Valence Tautomerism: New Challenges for Electroactive Ligands

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Valence tautomeric complexes combine redox-active ligands and transition metal ions with two or more accessible oxidation states, exhibiting two nearly degenerated electronic states with localized electronic structures. Charge distribution in such electronic isomers has an appreciable sensitivity to the environment so an external perturbation, like photons, temperature and/or pressure, may lead to an intramolecular electron transfer between both redox active units and therefore to a reversible interconversion between the two degenerated electronic states. Moreover, since each electronic isomer exhibits different optical, electronic and/or magnetic properties, these complexes are being proposed as candidates for future use in molecular electronic devices and switches. Most of the valence tautomeric complexes reported thus far are based on quinone or quinone-type ligands with a series of transition metal ions such as Co, Cu, Ni and Mn. Nevertheless, in the last few years, the number of electroactive ligands identified to be active in valence tautomeric complexes is being expanded by including new radical ligands such as polychlorotriphenylmethyl, phenoxyl or tetraphenylporphyrin radicals.

Introduction

Development of molecular-scale systems that exhibit intramolecular electron-transfer phenomena induced by external stimuli has attracted considerable attention.[1] The interest is twofold. First, the possibility of inducing a reversible change in the electronic distribution of a molecular system opens the door to their potential use in information storage and integrated molecular-sized devices. And second, from a theoretical point of view, to study the role of various parameters governing the intramolecular electron transfer (IET) rates. Mixed-valence systems are excellent candidates for such studies since they contain at least two redox sites with different oxidation states linked by a bridge that medi-

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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ates the transfer of electrons from one site to the other.[2] Depending on the strength of the interaction between the redox centers, Robin and Day[3] classified the mixed-valence systems into three main groups. The potential energy curves for the three types of mixed-valence compounds, which represent the systems for any geometry along the nuclear coordinate, are shown in Figure 1.

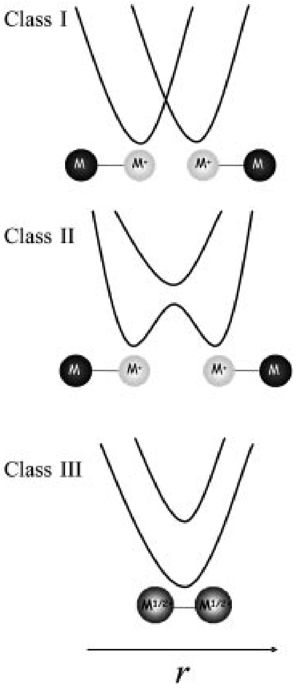


Figure 1. Potential energy curves for mixed-valence systems. The curves are arranged into three main groups according to the Robin and Day classification. In Class I the interaction between the redox centers is negligible; in Class II the interaction between the redox centers is weak or moderate and in Class III the electronic interaction is so intense that the electron is completely delocalized over the molecule.

In the Class I mixed-valence systems the interaction between the redox centers is zero or extremely weak and, therefore, the system only exhibits the properties of the isolated redox units. Even if the molecule acquires sufficient activation energy to reach the intersection region, the probability of electron exchange would be negligible. On the contrary, in Class III mixed-valence systems the electronic interaction is so intense that the electron is completely delocalized over the entire molecule. Then, the properties of each isolated unit are no longer observed and new properties associated with the delocalized species appear. Finally, for Class II systems the interaction between the redox centers is moderate. The electronic interaction has almost no effect on the potential energy curves in the vicinity of the equilibrium geometries but causes mixing in the vicinity of the crossing point. In other words, the electron is vibrationally localized in one of the redox centers due to the presence of an activation energy barrier (ΔG), although such a barrier may be overcome by an external optical or thermal stimulus, to promote an IET process.

The study of molecular mixed-valence class II systems was initiated by Taube's seminal work on compounds such as $[(NH_3)_5Ru\text{-bridge-}Ru(NH_3)_5]^{5+}$. Since then, most of the mixed-valence complexes that have been shown to exhibit intramolecular electron-transfer phenomena are homo- and heteronuclear metallic complexes where the two metal atoms with different oxidation states are connected through an organic bridging ligand.[4] From them, ruthenium complexes and ferrocene moieties have been widely used thanks to their great stability, ease of oxidation and their kinetic inertness.[5] Mixed-valence molecular systems where the electro-active units are pure organic groups have so far received less attention, probably due to their high instability,[6] although for these systems electron transfer could be fine-tuned in a far more precise manner thanks to the flexibility of organic synthesis. The different types of electroactive organic units used thus far are: i) anion radicals derived from conjugated diquinones and diimides,[7] ii) cation radicals derived from bis(tetrathiafulvalenes),[8] iii) cation radicals derived from bis(hydrazines),[9] iv) quinoid groups[10] and v) ion radicals derived from π-conjugated polyarylmethyl/polyarylamines[11] and polychlorotriphenylmethyl radicals.[12] In most of these cases the intramolecular electron transfer is mediated through an organic bridge and only in a few cases does it take place through a bridging metal ion.[13]

Finally, a third type of class II mixed-valence systems is the heterogeneous complexes combining both redox-active ligands and transition metal ions. Some complexes with non-innocent electro-active ligands exhibit a reversible intramolecular electron transfer between the metal ion and the ligand, leading to an internal charge redistribution and therefore to the existence of two different electronic isomers. This family of complexes, termed Valence Tautomeric (VT), is of considerable interest. First, they are unique model systems, which provide insight into the basic factors affecting intramolecular electron transfer in coordination complexes. And second, from an applied perspective, the large changes in the optical, structural, and magnetic properties that often accompany the valence tautomeric interconversion have potential applications in bistable molecular switching materials and devices. In this review, we will first give a brief introduction to the concepts of valence tautomerism, its origin, physical properties and interconversion mechanisms. In a subsequent section, we will make a compendium of the different redox-active ligands used thus far in valence tautomeric complexes, and we will finally mention some new ideas based on the combination of valence tautomeric equilibrium with additional redox reactions involved with the redox-active ligand.

Valence Tautomerism

Valence tautomeric metal complexes with at least two redox-active centers, the metal ion and an electro-active ligand, are characterized by the existence of two electronic isomers (valence tautomers) with different charge distributions, and consequently, different optical, electric and magnetic properties. The interconversion between the different electronic isomers is accomplished by a reversible intramolecular electron transfer involving the metal ion and the redox active ligand, analogous with that observed for Prussian blue analogs.[14] A schematic representation of valence tautomerism together with the corresponding potential energy curve plotted as a function of the nuclear coordinate, is shown in Figure 2.

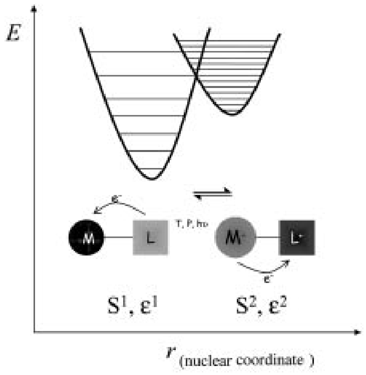


Figure 2. Potential energy curves for a valence tautomeric complex with a schematic representation emphasizing the intramolecular electron transfer between the metal ion and the ligand.

One of the first descriptions of valence tautomerism and an excellent example of the above mentioned charge distribution sensitivity is exhibited by the cobalt bis(quinone) complex $[Co^{III}(3,5\text{-DTBCat})(3,5\text{-DTBSQ})(bpy)]$ (**1**), where 3,5-DTBCat^{2-} and 3,5-DTBSQ^{-} refer, respectively, to the catecholate (Cat^{2-}) and semiquinonate (SQ^{-}) forms of 3,5-di-*tert*-butyl-o-quinone, and bpy is 2,2′-bipyridine.[15] In solution, the equilibrium in Equation (1) can be induced by variations of temperature and monitored by magnetic measurements and spectroscopic techniques such as UV/Vis, NMR and/or EPR spectroscopy.[16]

$$[Co^{III}(3,5\text{-DTBCat})(3,5\text{-DTBSQ})(bpy)]\ (\mathbf{1},\ ls\text{-}Co^{III}) \rightleftharpoons [Co^{II}(3,5\text{-DTBSQ})_2(bpy)]\ (\mathbf{1},\ hs\text{-}Co^{II}) \qquad (1)$$

For instance, a solution of complex **1** in toluene at low temperatures shows a band at 600 nm characteristic of the **1**, *ls*-Co^{III} tautomer. An increase of temperature promotes an intramolecular electron transfer so the **1**, *ls*-Co^{III} converts into the **1**, *hs*-Co^{II} tautomer as one of the ligands is oxidized by one electron from a Cat^{2-} to an SQ^{-} ligand. As a consequence, the intensity of the 600 nm band decreases and a band at 770 nm characteristic of the **1**, *hs*-Co^{II} tautomer increases in intensity (see Figure 3). Accompanying the optical changes, variations in the magnetic response are also observed. The **1**, *ls*-Co^{III} isomer has an $S = 1/2$ ground state whereas the **1**, *hs*-Co^{II} isomer has an $S = 2$ ground state.

This interconversion is an entropy-driven process, analogous with the extensively studied low-spin to high-spin crossover phenomena. The large entropy gain arises from: 1) a gain in electronic entropy due to the higher spin state degeneracy of the *hs*-Co^{II} form and 2) the higher density of vibrational states of the *hs*-Co^{II} form due its longer metal-ligand bond lengths. Thus thermal population of tautomeric states is dictated by the Gibbs free energy expression shown in Equation (2). At low temperatures, $T\Delta S$ is negligible compared to ΔH, and consequently if $\Delta H > kT$ only the *ls*-Co^{III} state is populated. An increase in the temperature will increase the $T\Delta S$ contribution, making it non-negligible and favoring the population of the *hs*-Co^{II} state, up to a critical temperature T_c where $\Delta G = 0$ and $\Delta H = T\Delta S$. A further increase in the temperature will change the sign of ΔG.

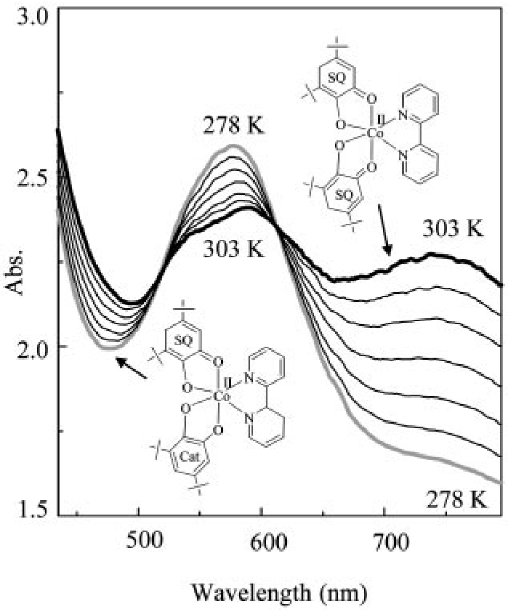


Figure 3. Temperature dependence of the electronic absorption spectrum of a CH_2Cl_2 solution of complex **1**.

$$\Delta G = \Delta G_{hs\text{-}Co^{II}} - \Delta G_{ls\text{-}Co^{III}} = \Delta H - T\Delta S \qquad (2)$$

It is important to emphasize that whereas most of the valence tautomeric complexes reported thus far exhibit a temperature-dependent interconversion in solution, the number of examples exhibiting a valence-tautomeric interconversion in the solid state is rather limited. For this, the presence of solvate molecules within the crystalline network and their effects on the phonon relaxation, play a critical role. For instance, a plot of the magnetic susceptibility vs. temperature for a sample of complex **2** recrystallized from four different solvents is shown in Figure 4. In this figure it is shown that for complex $[Co^{III}(3,5\text{-DTBSQ})(3,5\text{-DTBCAT})(phen)]\cdot C_6H_5CH_3$ (**2**), the tautomeric interconversion between the **2**, *ls*-Co^{III} and **2**, *hs*-Co^{II} isomers can be reversibly driven with temperature and monitored by large changes in the magnetic susceptibilities, with an interconversion that occurs abruptly within a narrow temperature range of ca. 30 °C. On the contrary, a polycrystalline sample recrystallized from ethanol has a μ_{eff} value essentially independent of the temperature and close to the value of 1.7 μ_B expected for the low-spin isomer. For samples recrystallized from acetonitrile and dichloromethane, incomplete transitions were observed (see Figure 4).[17]

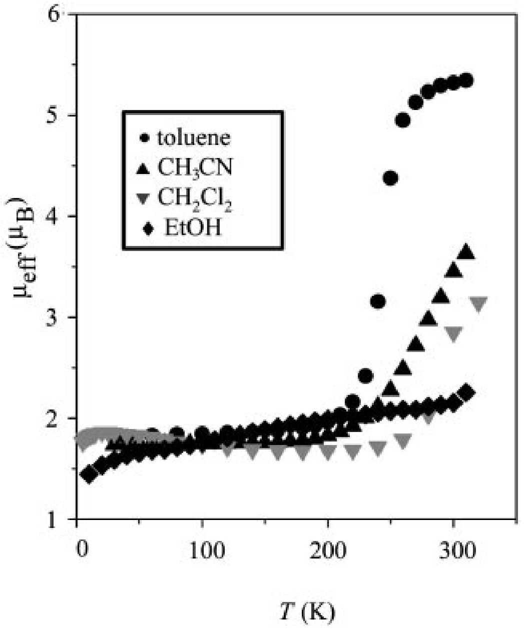


Figure 4. Plots of the effective magnetic moment (μ_{eff}) vs. temperature for complex **2** in different solvents: toluene, acetonitrile, dichloromethane, and ethanol.

Moreover, since valence tautomeric complexes are electronically labile, they exhibit significant vibronic interactions and therefore an appreciable sensitivity to the environment. As a consequence, intramolecular electron transfer can be induced not only by temperature variations but also by irradiation or pressure.

Light-Induced Tautomerism

Adams et al. reported results of the first picosecond time-resolved optical experiments on valence tautomeric complexes in solution.[18] In such work, pulsed laser photolysis, both on the picosecond (90 ps pulse) and the nanosecond (24 ns pulse) time-scales, were carried out for a series of complexes with the general formula $[Co(3,5\text{-DTBSQ})_2\text{-}(N\text{-}N)]$. The authors showed that when the complex is in the *ls*-Co^{III} form, a laser pulse could it excite it to a LMCT excited state. Such excited states experience a rapid intersystem crossing to the *hs*-Co^{II} state with a subsequent electron recombination to finally yield the *ls*-Co^{III} isomer. At room temperature, the rate of *hs*-Co^{II} to *ls*-Co^{III} conversion (k_{bvt}) ranges from 6.1×10^7 to 6.7×10^8 s^{-1} and its temperature dependence follows an Arrhenius-like behavior in the 140–300 K range. However, below 140 K, deviations from linearity are seen, most likely due to the involvement of quantum mechanical tunneling. Valence tautomerism for this family of complexes was also shown to take place in the solid state after illumination at low temperatures.[19] For instance, variations on the μ_{eff} vs. T plot of $[Co^{III}(3,5\text{-DTBSQ})(3,5\text{-DTBCAT})(phen)]\cdot C_6H_5Cl$ (**2**) before and after illumination are shown in Figure 5.[20] Similar interconversion in the solid state has been reported by Dei et al. for the new dinuclear complex $[\{Co(cth)\}_2(dhbq)](PF_6)_3$ (**3**), both by irradiation with a laser connected to the SQUID magnetometer and by reflectivity spectra.[21] Their results showed that the light-induced phenomenon is perfectly reversible although the photoinduced population rate corresponds to only 43% of the sample, most likely due to opacity phenomena.

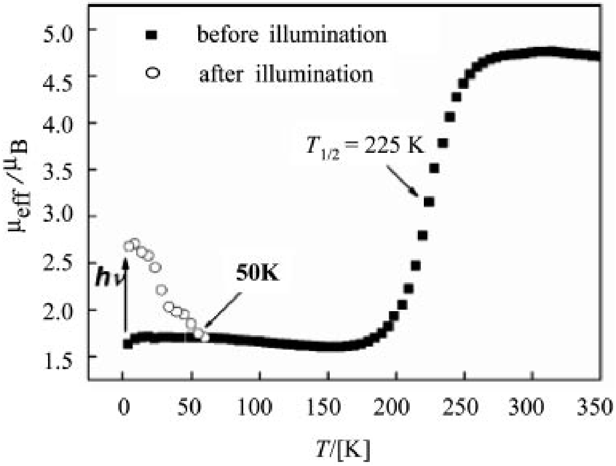


Figure 5. Plot of the χT product as a function of temperature T for complex **3** measured before and after irradiation at 647 nm. The bump at 45 K on the irradiation curve is a result of a small amount of oxygen.

Finally, additional femtosecond spectroscopic experiments by Neuwahl et al. in a simple cobalt-dioxolene derivative in solution demonstrated the involvement of not two but at least three states in a two-step process for a valence tautomeric interconversion in solution.[22] Besides the Co^{III}-Cat and Co^{II}-Sq pairs involved in the tautomerism, the third species may originate from several possible electronic isomers, such as a Co^{III}-Cat species with divergent electronic congurations or a low-spin Co^{II}-Sq isomer, which is expected to be characterized by a triplet electronic ground state.

Pressure-Induced Tautomerism

The X-ray structure analysis of complex **2** at three different temperatures (137, 238 and 295 K) revealed an average metal-ligand bond length increase of 0.18 Å on passing from the **2**, *ls*-Co^{III} to the **2**, *hs*-Co^{II} tautomer. As shown in Figure 6, such a change is due to a drastic change in the population of the antibonding e_g* orbitals.

Such increase of the molecular size when passing from the low-spin to the high-spin isomer has also been used to modulate valence tautomerism by pressure effects.[23] Verdaguer et al.[24] studied the nonsolvated complex **2** and its related solvated form $[Co^{II}(3,5DTBSQ)_2(phen)]\cdot C_6H_5CH_3$ by EXAFS and XANES. EXAFS data indicated that the **2**, *hs*-Co^{II} tautomer has bond lengths of Co–O = 2.08 Å and Co–N = 2.13 Å whereas the **2**, *ls*-Co^{III} tautomeric complex is smaller with Co–O = 1.91 Å and Co–N = 1.93 Å. Both complexes could be reversibly driven from the larger **2**, *hs*-Co^{II} tautomer to the smaller **2**, *ls*-Co^{III} tautomeric form upon application of pressure, within the 0.075–0.700 GPa

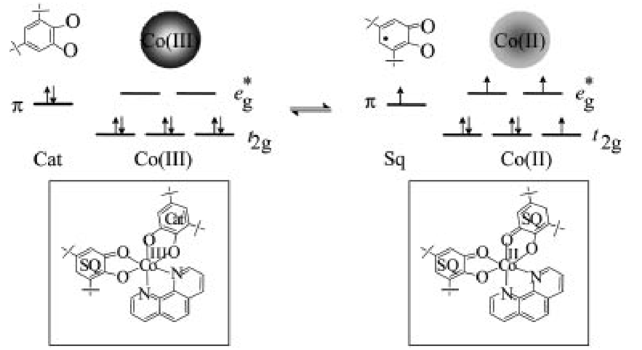


Figure 6. Representation of the orbital occupancy, both metal and ligand based, on the two different tautomeric forms for complex **2**.

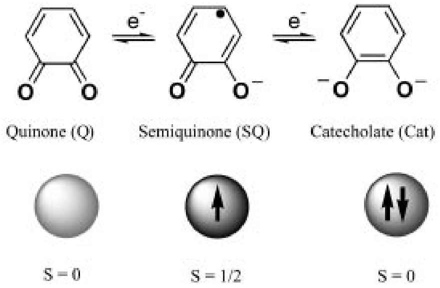
range for the solvated form and 0.10–2.5 GPa for the nonsolvated form. In addition to EXAFS and XANES, pressure-induced valence tautomerism has also been recently monitored by changes in the magnetic response.[25]

Redox-Active Ligands

So far, many different types of redox-active ligands have been described in the literature. Among them are π-conjugated molecules with coordinating capabilities such as quinone-types,[26] crown-ethers,[27] ferrocene,[28] tetrathiafulvalenes derivatives,[29] and polymers/oligomers,[30] such as polyanilines and polythiophenes.[31] However, we must emphasize that even though the number of metal complexes based on redox-active ligands is considerable, those exhibiting valence tautomerism are rather limited since they must simultaneously satisfy two conditions: 1) the degree of covalency in the interaction between metal ion and electroactive ligand must be low, and 2) the energy of their frontier orbitals must be similar.[32] In other words, it is necessary that these complexes exhibit localized electronic structures, low orbital mixing, and a small energy difference between the two electronic tautomers. Most of the valence tautomeric complexes reported thus far are based on quinone or quinone-type ligands with a series of transition metal ions. Nevertheless, in the last few years the number of electroactive ligands inducing valence tautomerism is being expanded by including new electroactive ligands such as schiff-base, phenoxyl, tetraphenylporphyrin and polychlorotriphenylmethyl radicals. Examples of each case are revised below.

Quinone Ligands

Metal dioxolene complexes have been the subject of a vigorously growing and fascinating research field for a long time due to their rich structural, physical and chemical properties.[33] In addition to exhibiting valence tautomerism, the subject of the present review, several other interesting features such as the design of paramagnetic molecules with predetermined spin topologies[34] and activation of small molecules like O_2 and N_2 have also been described.[35] Most of these interesting features are related to their rich redox activity, since they are "noninnocent" electroactive ligands that may exist as neutral quinones (Q), radical semiquinones (SQ^-) or dianionic catecholates (Cat^{2-}) (Scheme 1), although in valence tautomeric complexes they are only found in the SQ^- and Cat^{2-} forms due to the limiting binding ability of the quinone ligand.[36] Charge localization within the metal-quinone chelate ring has been observed for different transition metal complexes (cobalt, manganese, nickel and copper among them),[37] allowing the observation in some cases of valence tautomerism. However, in other cases such as for ruthenium complexes, charge distribution is less clear and a delocalized electronic structure may be an appropriate description.[16]



Scheme 1.

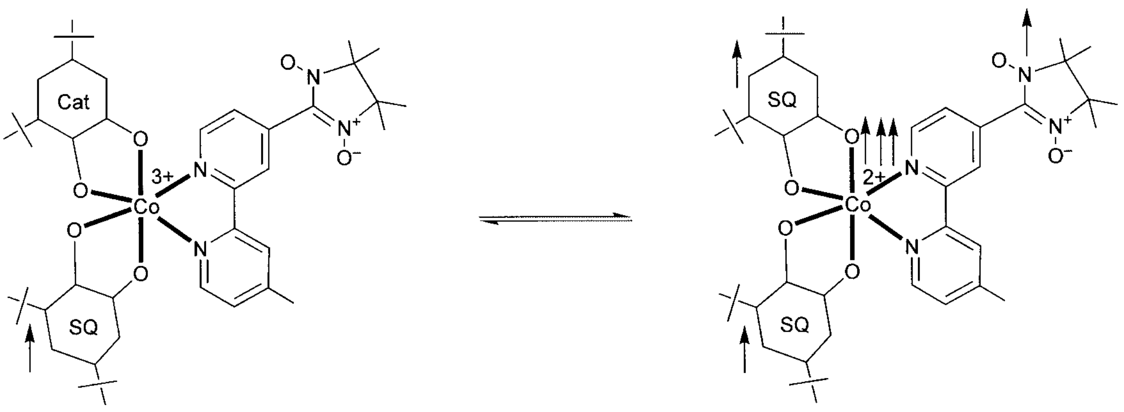
Cobalt Complexes

The best investigated family of quinone-based valence tautomeric complexes is that of cobalt-dioxolene molecules, where the valence tautomeric interconversion involves an intramolecular electron transfer between a six-coordinate cobalt ion and a coordinated dioxolene ligand. The simplest cobalt-quinone complexes undergoing valence tautomerism belong to the family of ionic complexes with the general formula [ML(diox)]Y, where L = tetraazamacrocycle ancillary ligand, diox = 9,10-dioxophenantrene and Y = PF_6, BPh_4, I.[25] Such complexes undergo a temperature- and pressure-induced intramolecular electron-transfer equilibrium with a transition temperature that varies with the volume and coulombic interaction of the counterion Y. Moreover, substitution of CH_2Cl_2 solvent molecules with their deuterated analogs drastically modifies its magnetic properties giving rise to a thermal hysteresis, an important issue if future technological applications are envisaged for these molecular systems.[38]

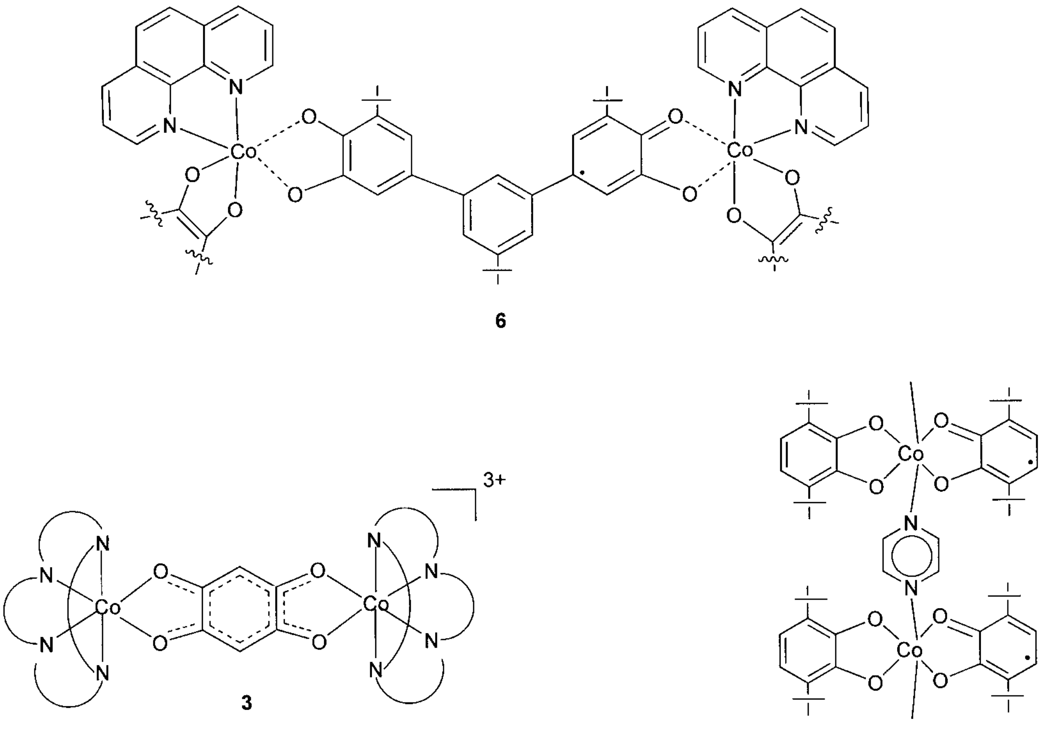
Before the previous monodioxolene complexes were reported, most cobalt complexes shown to exhibit valence tautomerism were of the general formula $[Co(N\text{-}N)(Q)_2]$, where N-N is a diazine ligand, Q = 3,5- and 3,6-di-*tert*-butylcatecholato or semiquinone form. Several interesting features have been observed for this family of complexes, among them a marked effect of the nature of the quinone and ancillary ligands on the tautomerism. For instance, whereas in complex [Co(bpy)(3,6-DBSQ)(3,6-DBCat)] bipyridine ligands of adjacent molecules stack to form a one-dimensional lattice resulting in a remarkable photomechanical effect upon irradiation, replacement by the 3,5-di-*tert*-

butylcatecholato induces a dimerization. As far as the ancillary ligand is concerned, Hendrickson et al.[39] and Pierpont et al.[40] have also concluded that it is possible to systematically control valence tautomerism by changing the counterligand chelate ring flexibility and their donor abilities. Another interesting example has been described by Awaga et al., who reported valence tautomerism in the spin-labeled complex [Co(nnbpy)(3,5-DTBSQ)$_2$] (**4**), where nnbpy is a bipyridine substituted nitronyl nitroxide radical. Even though the temperature dependence of the magnetic susceptibility indicates a tautomeric interconversion above 250 K, the radical ligand behaves as a Curie spin over the whole temperature region.[41] A schematic representation of the valence tautomerism observed for complex **4** is shown in Scheme 2.

In addition to variations in the number and nature of the electroactive and counter ligands, different polynuclear tautomeric complexes have also been reported (see Scheme 3). For instance, Dei et al. reported the dinuclear complex [{Co(cth)}$_2$(dhbq)](PF$_6$)$_3$ (**3**) that undergoes a gradual thermal tautomeric transition at around 175 K and quantitative photoconversion.[21] Pierpont et al. followed this approach to establish the photomechanical polymer [Co(pyz)(3,6-DBQ)$_2$]$_n$ (**5**). This coordination polymer exhibited a temperature-induced tautomeric interconversion in the solid state that is derived from a mechanical process



Scheme 2.



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3

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Scheme 3.

due to variations on the bond lengths although no hysteresis effects were observed.[42] On the contrary, such hysteresis was observed more recently by Schultz et al., who used a bis-bidentate ligand to obtain the coordination polymer $[Co(phen)L]\cdot 0.5CH_2Cl_2$ (**6**). This cobalt-dioxolene polymer exhibits the necessary cooperative properties that lead to thermal hysteresis in a valence tautomeric equilibrium, even though the transition could be classified as gradual.[43]

Copper Complexes

Some copper complexes containing dioxolene ligands may yield, under the right conditions, the valence tautomeric interconversion shown in Equation (3) and Figure 7.[44]

$$[Cu^{II}(DTBCat)(L)] \rightleftharpoons [Cu^{I}(DTBSQ)(L)] \quad (3)$$

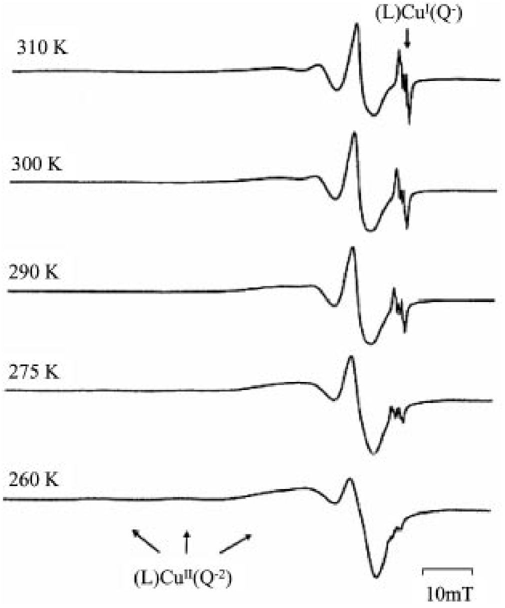


Figure 7. EPR spectra illustrating the temperature-dependent redox isomerism (**3**), with L = mtb and Q = 3,5-di-*tert*-butyl-*o*-quinone, in THF solution.

One of the first examples of valence tautomerism involving the Cu^{II}/Cu^{I} pair was reported in a copper containing amine oxidase enzyme that catalyzes the oxidation of amines to aldehydes,[45] an important process involved in relevant biological functions such as growth regulation and tissue maturation. Indeed, the oxidation of primary amines to aldehydes takes place through a two-electron reduction of O_2 to H_2O_2 catalyzed by the active copper center of the homodimeric enzyme. For this to be achieved and to circumvent spin conservation problems an interconversion from its initial Cu^{II}-catecholate form to the Cu^{I}-semiquinone form, mediated by an intramolecular electron transfer between both units, takes place. Dooley et al. presented evidence for the generation of such a Cu^{I}-semiquinone natural form on several amine oxidases under anaerobic conditions by taking advantage of the very different EPR characteristics (*g* factor and hyperfine-coupling constants) between the pairs Cu^{II}/diamagnetic ligand and Cu^{I}/radical ligand.[45] These studies suggested that the Cu^{I}-semiquinone and the Cu^{II}-catecholate forms are in equilibrium; the Cu^{II}-catecholate form being more stable at low temperatures and the Cu^{I}-semiquinone form at high temperatures.

These exciting results and other biological and commercial processes have motivated the synthesis and characterization of different copper-quinone synthetic models. These studies have shown that the electronic distribution in a series of complexes with the general formula $[(Q^{n-})Cu^{n+}L]$ depends on the donor or acceptor characteristics of the ligand L. With strong π-acceptor ligands, such as L = CO, CNR, PR_3 or AsR_3, the Cu^{I}-semiquinone form is favored, whereas the use of non π-acceptor ligands, such as amine ligands, favors the Cu^{II}-semiquinone form.[46] For instance, Kaim et al. have reported the use of a thioether ligand that favors the Cu^{I}-semiquinone form to induce sensitive valence tautomerism in paramagnetic copper complexes related to amine oxidase enzymes.[47] Similar studies have also been done by Speier et al., who described the existence of valence tautomerism for the species $[Cu(py)_2(PhenQ)_2]$ (**7**).[48] The temperature dependence of the isotropic ESR spectrum of complex **7** in a pyridine solution indicates that at 373 K the complex is in the form $[Cu^{I}(PhenSQ)]$ whereas at 233 K the $[Cu^{II}(PhenCat)]$ tautomer is present, exclusively.

Manganese Complexes

A few years after the first report on cobalt tautomerism, similar temperature-dependent shifts in electronic spectra were observed for a related complex of manganese.[49] The main difference is that valence tautomerism in this case involves three different tautomeric forms associated with three different oxidation states where the manganese ions can be found. Complex $[Mn(py)_2(3,5\text{-}DBCat)_2]$ (**8**) experienced a reversible change in color from the intense purple of the Mn^{IV} form to the pale green-brown characteristic color of the Mn^{II} form. The interconversion takes place through a Mn^{III} form, which usually exhibits similar colors to that of the Mn^{IV} form, as confirmed later in the solid state[50] and in solution.[51] More recently, valence tautomerism in an adduct of a tetrazamacrocycle complex of manganese with a single *o*-benzoquinone ligand has also been reported.[52] The tautomeric interconversion involves two species with nearly degenerate electronic states and a strong sensitivity to variations of the counterion.

Iron and Nickel Complexes

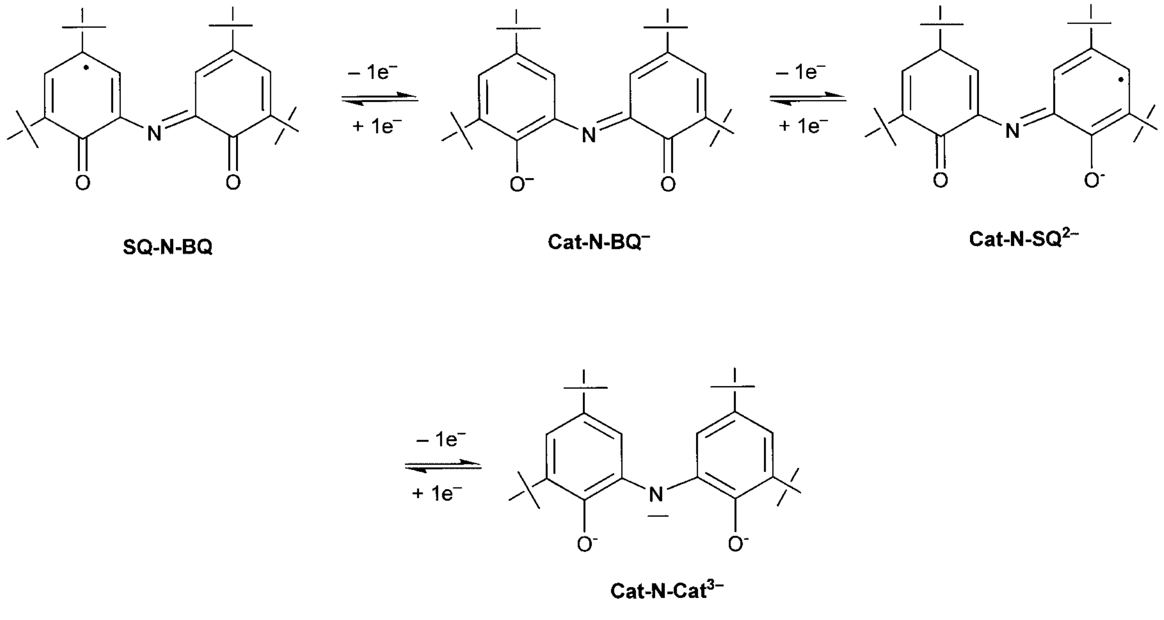
Very recently, two new examples of nickel and iron-quinone complexes have been reported to exhibit valence tautomerism. Tanaka et al. reported complexes $[Ni(PyBz_2)(tBu_2SQ)]PF_6$ (**9**) and $[Ni(MePyBz_2)(tBu_2Cat)]PF_6$ (**10**) as the first examples for the successful control of valence tautomerism between the Ni^{II}-SQ and Ni^{III}-Cat frameworks.[53] Moreover, drastic differences in the electronic states of both complexes are observed due to the steric effects induced by the *o*-methyl group in the $MePyBz_2$ ligand, which weakens the coordination of the pyridine moiety to the nickel ion compared with the unsubstituted $PyBz_2$ ligand. On the other hand, Banerjee et al. reported a semiquinone-catecholate based mixed valence complex [Fe(bispicen)-(Cl_4Cat)(Cl_4SQ)]·DMF (**11**), for which valence tautomerism has been followed by electronic absorption spectroscopy. The tautomer Fe^{III}-(Cl_4Cat)(Cl_4SQ) is favored at low temperatures, while at an elevated temperature, the Fe^{II}-$(Cl_4SQ)_2$ tautomeric form dominates. This is the first example where a mixed valence semiquinone/catecholate iron(III) complex undergoes intramolecular electron transfer.[54]

Phenoxyl Ligands

Transition metal complexes in which one or more of the ligands is present as a phenoxyl radical have attracted much interest due to their broad occurrence in technical processes[55] and enzymatic metalloproteins such as galactose oxidase (GAO)[56] or glyoxal oxidase (GLO).[57] Phenoxyl radicals are monovalent oxygen radical species that exhibit delocalization of the unpaired electron over the aromatic ring and in most cases *ortho* and *para* substituents that give steric protection.[58] For instance, it has been shown that *tert*-butyl substituents at the *ortho* and *para* positions of the phenolates facilitate one-electron oxidation to the corresponding phenoxyl radicals, because these substituents decrease the oxidation potential of the phenolates and provide enough steric bulk to suppress bimolecular decay reactions of the generated phenoxyl radicals.[59] Several groups have prepared metal-phenoxyl complexes giving new insights into the chemical factors that govern the generation and stability of this type of radicals,[60] among those worth mentioning are the ones produced by Wieghardt et al. They have established that bidentate *O,N*-coordinated *o*-aminophenolato ligands can be found in one of the following different protonation and oxidation levels: *o*-imidophenolate(2^-) anions, *o*-iminobenzosemiquinonate(1^-) radical monoanions or even *o*-iminobenzoquinone. All these forms can exist in coordination compounds as confirmed by low-temperature X-ray crystallography.[61] In addition, *o*-iminobenzosemiquinonate(1^-) anions are paramagnetic (S = 1/2) ligands that couple either ferro- or antiferromagnetically when coordinated to a paramagnetic transition metal ion, depending on the symmetry of the magnetic d orbital of the metal ion.

A further step has been the study and characterization of *O,N*-coordinated type ligands containing two phenolate donor groups. These ligands, in addition to producing phenoxyl radicals in the presence of air, exhibit better chelating capabilities and good π-donor atoms that stabilize higher oxidation states,[62] which has allowed the observation of valence tautomerism in some of their complexes. The advantages of valence tautomeric Schiff-base complexes over transition metal complexes with *o*-quinone ligands are considerable. First, valence tautomeric Schiff-base complexes display higher stabilities relative to atmospheric oxygen in solution and in the solid state. Second, the differences between the optical properties of isomers involved in the valence tautomerism of the cobalt Schiff-base complex are enhanced when compared to those observed for cobalt complexes with *o*-quinone ligands. Third, the Schiff-base ligand exhibits a richer electrochemical behavior since it can exist in different oxidation forms, ranging from +1 to –3, which may lead to stable coordination complexes with several metal ions in a variety of oxidation states. For instance, the tridentate ligand [(2-hydroxy-3,5-di-*tert*-butyl-1-phenyl)imino]-3,5-di-*tert*-butyl-1,2-benzoquinone ligand (Cat-N-BQ), may in principle exist in different oxidation states although it usually coordinates in the mononegative Cat-N-BQ or dinegative Cat-N-SQ radical forms (see Scheme 4).[63]

Using such a ligand, in 1988 Pierpont et al. reported the new complex [Co^{III}(Cat-N-BQ)(Cat-N-SQ)] (**12**), although at that time no evidence for tautomeric interconversion was shown to take place.[64] A few years later, the temperature



Scheme 4.

dependence of the spectral and magnetic properties of solutions of this compound in nonpolar solvents suggested the existence of the valence tautomeric equilibrium shown in Equation (4). The temperature dependence of the ^{1}H NMR spectrum of a [D$_8$]toluene solution of complex [Co^{III}(Cat-N-BQ)(Cat-N-SQ)] is shown in Figure 8.[65]

$$[Co^{III}(Cat\text{-}N\text{-}BQ)(Cat\text{-}N\text{-}SQ)] \rightleftharpoons [Co^{II}(Cat\text{-}N\text{-}BQ)_2] \quad (4)$$

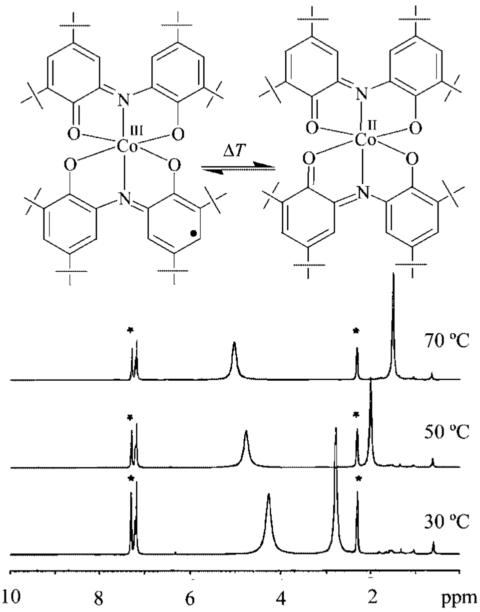
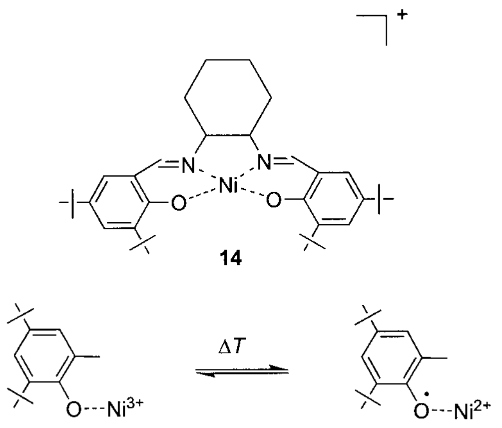


Figure 8. Temperature dependence of the ^{1}H NMR spectrum of a [D$_8$]toluene solution of [Co(Cat-N-BQ)(Cat-N-SQ)]. The observed signals are due to the *tert*-butyl groups of the ligand. Resonances associated with ring protons are not shown.

The interconversion temperature (T_c) was determined to be close to 300 K by the ratio between the enthalpy and the entropy changes in solution but no tautomerism was observed in the solid state, as evidenced by the lack of changes in the variable-temperature magnetic susceptibility data. This fact was initially attributed to the lack of solvate molecules within the crystalline network, which are assumed to impart a "softness" to the lattice that makes it possible to appreciate the dimensional change in the complex. However, in subsequent work, the same authors showed that complex **12** exhibits a tautomeric interconversion in the solid state but at much higher temperatures than in solution.[66] The large difference between the interconversion T_c in the solid state and in solution is suggested to come from the entropy changes associated with the modifications of vibronic interactions.

Valence tautomerism has also been reported for the related manganese complex [Mn^{IV}(Cat-N-SQ)$_2$] (**13**). In this case, valence tautomerism involves three different tautomeric isomers associated with the three different oxidation states in which the manganese ion can be found: Mn^{IV}, Mn^{III} and Mn^{II}.[67] Variable-temperature magnetic susceptibility data for a crystalline sample of complex **13** is characterized by a constant μ_{eff} value of 1.9 μ_B consistent with the formulation [Mn^{IV}(Cat-N-SQ)$_2$] (**13**, Mn^{IV}). This fact evidenced the lack of valence tautomerism for complex **13** in the solid state, at least in the temperature range studied. For this reason, variable-temperature magnetic susceptibility data for a [D$_8$]toluene solution of complex **13** were recorded. From 5 to 270 K complex **13** exhibits a constant μ_{eff} value of 1.8–1.9 μ_B in solution, characteristic of the **13**, Mn^{IV} tautomer. Then, from 270 to 360 K the value of μ_{eff} increases gradually to a value of 4.8 μ_B, which is over the spin-only value of 3.9 μ_B (g = 2) expected for the **13**, Mn^{III} isomer but below that expected for the **13**, Mn^{II} tautomer (5.9 μ_B). Since the tautomeric interconversion in solution usually occurs gradually over a large temperature range (>80–100 °C) it was impossible to completely shift the tautomeric equilibrium to the [Mn^{II}(Cat-N-Q)$_2$] isomer. Further support of the existence of the valence tautomerism shown in Scheme 4 was provided by variable temperature electronic absorption spectra for a toluene solution of complex **13** in the 293–353 K temperature range.

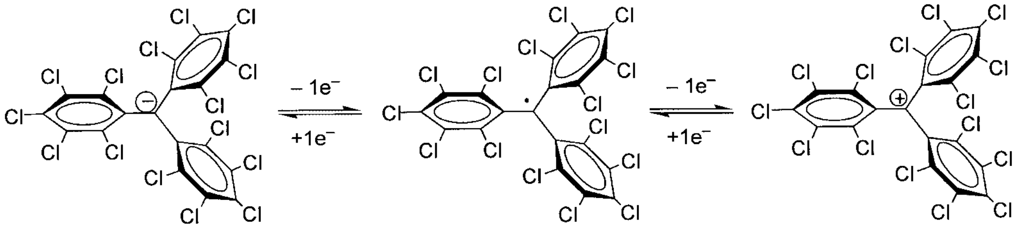
In addition to the Schiff-base ligands previously described and in the course of studies on metal-phenoxyl radical complexes, Shimazaki et al. have recently reported that the one-electron oxidized form of a new mononuclear nickel(II)-bis(salicylidene)diamine complex exhibits valence tautomerism. Indeed, the one-electron oxidation of **14** has been found to be temperature dependent in CH$_2$Cl$_2$ yielding the corresponding Ni^{III}-phenolate complex at $T < -120$ °C and the Ni^{II}-phenoxyl radical species at $T > -100$ °C, which is regarded as a tautomerism of the oxidation states governed by temperature.[68] A schematic representation for the tautomeric equilibrium of this species in solution is shown in Scheme 5.



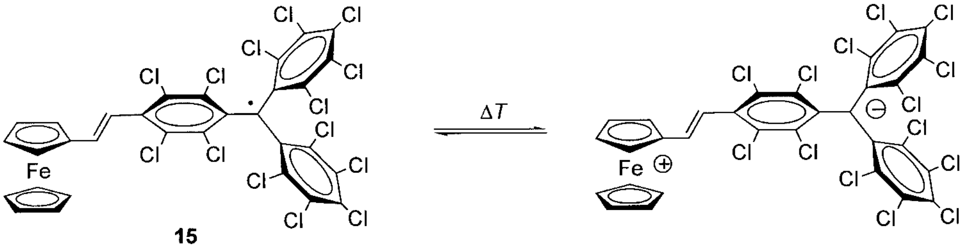
Scheme 5.

Polychlorotriphenylmethyl Radicals

Perchlorotriphenylmethyl radicals (PTM) have their central carbon atom, where most of the spin density is localized, sterically shielded by an encapsulation with six bulky chlorine atoms that increases its life expectancy and thermal and chemical stability.[69] Moreover, the cyclic voltammetry of perchlorotriphenylmethyl radicals shows the formation of two different stable ionic species that correspond



Scheme 6.



Scheme 7.

to the oxidation and reduction of this radical (see Scheme 6). This allows the corresponding anions and cations to be obtained, either chemically or electrochemically, both in solution and in solid state, which also show considerable stabilities in accordance with the steric shielding of their central carbon atoms. Such persistence as well as the particular structural and conformational characteristics of radicals of this family, has enabled them to be functionalized in order to build pure organic open-shell dendrimers with high-spin ground states[70] and pure-organic mixed-valence molecular wires exhibiting intramolecular electron-transfer phenomena.[71]

More recently, Veciana et al. have described the use of perchlorotriphenylmethyl radicals, properly functionalized with carboxylic groups, to obtain complexes combining paramagnetic metal ions and pure organic radicals as ligating sites. Even though this approach has been successfully used to obtain novel mononuclear[72] and extended transition metal complexes exhibiting nonconventional structural motifs, such as nanoporous frameworks with exotic magnetic behavior,[73] no valence tautomerism has been reported on such complexes so far. Nevertheless, the same authors did report valence tautomerism on a new family of molecular systems comprising PTM radicals and ferrocene

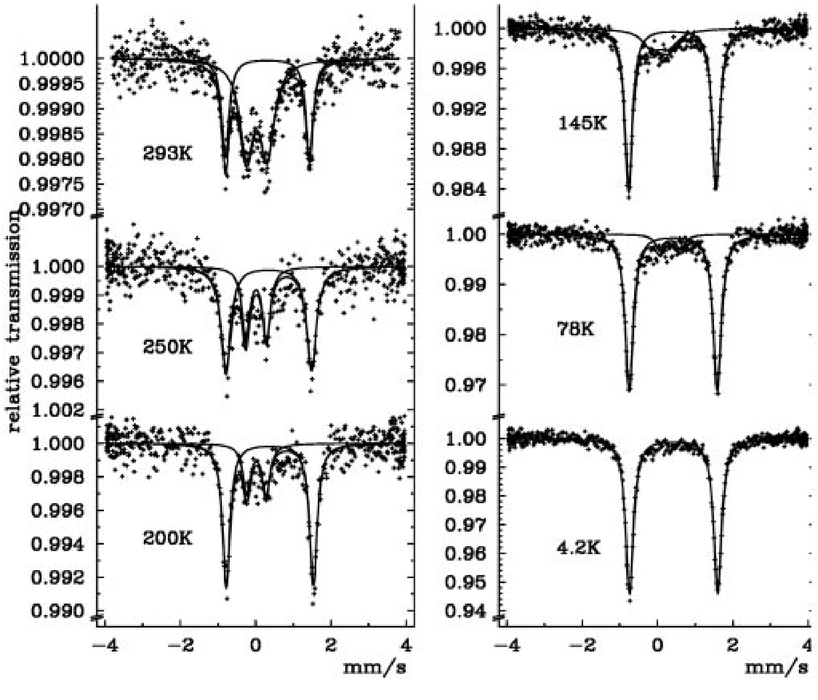


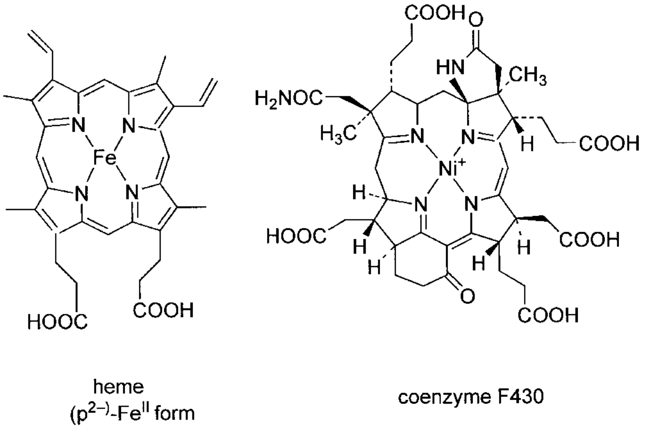
Figure 9. ^{57}Fe Mössbauer spectra of radical **15** as a function of temperature, showing the interconversion between the Fe^{III} and Fe^{II} redox states.

units (see Scheme 7).[74] Ferrocene chromophores are interesting not only because of their electron donor capacities and rich electrochemistry but also because they are electroactive species whose oxidation state can be controlled by means of a chemical or electrochemical stimulus, with their oxidized states being of open-shell character.

As far as we know, this is the only example described, so far, where valence tautomerism was followed by variable-temperature Mössbauer experiments. The ^{57}Fe Mössbauer spectra of radical **15** as a function of temperature are shown in Figure 9. As can be seen in this figure, the Mössbauer spectrum of **15** exhibited a temperature-dependent behavior, in solid state, that is in agreement with the observation of a temperature-dependent intramolecular electron transfer from the ferrocene center to the radical as shown from left to right in Scheme 7. The conversion appears to be gradual up to room temperature and fully reversible as confirmed by repetitive temperature-variable Mössbauer experiments.

Metalloporphyrins

The cation radicals of metalloporphyrins have been extensively studied because they serve as model systems for biological-redox intermediates. In these systems, the formation of a ring vs. a metal centered cation is determined by factors such as the intrinsic redox potentials of the porphyrin ring and metal center, the number and type of ligands on the metal ion and the nature of the solvent. Thanks to such electronic lability, some metalloporphyrins are susceptible to exhibiting valence tautomerism. A well-recognized case is the heme system, in which the porphinoid macrocyclic ligand can participate directly in the electron-transfer process, or nickel complexes of porphinoid ligands related to the function of factor F430 in the methane-releasing coenzyme M reductase.[75] A drawing of the heme and coenzyme F430 are shown in Scheme 8.



Scheme 8.

In addition to the occurrence in natural systems, in 1975 Dolphin et al. showed the existence of a reversible intramolecular electron transfer in an oxidized nickel tetraphenylporphyrin (TPP).[76] The reversible temperature-dependent transformation can be described as shown in Equation (5).

$$[\mathrm{Ni^{II}(TPP)}]^{\cdot+}\,\mathrm{ClO_4^-} \rightleftharpoons [\mathrm{Ni^{III}(TPP)}]^{+}\,\mathrm{ClO_4^-} \quad (5)$$

At room temperature, oxidation of complex Ni(TPP) (where TPP = tetraphenylporphyrin) yields a green solution associated with the electronic form $[\mathrm{Ni^{II}(TPP^{\cdot})^{+}}]$ with a π-cation radical. Upon freezing at 77 K, the green solution becomes orange. These spectral changes are consistent with conversion to a low-spin $[\mathrm{Ni^{III}(TPP)}]^{+}$ ($S = 1/2$) in which the unpaired electron resides in a metal ion orbital, as confirmed by temperature-dependent ESR spectroscopy. Kadish et al. also studied electron-transfer mechanisms of five different nickel(II) porphyrins by replacing the phenyl groups with alkyl groups, all of them exhibiting a temperature-dependent valence tautomerism.[77] In addition to variations on the porphyrin ring, it has been proposed that axial ligation also plays a significant role in mediating the tautomerism. For instance, Bocian et al.[78] have shown based on spectroscopic data that relatively stable $[\mathrm{Ni^{III}(TPP)}]^{+}$ can be obtained, even at ambient temperatures, when coordinating ligands such as THF, py and CH_3CN, are present. The spectroscopic data indicate that the conversion to $\mathrm{Ni^{III}}$ species is facilitated by mixing of the metal ion and porphyrin ring orbitals, the latter of which contains the hole in the π-cation form.

Redox-Tuned Valence Tautomerism

The redox activity of the ligands not only allows for the existence of valence tautomerism but also for additional switching capacities resulting from an electrochemical process. Such a strategy has been shown to be very useful for the systematic tuning of the critical temperature (T_c), at which there are equal amounts of both tautomers, as well as of the net magnetic moments and optical properties of the tautomeric isomers. Different examples of redox-tuned valence tautomerism are revised below.

Quinone Ligands

A study of the influence of the temperature on the cyclic voltammetric behavior of complex $[\mathrm{Co^{III}}$(3,5-DTBCat)(3,5-DTBSQ)(bpy)] (**1**, *ls*-$\mathrm{Co^{III}}$) revealed interesting features. This was the first time that changes in the redox properties of both isomers were followed.[79] As shown in Figure 10, at 273 K the **1**, *ls*-$\mathrm{Co^{III}}$ tautomer shows two well-defined processes at $E_{1/2}$ of –0.34 and +0.25 V vs. Ag wire. The redox couple observed at $E_{1/2}$ = –0.34 V is associated with the reduction of the semiquinone ligand to the catecholate form, whereas the second redox process is characteristic of the oxidation of the catecholate ligand to the semiquinone form. As the temperature is increased, slight shifts of the redox processes into the direction of more positive potentials and the apparition of new redox processes at approximately $E_{1/2}$ = –0.75 and +0.40 V, are observed. Since the tautomeric interconversion in solution occurs gradually over a large temperature range, it was impossible to completely shift the tautomeric equilibrium to the **1**, *hs*-Co^{II} isomer. For this reason, the voltammetric response of complex [Co^{III}(3,5-DTBCat)(3,5-DTBSQ)(phen)] (**2**) at different temperatures was also studied (see Figure 10). The cyclic voltammogram of **2** in CH_2Cl_2 at 273 K shows a similar pattern to that observed for **1** at 303 K with a mixture of **2**, *ls*-Co^{III} and **2**, *hs*-Co^{II} since it exhibits a lower temperature interconversion. As the temperature is increased, **2**, *ls*-Co^{III} converts completely into the **2**, *hs*-Co^{II} tautomer, whose cyclic voltammogram shows a one-reduction process at $E_{1/2} = -0.20$ V vs. Ag wire, and two irreversible one-electron oxidation processes. The reduction process is associated with the reduction of the two semiquinone ligands to the catecholate form whereas the oxidation processes are mostly associated with the irreversible oxidation of the semiquinone ligand to the quinone form and to the oxidation of the metal center.

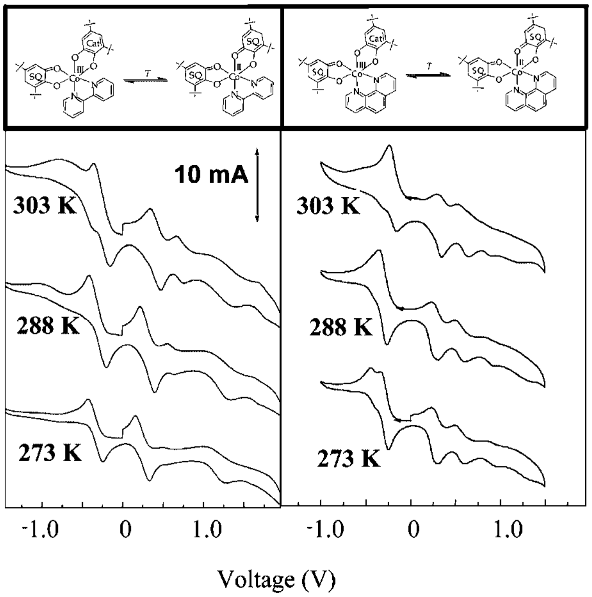
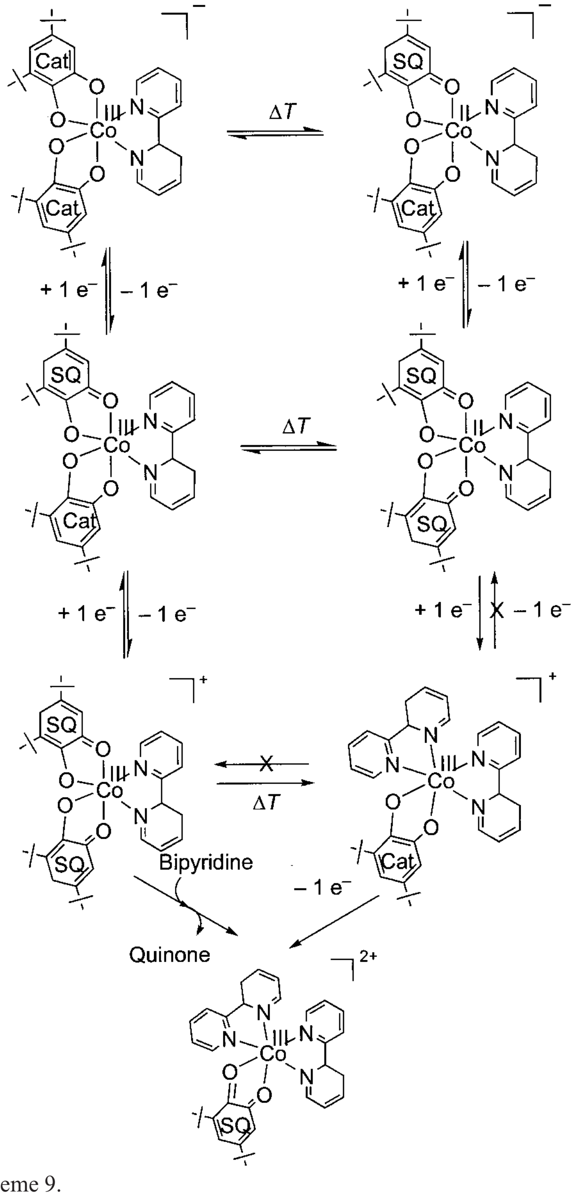


Figure 10. Variable-temperature electrochemical experiments for complexes **1** and **2** in CH_2Cl_2.

Such temperature-dependent redox behavior was also used to selectively oxidize or reduce each one of the tautomeric isomers.[80] Reduction of [Co^{III}(3,5-DTBCat)(3,5-DTBSQ)(bpy)] in CH_2Cl_2 at 273 K with 1 equivalent of $CoCp_2$ yielded [Co^{III}(3,5-DTBCat)$_2$(bpy)][$CoCp_2$] (**1**$^-$, *ls*-Co^{III}) as a dark-green microcrystalline material, whereas reduction of the corresponding high-spin isomer [Co^{II}(3,5-DTBSQ)$_2$(bpy)] (**1**, *hs*-Co^{II}) yielded a purple microcrystalline material characterized as [Co^{II}(3,5-DTBCat)(3,5-DTBSQ)(bpy)][$CoCp_2$] (**1**$^-$, *hs*-Co^{II}). Moreover, the electronic absorption spectra of **1**$^-$, *ls*-Co^{II} and **1**$^-$, *hs*-Co^{II} in acetone exhibited a temperature dependence consistent with the valence-tautomeric equilibrium shown in Scheme 9. This allowed the establishment of an array of four states showing different optical and magnetic ground states, controlled by two temperature-controlled valence-tautomeric equilibria and two reversible redox processes. The possibility of entering the cycle at each state and advancing through the square array in a clockwise and counter-clockwise direction was also established.



Scheme 9.

Such an array was not obtained for the corresponding oxidized species. Indeed, complex **1**, *ls*-Co^{III} was oxidized by a H_2O_2/HCl mixture yielding an olive-green microcrystalline material characterized as [Co^{III}(3,5-DTBSQ)$_2$(bpy)]·Cl (**1**$^+$, *ls*-Co^{III}). However, oxidation of complex **1**, *hs*-Co^{II} with 1 equivalent of $AgBF_4$ surprisingly yielded [Co(3,5-DTBCat)(bpy)$_2$](BF_4)·$2CH_2Cl_2$ (**16**). A feasible mechanism for obtaining complex **16** is shown in Scheme 9. Single oxidation of one semiquinone to the quinone form occurs, but the resulting quinone ligand is not basic enough to interact with first-row transition metal ions and therefore the ligand is lost to introduce a new bipyridine ligand that keeps the octahedral coordination around the cobalt ion. A similar mechanism was found for the double oxidation of **1**, *ls*-Co^{III} by $AgBF_4$ and **1**, *hs*-Co^{II} by a mixture of $HClO_4/H_2O_2$ to yield in both cases $[Co^{III}(3,5\text{-DTBSQ})(bpy)_2]\cdot X_2$, where X = BF_4 or ClO_4, respectively.[81]

Phenol Ligands

To avoid the low donor capabilities of quinone ligands, Rovira et al. established an array of four states based on the oxidation of the tautomeric complex $[Co^{III}(Cat\text{-}N\text{-}BQ)(Cat\text{-}N\text{-}SQ)]$ (**12**).[82] The advantage of this complex lies in the rich electrochemical behavior of the Schiff-base ligand, which can exist in up to five different oxidation forms, ranging from +1 to –3. Its cyclic voltammogram shows a one-electron oxidation process at $E_{1/2}$ = +0.18 V and a reversible one-electron reduction at $E_{1/2}$ = –0.38 V, both being associated with electrochemical processes occurring at ligand-based orbitals. Potential controlled electrolysis experiments demonstrated the reversibility of both redox processes, indicating no structural changes such as ligand loss or decomposition on the time-scale of the experiment. Therefore, the charged species formed from partial oxidation of complex **12** was generated chemically. Interestingly, the variable-temperature absorption spectra of a toluene solution of complex $[Co^{III}(Cat\text{-}N\text{-}BQ)_2]^+$ (**12⁺**) shows the existence of an equilibrium consistent with the existence of a temperature-induced valence tautomerism [Equation (6)].

$$[Co^{III}(Cat\text{-}N\text{-}BQ)_2]^+ \rightleftharpoons [Co^{II}(Cat\text{-}N\text{-}BQ)(SQ\text{-}N\text{-}BQ)]^+ \qquad (6)$$

This allowed the establishment of an array of four states showing different optical and magnetic ground states by using a reversible oxidation process as an additional stimulus. In a further step, to expand the number of states within the array, Ruiz-Molina et al. converted the valence tautomeric equilibrium of complex $[Mn^{IV}(Cat\text{-}N\text{-}SQ)_2]$ (**13**, Mn^{IV}) by an additional reversible oxidation process to an array of six states. The cyclic voltammogram of complex **13** shows two oxidation processes at $E_{1/2}$ = +0.68 V and $E_{1/2}$ = +0.15 V and a reversible reduction at $E_{1/2}$ = –0.46 V (vs. Ag wire), which have been identified as electrochemical processes involving ligand-based orbitals. Therefore, the charged species **13⁺** formed from partial oxidation of complex **13** was generated chemically. Moreover, the variable-temperature magnetic susceptibility data and electronic spectroscopy for a [D$_8$]toluene solution of a toluene solution was consistent with the valence tautomerism shown in Equation (7).

$$[Mn^{IV}(Cat\text{-}N\text{-}Q)(Cat\text{-}N\text{-}SQ)]^+ \rightleftharpoons [Mn^{III}(Cat\text{-}N\text{-}Q)_2]^+ \rightleftharpoons [Mn^{II}(Cat\text{-}N\text{-}Q)(SQ\text{-}N\text{-}Q)]^+ \qquad (7)$$

Polychlorotriphenylmethyl Radicals

The polychlorotriphenylmethyl radical **17**, derived from the valence tautomeric complex **15**, by replacing the ferrocene unit by a permethylated ferrocene, has been converted into an array of three redox states that exhibit distinct physical properties by reduction into their diamagnetic anionic form **17⁻** and/or oxidation into the ferrocenium radical derivative **17⁺**.[83] Interest in these molecular systems is considerable since they not only exhibit variations in color and magnetic properties but also show nonlinear optical responses due to their octupolar nature and their donor-acceptor dyad topology. Indeed, the color of the [K([18]-crown-6)]⁺**17⁻** salt is deep purple, radical **17** is brown, the **17⁺**BF_4^- salt is yellow, and the hydrocarbon **17**-H is pale pink. In accordance with their distinct colors, the optical absorption spectra of the three species **17**, **17⁺**, **17⁻** show striking differences. Among them, is a remarkable broad intervalence charge-transfer (IVCT) absorption band in the NIR region observed for radical **17**, centered at 1520 nm which is associated with an intramolecular electron transfer from the ferrocene donor unit to the radical acceptor unit (the PTM unit). On the other hand the IVCT band is absent, in agreement with the lack of electron-donor character of the organometallic unit when it is oxidized or reduced. The dynamic hyperpolarizabilities of these three species were measured by hyper-Rayleigh scattering (HRS) experiments. In accordance with the presence of an intense IVCT band, radical **17** gives a large nonlinear optical response with a dynamic hyperpolarizability value β = 545(±30) × 10^{-30} esu. This value is reduced almost ninefold to 66(±7) × 10^{-30} esu for **17⁺**, and even more for the carbanion **17⁻** which has a β = 30(±3) × 10^{-30} esu. The magnetic properties of the three species that have been studied are also different. Thus, while [K([18]crown-6)]⁺**17⁻** is diamagnetic, the paramagnetic susceptibility of compounds **17** and **17⁺**BF4⁻ in the solid state between 4–300 K showed quasi-ideal paramagnetic behavior with effective magnetic moments of 1.72 for **17** and 2.50 μ_B for **17⁺**BF4⁻ at 300 K; as expected for systems with S = 1/2 and S = 2 × 1/2 units.

To demonstrate the complete reversibility of the redox reactions of radical **17**, several oxidation and reduction cycles were performed. As shown in Figure 11, the optical

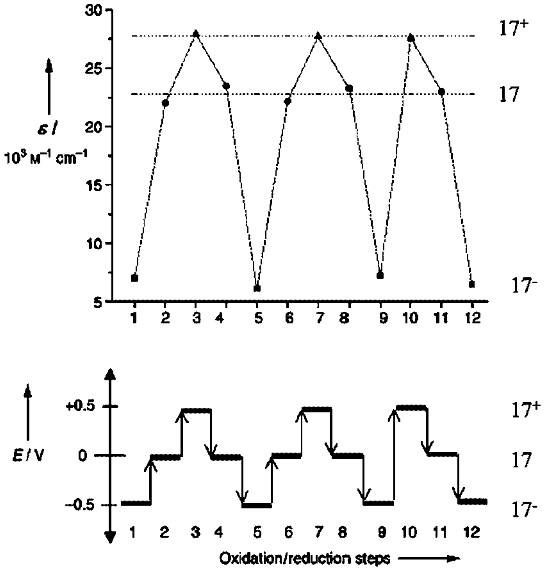


Figure 11. Cyclic stepwise oxidations and reductions carried out in THF with a chronoamperometric technique monitoring the changes in the visible spectrum for **17**-H, [K([18]crown-6)]⁺**17⁻**, **17**, and **17⁺**BF_4^-.

spectrum was recorded, after each step, and could be fully recovered after each cycle. Analogous switching behavior was also detected with EPR spectroscopy by studying the magnetic response in solution of the redox-switchable molecular array. Such chemical transformations along with the conversions by electrical stimuli led us to expect a plethora of signal transduction mechanisms should this molecular switchable array be used as a molecular logic gate. Therefore, radical **17** appeared as an ideal candidate for developing a multiproperty three-state switching molecular device governed by electrical and/or thermal inputs.

Acknowledgments

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