obtained.

Switchable molecules can be obtained also in the case of one quinonoid molecule bound to the metal ion provided pairs of isomers have comparable energies, as indicated above. These systems have been called valence tautomers,[18] the interconversion involving an intramolecular electron transfer. They may be in equilibrium with each other, and the temperature at which the two species are present in equal amounts is defined as the critical temperature, T_c. Since the two forms have different bond lengths in the solid state,[17]cooperative effects can be observed at variable temperatures, pressures, or both. Valence tautomers showing detectable hysteresis are scarce. A very small hysteresis effect (5 K) was found to characterize the tautomeric interconversion of the $Co^{III}(Phen)(DBCat)(DBSQ)\cdot C_6H_5CH_3$ complex to the $Co^{II}(DBSQ)_2\cdot C_6H_5CH_3$ species (Phen = 1,10-phenanthroline, DBCat, DBSQ = catecholato and semiquinonato form of 3,5-di-*tert*-butyl-*o*-benzoquinone).[19] The large 230 K effect observed for the $Co(py_2O)(DBCat)(DBSQ)$ cannot be attributed to lattice effects, but to the peculiar properties of the ancillary py_2O ligand.[20]
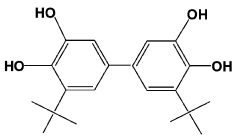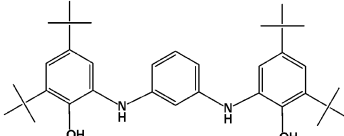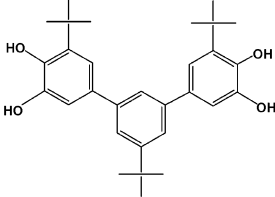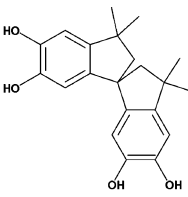
Several examples of mixed valence quinonoid complexes have been reported in the literature, though their technological potentialities have never been considered in detail.[17,21−23] To increase the possibility of charge delocalization within the ligands, symmetrical bis-*o*-dioxolene compounds, either directly linked to each other or connected through an organic spacer, have been investigated. These ligands were designed in such a way that they may act as bis-bidentate toward two different metal ions. According to their electronic features, mixed valence complexes belonging to the three aforementioned Robin and Day classes may be obtained.
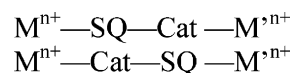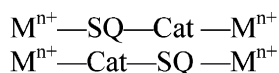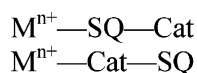
In addition, these systems provide a further opportunity of investigation. An important point, which we have omitted so far, is that semiquinones are magnetic, and therefore these systems can be used also to develop new classes of molecular-based magnets.[24−29] Further they allow us to investigate the interplay of intramolecular charge transfer and magnetic properties. In this Account, we will focus on two classes of metal quinonoid systems, namely, mixed valence and valence tautomeric species, trying to show how these molecules offer exciting perspectives for developing new classes of materials.

Mixed-Valence Quinonoid Metal Complexes

Mixed-valence quinonoid metal complexes contain at least two dioxolene moieties in different oxidation states. The two dioxolenes may be coordinated to the same metal ion or may belong in the simplest case to a bis-dioxolene ligand. The mixed-valence behavior of the former family of metal complexes has been discussed in the past.[17,30,31] Here we focus the discussion on the latter class of compounds. The bis-dioxolene ligands that we have considered are shown in Table 1.

Table 1. Free Energies Changes (V) for the Comproportionation Reaction $M_2(CTH)_2(SQ-SQ)^{4+}$ + $M_2(CTH)_2(Cat-Cat)^{2+} \rightarrow 2M_2(CTH)_2(SQ-Cat)^{3+}$ (M = Cr(III), Co(III) for Ligands 1−4[28,33,44]

	(1)	(2)	(3)	(4)
ΔE (V)	0.5	0.23	0.10	0.14

Scheme 2

$$M^{n+}-SQ-Cat \qquad M^{n+}-SQ-Cat-M^{n+} \qquad M^{n+}-SQ-Cat-M'^{n+}$$
$$M^{n+}-Cat-SQ \qquad M^{n+}-Cat-SQ-M^{n+} \qquad M^{n+}-Cat-SQ-M'^{n+}$$

The oxidation of a deprotonated bis-catecholate tetranegative anion affords four different products thus giving rise to the following redox chain:

$$[Cat-Cat]^{4-} \rightarrow [SQ-Cat]^{3-} \rightarrow [SQ-SQ]^{2-} \rightarrow$$
$$[Q-SQ]^- \rightarrow Q-Q$$
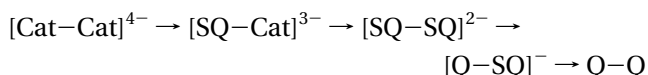
The trinegative $[SQ-Cat]^{3-}$ and mononegative $[Q-SQ]^-$ species of the above redox chain are obviously always paramagnetic radicals ($S = \frac{1}{2}$), which can also be considered mixed valence systems. As a general paradigm the class I, II, or III behaviors of these bis-dioxolene radical ligands is related to the possibility of electronic conjugation. Thus the attention must be focused to the nature of the spacer and to the dihedral angle between the dioxolene planes.[21−23,32−34] Due to the poor donor properties of the quinone ligand, only the metal complexes formed by the $SQ-Cat^{3-}$ bis-dioxolene were considered in our work.

There are several different possibilities of isolating mixed valence metal bis-quinononid species, as sketched in Scheme 2, which can in principle act as switchable molecules. Below we report examples of various classes.

The possibility of isolating a mixed valence species $ML(SQ-Cat)ML^{n+}$ (L = ancillary ligand), where the bis-dioxolene acts as bis-bidentate bridging ligand toward two identical metal acceptors, is associated with the ΔG change of the equilibrium

$$ML(Cat-Cat)ML^{(n-1)+} + ML(SQ-SQ)ML^{(n+1)+} \rightleftarrows$$
$$2ML(SQ-Cat)ML^{n+}$$
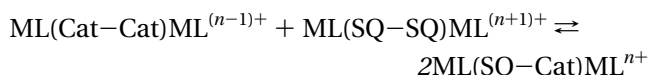
defined by the difference of the redox potentials of the $SQ-Cat/Cat-Cat$ and $SQ-SQ/SQ-Cat$ couples of the coordinated bridging ligand. This quantity is sufficiently large for metal complexes formed by ligands **1** and **2** but not for **3** and **4**. In the latter cases, the comproportionation constants are too small (about 30 and 200 for **3** and **4**, respectively), and it is rather difficult to obtain pure solids containing only the mixed valence species. However, as we shall discuss below, sufficiently pure complexes were obtained using ligand **4**.

The bis-5,5′-*tert*-butyl-3,3′,4,4′-tetrahydroxybiphenyl ligand **1** contains two dioxolenes directly linked by a C−C bond. The electronic coupling between the two redox active dioxolene moieties of the mixed valence $SQ-Cat^{3-}$ form is expected to be strongly dependent on the dihedral angle between the aromatic planes.[21−23,32−34] Indeed, a class II character is expected for a dihedral angle close to 90°, whereas complete π conjugation and then a class III behavior are expected for a dihedral angle far from this value. Metal complexes of formula $M_2(CTH)_2$-$(SQ-Cat)(PF_6)_3$ containing the $SQ-Cat^{3-}$ as bridging ligand were obtained as chromium(III) and cobalt(III) derivatives using the tetraazamacrocycle CTH as ancillary ligand (CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).[35] These complexes were postulated to contain dinuclear cations in which the metal ions are coordinated to one dioxolene and the remaining coordination sites are occupied by the macrocyclic ligand that assumes a folded conformation.

A key evidence for these conclusions came from the EPR spectrum of the cobalt complex in fluid solution, consisting of 17 equally spaced lines (Figure 2a). This feature was attributed to the hyperfine coupling of the completely delocalized unpaired electron of the bridging ligand with two equivalent metal ions and with two equivalent ${}^1H$ nuclei. Indeed the observed metal ion hyperfine coupling (4.2 G) is about half of those observed for mononuclear cobalt−semiquinonato complexes (8−10 G). The EPR spectra and magnetic properties of the Cr(III) derivative, as well as DFT calculation, were found to be consistent with those of a well-isolated sextet electronic ground state, which arises from the strong antiferromagnetic coupling ($500 < J < 800$ cm^{-1}) of the two $S = \frac{3}{2}$ chromium ions with the $S = \frac{1}{2}$ paramagnetic ligand.

The electronic spectra of the two complexes are rather similar to each other and apparently are dominated by the internal transitions of the ligand (internal $\pi \rightarrow \pi^*$ SOMO) (Figure 2b). In terms of the usual mixed valence approach, the pattern of bands appearing in the infrared region could be tentatively assigned to an intramolecular
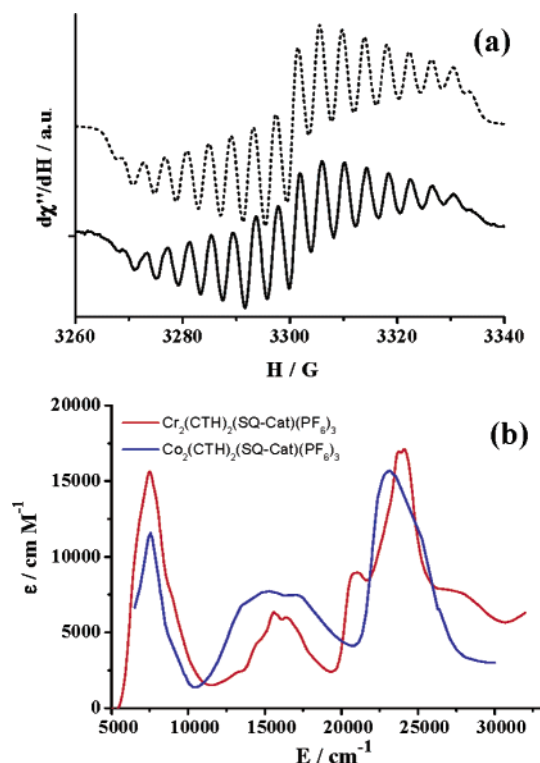
FIGURE 2. (a) EPR fluid solution of Co(III) derivative of ligand **1** together with best simulation spectrum (dotted line); (b) electronic spectra of Cr(III) and Co(III) derivatives of ligand **1**.

FIGURE 3. Spectroelectrochemical reductive progression of a dichloromethane solution containing the $[Ru_2(bpy)_4(SQ-Cat)]^+$ species. In the inset, the differences between the -0.70 V spectrum and all the other spectra are shown.

ligand-to-ligand charge-transfer band. The absorption occurring at about 7000 cm^{-1} in the spectra of the two derivatives shows a moderate solvatochromism (seven solvents used), the maximum shift of about 250 cm^{-1} being observed on passing from dichloroethane to dimethyl sulfoxide. The assignment of intramolecular dioxolene-to-dioxolene charge-transfer character to this transition, coupled with the EPR evidences, suggests a class III character of the radical ligand. Indeed DFT calculations on the trinegative SQ−Cat ligand as well its cobalt derivative support the hypothesis of a fully symmetrical delocalized description.

A different situation is found in complexes of *N,N'*-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,3-phenylenediamine ligand **2**. With bis(bipyridyl)ruthenium(II) as acceptor, the complex $[Ru_2(bpy)_4(SQ-SQ)](PF_6)_2$ was synthesized.[36] Magnetic and EPR measurements suggest that this compound contains the bis(iminosemiquinonato) form of **2** bridging the two ruthenium metal acceptors. The diradical ligand is characterized by a triplet ground state as a consequence of the ferromagnetic interaction between the two iminosemiquinonato moieties (*J* ca. −80 cm^{-1}). Though this result follows the expectations,[37−40] it should be mentioned that in the Co$^{III}_2$(SQ−SQ)$_3$ complex formed by the same ligand, we have recently observed an antiferromagnetic interaction.[41] The analysis of the X-ray structure suggested that this behavior is induced by the large dihedral angles between the two iminodioxolene planes. Indeed the observed values (ca. 70° and 85°) are significantly different from those expected for the free
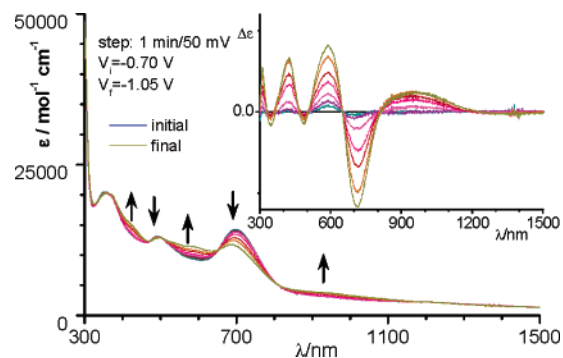
ligand (ca. 15−20°) as the result of the steric constraints imposed by the coordination to the metal centers.

As shown in Table 1, the difference in the redox potentials of the SQ−Cat/Cat−Cat and SQ−SQ/SQ−Cat couples of the coordinated ligand **2** (0.23 V) shows that it is possible to obtain solutions containing the mixed valence $[Ru_2(bpy)_4(SQ-Cat)]^+$ species without significant amount of side products. The spectroelectrochemical reductive progression (Figure 3) evidences the existence of several isosbestic points thus indicating the occurrence of an equilibrium involving only two chromophores. The observed spectra, which do not show intervalence bands, may be related to those of simple monoimino−semiquinonato and catecholato of the corresponding mononuclear ruthenium derivatives.[21,42,43] These results therefore suggest the attribution of a class II character to the coordinated bridging ligand as a result of the low electronic delocalization within the ligand. Again it is believed that the dihedral angle between the two dioxolene ligands plays a determining role, since a class III behavior is expected if the molecule adopted a planar conformation.

As we mentioned previously, the thermodynamic properties of the mixed valence species of the ligand **3** preclude isolation of ML(SQ−Cat)ML^{n+} complexes without significant presence of the bis-cathecholate and bis-semiquinonato species. However the ferromagnetic interactions characterizing the latter derivatives are weaker than expected on the basis of the topology of the biradical, the exchange coupling constant *J* being ca. 30−35 cm^{-1}.[28] This behavior was again attributed to the variation of the coupling induced by the torsion between the two dioxolene planes, which is expected to strongly reduce the conjugation of the system. Following these results, we concluded that, provided that no significant structural changes occur on reduction, the mixed valence complexes of **3** are expected to show a class II behavior and could then be appealing for switching purposes.

The magnetic characterization of the bis-semiquinonato M$^{III}_2$(CTH)$_2$(SQ−SQ)(PF$_6$)$_4$ derivatives (M = Co, Cr) obtained by using the bis-dioxolene 3,3,3′,3′-tetramethyl-5,6,5′,6′-tetrahydroxy-1,1′-spiro-bis(indane) (CatH$_2$−CatH$_2$) **(4)** as bridging ligand shows that the two radical moieties experience a very weak antiferromagnetic interaction.[44] A
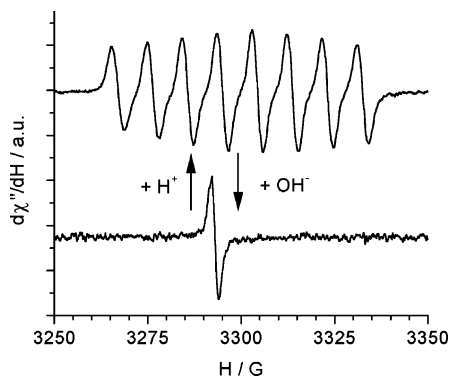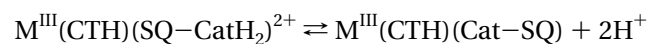
FIGURE 4. EPR spectra of a fluid acetonitrile solution of Co(SQ−CatH$_2$) (upper) and Co(Cat−SQ) derivatives of ligand **4** obtained in acidic and basic conditions, respectively, evidencing the occurrence of a reversible pH-controlled intramolecular electron-transfer process.

FIGURE 5. Electronic spectra of acetonitrile solutions of Cr(CTH)-(SQ−CatH$_2$) (—) and of Cr(Cat−SQ) (− − −) derivatives of ligand **4** obtained in acidic and basic solutions, respectively. The features of the band occurring at 14 650 cm^{-1} for acidic solution were assigned to the strongly forbidden $^4A \rightarrow {}^2E$ transition of the metal ion, allowed by the antiferromagnetic interaction with the coordinated radical ligand. 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(Cat−SQ) chromophore.

class I character can be therefore reasonably suggested for the mixed valence M(CTH)(Cat−SQ)M(CTH)$^{3+}$ complexes, as supported by the EPR spectrum of the cobalt derivative, which shows an eight line spectrum identical to that of Co(CTH)(DBSQ)$^+$ cation.[45] However some aspects of the chemical properties of this ligand deserve consideration. The two-electron oxidation of Cat−CatH$_4$ in acidic solution yields the catecholate−quinone (CatH$_2$−Q) form of the molecule.[46] Electronic and EPR spectra suggest that the mixed valence character of the molecule is removed in alkaline solution, where the deprotonated paramagnetic bis-semiquinonato species is obtained according to the equilibrium

$$Q-CatH_2 + 2OH^- \rightleftharpoons SQ-SQ^{2-}$$

Complexes of formula M(CTH)(SQ−CatH$_2$)(PF$_6$)$_2$ (M = Cr^{III}, Co^{III}, and SQ−CatH$_2$ = semiquinonato form of the CatH$_2$-Q ligand) were prepared by oxidative addition of CatH$_2$−Q to the appropriate M(CTH)$^{2+}$ derivatives.[46] Their physical characterization strongly suggests that these complexes are six-coordinate, with the semiquinonato ligand coordinated to the metal ion. Both EPR and electronic spectra (Figures 4 and 5) provide evidence that when the not-coordinated catecholate moiety is deprotonated in alkaline medium, both the M^{III}(CTH)(SQ−CatH$_2$)$^{2+}$ complexes yield the M^{III}(CTH)(Cat−SQ) species according to the equilibrium

$$M^{III}(CTH)(SQ-CatH_2)^{2+} \rightleftharpoons M^{III}(CTH)(Cat-SQ) + 2H^+$$

Again the process is associated with an intramolecular electron transfer between the two dioxolene ligands. The analysis of the magnetic properties provided additional evidence that the free ligand and its metal complexes show pH-controlled charge distribution. Indeed in the Cr^{III}(CTH)(SQ−CatH$_2$)$^{2+}$ the semiquinonato ligand is coordinated to the metal ion and the electronic ground state of the complex is expected to be a triplet as a result of the antiferromagnetic coupling interaction between the $S = {}^3/_2$ metal ion and the $S = {}^1/_2$ coordinated radical ligand. This interaction is removed in the deprotonated
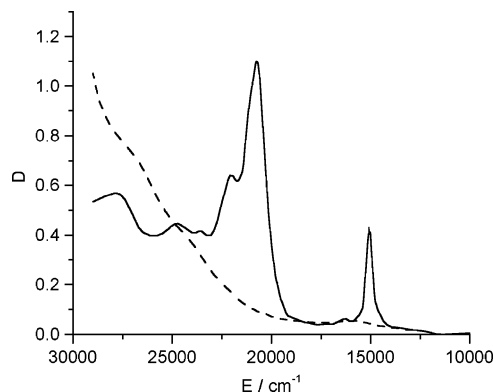
complex, and the magnetic properties of the system are due to the presence of two weakly interacting paramagnetic centers.

In principle, it is possible to design M−SQ−Cat−M′ (M ≠ M′) species that undergo intramolecular electron transfer to yield the isomeric M−Cat−SQ−M′ species. In fact, the potentials of ligand-centered redox processes of the homodinuclear cobalt(III) and chromium(III) M$_2$(CTH)$_2$-(Cat−Cat)$^{2+}$ complexes, containing **4** as bridging ligand, are nearly identical, the difference being less than 20 mV. In principle, the two isomers (a) (CTH)Cr^{III}(SQ−Cat)Co^{III}-(CTH)$^{3+}$ and (b) (CTH)Cr^{III}(Cat−SQ)Co^{III}(CTH)$^{3+}$, which contain the semiquinonato moiety coordinated to Cr^{III} or to Co^{III}, respectively, may coexist. The (a) isomer is expected to be characterized by a triplet ground state (χT(expected) = 1 emu mol^{-1} K), whereas the (b) isomer is expected to show a χT value close to 2.25 emu mol^{-1} K as a result of the presence of uncorrelated $S = {}^3/_2$ and $S = {}^1/_2$ spin centers. Since the spin multiplicities of the two isomers are 3 and 8, respectively, the electronic entropy difference between the two isomers is $\Delta S = k \ln {}^8/_3$. On this basis, if the electron-transfer process between the two dioxolene moieties were allowed, one would expect the relative population of the two isomers to depend on temperature.

The synthesis of a heterodinuclear complex is possible provided that one of the two metal complex moieties experience kinetic inertness toward ligand substitution. In this sense, both the chromium(III) and cobalt(III) complexes are suitable starting materials. The complex of analytical formula [Co^{III}Cr^{III}(CTH)$_2$(SQ−Cat)](PF$_6$)$_3$ was synthesized by using the following procedure.[44] The oxidation of the Cr^{III}(CTH)(SQ−CatH$_2$)$^{2+}$ cation yielded the Cr^{III}(CTH)(SQ−Q)$^{2+}$ species, which was isolated as PF$_6$ salt. The oxidative addition of this quinone species to the Co(CTH)$^{2+}$ complex, followed by the addition of an equimolar amount of the same complex, led to the isolation of a compound of formula [Cr(CTH)(Cat−Cat)-

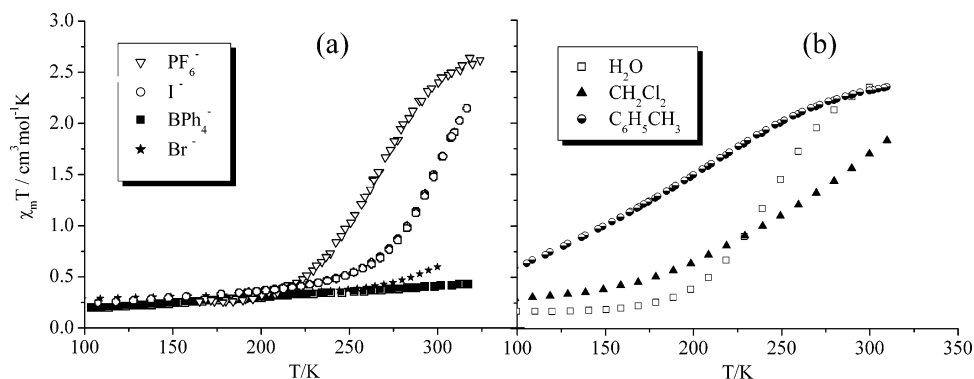**FIGURE 6.** Plot of $\chi_M T$ versus T of (a) Co(CTH)(Phendiox)Y (Y = PF$_6$·H$_2$O, I, BPh$_4$, and Br) and (b) Co(CTH)(Phendiox)PF$_6$·solv (solv = H$_2$O, 1.5CH$_2$Cl$_2$, and C$_6$H$_5$CH$_3$).

Co(CTH)](PF$_6$)$_2$, which was in turn oxidized and isolated as [Co^{III}Cr^{III}(CTH)$_2$(SQ−Cat)](PF$_6$)$_3$ and then purified by column chromatography. Its electronic spectrum and magnetic properties at room temperature—intermediate between those expected for the two charge distributions—supported the presence of both isomers. However the temperature-dependent susceptibility data showed no changes on decreasing temperature, thus indicating the absence of any equilibrium involving the two isomers. This may be attributed to the class I nature of the bridging mixed valence ligand **4**.

Valence Tautomerism in Cobalt−Quinonoid Complexes

The discovery that the Co^{III}(N−N)(Cat)(SQ) complexes may undergo valence tautomeric behavior in solution and then in the solid state has been made several years ago,[18,19] but the design and the development of these molecular systems remain rather difficult, and the majority of the reported investigations follow the chemical track of the first compound.[11−13,17] To produce materials with desired properties, for example, with large hysteresis at room temperature, it is necessary to understand the structure−property relations not only at the molecular but also at the supramolecular level. The latter is still far from being achieved and making molecular materials with desired properties is still much more an art than a science.

To design a complex undergoing valence tautomerism, it is important to remember that the electron-transfer process may occur when the free energies of the interacting counterparts are similar. This means that the redox potentials associated with the Co^{III}/Co^{II} and SQ/Cat couples must be similar. We found that this approach based on electrochemical data can be successful, since it allowed us to synthesize two new families of valence tautomeric cobalt−dioxolene complexes. They are the CoL(Phendiox)Y·solv (L = tetradentate macrocyclic ligand with secondary amine donors, Phendiox = catecholato or semiquinonato form of 9,10-dioxophenanthrene, Y = Br, I, PF$_6$, or BPh$_4$, solv = H$_2$O, 0.5C$_6$H$_5$CH$_3$, or 1.5CH$_2$Cl$_2$)[44,47,48] and the Co$_2$(CTH)$_2$(DHBQ)(PF$_6$)$_3$ (DHBQ = deprotonated form of 2,5-dihydroxy-1,4-benzoquinone).[49] Since the Co^{III}Cat form is essentially diamagnetic and the Co^{II}SQ one paramagnetic, magnetic susceptibility measurements at

various temperatures give unequivocal proof that all the CoL(Phendiox)Y·solv derivatives undergo valence tautomeric equilibria (Figure 6). Indeed, all these systems are diamagnetic at low temperatures, but starting from ca. 150 K, they become paramagnetic, and the χT values increase with increasing temperatures. The transitions can be classified as gradual and are associated with a color change of the samples from yellow at low temperatures to deep brown at high temperatures. The transition is reversible as on cooling the samples the yellow color is restored and no significant hysteresis effects were detected. The analysis of the crystal structures of the Co(CTH)(Phendiox)PF$_6$· 1.5CH$_2$Cl$_2$ at 198 and 295 K, as well as temperature-dependent IR spectra, shows that the transition

$$Co^{III}(CTH)(Phencat)^+ \rightleftarrows Co^{II}(CTH)(PhenSQ)^+$$
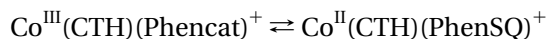
is associated with a lengthening of the bonds. In particular, the Co−O distance is 1.90 Å at low temperature and was estimated as 2.09 Å when the transition is complete.[50] The presence of different counterions deeply influences the value of T_c. The magnetic properties of Co(CTH)-(Phendiox)PF$_6$·H$_2$O additionally show a pressure dependence, T_c increasing as the pressure increases.[47] This result follows the expectations, given the larger volume of the Co^{II}−SQ species with respect to the Co^{III}−Cat one.

The magnetic behavior of these systems also depends on the nature and the presence of solvent molecules in the lattice (Figure 6). Indeed the χT vs T traces of the hydrate and dichloromethane solvates are completely different from each other. This result is well-known and well-documented for all the thermochromic molecular systems so far investigated since in general it is associated with changes of the crystal lattice. However we have recently obtained an unexpected result on replacing the dichloromethane molecules by d_2-dichloromethane.[51] In the latter situation, the complex shows a different magnetic behavior (Figure 7), the transition being more abrupt and showing a significant thermal hysteresis. The transition critical temperatures measured on heating the samples and cooling are $T_{c\uparrow}$ = 244 K and $T_{c\downarrow}$ = 236 K, respectively, values to be compared with the $T_{c\uparrow}$ = 300 K observed for the nondeuterated sample.

This unexpected anomaly was justified on the basis of the X-ray diffractograms of the two complexes, which were
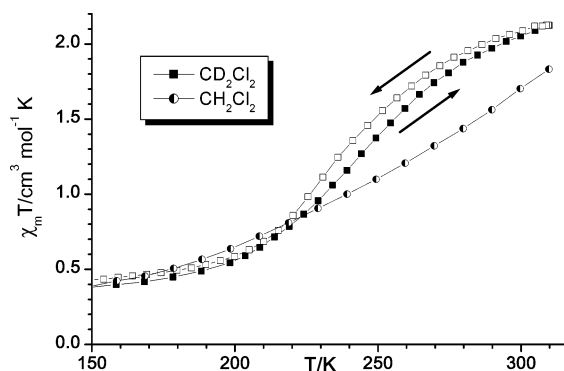
FIGURE 7. Temperature dependence of the $\chi_M T$ product for [Co(CTH)(Phendiox)]PF$_6$·1.5CH$_2$Cl$_2$ and for the CD$_2$Cl$_2$ analogue. For the latter, data collected either on heating (■) or on cooling (□) are shown.

FIGURE 8. Variable-temperature electronic absorption spectra of 1,2-dichlorobenzene solutions of [Co(tpy)(Cat−N−SQ)]PF$_6$ from 294 (A) to 346 K (B). In the inset is shown the temperature dependence of X-band EPR spectra of the same solution.

Scheme 3

found to be different from each other and did not significantly change on decreasing temperature. On the other hand, the X-ray diffractometric analysis and magnetic measurements of single crystals of the deuterated solvate, grown by slow evaporation of deuteriodichloromethane−hexane solutions, showed that the crystal structure and the magnetic properties of the obtained compound were identical to those of the previously reported nondeuterated one. It was therefore concluded that the deuterated solvate may give rise to two crystalline forms, which are characterized by different cooperative effects. Because this polymorphism was not detected for the nondeuterated solvate, it is apparently due to isotopic effects. To our knowledge, this effect has never been observed in molecular systems showing spin transitions and suggests that the energy difference of solvent vibrational modes in the lattice may be a critical factor in determining the cooperativity of the whole.

Attempts were made to use more complex dioxolene ligands, as in [Co^{III}(Cat−N−BQ)(Cat−N−SQ)] and [Co^{III}(tpy)(Cat−N−SQ)]Y (tpy = 2,2′:6′,2″-terpyridine, Cat−N−BQ, Cat−N−SQ = mononegative and radical dinegative Schiff base diquinone ligand (see Scheme 3), Y = PF$_6$, BPh$_4$) of which the proposed charge distributions are supported by structural and spectroscopic data.[52] The temperature-dependent electronic and spectral properties of the solutions of the two compounds suggest the existence of a thermally driven valence tautomeric interconversion Co^{III}(Cat−N−SQ) → Co^{II}(Cat−N−BQ) complex, the divalent metal ion being in high-spin configuration (Figure 8). At room temperature, UV−vis spectra provide evidence of tautomeric equilibrium (but EPR spectra show that the Co^{III}(Cat−N−SQ) species disappears at ca. 200 K). The same interconversion processes were found to occur also in the solid state with a significantly higher T_c value (about 600 K) than in solution. The large difference between the interconversion T_c in the solid state and in solution are suggested to come from the entropy changes associated with the modifications of vibronic interactions.

Another approach to increase the cooperative interactions is to move to polynuclear metal complexes.[49] On this way, the first step is to prepare dinuclear species such as Co$_2$(CTH)$_2$(DHBQ)(PF$_6$)$_3$, which was obtained by one-
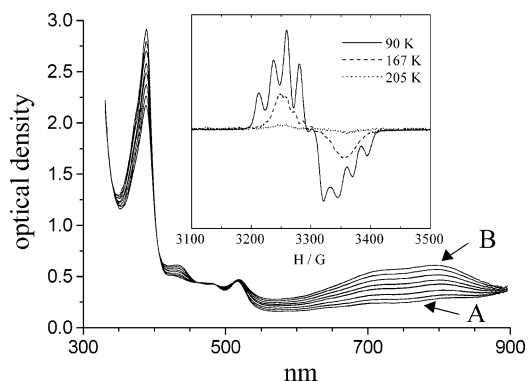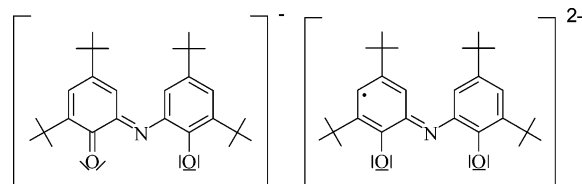
electron chemical oxidation of solutions containing the [hs-Co$^{II}_2$(CTH)$_2$(DHBQ^{2-})]$^{2+}$ cation. The one-electron oxidation of the system was carried on with the aim of increasing the redox potential of the DHBQ^{3-}/DHBQ^{2-} couple. The tripositive cation can be formulated as (i) the [Co^{II}(DHBQ$^-$)Co^{II}] complex if a ligand-centered oxidation process is operative, (ii) the mixed valence [Co^{II}(DHBQ^{2-})Co^{III}] complex if a metal-centered oxidation process occurs, and (iii) the [Co^{III}(DHBQ^{3-})Co^{III}] complex, if the oxidation involves both the metal ions and the reduction of the ligand occurs, as it has been found for the iron analogue.[53]

The electronic and IR spectra and the magnetic susceptibility at room temperature of Co$_2$(CTH)$_2$(DHBQ)(PF$_6$)$_3$ strongly support the formulation of the compound as a mixed valence hs-Co^{II}−Co^{III} derivative (hypothesis ii). However temperature-dependent magnetic susceptibility measurements show that a transition between two different species occurs below 200 K (Figure 9). Its EPR spectrum at 4 K shows a strong signal at $g = 2.00$, thus supporting the existence of a radical ligand at this temperature. The temperature variation of this signal rules out the existence of a spin crossover equilibrium involving the Co^{II} ions and proves that a valence tautomeric interconversion to a [Co^{III}(DHBQ^{3-})Co^{III}]$^{3+}$ species is occurring.

Even more interesting is that this complex was found to undergo to valence tautomerism upon light irradiation. Indeed if light irradiation at 647.1−676.4 nm is applied at low temperature the magnetic moment immediately increases up to $\chi_M T$ of 1.2 cm^3 K mol^{-1} (Figure 9). When the light is switched off and the temperature raised, the $\chi_M T$ product decreases smoothly recovering the value measured before irradiation around 60 K. This behavior shows that the light-induced phenomenon is perfectly reversible. The strong opacity of the sample (dark purple) preventing the penetration of light in bulk, limited the
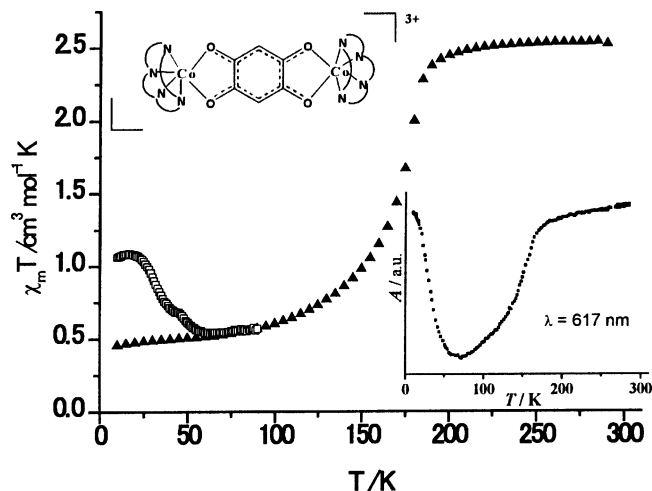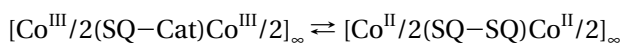
FIGURE 9. Temperature dependence of $\chi_M T$ of complex [{Co(CTH)}$_2$(DHBQ)](PF$_6$)$_3$ measured before (▲) and after (□) irradiation at 647 nm. The temperature dependence of the reflectivity at 617 ± 5 nm is also reported in the bottom right inset. On the top left inset, a schematic view of the cationic part of the complex is shown.

highest photoinduced rate of population to about 40% if we consider that the ls-Co^{III}−(DHBQ^{3-})−ls-Co^{III} → hs-Co^{II}−(DHBQ^{2-})−ls-Co^{III} process occurs. Indeed the investigation of the temperature dependence of the reflectivity signals showed that an almost quantitative interconversion occurs at the surface.

In addition to the potential technological impact of this photoswitchable material, we wish to stress that this result was obtained by successfully tuning the electronic properties of the system by molecular synthesis techniques. This approach opens the possibility of obtaining a series of compounds undergoing valence tautomeric transitions involving species with properly designed electronic ground states. This is related to the dinuclear character of the complex, which contains a tripositive metal ion (diamagnetic in this case, but which can be substituted with paramagnetic ones) acting as ancillary counterpart.

The final step to enhance cooperative effects is that of synthesizing polymeric species. With this in mind, we have synthesized the cobalt-1,10-phenanthroline adduct of the bis-dioxolene ligand **3**, the analytical and spectroscopic properties of which are consistent with the formula [Co-(phen)(SQ−Cat)·CH$_2$Cl$_2$]$_\infty$.[54] This compound was postulated to contain the metal ions with the same donor set of the aforementioned mononuclear Co^{III}(N−N)(Cat)(SQ) complexes,[18,19] the bis-bidentate ligand acting as bridging ligand toward two different metal ions. The temperature-dependent magnetic properties of this compound (Figure 10) are consistent with the presence of a Co^{III}(SQ−Cat) dominant species at low temperatures undergoing a thermally driven valence tautomeric transition to hs-Co^{II}-(SQ−SQ) according to the equilibrium

$$[Co^{III}/2(SQ-Cat)Co^{III}/2]_\infty \rightleftharpoons [Co^{II}/2(SQ-SQ)Co^{II}/2]_\infty$$

The transition can be classified as gradual and at 310 K, the highest temperature we have measured, is far from being complete. Nevertheless the transition is character-
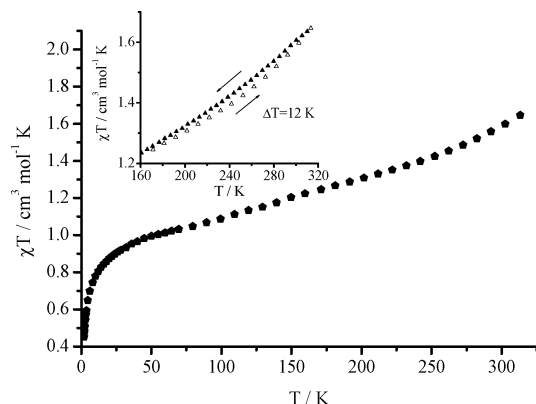

FIGURE 10. Temperature dependence of χT product for the cobalt-1,10-phenanthroline adduct of ligand **3**. The polymeric species undergoes a smooth valence tautomeric interconversion process, which is not complete at 310 K. The inset shows the details of the observed thermal hysteresis.

ized by a thermal hysteresis of about 12 K, thus suggesting that the designed connectivity of the lattice induces the desired cooperative effects.

Concluding Remarks

We have shown that quinonoid metal complexes are potentially very interesting molecular-based materials because they couple charge distribution bistability and magnetic properties. To design materials with tailored properties an understanding of the molecular properties and of the supramolecular organization in suitable lattices is required, and much work is still needed for this scope. We are currently developing synthetic strategies in this direction. Finally these systems offer also exciting properties to be measured on individual molecules with STM and related techniques when properly organized on suitable surfaces.

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