Valence Tautomerism in a Cobalt Complex of a Schiff Base Diquinone Ligand

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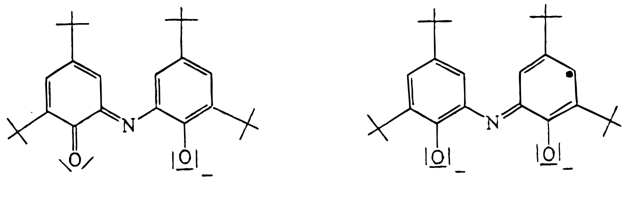
Introduction

Molecules exhibiting interconversion between energetically close-lying electronic states are actively investigated as possible candidates for information storage.[1] There are several classes of potentially bistable molecules, like thermochromic compounds,[2] mixed valence compounds,[3−6] spin crossover complexes,[7−12] and valence tautomers.[13−16] The last term defines two molecules related by an intramolecular electron-transfer process, i.e. A−D and A$^-$−D$^+$, thus involving two electronic isomers characterized by different charge distributions and then by different physical and chemical properties.

It is apparent that, to obtain molecular adducts A−D characterized by valence tautomerism, two conditions must be simultaneously satisfied: (i) the covalency of the interaction between A and D must be low; (ii) the energies of the frontier orbitals of the two counterparts must be similar. These conditions are hard to meet simultaneously, and so far only molecular complexes of general formula M(N−N)(diox)$_2$ (M = Co, Mn; N−N = diazine ligand; diox = catecholato, semiquinonato) have been reported showing this property, with transition temperatures T_c ranging from 100 to 350 K.[13,17−22] In all of these systems the tautomeric equilibrium involves the internal electron transfer between a catecholato ligand and the acceptor metal ion, yielding a metal semiquinonato adduct as a product. All of these systems are so far variations on the same theme, in the sense that they have in common the same class of dioxolene ligands. To find molecules that are bistable around room temperature, it is necessary to increase the number of ligands that can be used for complexation. We have now found that a Schiff base diquinone ligand forms two valence tautomeric species with cobalt ions with a transition temperature around room temperature. Here we wish to report the spectroscopic characterization of this system in solution.

Chart 1



Cat−N−BQ

Cat−N−SQ

Results and Discussion

It is well-known[23−27] that 3d metal ions react with 3,5-di-*tert*-butylcatechol and aqueous ammonia in the presence of air, yielding bis complexes of the Schiff base biquinone ligands, which can be described, depending on the nature of the metal ions, either as the monoanion of the 2-(2-hydroxy-3,5-di-*tert*-butylphenylimino)-4,6-di-*tert*-butyl-cyclohexa-3,5-dienone (Cat-N-BQ (**I**)) or the corresponding dianionic semiquinonato analogue (Cat-N-SQ (**II**)) (Chart 1). The cobalt complex can be formulated on the basis of crystallographic characterization as a Co^{III}(Cat-N-BQ)(Cat-N-SQ), in which the diamagnetic metal ion is pseudo-octahedrally coordinated to the two tridentate meridional ligands in the two different oxidation states.[24] Ir, RR, magnetic, and EPR data are well consistent with this description.[24,26,28]

We have now found, however, that the solutions of this complex in nonpolar solvents such as toluene or 1,2-dichloroethane show, as reported, an EPR signal at low temperatures but are EPR silent at room temperature and that their colors turn reversibly from brick brown to green-blue when warmed. This behavior was not observed in a previous study.[24] The variable-temperature absorption spectra of a toluene solution of this compound (Figure 1) show the existence of an equilibrium involving two chromophores as indicated by the presence of two isosbestic points. As the temperature of the solution is increased the intensity of the bands at 797 and 721 nm increases,

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(1) Kahn, O.; Launay, J. P. *Chemtronics* **1988**, *3*, 140.
(2) Sone, K.; Fukuda, Y. *Inorganic Thermochromism*; Springer-Verlag: Berlin, 1987.
(3) Day, P. *Int. Rev. Phys. Chem.* **1981**, *1*, 149.
(4) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.
(5) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.
(6) Prassidis, K. (Ed.) *Mixed Valency Systems: Applications in Chemistry, Physics, and Biology*; NATO ASI Series C343; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.
(7) Gütlich, P. *Struct. Bonding* **1981**, *44*, 83.
(8) Konig, E. *Progr. Inorg. Chem.* **1987,** *35*, 527.
(9) Beattie, J. K. *Adv. Inorg. Chem.* **1988**, *32*, 1.
(10) Toftlund, H. *Coord. Chem.* **1989,** 94, 67.
(11) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Eng.* **1994**, *33*, 2024.
(12) Kahn, O.; Martinez, C. J. *Science* **1998**, *279*, 44.
(13) Pierpont, C. G.; Lange, C. W. *Prog. Coord. Chem.* **1993**, *41*, 381.
(14) Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 8221.
(15) Gütlich, P.; Dei, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2734.
(16) Hendrickson, D. N.; Adams, D. M.; Wu, C.-C.; Aubin, S. M. J. in *Magnetism: A Supramolecular Function*; Kahn, O., Ed.; NATO ASI Series C484; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996; p 357.
(17) Abakumov, G. A.; Cherkasov, V. K.; Bubnov, M. P.; Ellert, O. G.; Dobrokhotova, Z. B.; Zakharov, L. N.; Struchkov, Y. T. *Dokl. Akad. Nauk.* **1993**, *328*, 12.
(18) Jung, O. S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 2227.
(19) Jung, O. S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 1127.
(20) Attia, A. S.; Pierpont, C. G. *Inorg. Chem.* **1995**, *34*, 1172.
(21) Jung, O. S.; Jo, D. H.; Lee, Y. A.; Sohn, Y. S.; Pierpont, C. G. *Angew. Chem., Int. Ed. Eng.* **1996**, *35*, 1694.
(22) Jung, O. S.; Jo, D. H.; Lee, Y. A.; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1997**, *36*, 19.
(23) Girgis, A. Y.; Balch, A. L. *Inorg. Chem.* **1975**, *14*, 2724.
(24) Larsen, S. K.; Pierpont, C. G. *J. Am. Chem. Soc.* **1988**, *110*, 1827.
(25) Simpson, C. L.; Boone, R. S.; Pierpont, C. G. *Inorg. Chem.* **1989**, *28*, 4379.
(26) Bruni, S.; Caneschi, A.; Cariati, F.; Delfs, C.; Dei, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1994**, *116*, 1388.
(27) Speier, G.; Csihony, J.; Whalen, A. M.; Pierpont, C. G. *Inorg. Chem.* **1996**, *35*, 3519.
(28) Swarnabala, G.; Rajasekharan, M. U.; Padhye, S. *Chem. Phys. Lett.* **1997**, *267,* 539.

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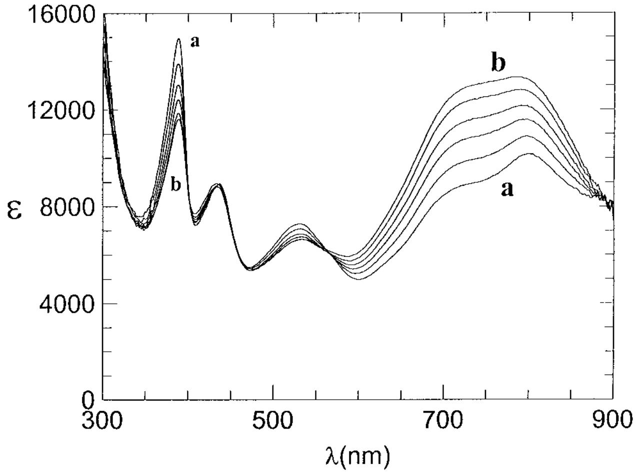

Figure 1. Temperature dependence of the electronic absorption spectrum of a toluene solution of Co(Cat-N-BQ)(Cat-N-SQ): (a) 296 K; (b) 337 K.

whereas that of the bands at 533, 439, and 391 nm decreases. When the observed spectra are compared with those of the $Zn(Cat\text{-}N\text{-}BQ)_2$, which show two intense bands at 793 and 736 nm,[23] as well as with those of the $M(Cat\text{-}N\text{-}SQ)_2$ (M = Ge, Sn),[26] showing bands at 1010, 559, and 385 nm, it is apparent that the spectrum of the cobalt complex is dominated by the internal transitions of the coordinated ligands. Support for this statement arises from the comparison with the spectrum of the Al(Cat-N-BQ)(Cat-N-SQ) complex (see Experimental Section). Thus the observed spectra show that the molar fraction of the species containing the Cat-N-SQ ligand decreases on increasing temperature, whereas that of the species containing the Cat-N-BQ ligand increases. The temperature-dependent electronic spectrum is therefore consistent with the presence of the redox equilibrium

$$Co^{III}(Cat\text{-}N\text{-}BQ)\ (Cat\text{-}N\text{-}SQ) \rightleftharpoons Co^{II}(Cat\text{-}N\text{-}BQ)_2 \quad (1)$$

involving a ligand-to-metal electron-transfer process.

Further support of the existence of the above equilibrium is provided by magnetic susceptibility data obtained with the Evans method[29] for toluene-d_8 solutions of this compound in the range 295−360 K. The observed χT values increase as the temperature of the solutions increases, reaching a plateau at 355 K characterized by the χT value of 3.21 emu mol^{-1} K. The experimental data have been analyzed on the assumption of the existence of equilibrium (eq 1), assuming a $\mu_{eff} = 1.75\ \mu_B$ ($\chi T = 0.38$ emu mol^{-1} K) for the reactant species, in agreement with the data obtained for the solid, and $\mu_{eff} = 5.07\ \mu_B$ ($\chi T = 3.21$ emu mol^{-1} K) for the product, as extrapolated from solution χT values. The latter value is consistent with the expected one for a pseudo-octahedral high-spin cobalt(II) complex. Finally the magnetic susceptibility data have been used to calculate the thermodynamic quantities associated with eq 1. The values obtained are $\Delta H = 42.0$ (0.8) kJ mol^{-1} and $\Delta S = 140(3)$ J mol^{-1} K^{-1}. These values are of the same order of magnitude as those reported for valence tautomeric equilibria involving $Co(N{-}N)(diox)_2$ complexes.[16,30−32]

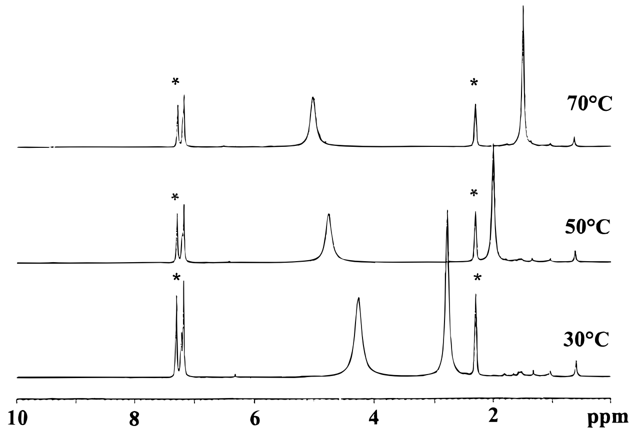

Figure 2. Temperature dependence of the ^1H NMR spectrum of a toluene-d_8 solution of Co(Cat-N-BQ)(Cat-N-SQ). The observed signals are due to the *tert*-butyl groups of the ligand. Resonances associated with ring protons are not shown. Signals labeled with * are due to the solvent.

The variable temperature ^1H NMR spectra of a toluene-d_8 solution of the complex are shown in Figure 2. The signal half-widths of the *tert*-butyl groups are significantly smaller than expected for a radical species, and the temperature dependence of the associated isotropic shifts does not follow a Curie−Weiss behavior, thus indicating that pseudocontact shifts are also operative. One confirmation of this comes from the spectra of the Al(Cat-N-BQ)(Cat-N-SQ) complex, which shows the spectral behavior expected for a radical derivative. In this case the signal half-widths of the *tert*-butyl groups of the two ligands, which are equivalent on the NMR time scale, are significantly broad, and the temperature tependence of the observed isotropic shifts follows the Curie−Weiss law. The spectral parameters observed for the cobalt complex are consistent with the presence of a paramagnetic compound characterized by a short electronic relaxation time and a large magnetic anisotropy like a high-spin cobalt(II) in pseudo-octahedral symmetry. It is also apparent from these data that the EPR signal is not detected in solution because of the short electronic relaxation time of the system. The reported solution spectrum is not consistent with a Co^{III}(Cat-N-SQ) species, as suggested by the same authors,[24] on the other hand, but it seems consistent with a Co^{III}(3,5-di-*tert*-butylsemiquinonato) impurity.

The present data therefore strongly suggest that the Co^{III}(Cat-N-BQ)(Cat-N-SQ) complex undergoes a valence tautomeric equilibrium in solution. It is clear that this transformation is entropy driven and the observed large entropy change can be ascribed to changes in vibrational and, even to a minor extent, electronic contributions.[33] In fact, as previously suggested,[13−15,30,31] changes in spin and orbital degeneracy of the electronic ground state between the reactant and the product cannot explain the observed entropy change of 140 J mol^{-1} K^{-1}. Indeed in the octahedral symmetry approximation the expected electronic entropy change cannot be greater than 15 J mol^{-1} K^{-1}. Entropy changes due to the different solvation of reactants and products are expected to be very small.[34] It is therefore suggested, as for spin-crossover complexes and the previously reported valence tautomers, that also for the present system the vibrational entropy change is the main factor influencing the observed equilibrium. As a general consideration, the valence tautomerism originates from a change in the electronic popula-

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(29) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(30) Pierpont, C. G.; Jung, O. S. *Inorg. Chem.* **1995**, *34*, 4281.
(31) Adams, D. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 11515.
(32)) Roux, C.; Adams, D. M.; Itiè, J. P.; Polian, A.; Hendrickson, D. N.; Verdaguer, M. *Inorg. Chem.* **1996**, *35*, 2846.
(33) Richardson, D. E.; Sharpe, P. *Inorg. Chem.* **1993**, *32*, 1809.
(34) Dei, A. *Inorg. Chem.* **1993**, *32*, 5730.

tion of the antibonding e_g orbitals with a consequent increase of the distance of the metal−ligand donor atoms. For the Co^{III}(Cat-N-BQ)(Cat-N-SQ) complex the Co−O and Co−N distances are 1.90 and 1.87 Å,[24] respectively, whereas in the Ni(Cat-N-BQ)$_2$ the Ni−O and the Ni−N distances are 2.03 and 2.02 Å, respectively.[25] The different charge distribution in the latter compound leads to an increase of the metal−donor atom distance of 0.14 Å and a similar difference can be reasonably expected for the Co^{II}(Cat-N-BQ)$_2$ complex. This consideration supports the hypothesis of a large vibrational entropy change contribution for the valence tautomeric transition here discussed.

To utilize bistable molecules for switching application, it is necessary that the transition be characterized by hysteresis and this requires that the process occurs in condensed phases.[1] We were unable to detect in the solid state the existence of a similar transition for this compound. A reversible change of color occurs when the sample is warmed to 550 K. The DSC trace evidences two first-order transitions at 550 and 565 K with associated enthalpy changes of 3.9 and 1.1 kJ mol^{-1}, respectively. However, the lack of magnetic and spectroscopic data at high temperatures does not allow any conclusion about the nature of these transitions.

We feel that this system is worth of consideration for two reasons. First, it describes a valence tautomeric equilibrium involving a cobalt complex in which the electronic ground states of the two species are well defined. This is not true, for example, for all the reported Co^{II}(N−N)(SQ)$_2$ complexes, whose magnetic properties are rather poorly understood.[13,14,16−22] The second and more important reason is that valence tautomerism characterizes a complex formed by a ligand which contains a nitrogen donor atom in addition to the dioxolene oxygen donors. This means that there is low delocalization within the metallocycle chelate ring and suggests that it could be possible to utilize a less restricted class of chelating ligands for designing metal complexes exhibiting valence tautomerism.

Experimental Section

Physical Methods. EPR spectra were recorded with a Varian E-9 spectrometer working at X-band frequency. Room-temperature electronic spectra were recorded in the range 5000−40 000 cm^{-1} on a Perkin-Elmer Lambda 9 spectrophotometer. Temperature-dependent electronic spectra were recorded on a Shimadzu 2101 PC spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance DPX spectrometer operating at 200 MHz. Differential calorimetry experiments were carried out on a Perkin-Elmer DSC 9 apparatus.

Synthetic Procedure. The Co(Cat-N-BQ)(Cat-N-SQ) and Zn(Cat-N-BQ)$_2$ complexes where prepared according to literature methods.[23,24] The Al(Cat-N-BQ)(Cat-N-SQ) complex was prepared in a similar fashion using aluminum trichloride as metal salt. Anal. Found: C, 76.75; H, 9.26; N, 3.17. $C_{56}H_{80}AlN_2O_4$ requires C, 77.11; H, 9.25; N, 3.21. ESR, $g = 2.00$ (no hyperfine structure detected). UV−vis, nm (ϵ): 960 (12 400), 916 (12 100), 858 (11 900), 777 (16 800), 720 (14 900), 538 (4500), 455 (10 645), 435 sh, 393 (39 800), 370 sh, 345 sh.

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