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# Temperature-Induced Solid-State Valence Tautomeric Interconversion in Two Cobalt–Schiff Base Diquinone Complexes

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The mixed-ligand complexes [Co$^{III}$(tpy)(Cat-N-SQ)]Y and [Ni$^{II}$(tpy)(Cat-N-BQ)]PF$_6$ (tpy = 2,2′:6′,2′′-terpyridine; Cat-N-BQ, Cat-N-SQ = mononegative and radical dinegative Schiff base diquinone ligand; Y = PF$_6$, BPh$_4$) were prepared. Structural and spectroscopic data support the different charge distribution of the two compounds. The temperature-dependent electronic and spectral properties of solutions containing the [Co$^{III}$(tpy)(Cat-N-SQ)]$^+$ suggest that this compound undergoes a thermally driven valence tautomeric interconversion to [Co$^{II}$(tpy)(Cat-N-BQ)]$^+$ complex, the metal ion being in high-spin configuration. The comparison of the electrochemical properties of the cobalt and nickel derivatives supports the observed behavior. The same interconversion process was found to occur also in the solid state with a significant higher $T_c$ value than in solution. It was found that the previously reported [Co$^{III}$(Cat-N-BQ)(Cat-N-SQ)] shows a similar behavior. 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.

## Introduction

Metal−dioxolene complexes undergoing valence tautomerism provide an important class of compounds for understanding the details of the intramolecular electron-transfer processes involving a transition metal ion and a coordinated redox active ligand.[1−23] Though it has been shown that several 3d metal−dioxolene complexes ions are characterized by this unusual property, there is no doubt that cobalt derivatives are the most interesting ones, due to the changes of magnetic properties associated to the changes in charge

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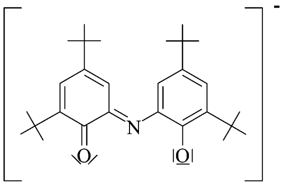
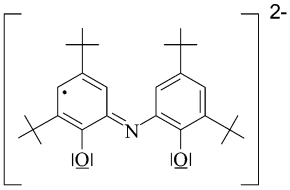
distribution. Indeed in all of the examples reported to date for this metal ion the interconversion involves an intramolecular electron transfer from a coordinated catecholato ligand to a six-coordinate diamagnetic Co(III) ($t_{2g}^6$($O_h$)), yielding a Co(II)−semiquinonato species. In this species the metal ion is in the high-spin electronic configuration ($t_{2g}^5e_g^2$, $S$ = 3/2). As observed for spin-crossover systems,[24] the process is essentially entropy driven, the Co(III)−catecholato species being favored at low temperatures and the Co(II)−semiquinonato at high temperatures. It is well established that the transition between the two forms can be also induced by pressure changes or by continuous optical irradiation, thus making these compounds potential candidates for bistable molecular switches. Recent studies have shown the possibility of inducing reversible optical electron transfer with the formation of long-lived products at very low temperatures by using appropriate irradiating sources.[25−29] These pioneering experiments were carried out on solid samples of cobalt−dioxolene complexes undergoing valence tautomeric transitions in the solid state.

All the cobalt complexes which exhibit valence tautomerism in condensed phase are molecular dioxolene complexes of general formula Co(N-N)(diox)$_2$ (N-N = diazine ligand; diox = 3,5- and 3,6-di-*tert*-butylcatecholato or the parent semiquinonato) or related polynuclear complexes formed by tetraoxolene ligands acting as bis-bidentate.[23] The ionic Co(CTH)(diox)Y complexes (CTH = tetraazamacrocycle; diox = catecholato or semiquinonato forms of 9,10-dioxyphenanthrene; Y = I, PF$_6$, BPh$_4$) display similar behavior.[22] In this framework it seems highly desirable to enlarge the families of cobalt−dioxolene type derivatives showing valence tautomerism in the solid phase by increasing the number of ligands which can be used for complexation. Bearing this in mind, we have reconsidered the cobalt complexes formed by the monoanion of the tridentate ligand 2-((2-hydroxy-3,5-di-*tert*-butylphenyl)imino)-4,6-di-*tert*-butylcyclohexa-3,5-dienone (Cat-N-BQ (**I**)) as well as by its dianionic semiquinonato radical analogue (Cat-N-SQ (**II**)),



*Cat-N-BQ*
**(I)**



*Cat-N-SQ*
**(II)**

Though the molecule may in principle exist in five different oxidation states, it is usually coordinated as mononegative Cat-N-BQ or dinegative Cat-N-SQ radical, as mentioned above. However it should be mentioned that, as evidenced by Wieghardt and Chauduri,[30] this ligand may exhibit sometimes a more complicated behavior.

The formulation of the cobalt complex as mixed-ligand Co$^{III}$(Cat-N-BQ)(Cat-N-SQ) derivative on the basis of the structural parameters is consistent with the spectroscopic and magnetic properties of the solid compound.[31] Indeed the observed constant $\chi_M T$ value of 0.4 emu K mol$^{-1}$ in the range 4−300 K and the single line at $g$ = 2.00 in its powder EPR spectrum well agree with the existence of a radical ligand coordinated to a diamagnetic d$^6$ low-spin Co(III) ion. In addition the IR and RR spectra indicate the presence of different C−O, C═O, and C═N stretching modes.[32] This suggests that at room temperature the electron-transfer process between the two coordinated ligands is slow on the vibrational time scale, thus indicating a class I character for this mixed valence compound. However the temperature dependence of the spectral and magnetic properties of solutions of this compound in nonpolar solvents suggests the existence of the valence tautomeric equilibrium

$$\underset{S\,=\,1/2}{\mathrm{Co^{III}(Cat\text{-}N\text{-}BQ)(Cat\text{-}N\text{-}SQ)}} \rightleftharpoons \underset{S\,=\,3/2}{\mathrm{Co^{II}(Cat\text{-}N\text{-}BQ)_2}}$$

with interconversion temperature $T_c$, determined by the ratio between the enthalpy and the entropy changes, equal to 300 K. Since no evidence of this process was found in the solid state in the 4−300 K range, it has been suggested to reconsider this interpretation by taking into account intramolecular cyclization processes.[1] Speier and Pierpont have found that this molecular rearrangement yields the phenoxylazinylate radical ligand which may also give rise to electron-transfer reactions.[33] Although this doubt has reasonable chemical grounds, we believe that in the solid state $T_c$ may be simply shifted to higher temperatures due to the formation of the lattice. This hypothesis has been recently supported by the results on Co$^{III}$(Cat-N-BQ)$_2$BF$_4$.[21] The spectral properties of the solutions of this compound suggest the existence of the equilibrium

$$\underset{S\,=\,0}{\mathrm{Co^{III}(Cat\text{-}N\text{-}BQ)_2^{\,+}}} \rightleftharpoons \underset{S\,=\,1-2?}{\mathrm{Co^{II}(Cat\text{-}N\text{-}BQ)(Cat\text{-}N\text{-}SQ)^+}}$$

but there is no evidence of such a process in the solid state. To test our hypothesis, we measured magnetization at higher temperatures than 300 K. We also investigated the possibility to induce electron transfer by appropriate irradiation at low temperatures. The results of these investigations are reported below.

To reach a better description of the cobalt−diquinone moiety, the synthesis of metal complexes containing a single chelated redox-active tridentate ligand was also attempted.

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Notwithstanding the expectations, six-coordinated Co(III) complexes of formula Co(tpy)(Cat-N-SQ)Y (Y = $PF_6$, $BPh_4$) were obtained using the 2,2′:6′,2″-terpyridine (tpy) as ancillary ligand. The crystal structure and the physical properties of these compounds are here reported and compared with those of the Ni(II) analogue.

## Experimental Section

**Synthesis.** The Co(Cat-N-SQ)(Cat-N-BQ) complex was prepared according to the previously reported procedure.[31] The complexes of general formula Co(tpy)(Cat-N-SQ)Y (Y = $PF_6$, $BPh_4$) and Ni(tpy)(Cat-N-BQ)$PF_6$ were prepared by mixing solutions of the appropriate metal(II) chloride (1 mmol), 2,2′:6′,2″-terpyridine (1 mmol), and 3,5-di-*tert*-butylcatechol (2 mmol) in ethanol. A 1 mL volume of aqueous concentrated ammonia was then added to the resulting suspension. The mixtures were stirred 4 h at room temperature and then filtered to remove small quantities of Co(Cat-N-SQ)(Cat-N-BQ) or Ni(Cat-N-BQ)$_2$. Solid microcrystalline compounds were obtained by addition of an aqueous solution of $KPF_6$ or acetone solution of $NaBPh_4$. They were filtered out and then recrystallized from methanol or dichloromethane/pentane mixtures. (Anal. Found for Co(tpy)(Cat-N-SQ)$PF_6$: C, 59.68; H, 5.81; N, 6.74. Calcd for $C_{43}H_{51}CoF_6N_4O_2P$: C, 60.05; H, 5.98; N, 6.52. Found for Co(tpy)(Cat-N-SQ)$BPh_4$: C, 77.24; H, 6.95; N, 5.40. Calcd for $C_{67}H_{71}BCoN_4O_2$: C, 77.79; H, 6.92; N, 5.42. Found for Ni(tpy)(Cat-N-BQ)$PF_6$: C, 59.72; H, 6.01; N, 6.68. Calcd for $C_{43}H_{51}F_6N_4NiO_2P$: C, 60.12; H, 5.99; N, 6.53.)

**Physical Measurements.** X-ray data collection was performed on a CCD-1K three-circle Bruker diffractometer equipped with Cu Kα radiation and Göbel mirrors monochromator using SMART 5.625 software. Intensities were corrected for absorption (SADABS). The structure was successfully solved by direct methods (SIR97)[35] which gave the position of all non-hydrogen atoms but few carbon atoms of the *tert*-butyl groups, which where later identified by successive Fourier difference syntheses using SHELXL97.[36] The structure was refined against $F^2$ with full-matrix least-squares refinement. Hydrogen atoms were added in calculated positions by assuming idealized bond geometries. Anisotropic thermal factors were used for all non-hydrogen atoms. Details of data collection and structure refinement are given in Table 1.

The magnetization measurements at low temperatures and at high temperatures have been performed with an Oxford Instruments vibrating-sample magnetometer (VSM) working between 0 and 12 T and in the 1.5−1000 K temperature range. The high temperatures measurements were carried out with a furnace insert that operates between 300 and 1000 K while below room temperature it has been measured with a low-temperature insert with magnetic fields equal to 2 and 1 T, respectively. The diamagnetic corrections have been evaluated with the help of Pascal's tables.

EPR spectra were recorded with a Varian E-9 spectrometer working at X-band frequency equipped with an Helium flux cryostat ESR9 from Oxford Instruments. Room-temperature electronic spectra were recorded in the range 5000−30 000 cm$^{-1}$ on a Perkin-Elmer Lambda 9 spectrophotometer. The electrochemical analysis by cyclic voltammetry was carried out by using an electrochemical unit (Amel model 553 potentiostiat equipped with Amel 860, 560, and 568 elements) and a classical three-electrode cell. The working electrode was a platinum microsphere, the auxiliary electrode was a platinum disk, and the reference electrode was a calomel electrode in aqueous saturated KCl (SCE). All potentials are reported for cyclic voltammograms of $10^{-3}$ M 1,2-dichloroethane solutions of the complexes as referenced vs ferrocenium/ferrocene couple. Under the experimental conditions used (25 °C, 0.1 M $NBu_4PF_6$) this couple lies at +0.455 V vs SCE. Temperature-dependent electronic spectra were recorded on a Shimadzu 2101 PC spectrophotometer.

**Table 1.** Crystal Data and Structure Refinement for [Co(tpy)(Cat-N-SQ)]$BPh_4$

| | |
|---|---|
| fw | 1034.02 |
| temp | 293(2) K |
| wavelength | 1.541 78 Å |
| cryst system, space group | orthorhombic, *Pnn*2 |
| unit cell dimens | $a = 41.396(2)$ Å |
| | $b = 14.383(1)$ Å |
| | $c = 20.626(1)$ Å |
| | $\alpha = 90.000(2)°$ |
| | $\beta = 90.000(2)°$ |
| | $\gamma = 90.000(2)°$ |
| V | 12281(2) Å$^3$ |
| Z | 8 |
| calcd density | 1.119 mg/m$^3$ |
| abs coeff | 2.528 mm$^{-1}$ |
| *F*(000) | 4392 |
| cryst size | 0.8 × 0.4 × 0.2 mm |
| $\theta$ range for data collcn | 2.13−50.49° |
| limiting indices | $-41 \leq h \leq 39$ |
| | $-14 \leq k \leq 14$ |
| | $-20 \leq l \leq 20$ |
| reflcns collcd/unique | 27 821/11 803 [R(int) = 0.0682] |
| completeness to $\theta$ | 50.49 98.0% |
| refinement method | full-matrix least squares on $F^2$ |
| data/restraints/params | 11 803/1/1321 |
| GooF on $F^2$ | 1.039 |
| final R indices [$I > 2\sigma(I)$] | R1 = 0.0700 |
| | wR2 = 0.1081 |
| R indices (all data) | R1 = 0.1277 |

Photomagnetism experiments were performed using a 75 W xenon lamp as light source (Müller Elektronik Optik XH100), in combination with suitable broad-band interference filters. The light was guided by a large core (1000 μm) optical fiber (Fort Fiber Ottiche HCP M1000T) into a Cryogenic S600 SQUID magnetometer or an EPR spectrometer. In the former case a few milligrams of compound were pressed onto a premade 5 mm KBr pellet. In the latter, the loose ground powder was used.

## Results

The compounds of general formula [M(tpy)(L)]Y (M = Co, Ni; L = Cat-N-BQ or Cat-N-SQ; Y = $PF_6$, $BPh_4$) were prepared by mixing solutions containing the appropriate metal salt, the terpyridine ancillary ligand, and 3,5-di-*tert*-catechol in stoichiometric ratio 1:1:2 followed by the addition of aqueous concentrated ammonia. The addition of solutions containing the appropriate counteranion allowed the precipitation of the mixed ligand complex cation in high yield (>80%). This procedure does not hold if copper, iron, or manganese salts are used. In this case the precipitation of the [M(L)$_2$] species occurs.

The isolation of these cobalt and nickel complexes is rather surprising. As a matter of fact, it is reasonable to expect that in methanol the equilibrium

$$2M(tpy)(L)^+ \rightleftharpoons M(tpy)_2^{2+} + M(L)_2 \qquad (1)$$

should be shifted to the right, according to the low solubility

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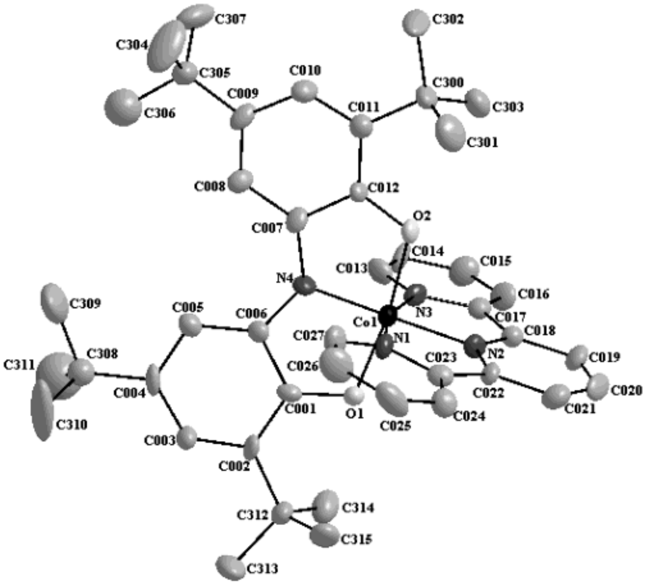


**Figure 1.** Molecular structure of $[Co(tpy)(Cat\text{-}N\text{-}SQ)]^+$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 20% probability.

of the neutral $M(L)_2$ species and to the difference of solvation free energies of the two ionic species which is expected to depend on the squared ionic charge. Therefore, the precipitation of the neutral species when copper, iron, or manganese salts are used appears an obvious experimental result. Instead, as it will be shown below all the physical properties of the cobalt and nickel complexes support the mixed-ligand character of the isolated compounds.

**Crystal Structure of Co(tpy)(Cat-N-SQ)BPh$_4$.** All attempts to obtain a single crystal of $[Co(tpy)(Cat\text{-}N\text{-}SQ)]PF_6$ suitable for X-ray diffractometric analysis were unsuccessful. Good quality crystals were instead obtained on replacing the $PF_6^-$ counterion with $BPh_4^-$. $[Co(tpy)(Cat\text{-}N\text{-}SQ)]BPh_4$ crystallizes in the orthorhombic, *Pnn*2 space group. The crystallographic symmetry is lower than that of the cation because of the presence of the $BPh_4$ anion in the unit cell. The crystal structure is shown in Figure 1, while selected bond distances are reported in Table 2. The compound consists of a $[Co(tpy)(Cat\text{-}N\text{-}SQ)]^+$ cation, the metal ion adopting a pseudooctahedral geometry, and $BPh_4$ anions. The two ligands, tpy and Cat-N-SQ, act as tridentate ligands and are coordinated in a meridional configuration with the two planes nearly perpendicular to each other. The coordination geometry around the Co(III) ions deviates from a regular octahedron due to the small bite angle of the terpyridine ligand which forces the N−Co−N angle with the terminal N atoms to be smaller than 180° (the average value is 164.1°). Also the O−Co−O angles are smaller than 180°, being between 172.95(5)° (Co(2)) and 170.23(6)° (Co(3)). Three different crystallographic sites can be distinguished for the Co ions: Co(1) is located on a general position while Co(2) and Co(3), together with the central nitrogen atoms of the two ligands coordinated to both atoms (N(5), N(7), N(8), and N(10)), lie on two different binary axes and therefore have an occupation factor of 1/2 so that only 2 molecules/asymmetric unit are present. The structural parameters of the coordinated Schiff base diquinone are consistent with the Cat-N-SQ radical character. Indeed the average Co−N and Co−O bond distances are 1.93 and 1.89 Å, respectively, and well agree with the expectations for a tripositive low-spin metal acceptor. The same bond distances in the $[Co(Cat\text{-}N\text{-}BQ)_2]^+$ complex were found to be 1.85 and 1.92 Å,[21] whereas in the [Co(Cat-N-BQ)(Cat-N-SQ)] complex were found to be 1.87 and 1.90 Å (average) for Co−N and Co−O, respectively.[31] The observed difference is explained by reminding that in the $[Co(Cat\text{-}N\text{-}BQ)_2]^+$ the ligand has a different oxidation state, whereas in the [Co(Cat-N-BQ)(Cat-N-SQ)] complex the two Schiff base diquinone ligands have different oxidation states and the observed structural parameters are averaged. The larger value of the Co−N distance reflects a lower donor power of the nitrogen atom, as expected from the electronic properties of the Cat-N-SQ ligand. The observed C−O bond lengths (∼1.33 Å) in the [Co(tpy)(Cat-N-SQ)] are well consistent with the dinegative radical nature of the Schiff base diquinone ligand. Again this value falls in the expected range once compared with those observed for $[Co(Cat\text{-}N\text{-}BQ)_2]^+$ and [Co(Cat-N-BQ)(Cat-N-SQ)] (1.30 and 1.31 Å, respectively). Similar conclusions can be obtained from the inspections of the C−N bond lengths which average 1.38 Å (1.36 Å in [Co(Cat-N-BQ)(Cat-N-SQ)] and 1.35 Å in $[Co(Cat\text{-}N\text{-}BQ)_2]^+$). Significant differences are observed in the C−C ring bond distances which, on average, are shorter between carbon atoms at 3−4 and 5−6 positions, as indeed observed on the [Co(Cat-N-BQ)(Cat-N-SQ)] compound, indicating a localized electronic structure. Finally, a significant twist of the phenyl ring planes was observed for at least two of the three ligands in the asymmetric unit: the twist angles are in fact 15.9 and 5.8° for the ligands coordinated at Co(3) and Co(1), respectively, while it is only 1.7° for the ligand coordinated at Co(2).

**Table 2.** Selected Bond Lengths (Å) for $[Co(tpy)(Cat\text{-}N\text{-}SQ)]BPh_4$

| | | | |
|---|---|---|---|
| Co(1)−N(1) | 1.922(7) | Co(2)−N(9) | 1.971(6) |
| Co(1)−N(2) | 1.886(8) | Co(2)−N(10) | 1.845(10) |
| Co(1)−N(3) | 1.912(7) | Co(2)−O(4) | 1.880(5) |
| Co(1)−N(4) | 1.834(8) | Co(3)−N(5) | 1.806(13) |
| Co(1)−O(1) | 1.879(5) | Co(3)−N(6) | 1.943(8) |
| Co(1)−O(2) | 1.879(5) | Co(3)−N(7) | 1.882(12) |
| O(1)−C(001) | 1.331(9) | Co(3)−O(3) | 1.910(6) |
| O(2)−C(012) | 1.329(8) | O(3)−C(41) | 1.310(10) |
| C(001)−C(006) | 1.439(10) | O(4)−C(42) | 1.336(9) |
| C(007)−C(012) | 1.453(10) | N(5)−C(33) | 1.360(13) |
| N(1)−C(023) | 1.381(11) | N(6)−C(28) | 1.347(12) |
| N(1)−C(027) | 1.308(11) | N(6)−C(32) | 1.354(12) |
| N(2)−C(018) | 1.316(10) | N(7)−C(36) | 1.387(11) |
| N(2)−C(022) | 1.339(9) | N(8)−C(53) | 1.354(10) |
| N(3)−C(013) | 1.266(10) | N(9)−C(48) | 1.346(10) |
| N(3)−C(017) | 1.387(11) | N(9)−C(52) | 1.351(11) |
| N(4)−C(006) | 1.371(10) | N(10)−C(47) | 1.379(9) |
| N(4)−C(007) | 1.384(10) | C(006)−C(001) | 1.439(10) |
| C(018)−C(017) | 1.490(11) | C(33)−C(32) | 1.481(14) |
| C(022)−C(023) | 1.434(11) | C(47)−C(42) | 1.392(10) |
| Co(2)−N(8) | 1.818(11) | | |

**Spectroscopic, Magnetic, and Electrochemical Characterization.** On the basis of the magnetic and spectral properties, we can postulate that the nickel derivative contains the pseudooctahedral $[Ni^{II}(tpy)(Cat\text{-}N\text{-}BQ)]^+$. The compound is paramagnetic, and its $\chi_M T$ value of 1.05 emu K mol$^{-1}$ at

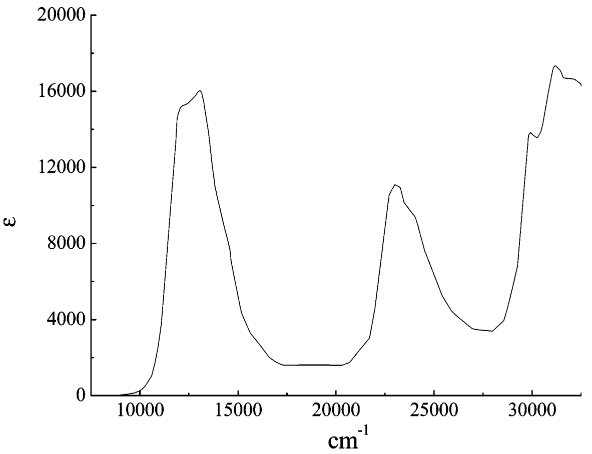


**Figure 2.** Electronic absorption spectrum of an acetonitrile solution of [Ni(tpy)(Cat-N-SQ)]$PF_6$.

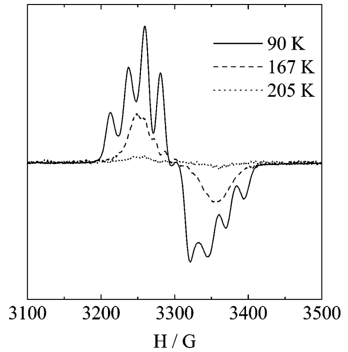


**Figure 3.** Temperature dependence of the X-band EPR spectra of [Co(tpy)(Cat-N-SQ)]$PF_6$ in 1,2-dichlorobenzene solution.

room temperature is consistent with a triplet electronic ground state as expected for a six-coordinated $3d^8$ metal ion. Its electronic spectrum in 1,2-dichloroethane is shown in Figure 2 and is rather similar to that of the [Ni(Cat-N-BQ)$_2$] and [Zn(Cat-N-BQ)$_2$],[32,34] thus indicating that the spectrum is dominated by the internal transitions of the Schiff base diquinone ligand.

In addition to its structural properties the formulation of the cobalt analogue at room temperature as $[\mathrm{Co^{III}(tpy)(Cat\text{-}N\text{-}SQ)}]^+$ is well supported by its magnetic and spectroscopic properties. The EPR powder spectra of both the $PF_6$ and $BPh_4$ complexes show a signal at $g = 2.00$ in the 4−300 K range as expected for a compound containing a radical ligand coordinated to a diamagnetic metal ion. Its reflectance spectrum in the range 5000−30 000 $cm^{-1}$ shows the same internal ligand transitions which characterize all the [M(Cat-N-SQ)$_2$] complexes (M = Ti, Ge, Sn).[32] The solutions of $[\mathrm{Co^{III}(tpy)(Cat\text{-}N\text{-}SQ)}]^+$ in nonpolar solvents such as 1,2-dichlorobenzene do not show any EPR spectrum at room temperature. Indeed temperature-dependent EPR spectra show that the hyperfine split resonance absorption centered at $g = 2.00$ disappears at 200 K (Figure 3). A similar behavior was observed for nonpolar solutions of [Co(Cat-N-BQ)(Cat-N-SQ)].[16] In the present investigation we have found that for this compound the signal vanishes at 70 K.

The variable-temperature electronic absorption spectrum of 1,2-dichlorobenzene solutions of the $\mathrm{Co^{III}}$(tpy)(Cat-N-SQ)-($PF_6$) complex (Figure 4) shows the existence of an equilibrium involving two chromophores as indicated by the presence of three isosbestic points. The observed behavior is quite analogous to that observed for the Co(Cat-N-BQ)-(Cat−NSQ) complex.[16] The intensities of the absorptions at 800, 720, and 430 nm increase with the temperature, those bands being attributed to the Cat-N-BQ$^-$ chromophore, whereas the intensity of the band at 385 nm associated with the Cat-N-SQ$^{2-}$ ligand decreases. Unfortunately the low solubility of this compound in nonpolar solvents has precluded the possibility of determining the magnetic susceptibilities using the Evans method. On the other hand the $^1$H NMR spectra show that solvolysis and ligand disproportionation processes occur if polar solvents such as dimethyl sulfoxide are used.

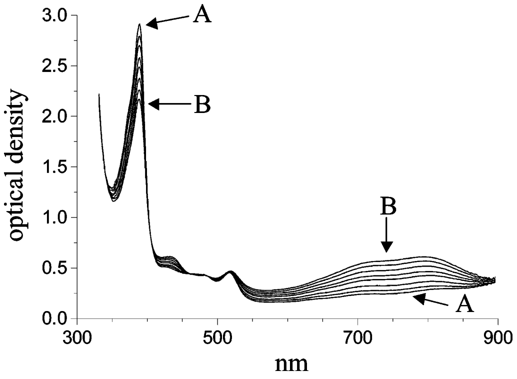


**Figure 4.** Variable-temperature electronic absorption spectrum of 1,2-dichlorobenzene solutions of [Co(tpy)(Cat-N-SQ)]$PF_6$ from 294 K (A) to 346 K (B).

The results from both EPR and electronic spectra well agree with the existence of an entropy driven interconversion equilibrium

$$[\mathrm{Co^{III}(tpy)(Cat\text{-}N\text{-}SQ)}]^+ \rightleftharpoons [\mathrm{Co^{II}(tpy)(Cat\text{-}N\text{-}BQ)}]^+ \qquad (2)$$

involving a ls-cobalt(III) complex of a radical ligand ($S = 1/2$) species which yields an high-spin cobalt(II) metal complex of a closed-shell ligand. The possibility of a spin-crossover equilibrium involving ls- and hs-cobalt(II) species is clearly ruled out by the observed pattern of electronic transitions, which are typical of the Cat-N-SQ$^{2-}$ ligand at low temperature and of the Cat-N-BQ$^-$ at high temperature, and by the EPR parameters ($g = 2.00$), which are not consistent with the presence of a ls-$d^7$ cobalt(II) complex. The temperature behavior of the EPR spectra is consistent with the formation of a paramagnetic species, characterized by a very short electronic relaxation time. Such fast electronic relaxation time is usually observed in six-coordinated high-spin Co(II) derivatives. It is rather obvious that if a fast interconversion equilibrium involves two paramagnetic species A and B characterized by electronic relaxation times $\tau_{eA}$ and $\tau_{eB}$, the total relaxation time of the system, $\tau_e$, is given by

$$1/\tau_e = x_A/\tau_{eA} + (1 - x_A)/\tau_{eB} \qquad (3)$$

where $x_A$ and $1 - x_A$ are the molar fractions of A and B, respectively. It is important to stress out that if $\tau_{eB}$ is much

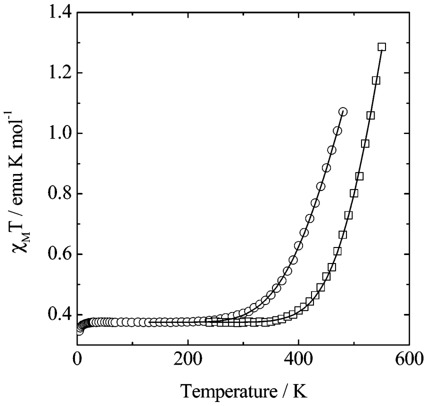


**Figure 5.** $\chi_M T$ vs $T$ plot for [Co(tpy)(Cat-N-SQ)]$PF_6$ (circles) and [Co(Cat-N-BQ)(Cat-N-SQ)] (squares).

shorter than $\tau_{eA}$, $\tau_e$ is controlled by $\tau_{eB}$, even if A is the dominant species. The electronic relaxation time of [$Co^{III}$(tpy)(Cat-N-SQ)]$^+$ is expected to be much slower than that of the valence tautomer [$Co^{II}$(tpy)(Cat-N-BQ)]$^+$ if the metal ion adopts a high-spin electronic configuration. Thus, the observed experimental data could be consistent with the existence of the above shown valence tautomeric equilibrium (2).

The magnetic behavior of [$Co^{III}$(tpy)(Cat-N-SQ)]$PF_6$ as a $\chi_M T$ vs $T$ plot is shown in Figure 5, where $\chi_M$ is the molar magnetic susceptibility and $T$ the temperature. In the temperature range 10−200 K the $\chi_M T$ value is nearly equal to what is expected for one spin 1/2, which corresponds to a single unpaired electron on the semiquinonato ligand, with $g_{SQ} = 2.00$ (0.375 emu K mol$^{-1}$). The decrease of $\chi_M T$ at lower temperatures might be ascribed to saturation effects and/or intermolecular interactions. The most interesting feature appears above 200 K. Indeed, $\chi_M T$ increases with temperature and reaches 1.1 emu K mol$^{-1}$ at 490 K. These changes in $\chi_M T$ are consistent with the thermally induced valence tautomeric interconversion (2). If the transition were complete, we would expect the paramagnetism of hs-cobalt(II) in the high-temperature limit which, because of the spin−orbit coupling in the ground state $^4T_{2g}$, would correspond to $\chi_M T \approx 3$ emu K mol$^{-1}$.[35] Unfortunately, the material starts to decompose at 490 K, long before the transition is completed and even before we observe the inflection point. Nevertheless, one may track the thermodynamic parameters of the transition in writing $\chi_M T$ as

$$\chi_M T = \chi_M T_{SQ} + \gamma_{hs-Co(II)}(\chi_M T_{hs-Co(II)} - \chi_M T_{SQ}) \qquad (4)$$

with

$$\gamma_{hs-Co(II)} = \frac{1}{\exp\left(\frac{\Delta H}{RT} - \frac{\Delta S}{R}\right) + 1}$$

where $\chi T_{hs-Co(II)}$ and $\chi T_{SQ}$ are the $\chi T$ values for isolated high-spin cobalt(II) and low-spin cobalt(III)−semiquinonato, respectively. $\gamma_{hs-Co(II)}$ is the molar fraction of high-spin cobalt(II). $\Delta H$ and $\Delta S$ are respectively the enthalpy and the entropy changes associated with the rearrangement of the electronic configuration. When $\chi_M T_{SQ} = 0.375$ and $\chi_M T_{hs-Co(II)} = 3.2$ emu K mol$^{-1}$ are fixed, the least-squares fitting of $\chi_M T$ with (4) gives a fairly good agreement with $\Delta H = 24.3$ kJ mol$^{-1}$ and $\Delta S = 41.3$ J K$^{-1}$ mol$^{-1}$ ($T_c = \Delta H/\Delta S = 588$ K). It is important to keep in mind that this model is valid only if (i) there are no interactions between the molecules and (ii) $\chi_M T_{hs-Co(II)}$ is temperature independent above 250 K. Surprisingly it is not possible to observe any thermally induced valence tautomeric interconversion for the tetraphenylborate analogue [Co(tpy)(Cat-N-SQ)]($BPh_4$) at lower temperatures than the decomposition of the material; $\chi_M T$ remains equal to 0.37 emu K mol$^{-1}$ in the investigated range 4−400 K.

The same measurements were also performed for [Co(Cat-N-BQ)(Cat-N-SQ)] in the solid phase. The thermal variation of $\chi_M T$ is shown in Figure 4. The magnetic behavior of this material is very similar to that of [Co(tpy)(Cat-N-SQ)]$PF_6$. It shows a thermally induced valence tautomeric interconversion at a temperature slightly higher than for [$Co^{III}$(tpy)(Cat-N-SQ)]$PF_6$, and again the material decomposes before the conversion is completed. The fitting of the data assuming the same $\chi_M T$ values used for the previously discussed complex gives an excellent agreement with $\Delta H = 44.4$ kJ mol$^{-1}$ and $\Delta S = 74.4$ J K$^{-1}$ mol$^{-1}$ ($T_c = \Delta H/\Delta S = 597$ K) (see Figure 4). Once compared with the thermodynamic quantities obtained for the same process in toluene solution, $\Delta H = 42$ kJ mol$^{-1}$ and $\Delta S = 140$ J K$^{-1}$ mol$^{-1}$,[16] it appears that the $T_c$ difference is essentially due to the entropy factor.

The possibility of inducing the valence tautomeric interconversion of [Co(tpy)(Cat-N-SQ)]$PF_6$ and [Co(Cat-N-BQ)(Cat-N-SQ)] by irradiating at low temperatures the solid complexes and their solutions in organic polymers was also investigated. The compounds were irradiated in situ at 400 nm using a 50 nm fwhm interference filter at 5 K. No changes in magnetic moments were observed. The same experiments were repeated using an EPR spectrometer. However, neither diminution of the $g = 2.00$ radical signal nor a signal attributable to Co(II) species could be observed. In summary, irradiation of the complex does not lead to the valence tautomeric state or its lifetime is too short to reach a photostationary state in which it is significantly present.

**Electrochemistry.** Cyclic voltammetry experiments of deaerated 1,2-dichloroethane solutions of [Ni(tpy)(Cat-N-BQ)]$PF_6$ show three redox couples at −0.35, −0.90, and −1.60 V vs ferrocenium/ferrocene couple, respectively. The first and the third process are not reversible. It can be reasonably suggested that all the processes are ligand centered, the first two involving the coordinated Schiff base diquinone ligand. Indeed the one electron oxidation of mononegative Cat-N-BQ$^-$ yields the neutral SQ-N-BQ radical, which is expected to be a weak Lewis base. The resulting Ni(tpy)(SQ-N-BQ)$^{2+}$ species is expected to be unstable, and dissociation follows the oxidation process.[36] This behavior is usually observed for all the metal−quinone/metal−semiquinonato couples we have investigated in the past, unless the electronic properties of the metal ion would determine a slow dissociation rate mechanism.[37] The second process (revers-

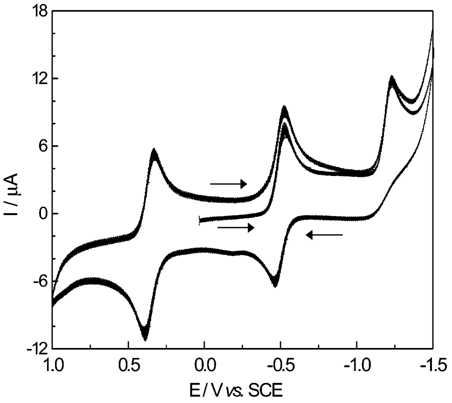


**Figure 6.** Cyclic voltammogram at room temperature of a 1,2-dichloroethane 0.1 M $[NBu_4]PF_6$ solution of [Co(tpy)(Cat-N-SQ)]$PF_6$. In our experimental apparatus the $Fc^+/Fc$ couple is at +0.455 V vs the standard calomel electrode (SCE).

ible) occurring at −0.90 V can be reasonably assigned to the [Ni(tpy)(Cat-N-BQ)]$^+$/[Ni(tpy)(Cat-N-SQ)] couple. It should be stressed that the same process for the neutral [Ni-(Cat-N-BQ)$_2$] occurs[36] at −1.20 V and there is no evidence of it in our cyclic voltammogram. This finding strongly supports the fact that for this compound equilibrium **(1)** is strongly shifted to the left. The third process (irreversible) occurring at −1.60 V is rather difficult to assign. It could involve either the Schiff-base diquinone ligand or the ancillary tpy ligand. The occurrence of a redox process at a similar potential in the voltammogram of the cobalt complex suggests that the metal ion is probably not involved in this couple.

The electrochemical behavior of [Co(tpy)(Cat-N-SQ)]$PF_6$ is rather different. Its cyclic voltammograms show two reversible processes at −0.11 and −1.00 V and an irreversible one at −1.65 V vs $Fc^+/Fc$ couple (Figure 6). The free energy value and the reversible character of the process occurring at −0.11 V suggest that the process is rather different from that −0.35 V observed for the nickel complex. In addition the value of −1.00 V, altough not too different, is significantly lower than the −0.90 V value found for the nickel derivative. Indeed it is usually found in a family of metal−polyoxolene complexes that if different metal ions have the same oxidation number, the ligand-centered redox processes are characterized by very similar free energy values.[32,36−38] Therefore, we suggest that the electron-transfer process occurring at −0.11 V is dominantly ligand centered and should be attributed to the couple

$$[\mathrm{Co^{III}(tpy)(Cat\text{-}N\text{-}BQ)}]^{2+} + e^- \rightleftharpoons [\mathrm{Co^{III}(tpy)(Cat\text{-}N\text{-}SQ)}]^+ \qquad (5)$$

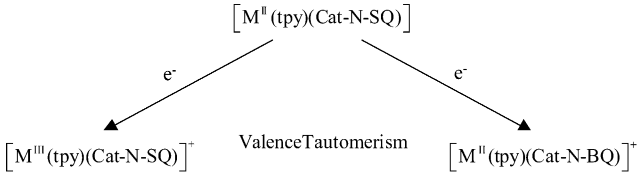
whereas the one occurring at −1.00 V should be associated with the metal-centered redox process

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

This assignment is supported by (i) the electronic spectra which show that at room temperature the cobalt(III)−semiquinonato species is the dominant one and (ii) the reversible character of process (5) as expected for a ligand-centered redox process, like the one observed at −0.90 V as observed also for the nickel complex. The assignment of the irreversible process occurring at −1.65 V is rather tentative, as mentioned above. Finally, it should be stressed out that the cyclic electrochemical behavior of [Co(Cat-N-BQ)(Cat-N-SQ)][36] is totally different from the one observed for this compound. Again this supports the suggestion that equilibrium (1) in this solvent is strongly shifted to the left.

## Discussion

The charge-localized nature of the metal−Schiff base diquinone metal complexes under investigation clearly shows up from the differences of the geometrical features of the coordinated ligands.[21,30−32,36] The crystallographic characterization of [Co(tpy)(Cat-N-SQ)]$BPh_4$ well supports the proposed charge distribution. If this description is correct and can be extended to the other derivatives, the one electron oxidation of a not yet isolated [M$^{II}$(tpy)(Cat-N-SQ)] complex may be considered to be (i) ligand centered, yielding the [M$^{II}$(tpy)(Cat-N-BQ)]$^+$ cation, or (ii) metal centered thus affording the [M$^{III}$(tpy)(Cat-N-SQ)]$^+$ complex, according to the following scheme:



*It is rather obvious that the process requiring less energy will be favored. Our experimental results show that for the nickel complex the ligand-centered process occurs, whereas the metal-centered one is dominant in the case of the cobalt compound.*

The difference between the free energy changes associated with the two redox processes defines the free energy change of the valence tautomeric equilibrium. Since only one of the two quantities can be experimentally measured, it is impossible to calculate this difference using experimental data. However, as mentioned above, the examination of the electrochemical behavior of the [M(Cat-N-BQ)$_2$] complexes[32,36] suggests that the ligand-centered redox potentials are approximately independent from the nature of metal ion when metal ions with the same oxidation state are considered. In fact, for the Ni(II) and the Zn(II) complexes two reversible electron-transfer processes were found, which can be assigned to the equilibria

$$[\mathrm{M^{II}(Cat\text{-}N\text{-}BQ)_2}] + e^- \rightleftharpoons [\mathrm{M^{II}(Cat\text{-}N\text{-}BQ)(Cat\text{-}N\text{-}SQ)}]^-$$

and

$$[\mathrm{M^{II}(Cat\text{-}N\text{-}BQ)(Cat\text{-}N\text{-}SQ)}]^- + e^- \rightleftharpoons [\mathrm{M^{II}(Cat\text{-}N\text{-}SQ)_2}]^{2-}$$

For the nickel derivative the two processes occur at −1.20

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and −1.53 V vs $Fc^+/Fc$, whereas for the zinc one they occur at −1.17 and −1.50 V vs $Fc^+/Fc$. The striking similarity of the measured quantities can be explained taking into account the basic electrostatic nature of the metal−Schiff base diquinone ligand interaction and the facts that the two metal ions are expected to have similar charge/radius ratios and that the solvation free energy changes are reasonably independent from the nature of the metal ions.[38] If we translate these considerations to our discussion, the free energy change associated with the couple $[Co^{II}(tpy)(Cat\text{-}N\text{-}BQ)]/[Co^{II}(tpy)(Cat\text{-}N\text{-}SQ)]^-$ would be similar to that of the nickel complex. Indeed it should be considered that, concerning their electronic configurations, the two complexes differ only in the presence of one electron in the $t_{2g}$ orbitals, whose contribution to the bonding interactions in these complexes are negligible. Therefore, if this hypothesis holds, the free energy change associated with the valence tautomeric equilibrium

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

can be calculated to be of the order of 10 kJ $mol^{-1}$ at room temperature. This means that the order of magnitude of the molar fraction of the Co(II) species in solution is about 0.02 in agreement with the electronic spectra. It should be reminded that a similar assumption was found to work reasonably in the correlation of the metal-to-ligand charge-transfer spectra of 1:1 catecholato Fe(III) complexes and their electrochemical properties.[38]

It is worth noting that for [Co(Cat-N-BQ)(Cat-N-SQ)] the analogous equilibrium in toluene is characterized by a free energy change (about 0.4 kJ $mol^{-1}$), which is significantly lower than that for $[Co(tpy)(Cat\text{-}N\text{-}SQ)]^+$. Following the isoelectric character of the interconversion equilibrium, the different solvents are not expected to play a key role in these free energy changes. Hence, the observed difference between these quantities should reflect a greater stabilization of Co(III) when it is coordinated to the tpy ligand than when it is coordinated to Cat-N-BQ. This result parallels the one observed for $[Co(N\text{-}N)(diox)_2]$ complexes. Indeed it was found that the critical temperature $T_c$ reflects the donor power of the ancillary diazine ligand toward the metal ion.[1−3,7,9,12,39] Thus, low donor Lewis bases are expected to less stabilize Co(III) than Co(II), whereas the reverse is true with strong bases. This point might constitute an important empirical rule and should be considered when the design of a valence tautomer is planned. However the available data show that these considerations hold only in solution.

To date all the cobalt complexes known to undergo valence tautomerism in condensed phase were formed by simply chelating *o*-dioxolene ligands. The reason is that this intriguing interconversion process requires a low electronic delocalization within the metallocycle ring. Our investigations show that despite the fact that the M−N chemical bond is more covalent than the M−O, still we maintain the low electronic delocalization. The results here reported show that to design these systems ligands other than those containing only oxygen donor atoms can be considered. This suggestion is supported by some recently reported results on iminosemiquinonato metal complexes, whose structural and physical properties suggest a charge localized description.[40−43]

One of the most relevant points of this investigation is the large difference between $T_c$ in solution and in the solid state. As mentioned above, this value was found equal to 300 K for [Co(Cat-N-BQ)(Cat-N-SQ)] in toluene solution,[16] but the fit of magnetic data of the solid complex suggests that $T_c$ is about 300 K higher. We were unable to obtain the thermodynamic parameters of the solution equilibrium involving the $[Co(tpy)(Cat\text{-}N\text{-}SQ)]^+$ cation, because of the lack of the molar absorption coefficients of at least one of the two species undergoing the intramolecular electron-transfer process. However it can be qualitatively anticipated that $T_c$ should fall between 300 and 350 K, well below the 588 K determined for the solid compound. This result stresses the role of the medium effect as one of the determining factors in these equilibria. As said above, following the isoelectric character of the transitions, the enthalpy factors are not expected to play an important role.[38] This is supported by the fact that the enthalpy changes for the interconversion equilibrium in solution and in the solid state are similar (44 and 42 kJ $mol^{-1}$, respectively). The $T_c$'s shifts are therefore due to the entropy changes which are expected to drastically depend on the vibronic interactions.[12,44−46] In this respect it should be remembered that the unsolvated Co(phen)(DBSQ)(DBCat) does not show any transition in the temperature range 4−300 K, whereas the toluene and chlorobenzene solvates undergo to the transitions in the temperature range 200−260 K.[6] The results we report here are in full agreement with this observation.

Finally, as observed for the family of Co(CTH)(diox)Y complexes,[22] it is found that the critical temperature of the interconversion is strongly affected by the nature of the counterion. Indeed we were unable to detect any transition by replacing the hexafluorophosphate counterion with the tetraphenylborate before the decomposition. It seems that the effect of the anion on the transition temperature is not only governed by its volume but also by the Coulombic interactions. However, although it is rather obvious that in the solid state the nature of the lattice interactions and the packing effects play a key role, we are still far from an

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even qualitative complete comprehension of these systems in condensed phase.

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**Supporting Information Available:** CIF data file containing crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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