J. Am. Chem. Soc. 1993, *115*, 8221–8229

8221

Bistability in the [Co^{II}(semiquinonate)$_2$] to [Co^{III}(catecholate)(semiquinonate)] Valence-Tautomeric Conversion

David M. Adams,[1] Andrea Dei,[1,2] Arnold L. Rheingold,*,[3] and David N. Hendrickson*,[1]

Contribution from the Department of Chemistry-0506, University of California at San Diego, La Jolla, California 92093, and Department of Chemistry, University of Delaware, Newark, Delaware 19716
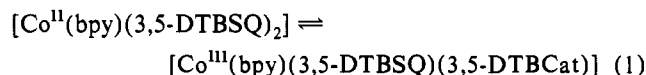
Received April 16, 1993

Abstract: The preparation and characterization of a series of valence-tautomeric cobalt complexes are presented. The diiminium ligand N⌒N in [Co(N⌒N)(3,5-DTBSQ)("3,5-DTBQ")] is 4,4'-diphenyl-2,2'-bipyridine (bpbpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2'-bipyrimidine (bpym), or 2,2'-bipyrazine (bpyz). It is shown that at room temperature the first three complexes are low-spin Co^{III} complexes with one semiquinonate-(1–) and one catecholate(2–) ligand. On the other hand, the phen, bpym, and bpyz complexes at room temperature are Co^{II} complexes with two semiquinonate ligands. The complex [Co(bpyz)(3,5-DTBSQ)$_2$] crystallizes in the space group *Ccc*2, which at 296 K has a unit cell with *a* = 16.233(6) Å, *b* = 26.894(10) Å, *c* = 8.472(2) Å, and *Z* = 4. Refinement with 1307 observed [*F* > 3.0σ(*F*)] reflections gave *R* = 0.0461 and *R*$_w$ = 0.0504. The complex [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$CH$_3$ crystallizes in the spage group *P*2$_1$/*c*, which at 295 K has a unit cell with *a* = 10.436(4) Å, *b* = 32.524(14) Å, *c* = 13.563(6) Å, *β* = 111.44(3)°, and *Z* = 4. Refinement with 2060 observed [*F* > 4.0σ(*F*)] reflections gave *R* = 0.0824 and *R*$_w$ = 0.0850. At room temperature both of these complexes have Co–O and Co–N bond lengths which indicate high-spin Co^{II} ions. The bond lengths in the quinone-derived ligands indicate that for both complexes the ligands are semiquinonate ligands. Variable-temperature UV–vis electronic absorption spectra are presented to show that in toluene solution all six of the complexes exhibit an equilibrium involving the Co^{II} and Co^{III} valence-tautomeric forms of the complex. An electron is transferred from the Co^{II} ion to one semiquinonate ligand to give the Co^{III} tautomer. Variable-temperature (2–320 K) magnetic susceptibility data are presented for polycrystalline samples of all of the complexes. The toluene solvate [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$CH$_3$ is the first complex to undergo the valence-tautomeric transformation in the solid state. Abrubtly in the 220–260 K region this toluene solvate converts between the Co^{II} and Co^{III} tautomeric forms in the solid state. X-ray structures at 238 and 173 K are presented to show that, upon cooling, this phen complex does convert from a Co^{II}(semiquinonate)$_2$ to a Co^{III}(semiquinonate)-(catecholate) complex. The chlorobenzene solvate of the phen complex also undergoes the tautomeric transformation, although less abruptly than the toluene solvate. The nonsolvated phen complex remains in the Co^{II} tautomeric form from 320 down to 2 K. It is shown that the valence-tautomeric transformation is entropy driven.

Introduction

Complexes of transition-metal ions and semiquinonate and catecholate ligands have localized bonding descriptions.[4] The parentage of the highest-occupied molecular orbitals of these complexes is dominantly either metal or ligand based. Furthermore, the catecholate and semiquinonate ligands have filled or partially filled molecular orbitals that are close in energy to transition-metal d orbitals. As a result, it is possible to change the charge distribution by changing one or more of three features of such a complex: the redox potential of the quinone-derived ligand, the nature of the other ligands,[5a] and the metal ion. For example, the charge distribution changes from [L$_2$Cu^{II}(3,5-DTBCat)] to [L$_2$Cu^{I}(3,5-DTBSQ)], where the ligands are the catecholate(2–) (Cat) and semiquinonate(1–) (SQ) forms of 3,5-di-*tert*-butyl-1,2-benzoquinone, respectively, as the ligand L is changed from a hard nitrogen donor to a soft phosphine donor.[5a] In the case of [Co(bpy)(3,5-DTBSQ)(3,5-DTBCat)], where bpy

is 2,2'-bipyridine, the metal ion is low-spin Co^{III} in the solid state.[6] On the other hand, a high-spin Co^{II} ion is found[7] in [Co(py)$_2$-(phenSQ)$_2$], where phenSQ$^-$ is the monoanion semiquinone of 9,10-phenanthrenequinone and py is pyridine. Changing the energy of the metal d orbital also leads to similar shifts in charge distribution. Neutral complexes of first-row metals have partially oxidized metals coordinated by partially reduced quinone-derived ligands [*e.g.*, Cr^{III}(SQ)$_3$, Mn^{II}(SQ)$_2$, and Fe^{III}(SQ)$_3$], whereas in the analogous complexes of the third-row metals the metal ions are in higher oxidation states with the quinone-derived ligands fully reduced [*e.g.*, W^{VI}(Cat)$_3$, Re^{VI}(Cat)$_3$, and Os^{VI}(Cat)$_3$].[8]

One of the most intriguing aspects of transition-metal semiquinonate/catecholate complexes is the thermally driven valence tautomerism which has been observed for some complexes in solution.[4] As summarized in eq 1, one cobalt complex has been

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

shown[6] to exist in solution in two valence-tautomeric forms. In toluene at room temperature the Co^{II} complex predominates. A decrease in the temperature leads to a stabilization of the Co^{III}

(1) University of California at San Diego.

(2) Professor A. Dei was on sabbatical leave from the Dipartimento di Chimica, Università di Firenze, 50144 Firenze, Italy.

(3) University of Delaware.

(4) (a) Pierpont, C. G.; Larsen, S. K.; Boone, S. R. *Pure Appl. Chem.* **1988**, *60*, 1331. (b) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(5) (a) Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 880. (b) Buchanan, R. M.; Wilson-Blumenberg, C.; Trapp, C.; Larsen, S. K.; Greene, D. L.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3070.

(6) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951.

(7) Floriani, C.; Henzi, R.; Calderazzo, F. *J. Chem. Soc., Dalton Trans.* **1972**, 2640.

(8) Bhattacharya, S.; Boone, S. R.; Fox, G. A.; Pierpont, C. G. *J. Chem. Soc.* **1990**, *112*, 1088, and references therein.

8222 *J. Am. Chem. Soc., Vol. 115, No. 18, 1993*

Adams et al.

tautomer such that at temperatures below ~250 K the Co^{III} form predominates. Valence tautomerism has been seen for a few other complexes. An X-ray structure and other data show that purple [Mn(3,5-DTBCat)$_2$(py)$_2$] is a Mn^{IV} complex with two coordinated catecholate ligands.[9] Dissolution of these purple crystals in toluene gives a green solution at room temperature, which likely contains the Mn^{II} tautomer [Mn^{II}(3,5-DTBSQ)$_2$-(py)$_2$]. When this toluene solution is cooled to temperatures below 250 K, it reversibly turns to the intense purple of the complex in the solid state. The dielectric of the solvent is also important, for a change from toluene to pyridine shifts the Mn^{IV}/Mn^{II} tautomeric transition temperature from ~250 to ~350 K. Similar solvent-dependent tautomeric equilibria have been reported[10] for [Fe(phenSQ)(phenCat)(bpy)].

From the above studies it is clear that complexes which exhibit valence tautomerism are electronically labile. Two electronic states are nearly degenerate, and this leads to vibronic interactions and an appreciable sensitivity to the environment. Other examples of electronic lability are found in mixed-valence[11] and spin-crossover[12] complexes. Electronically labile complexes are potential building blocks for molecular electronic devices.[13] An external perturbation (*e.g.*, photons, electric field, etc.) on a small collection of these complexes could lead to an interconversion between the two nearly degenerate states. In fact, Gütlich *et al.*[14] have shown that polycrystalline samples of Fe^{II} spin-crossover complexes maintained at low temperatures (<50 K) can be interconverted between the low- and high-spin states in the LIESST (light-induced excited spin state trapping) effect.

One goal of the present study is to systematically control the valence tautomerism of a series of cobalt semiquinonate/catecholate complexes. The 2,2′-bipyridine ligand in [Co(bpy)-(3,5-DTBSQ)(3,5-DTBCat)] was changed to other diiminium ligands. It was anticipated that by systematic variation of the redox potential of the diiminium ligand a series of complexes could be prepared where the valence-tautomeric preference would shift from Co^{III} to Co^{II}. In this paper, we will show that this is indeed possible, and we will discuss in detail the origin of the thermally driven valence-tautomeric equilibrium. It will also be shown that the valence-tautomeric transformation occurs in the solid state for certain complexes and that the transformation in the solid state can occur abruptly in a narrow temperature range.

(9) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041.

(10) Lynch, M. W.; Valentine, M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1982**, *104*, 6982.

(11) (a) Day, P. *Int. Rev. Phys. Chem.* **1981**, *1*, 149. (b) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107. (c) Hendrickson, D. N. In *Mixed Valence Systems: Applications in Chemistry, Physics and Biology*; Prassides, K., Ed.; NATO ASI Series; Kluwer Publishing Co.: Dordrecht, The Netherlands, 1991; pp 67–90. (d) Jang, H. G.; Wittebort, R. J.; Sorai, M.; Kaneko, Y.; Nakano, M.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 2265. (e) Mashuta, M. S.; Webb, R. J.; McCusker, J. K.; Schmitt, E. A.; Oberhausen, K. J.; Richardson, J. F.; Buchanan, R. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1992**, *114*, 3815. (f) Webb, R. J.; Hagen, P. M.; Wittebort, R. J.; Sorai, M.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 1791. (g) McCusker, J. K.; Jang, H. G.; Wang, S.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 1874.

(12) (a) Beattie, J. K. *Adv. Inorg. Chem.* **1988**, *32*, 1–53. (b) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527–622. (c) Rao, C. N. R. *Int. Rev. Phys. Chem.* **1985**, *4*, 19. (d) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83. (e) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293. (f) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543. (g) König, E.; Ritter, G.; Kulshreshtha, S. K. *Chem. Rev.* **1985**, *85*, 219. (h) Bacci, M. *Coord. Chem. Rev.* **1988**, *86*, 245. (i) Gütlich, P. In *Chemical Mössbauer Spectroscopy*; Herber, R. H., Ed.; Plenum Press: New York, 1984. (j) Maeda, Y.; Takashima, Y. *Comments Inorg. Chem.* **1988**, *7*, 41.

(13) (a) Kahn, O.; Krobert, J.; Jay, C. *Adv. Mater.* **1992**, *4*, 718. (b) Kahn, O.; Launay, J. P. *Chemtronics* **1988**, *3*, 140. (c) Launay, J. P. In *Molecular Electronic Devices II*; Carter, F. L., Ed.: Marcel Dekker: New York, 1987.

(14) (a) Gütlich, P.; Hauser, A. *Coord. Chem. Rev.* **1990**, *97*, 1. (b) Decurtins, S.; Gütlich, P.; Kohler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1. (c) Poganuich, P.; Decurtins, S.; Gütlich, P. *J. Am. Chem. Soc.* **1990**, *112*, 3270.

Experimental Section

Compound Preparation. All solvents were reagent grade (Aldrich) and were used as received. Prior to use in a reaction, the solvent was degassed by stirring under vacuum for 20–30 min. All reactions were carried out under an argon atmosphere. The starting material [Co$_4$-(3,5-DTBSQ)$_8$] was prepared by a published procedure[15] and was recrystallized from toluene to give [Co$_4$(3,5-DTBSQ)$_8$]·C$_6$H$_5$CH$_3$. Anal. Calcd (found) for [Co$_4$C$_{112}$H$_{160}$O$_{16}$]·C$_7$H$_8$: C, 68.38 (68.14); H, 8.10 (8.00); Co, 11.28 (11.52). All of the diiminium ligands except 2,2′-bipyrazine (bpyz) were purchased from commercial sources. A sample of 2,2′-bipyrazine was prepared as described in the literature.[16]

[Co(dpbpy)(3,5-DTBSQ)(3,5-DTBCat)]. [Co$_4$(3,5-DTBSQ)$_8$ (0.0436 g, 0.2 mmol) was suspended in 100 mL of toluene. In a separate flask, 0.246 g (0.8 mmol) of 4,4′-diphenyl-2,2′-bipyridine (dpbpy) was dissolved in 40 mL of toluene. The temperature in both blasks was increased to 100 °C. The dpbpy solution was then added dropwise to the tetramer solution over a period of 15 min. The color changed from the dark green of the tetramer to dark blue. The reaction mixture was cooled slowly to room temperature, and then it was reduced to half its volume. Filtering the solution gave a solid which was washed with 10 mL of toluene, yielding 0.50 g of a gray metallic solid. This product was recrystallized to give a blue-black microcrystalline solid by dissolving 100 mg of solid in 30 mL of toluene and subjecting the solution to slow evaporation under a steady flow of N$_2$ gas. Anal. Calcd (found) for [CoC$_{50}$H$_{56}$N$_2$O$_4$]: C, 74.33 (74.45); H, 6.98 (6.93); N, 3.47 (3.30); Co, 7.29 (7.04).

[Co(dmbpy)(3,5-DTBSQ)(3,5-DTBCat)]·$^1/_2$C$_6$H$_5$CH$_3$. A sample (0.758 g, 0.34 mmol) of [Co$_4$(3,5-DTBSQ)$_8$] was suspended in 100 mL of cyclohexane. In a separate flask, 0.253 g (1.39 mmol) of 4,4′-dimethyl-2,2′-bipyridine (dmbpy) was suspended in 100 mL of cyclohexane. The temperature in both flasks was increased to 80 °C to dissolve the starting materials. The dmpby solution was then added dropwise to the tetramer solution over a period of 0.5 h. A blue-green solid began to precipitate upon addition. The reaction mixture was stirred for 2 h at 80 °C and cooled slowly to room temperature. The product was filtered off as a metallic blue-green solid (0.620 g). The product was recrystallized by dissolving 100 mg in 30 mL of toluene and filtering hot, followed by slow evaporation under a stream of N$_2$ gas. Anal. Calcd (found) for [CoC$_{40}$H$_{52}$N$_2$O$_4$]·$^1/_2$C$_6$H$_5$CH$_3$: C, 71.59 (71.14); H, 7.73 (7.65); N, 3.84 (3.59); Co, 8.08 (8.07).

[Co(bpz)(3,5-DTBSQ)$_2$]. This complex was prepared in the same way as the dmbpy complex using cyclohexane for the initial reaction to give a blue-black microcrystalline solid. This product was recrystallized by dissolving 200 mg in 20 mL of benzene, filtering hot, and then subjecting the solution to slow evaporation under a steady flow of N$_2$ gas. Anal. Calcd (found) for [CoC$_{36}$H$_{46}$N$_4$O$_4$]: C, 65.74 (65.77); H, 6.99 (6.91); N, 8.51 (8.51); Co, 8.96 (8.85).

[Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$CH$_3$. [Co$_4$(3,5-DTBSQ)$_8$] (0.666 g, 0.3 mmol) was suspended in 100 mL of methylcyclohexane. In a separate flask, 0.220 g (1.22 mmol) of 1,10-phenanthroline (phen) was suspended in 100 mL of methylcyclohexane. These starting materials were dissolved by heating to 100 °C. The phen solution was then added dropwise over a period of 0.5 h to the tetramer solution. After approximately half of the phen solution was added, a dark green microcrystalline precipitate was visible. After the additon was complete, the reaction mixture was stirred for an additional 0.5 h at 100 °C. After cooling, filtration gave a dark green-brown microcrystalline solid (0.700 g). This solid was recrystallized by dissolving 200 mg in 100 mL of toluene and filtering hot, followed by slow evaporation under a flow of N$_2$ gas. Anal. Calcd (found) for [CoC$_{40}$H$_{48}$N$_2$O$_4$]·C$_6$H$_5$CH$_3$: C, 73.13 (73.17); H, 7.31 (7.36); N, 3.63 (3.61); Co, 7.63 (7.59).

[Co(phen)(3,5-DTBSQ)$_2$]. A 200-mg amount of the dark green-brown microcrystalline solid from the previous procedure was dissolved in methylcyclohexane by heating to 100 °C, filtered hot, and set aside under a flow of N$_2$ gas. After 1 day, dark green gossamer needles were isolated by filtration, (0.180 g). Anal. Calcd (found) for [CoC$_{40}$H$_{48}$N$_2$O$_4$]: C, 70.68 (70.66); H, 7.12 (7.45); N, 4.12 (3.70); Co, 8.67 (8.28).

[Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$Cl. A 200-mg amount of the dark green-brown microcrystalline solid was dissolved in 150 mL of chlorobenzene. The solution was set aside under a flow of N$_2$ gas to reduce the volume. A blue-black crystalline product (0.100 g) was obtained by filtration. Anal. Calcd (found) for [CoC$_{40}$H$_{48}$N$_2$O$_4$]·C$_6$H$_5$Cl: C, 69.73 (68.28); H, 6.74 (6.64); N, 3.83 (3.53); Co, 7.44 (7.43).

(15) Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439.

(16) Lafferty, J. F.; Case, F. H. *J. Org. Chem.* **1967**, *32*, 1591.

Valence-Tautomeric Cobalt Complexes

J. Am. Chem. Soc., Vol. 115, No. 18, 1993 8223

Table I. Crystallographic Data for [Co(bpyz)(3,5-DTBSQ)$_2$] (1) and [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$CH$_3$ (2)

Bipyrazine Complex	
C$_{36}$H$_{46}$CoN$_4$O$_4$	*Ccc*2
fw = 657.71	*T* = 296 K
a = 16.233(6) Å	λ = 0.717 03 Å
b = 26.894(10) Å	ρ_{calcd} = 1.181 g cm^{-3}
c = 8.472(2) Å	μ = 5.00 cm^{-1}
V = 3698.6(13) Å^3	R^a = 0.0461
Z = 4	$R_w{}^a$ = 0.0504

Phenanthroline Complex at Three Temperatures[b]	
C$_{47}$H$_{56}$CoN$_2$O$_4$	*P*2$_1$/*c*
fw = 771.9	*T* = 295 K
a = 10.436(4) Å	λ = 0.717 03 Å
b = 32.524(14) Å	ρ_{calcd} = 1.196 g cm^{-1}
c = 13.563(6) Å	μ = 4.44 cm^{-1}
β = 111.44(3)°	R^a = 0.0824
V = 4285(3) Å^3	$R_w{}^a$ = 0.0850
Z = 4	
C$_{47}$H$_{56}$CoN$_2$O$_4$	*P*2$_1$/*c*
fw = 771.9	*T* = 238 K
a = 10.425(3) Å	λ = 0.717 03 Å
b = 32.226(8) Å	ρ_{calcd} = 1.218 g cm^{-3}
c = 13.454(4) Å	μ = 4.48 cm^{-1}
β = 111.39(2)°	R^a = 0.0489
V = 4208.6(18) Å^3	$R_w{}^a$ = 0.0629
Z = 4	
C$_{47}$H$_{56}$CoN$_2$O$_4$	*P*2$_1$/*c*
fw = 771.9	*T* = 173 K
a = 10.391(6) Å	λ = 0.717 03 Å
b = 31.692(17) Å	ρ_{calcd} = 1.270 g cm^{-3}
c = 13.164(7) Å	μ = 4.71 cm^{-1}
β = 111.39	R^a = 0.0754
V = 4035.6(37) Å^3	$R_w{}^a$ = 0.0907
Z = 4	

^{a} $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/[\Sigma w|F_o|^2]^{1/2}$. ^{b} Temperatures (±1.2 K) are for the crystal and were calibrated by replacing the crystal with a similarly sized thermocouple.

[Co(bpym)(3,5-DTBSQ)$_2$]. This complex was prepared in methylcyclohexane as described above for the phen complex, except the initial solution was allowed to stand for 24 h after cooling. A liver-brown-green microcrystalline solid was isolated which did not need to be recrystallized. It should be noted that if an attempt is made to recrystallize the above micricrystalline solid, analytical data suggest that a dinuclear Co$_2$ complex (bridging bpym?) results.

Physical Method. Electronic absorption spectra were recorded with a Hewlett-Packard 8452A diode array spectrophotometer. Each spectrum was obtained as a signal average of 250 spectra collected at intervals of 0.1 s. Variable-temperature solution spectra were run using two different setups. For measurements above room temperature, a Hewlett-Packard Model 89054A thermostated cell holder connected to a Fisher Model 800 Isotemp circulating temperature bath was used. Temperature stability was better than ±0.5 K; the absolute accuracy is estimated to be ±2 K. Spectra were collected after the sample had been allowed to thermally equilibrate at each temperature for 15 min. For electronic spectra run at temperatures below room temperature, the sample cell was placed in a Janis Model 8DT-SVT-OPT dewar equipped with optical windows. Temperature control was achieved with a LakeShore Model DST-80D temperature controller and a Model DT-470-SD-13 silicon diode. This factory-installed diode is located below the sample region; we installed a second diode (LakeShore DT-500-DRC) to monitor temperature at a position approximately equidistant above the sample region and took the average of the readings on the two diodes as the temperature of the sample.

X-ray Crystal Structure Determination of [Co(bpyz)(3,5-DTBSQ)$_2$] (1). A blue-black crystal was mounted with epoxy cement on a glass fiber. Diffraction data collected at 296 K (see Table I) indicated that the crystal symmetry is orthorhombic. The noncentrosymmetric space group *Ccc*2 was chosen (instead of *Cccm*) as required by the placement of a chiral tris chelate complex on a special position. The structure was solved intuitively by placing the Co atom in an arbitrary position on the 2-fold axis. The correctness of the reported hand was determined by the refinement of a multiplicative term [1.11(8)] for Δ*f''*. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. All computations used

Chart I

4,4'-diphenyl-2,2'-bipyridine
(dpbpy)

4,4'-dimethyl-2,2'-bipyridine
(dmbpy)

1,10-phenanthroline
(phen)

2,2'-bipyrimidine
(bpym)

2,2'-bipyrazine
(bpyz)
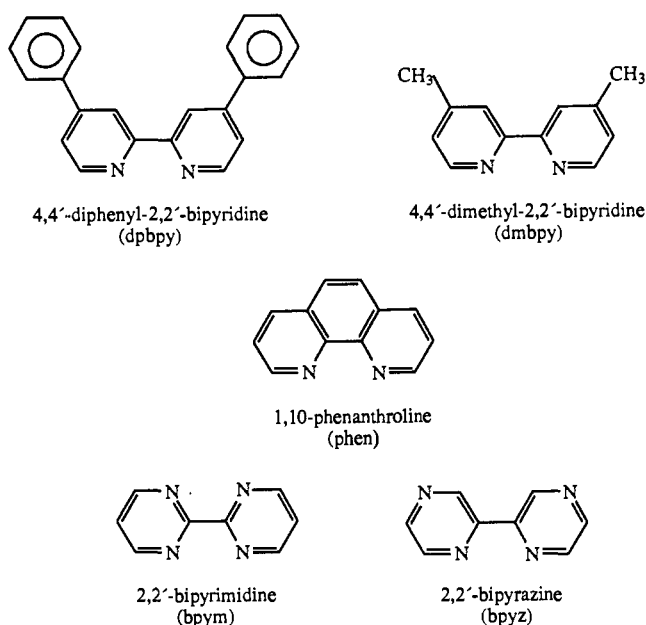
SHELXTL PC software (G. Sheldrick, Siemens XRD, Madison, WI). Details of the data collection are summarized in Table I.

X-ray Crystal Structure Determinations of [Co(phen)(3,5-DTBSQ)-(3,5-DTBCat)]·C$_6$H$_5$CH$_3$ (2). First, X-ray diffraction data were collected at 238 K for a glass fiber-mounted blue-black crystal by employing a closed-cycle refrigerator. The space group was determined to be monoclinic (*P*2$_1$/*c*). The Co atom was located by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. Details of the data collection are summarized in Table I. Sometime later, it was decided to determine the X-ray structure of this complex at two other temperatures, 295 and 173 K. Since the original crystal was lost, a second crystal which was found to be of lower diffraction quality was mounted. As summarized in Table I, diffraction data were collected at 295 K and refinement showed that the same *P*2$_1$/*c* symmetry was present at room temperature. This second crystal was then cooled in a liquid-nitrogen gas stream, and diffraction data were collected at 173 K. The crystal maintained the *P*2$_1$/*c* space group symmetry at 173 K. In all three structures, the toluene solvent molecule was not found to be disordered. However, as expected, the thermal parameters of the methyl carbon atoms were significantly larger than those of the ring carbon atoms. The details of the data collection and refinement at all three temperatures are given in Table I.

Results and Discussion

There were two main goals in the present research. The first goal was to prepare a series of cobalt complexes for which we could systematically vary the temperature for the valence-tautomeric equilibrium in eq 1 for complexes in solution. The second goal was to characterize the first example of a cobalt–semiquinonate complex which undergoes the valence-tautomeric transformation in the *solid state*. Since [Co(bpy)(3,5-DTBSQ)-(3,5-DTBCat)] is known to exhibit the equilibrium in eq 1 in toluene, the first goal was achieved by preparing a series of complexes where the 2,2'-bipyridine (bpy) ligand was systematically replaced by other chelating diiminium ligands (symbolized by N͡N) to give complexes with the composition [Co(N͡N)-(3,5-DTBSQ)("3,5-DTBQ")], where "3,5-DTBQ" is either the semiquinonate or catecholate form of the ligand. The diiminium ligands in Chart I were selected on the basis of availability and reduction potential.

In each case the reaction of the diiminium ligand with the Co^{II} tetrameric complex [Co$_4$(3,5-DTBSQ)$_8$] under an argon atmosphere gives the desired [Co(N͡N)(3,5-DTBSQ)("3,5-DTBQ")] complex. Single-crystal X-ray structures were determined for

8224 *J. Am. Chem. Soc., Vol. 115, No. 18, 1993*

Adams et al.

Table II. Effective Magnetic Moments for Polycrystalline Samples of [Co(N⌒N)(3,5-DTBSQ)("3,5-DTBQ")][a]

N⌒N diiminium ligand	μ_{eff} (μ_B)	
	100 K	300 K
dpbpy	1.84	2.00
dmbpy[b]	1.76	1.93
bpy[b]		1.92
phen[c]	1.73	5.12
bpym	4.04	5.08
bpyz	3.87	4.01

[a] The ligand "3,5-DTBQ" is either the semiquinonate or the catecholate ligand depending on the diiminium ligand and the temperature. [b] Crystallizes as the $C_6H_5CH_3$ hemisolvate. Data taken from this work and ref 6. [c] Crystallizes as the $C_6H_5CH_3$ monosolvate.

the phen and bpyz complexes. The data for these structures, together with data from variable-temperature UV–vis electronic absorption and magnetic susceptibility studies, clearly indicate whether a given complex is in the Co^III or Co^II valence-tautomeric form. For example, in Table II the effective magnetic moments (μ_{eff}) measured at 100 and 300 K for polycrystalline samples of the five new complexes and [Co(bpy)(3,5-DTBSQ)(3,5-DTB-Cat)] are given. These magnetic susceptibility data show that in the solid state the dpbpy, dmbpy, and bpy complexes are Co^III complexes with one unpaired electron per molecule. The values of μ_{eff} are in the 1.76–2.00-μ_B range from 100 to 300 K. Thus, the Co^III ion is low-spin d^6 with one catecholate (diamagnetic) and one semiquinonate ($S = 1/2$) ligand.

On the other hand, the phen, bpym, and bpyz complexes have μ_{eff} values of 5.12, 5.08, and 4.01 μ_B at 300 K. These three complexes are clearly [Co^II(N⌒N)(3,5-DTBSQ)₂] complexes at 300 K in the *solid state*. In these complexes the Co^II ion is high spin and there are two $S = 1/2$ semiquinonate ligands. Due to complications associated with the $t_{2g}^5 e_g^2$ Co^II ion configuration, the rationalization of the observed magnetic properties is not straightforward. There are likely *intra*molecular antiferromagnetic exchange interactions present between the $S = 3/2$ Co^II ion and each $S = 1/2$ ligand. This would give one $S = 5/2$, one $S = 1/2$, and two $S = 3/2$ states for each [Co^II(N⌒N)(SQ)₂] complex. Previous work[17] has shown that the Co^II–SQ^•⁻ exchange interaction is very weak ($J = -1$ to -5 cm⁻¹ for the $-2J\hat{S}_i \cdot \hat{S}_j$ exchange interactions). At temperatures above ~20 K, all of the above $S = 1/2, 3/2$, and $5/2$ states would be populated for such a [Co^II-(N⌒N)(SQ)₂] complex. If the Co^II ion possesses no orbital angular momentum and the Co^II–SQ^•⁻ interaction is absent, then the spin-only value of μ_{eff} per complex is expected to be 4.58 μ_B. This value is calculated by adding together the spin-only *Magnetic susceptibility* values for one $S = 3/2$ species and *two* $S = 1/2$ species.

The variation in properties in the above series of complexes reflects in part the changes in the reduction potentials[18] for the series of diiminium ligands: -2.40 (dmbpy), -2.18 (bpy), -2.04 (phen), -1.80 (bpym), and -1.70 V (bpyz). The bpyz ligand has the lowest (energy) unoccupied molecular orbital (LUMO) which can be used to π-back-bond with the cobalt ion. Thus, the bpyz ligand will stabilize the Co^II (electron-rich) form of the complex. Of course, both the π-back-bonding and σ-donation capabilities of the diiminium ligands come into play in determining whether the Co^II or Co^III valence tautomer is more stable. In this sense, it would be valuable to know the variation in the HOMO–LUMO gap for the series of ligands. However, if the σ-donation capability is not changing greatly in the series, then the tendency to stabilize the Co^II tautomer should follow the above reduction potentials: bpyz > bpym > phen > bpy > dmbpy.

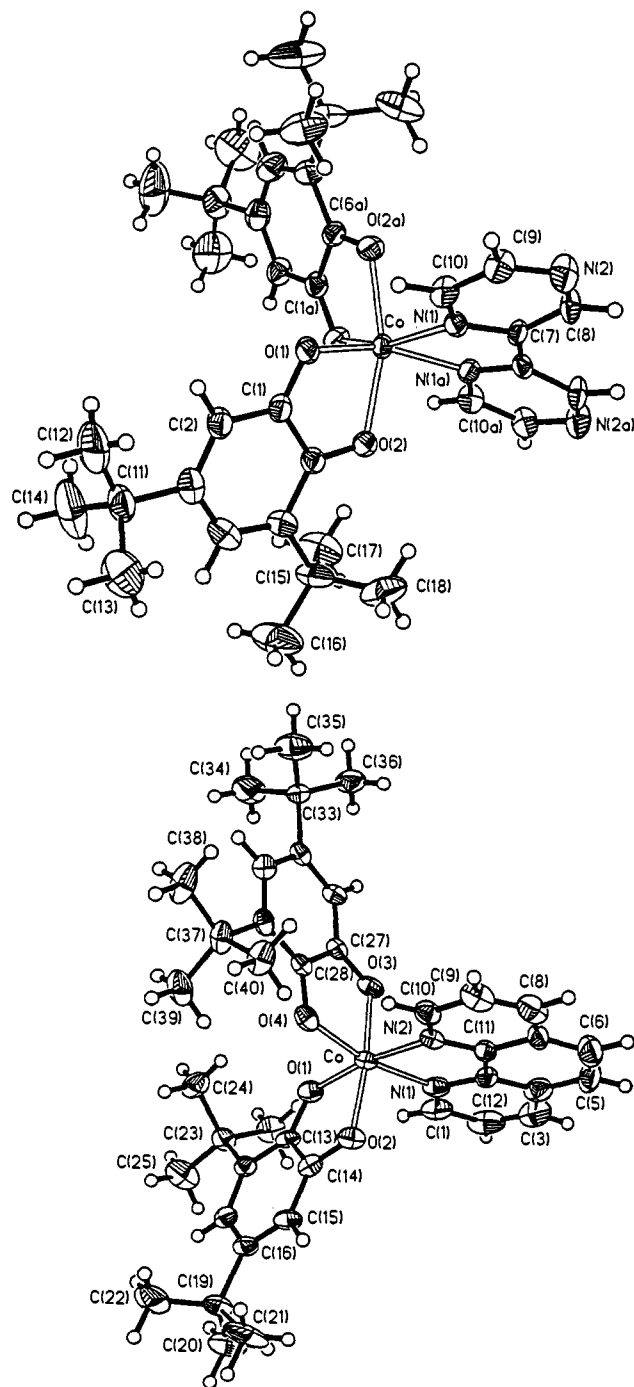Before the data base for the above complexes is discussed, an important point needs to be made. Some of the complexes

(17) Lynch, M. W.; Buchanan, R. M.; Pierpont, C. G.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1038.

(18) Kawanishi, Y.; Kitamura, N.; Tazuke, S. *Inorg. Chem.* **1989**, *28*, 2968.

Figure 1. Illustrations of [Co(bpyz)(3,5-DTBSQ)₂] (**1**) (top) at 296 K and Co^II complex in [Co(phen)(3,5-DTBSQ)₂]·$C_6H_5CH_3$ (**2**) (bottom) at 295 K based on single-crystal X-ray structures.

crystallize with solvent molecules in the lattice. For example, the phen complex crystallizes with one molecule of toluene. If these valence-tautomeric complexes are vibronic, it is likely that the nature of the solvate molecules could be important in determining the properties of a given crystalline compound.

Room-Temperature X-ray Structures. Single-crystal X-ray structures were determined at room temperature for [Co(bpyz)-(3,5-DTBSQ)₂] (**1**) and [Co(phen)(3,5-DTBSQ)₂]·$C_6H_5CH_3$ (**2**). A view of the bipyrazine complex **1** is given in Figure 1, and intramolecular bond distances and angles for complex **1** are collected in Table III. In the crystal of [Co(bpyz)(3,5-DTBSQ)₂] there is a hydrogen-bonding sheet network, involving hydrogen bonding between the para nitrogen atoms on one bpyz ligand and the ortho hydrogen atoms of a bpyz ligand on a neighboring complex, where the distance between the carbon and nitrogen is

Valence-Tautomeric Cobalt Complexes

J. Am. Chem. Soc., Vol. 115, No. 18, 1993 8225

Table III. Selected Bond Distances and Angles for
[Co(bpyz)(3,5-DTBSQ)$_2$] (1)[a]

Bond Distances (Å)			
Cobalt			
Co–O(1)	2.046(4)	Co–N(1)	2.130(4)
Co–O(2)	2.057(4)		
Semiquinonate Ligand			
O(1)–C(1)	1.291(7)	C(5)–C(6)	1.436(8)
O(2)–C(6)	1.270(7)	C(2)–C(3)	1.370(10)
C(1)–C(6)	1.470(8)	C(4)–C(5)	1.362(10)
C(1)–C(2)	1.420(9)	C(3)–C(4)	1.423(11)

Bond Angles (deg)			
Cobalt			
O(1)–Co–O(2)	79.3(2)	N(1)–Co–N(1A)	75.3(2)
O(2)–Co–N(1)	108.2(2)	O(1)–Co–N(1)	93.0(2)
O(2)–Co–O(1A)	90.2(2)	O(1)–Co–(1A)	104.2(2)
N(1)–Co–O(2A)	85.6(2)	O(2)–Co–O(2A)	163.0(2)
O(1)–Co–N(1A)	157.1(2)		
Semiquinonate Ligand			
Co–O(1)–C(1)	112.9(4)	O(1)–C(1)–C(6)	116.7(5)
Co–O(2)–C(6)	113.2(3)	O(2)–C(6)–C(1)	116.6(5)

[a] The two semiquinonate ligands are related by a crystallographic C_2 axis.

3.26 Å. In contrast, [Co(bpy)(3,5-DTBSQ)(3,5-DTBCat)]·C$_6$H$_5$-CH$_3$ (3) has been reported[6] to have weakly coupled pairs of bipyridine complexes where the intermolecular interaction results from an overlap of two bpy ligands (3.65-Å separation) on neighboring complexes. Complex 1 crystallizes in the *Ccc*2 space group, whereas complex 3 has *I*2/*a* symmetry at room temperature.

There is an even greater difference between complexes 1 and 3. The average chelate bond distances given in Table IV for complex 1 show that this is a high-spin Co^{II} complex with two semiquinonate ligands. Complex 1 has C_2 site symmetry where the two equivalent semiquinonate ligands have Co–O bond lengths of 2.046(4) and 2.057(4) Å and Co–N = 2.130(4) Å. For comparison purposes, the Co–O bond lengths for the low-spin Co^{III} complex 3 were reported[6] to range from 1.851(6) to 1.906-(6) Å with Co–N lengths of 1.940(7) and 1.857(7) Å. The average Co–O and Co–N bond lengths in complex 1 are ~0.18 Å longer than those in complex 3. The fact that complex 3 is a low-spin Co^{III} complex with one semiquinonate and one catecholate ligand was established[6] by the bond lengths of the ligands, the presence of an intervalence-transfer (IT) electronic absorption in the near-IR region reflecting the mixed-valence ligand structure, and the observation of a relatively isotropic EPR signal for an organic radical (*i.e.*, small Co hyperfine coupling).

It has been found[4] that *o*-catecholate and *o*-semiquinonate ligands coordinated to first-row transition-metal ions exist in distinct oxidation states. The bond lengths in a given ligand indicate whether it is in the catecholate or semiquinonate oxidation state. The C–O bond length for a catecholate ligand is, for example, 1.35(1) Å, and for a semiquinonate ligand it is 1.29(1) Å. The C–C bond lengths also reflect the more aromatic (delocalized) nature of a catecholate ligand, whereas a semiquinonate ligand should have more localized quinoid character. Table IV summarizes the average chelate C–O and C–C bond lengths found for coordinated ligands in complex 1 and in related complexes. The quinone-derived ligand in complex 1 has C–O bond lengths of 1.270(7) and 1.291(7) Å. The intra-ring C–C bond lengths in this same ligand range from two short values of 1.362(10) and 1.370(10) Å to longer values in the 1.420(9)-1.470(8)-Å range. The two crystallographically-equivalent ligands in complex 1 are clearly semiquinonate ligands.

A view of the phenanthroline complex in [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$CH$_3$ (2) at 295 K is shown in Figure 1. Selected bond lengths and angles are given in Table V. This complex crystallizes in the $P2_1/c$ space group, and the two quinone-derived ligands are not related by symmetry. One has Co–O bond lengths of 2.042(9) and 2.040(10) Å and the other values of 2.055(9) and 2.074(9) Å. These Co–O bond lengths indicate that complex 2 at 295 K is a high-spin Co^{II} complex. An examination of the C–O and C–C bond lengths in Table V show that the two quinone-derived ligands of the phen complex 2 are also semiquinonate ligands at 295 K. Each ligand has two short C–C bond lengths (1.32-1.38 Å) and four longer bond lengths (1.41-1.47 Å). Thus, at room temperature complexes 1 and 2 are high-spin Co^{II} complexes, each with two semiquinonate ligands.

UV–Vis Electronic Absorption Spectra. Variable-temperature electronic absorption spectra (320–820 nm) were run for all of the complexes except the bipyridine complex, for which data were reported[6] previously. In a toluene solution all of the complexes show temperature-dependent spectra which indicate the presence of the valence tautomerism equilibrium as given in eq 1. The temperature dependence of the electronic spectrum of [Co(dpbpy)(3,5-DTBSQ)(3,5-DTBCat)] in toluene is shown in Figure 2. At room temperature there is a band at 600 nm which is characteristic of the Co^{III} tautomeric form of the complex. As the temperature of the toluene solution is increased from 298 to 348 K, the intensity of the 600-nm band decreases while a band at ~770 nm increases in intensity. This 770-nm band is characteristic of the Co^{II} form of the complex, which also shows bands at ~655 and ~560 nm. The presence of isosbestic points indicates there are two difference species present; that is, the valence tautomerism equilibrium given in eq 1 is present. As can be seen in Figure 2, the molar extinction coefficients (ϵ) of the observed transitions are greater than 2500 M^{-1} cm^{-1}. It is likely that the observed transitions are all of the charge-transfer type.

Figure 3 shows the temperature dependence of the electronic absorption spectrum of a toluene solution of [Co(phen)(3,5-

Table IV. Comparison of Average Bond Distances (Å) for Semiquinonate and Catecholate Complexes

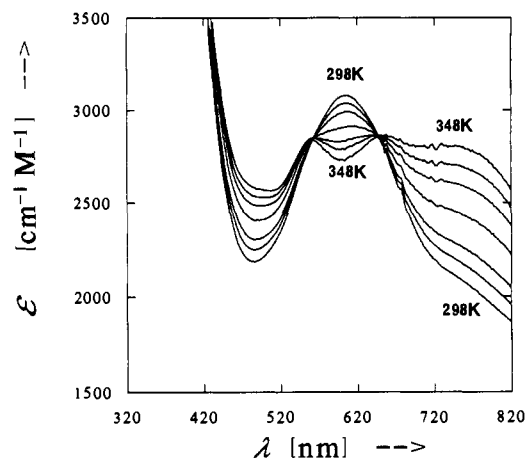| complex	M–N	M–O	C–O	C–C	ref
Semiquinonate Complexes					
[Ga(3,5-DTBSQ)$_3$]			1.293(10)	1.439(12)	d
[Co$_4$(3,5-DTBSQ)$_8$]		2.050(5)	1.285(7)	1.448(10)	e
[Co(bpyz)(3,5-DTBSQ)$_2$]	2.130(4)	2.052(5)	1.281(7)	1.470(8)	this work
[Co(phen)(3,5-DTBSQ)$_2$][a]	2.137(15)	2.052(10)	1.281(18)	1.465(19)	this work
[Co(bpy)(3,5-DTBSQ)(3,5-DTBCat)][b]	1.949(7)	1.897(6)	1.297(9)	1.446(11)	f
[Co(phen)(3,5-DTBSQ)(3,5-DTBCat)][c]	1.932(11)	1.917(8)	1.301(16)	1.437(16)	this work
Catecholate Complexes					
[Mn(py)$_2$(3,5-DTBCat)$_2$]			1.348(4)	1.402(4)	g
Na[V(3,5-DTBCat)$_3$]			1.340(20)	1.410(20)	h
[Co(bpy)(3,5-DTBCat)(3,5-DTBSQ)][b]	1.949(7)	1.869(6)	1.358(10)	1.376(12)	f
[Co(phen)(3,5-DTBCat)(3,5-DTBSQ)][c]	1.932(11)	1.864(8)	1.339(17)	1.405(16)	this work

[a] 295 K structure of the toluene solvate. [b] This is a toluene hemisolvate. [c] 173 K structure of the toluene solvate. [d] Adams, D. M.; Dei, A.; Rheingold, A.; Hendrickson, D. N. *Angew. Chem., Int. Ed. Engl.*, in press. [e] Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439–3444. [f] Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951–4957. [g] Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041–2049. [h] Cass, M. E.; Gordon, N. R.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3962–3967.

Table V. Selected Bond Distances and Angles for [Co(phen)(3,5-DTBSQ)("3,5-DTBQ")]·C₆H₅CH₃ (2)

Bond Distances (Å)

	173 K	283 K	295 K
		Cobalt	
Co–O(1)	1.915(8)	2.004(4)	2.042(9)
Co–O(2)	1.918(8)	2.011(4)	2.040(10)
Co–O(3)	1.867(8)	1.987(4)	2.055(9)
Co–O(4)	1.861(8)	2.002(4)	2.074(9)
Co–N(1)	1.939(11)	2.091(5)	2.135(15)
Co–N(2)	1.925(10)	2.073(5)	2.139(14)
		o-Quinone Ligands	
O(1)–C(13)	1.316(16)	1.291(8)	1.286(18)
O(2)–C(14)	1.287(16)	1.294(8)	1.293(18)
C(13)–C(14)	1.437(16)	1.463(7)	1.472(19)
C(14)–C(15)	1.405(20)	1.405(9)	1.417(23)
C(15)–C(16)	1.369(19)	1.356(9)	1.323(20)
C(16)–C(17)	1.432(17)	1.444(7)	1.454(18)
C(17)–C(18)	1.411(20)	1.368(9)	1.360(21)
C(18)–C(13)	1.381(17)	1.420(8)	1.414(18)
O(3)–C(27)	1.342(15)	1.302(7)	1.271(15)
O(4)–C(28)	1.336(17)	1.305(5)	1.273(18)
C(27)–C(28)	1.405(16)	1.448(7)	1.459(17)
C(28)–C(29)	1.417(18)	1.413(8)	1.436(20)
C(29)–C(30)	1.380(19)	1.386(9)	1.380(23)
C(30)–C(31)	1.399(16)	1.426(7)	1.419(18)
C(31)–C(32)	1.387(17)	1.371(8)	1.320(20)
C(32)–C(27)	1.415(18)	1.412(9)	1.422(22)

Bond Angles (deg)

	173 K	238 K	295 K
		Cobalt	
O(1)–Co–O(2)	85.5(4)	81.3(2)	79.0(4)
O(2)–Co–O(3)	177.6(3)	173.6(2)	170.9(4)
O(2)–Co–O(4)	91.4(4)	94.5(2)	95.8(4)
O(1)–Co–N(1)	93.5(4)	95.6(2)	95.8(4)
O(3)–Co–N(1)	86.8(4)	89.3(2)	90.4(4)
O(1)–Co–N(2)	175.4(4)	171.6(2)	169.2(5)
O(3)–Co–N(2)	91.2(4)	92.7(2)	94.4(4)
N(1)–Co–N(2)	83.5(4)	78.8(2)	77.3(5)
O(1)–Co–O(3)	92.1(4)	93.5(2)	94.0(4)
O(1)–Co–O(4)	91.2(3)	95.1(2)	96.2(4)
O(3)–Co–O(4)	88.8(4)	82.1(2)	79.1(4)
O(2)–Co–N(1)	93.2(4)	94.9(2)	96.0(5)
O(4)–Co–N(1)	173.6(5)	166.7(2)	164.5(5)
O(2)–Co–N(2)	91.1(4)	92.8(2)	93.3(5)
O(4)–Co–N(2)	92.0(4)	91.4(2)	92.0(5)
		o-Quinone Chelates	
Co–O(1)–C(13)	110.9(6)	113.1(3)	114.9(7)
Co–O(2)–C(14)	109.4(8)	112.0(3)	113.9(9)
O(2)–C(14)–C(13)	119.0(12)	117.1(6)	116.5(14)
O(1)–C(13)–C(14)	114.2(11)	115.8(5)	115.1(12)
Co–O(3)–C(27)	108.2(7)	112.0(3)	113.2(8)
Co–O(4)–C(28)	109.6(7)	112.5(3)	112.8(8)
O(4)–C(28)–C(27)	115.7(11)	115.8(5)	117.1(12)
O(3)–C(27)–C(28)	117.6(11)	117.7(5)	117.7(13)

Figure 2. Temperature dependence of the electronic absorption spectrum of a toluene solution of [Co(dpbpy)(3,5-DTBSQ)(3,5-DTBCat)] obtained at 298, 303, 308, 318, 328, 338, and 348 K. The molar extinction coefficient ε is plotted versus wavelength λ.
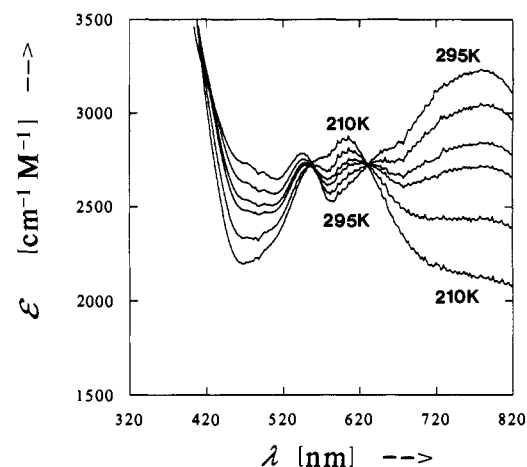
Figure 3. Temperature dependence of the electronic absorption spectrum of a toluene solution of [Co(phen)(3,5-DTBSQ)₂]·C₆H₅CH₃ (2) obtained at 295, 260, 240, 230, 220, and 210 K. The molar extinction coefficient ε is plotted versus wavelength λ.

DTBSQ)₂]. At 295 K in solution, this is a Co^{II} tautomer, as indicated by the intense broad band at ∼780 nm, with a shoulder at ∼660 nm and another weaker band at ∼550 nm. Increasing the temperature of this solution does not lead to much change in this spectrum. However, when the temperature of the toluene solution is decreased from 295 to 210 K, the intensity of the ∼780-nm band decreases appreciably, while a band at ∼600 nm appears and grows in intensity. At 295 K the phen complex in toluene is in the Co^{II} form, and on cooling to 210 K it converts to the Co^{III} form.

Similar temperature-dependent spectra were observed for toluene solutions of the dpbpy, dmbpy, and bpym complexes. In each case, it is possible to estimate a temperature at which there are approximately equal amounts of the Co^{II} and Co^{III} tautomeric forms present. This temperature follows the order ∼348 (dpbpy), ∼298 (dmbpy), ∼273 (bpy), ∼230 (phen), ∼190 (bpym), and

<190 K (bpyz). It is interesting to note that this is the same order as the reduction potentials for these diiminium ligands.

Valence Tautomerism in the Solid State. One of the major goals in this study was to discover whether the valence-tautomeric transformation could be carried out in the solid state. If these valence-tautomeric complexes are to exhibit optical bistability, then it is important to identify complexes which abruptly convert from one tautomer to the other in the solid state. Perhaps the best parameter to gauge whether a given complex is in the Co^{II} or Co^{III} form and whether it can interconvert in the solid state is magnetic susceptibility.

Variable-temperature (2–320 K) magnetic susceptibility data were gathered for polycrystalline samples of all of the complexes. Figure 4 shows plots of the effective magnetic moment (μ_{eff}) per molecule versus temperature for [Co(dpbpy)(3,5-DTBSQ)(3,5-DTBCat)] and [Co(dmbpy)(3,5-DTBSQ)(3,5-DTBCat)]·1/2C₆H₅CH₃. In the range 2–300 K, both of these complexes have μ_{eff} values which are essentially independent of temperature and close to the value of 1.7 μ_B. As indicated above, these two complexes are Co^{III} complexes with one catecholate ligand and one semiquinonate ligand. There is one unpaired electron localized on the semiquinonate ligand, and the spin-only value for μ_{eff} is expected to be 1.73 μ_B. In the case of the dmbpy complex, data were collected up to 340 K. Above ∼300 K, the value of μ_{eff} for this complex increases with increasing temperature to a value of 2.2 μ_B at 340 K.

Valence-Tautomeric Cobalt Complexes
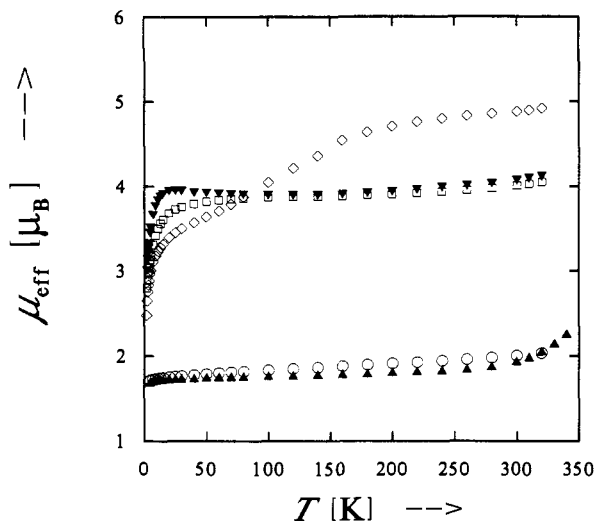
J. Am. Chem. Soc., Vol. 115, No. 18, 1993 8227

Figure 4. Plots of the effective magnetic moment (μ_{eff}) versus temperature for the following complexes: (O) [Co(dpbpy)(3,5-DTBSQ)(3,5-DTB-Cat)]; (▲) [Co(dmbpy)(3,5-DTBSQ)(3,5-DTBCat)]·$^1/_2$C$_6$H$_5$CH$_3$; (□) [Co(bpyz)(3,5-DTBSQ)$_2$]; (▼) nonsolvated [Co(phen)(3,5-DTBSQ)$_2$]; (◇) [Co$_4$(3,5-DTBSQ)$_8$]·C$_6$H$_5$CH$_3$.

Plots of μ_{eff} versus temperature for [Co(bpyz)(3,5-DTBSQ)$_2$] and a nonsolvated form of [Co(phen)(3,5-DTBSQ)$_2$] grown from methylcyclohexane are also shown in Figure 4. The two data sets are quite similar. For the bpyz complex, μ_{eff} at 320 K is 4.05 μ_B. When the temperature is decreased from 320 to 200 K, the value of μ_{eff} decreases to 3.91 μ_B. A further decrease in temperature leads to only a small decrease in μ_{eff} to 3.82 μ_B at 50.0 K, below which μ_{eff} falls off abruptly to 2.80 μ_B at 2.00 K. The relatively abrupt drop in μ_{eff} at low temperatures is likely due to a combination of zero-field splitting and "saturation" in the Zeeman interactions in the 10.0-kG field. The μ_{eff} data above $\sim$50 K for the bpyz and nonsolvated phen complexes indicate that they are Co^{II} complexes. The spin-only value of μ_{eff} expected for a high-spin Co^{II} ($S = ^3/_2$) complex with two $S = ^1/_2$ semiquinonate ligands when there are no exchange interactions present is 4.58 μ_B. In the 50–300 K range, the value of μ_{eff} for these two complexes is below the spin-only value. For comparison purposes, a plot of μ_{eff} per Co^{II} ion versus temperature is also shown in Figure 4 for the structurally characterized[15] Co^{II} complex [Co$_4$(3,5-DTBSQ)$_8$]. New data were collected in this work for [Co$_4$(3,5-DTBSQ)$_8$·C$_6$H$_5$CH$_3$ (see ref 17 for the previous data). The value of μ_{eff} per Co^{II} ion is 4.92 μ_B at 320 K. Figure 4 shows that this μ_{eff} per Co$_{II}$ ion value decreases gradually to 3.63 μ_B at 50 K. Since this complex is a tetrameric Co^{II} complex, there are probably weak intramolecular Co^{II}···Co^{II} exchange interactions, as discussed previously.[17] It can be concluded that, even though the μ_{eff} versus temperature curves for the bpyz and nonsolvated phen complexes track at somewhat smaller values than that for the tetrameric Co^{II} complex, these two complexes are high-spin Co^{II} complexes.

The situation becomes considerably more interesting in the case of [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$CH$_3$ (see Figure 5). A polycrystalline sample of this toluene solvate was cooled to 30.0 K in the SQUID susceptometer, where a μ_{eff} value of 1.72 μ_B was measured. Thus, the originally Co^{II} complex converts at low temperatures to the Co^{III} tautomeric form. This is the first complex which exhibits the valence-tautomeric transformation in the solid state.

As the temperature of the toluene-solvated phen complex is increased (Figure 5) from 30.0 to 200.0 K, there is little change in μ_{eff}. Then, abruptly in the 200–260 K region, the complex converts from a Co^{III} complex at 220 K to a Co^{II} complex at 260 K. The sample temperature was further increased to 310.0 K (μ_{eff} = 5.13 μ_B), whereupon it was then decreased back to 30.0

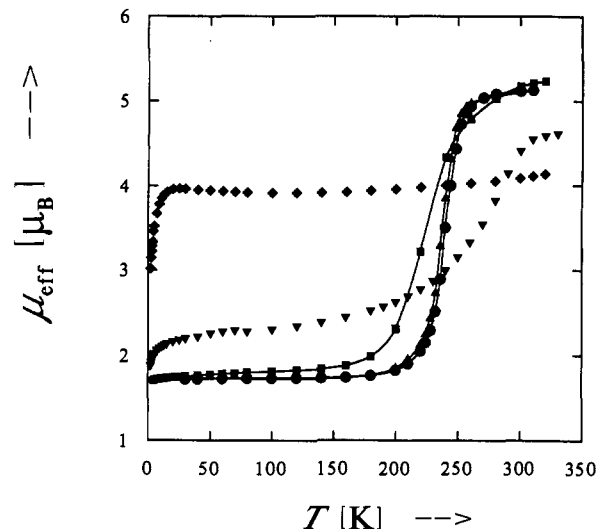**Figure 5.** Plots of the effective magnetic moment (μ_{eff}) versus temperature for the following complexes: (◆) [Co(phen)(3,5-DTBSQ)$_2$] recrystallized from methylcyclohexane; (■) [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$Cl; ((●) increasing temperature; (▲) decreasing temperature) [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$CH$_3$; (▼) a sample of [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$-CH$_3$ which was heated at 70 °C under vacuum for 12 h.

K. It can be seen that the transformation is essentially reversible with a small hysteresis of 5 deg ($\sim$4 h to run the full hysteresis loop). There are, at least, two important points to make. First, the abrupt transformation very likely does not occur in a simple equilibrium. The susceptibility data shown in Figure 5 were converted to values of the fraction of Co^{III} tautomer at a given temperature, n(Co^{III}). These data were then least-squares-fit to the expression $\ln(n/(1 - n)) = \Delta H/RT - \Delta S/R$ to give values of the enthalpy (ΔH) and entropy (ΔS) gains if the transformation occurs in an equilibrium. While the fit to the data is reasonable, the fitting parameters of $\Delta H = 83.7$ kJ/mol and $\Delta S = 345$ J/(mol K) are not at all reasonable. To be more specific, this extremely large ΔS value corresponds, from the $\Delta S = R \ln x$ equation, to a gain of $x = 1 \times 10^{18}$ degrees of freedom, which is impossible. The second point is that the toluene solvate molecules are critical. Two different forms of the nonsolvated phen complex were prepared: one resulted in the initial recrystallization from methylcyclohexane (see the Experimental Section) and the other resulted after grinding the microcrystalline sample of [Co(phen)-(3,5-DTBSQ)$_2$]·C$_5$H$_5$CH$_3$ and then heating the powder at 70 °C under vacuum for 12 h to remove the toluene solvate molecules. In both cases, the samples were analyzed to be [Co(phen)(3,5-DTBSQ)$_2$]. As can be seen in Figure 5, the sample recrystallized from methylcyclohexane persists as a Co^{II} complex throughout the 2–320 K region. Unfortunately, we do not have sufficiently good crystals of this nonsolvated form for an X-ray structure. On the other hand, the nonsolvated form which was obtained by pumping off the toluene solvate molecules does convert from a Co^{II} complex at 330 K to a predominantly Co^{III} complex at temperatures below $\sim$150 K. However, without the toluene solvate molecules the conversion occurs much more gradually. In fact, the conversion for the desolvated sample is apparently not complete at 330 K, nor has the sample completely converted to the Co^{III} form at low temperatures. At low temperatures there are probably residual Co^{II} complexes in the predominantly Co^{III} matrix. Desolvation would be expected to create considerable defects. Incomplete conversions for partially desolvated complexes has been reported[12] for spin-crossover complexes.

Additional evidence for the critical role which the toluene solvate molecules play in determining the abrupt transformation for the phen complex is available. By recrystallization of the nonsolvated complex in chlorobenzene, instead of toluene, a sample of [Co(phen)(3,5-DTBSQ)(3,5-DTBCat)]·C$_6$H$_5$Cl was prepared.
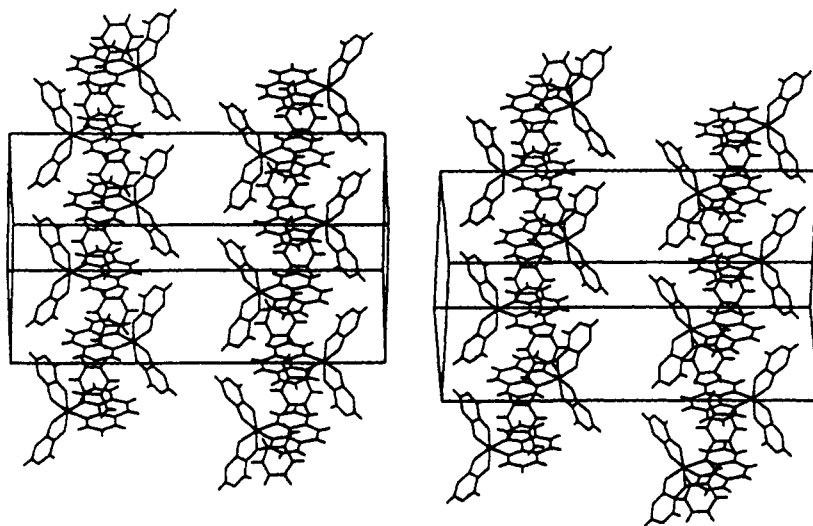
8228 *J. Am. Chem. Soc., Vol. 115, No. 18, 1993*

Adams et al.

Figure 6. Stereo packing diagram for [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$CH$_3$. The *tert*-butyl groups have been omitted for clarity.

The plot of μ_{eff} versus temperature for this chlorobenzene solvate (Figure 5) shows that it also undergoes the valence-tautomeric transformation in the solid state. Compared to the transformation of the toluene solvate, that of the chlorobenzene solvate starts at a lower temperature and is more gradual, taking over 100 deg for completion.

Preliminary solid-state ^{2}H NMR experiments on [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$D$_5$CD$_3$ have also been carried out. At temperatures below the abrupt conversion from the Co^{III} to the Co^{II} tautomer, the toluene solvate molecules have static phenyl rings where, as expected, the CD$_3$ group is rapidly ($>10^8$ s^{-1}) rotating on its local pseudo-C_3 axis. The ^{2}H NMR spectrum changes dramatically in the valence-tautomeric transformation region. It appears that the phenyl rings begin flipping about a pseudo-C_2 axis at the same temperature where the complexes convert from Co^{III} to Co^{II}. The results of more detailed ^{2}H NMR studies will be presented later.[19] The onset of motion in the toluene solvate molecules would be expected to contribute to the cooperativity that is likely present in the valence-tautomeric conversion of the toluene-solvated phen complex.

Variable-Temperature X-ray Structure of [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$CH$_3$ (2). X-ray structure determinations were carried out for this toluene solvate at 238 and 173 K in an effort to understand better the abrupt valence-tautomeric transformation. The $P2_1/c$ symmetry which was found at 295 K is also found in isomorphous unit cells at 238 and 173 K, even though these temperatures are in the middle and of below, respectively, the abrupt transformation. There is some contraction in the unit cell parameters (Table II) as the crystal temperature is lowered from 295 to 173 K. The unit cell volume decreases from 4285(3) Å^3 at 295 K to 4036(4) Å^3 at 173 K. Since there is no change in crystal symmetry, the phase transition is not first order, but must be of higher order. Each cobalt complex changes from a smaller Co^{III} complex at 173 K to a larger Co^{II} complex at 295 K. The toluene solvate molecules probably also convert from being static at 173 K to being dynamic at 295 K. The phase transition is of an order–disorder type.

Table V summarizes the changes in selected bond distances and angles for the toluene-solvated phen complex as it is cooled from 295 to 173 K. The temperature of 238 K is close to the midtemperature of the transformation. When this complex is cooled from 295 to 238 K, the two Co–O bond lengths of one quinone-derived ligand decrease by an average of 0.034(4) Å, whereas the two Co–O bond lengths on the other ligand decrease by an average of 0.070(2) Å. For the full range of 295–173 K,

the two Co–O bonds of the former ligand decrease by an average of 0.124(2) Å and the two Co–O bonds of the latter ligand decrease by an average of 0.200(12) Å. In the conversion from 295 to 173 K, the two Co–N bond lengths decrease by an average of 0.055-(11) Å, and from 295 to 173 K, there is an average change of 0.205(10) Å. Three observations can be made. First, the relatively large total decrease in Co–ligand bond lengths is consistent with a change from high-spin Co^{II} at 295 K to low-spin Co^{III} at 173 K. Second, in the initial conversion from 295 to 238 K, the decrease in Co–ligand bond lengths is only one-third to one-fourth of the total decrease in going from 295 to 173 K. This is the case in spite of the fact that 238 K is at the midpoint of the conversion. Third, the decreases in Co–O bond lengths are different for the two different quinone-derived ligands. There is a larger decrease [0.200(12) Å versus 0.124(2) Å] in the Co–O bond lengths associated with the ligand which has the O(3) and O(4) atoms. As is shown below, this ligand is converting from a semiquinonate(1–) ligand at 295 K to a catecholate(2–) ligand at 173 K. It is concluded that the other ligand persists as a semiquinonate moiety from 295 to 173 K.

The O(3)–C(27) and O(4)–C(28) bond lengths of one ligand increase from 1.271(15) and 1.273(18) Å, respectively, to 1.342-(15) and 1.336(17) Å when the temperature is decreased from 295 to 173 K. For a semiquinonate ligand, the C–O bond length is 1.29(1) Å, whereas for a catecholate ligand it is 1.35(1) Å. Thus, this ligand appears to be changing from semiquinonate at 295 K to catecholate at 173 K. In contrast, there are smaller increases in the O(1)–C(13) and O(2)–C(14) bond lengths for the other ligand from 1.286(18) and 1.293(18) Å, respectively, at 295 K to values of 1.316(16) and 1.287(16) Å at 173 K. This second ligand maintains characteristics of a semiquinonate ligand throughout the temperature region.

A stereo packing diagram for [Co(phen)(3,5-DTBSQ)$_2$]·C$_6$H$_5$-CH$_3$ is shown in Figure 6. Stacks of complexes are found, where in each stack there are appreciable phen···phen interactions between the complexes. Phen ligands on neighboring complexes are oriented such that their planes are nearly parallel (dihedral angles of 3.5° at 295 K at 1.2° at 173 K). The interplanar distance is 3.48 Å at 295 K and decreases to 3.36 Å at 173 K. This intermolecular interaction would be important in the valence-tautomeric phase transition. The cooperativity between one stack of complexes and another could be established by the onset of motion of the toluene solvate molecules.

Origin of the Valence-Tautomeric Transformation. Why do the above complexes convert from a Co^{III} complex with one catecholate and one semiquinonate ligand at low temperatures to the larger Co^{II} complex with two semiquinonate ligands as the

(19) Adams, D. M.; Rheingold, A. L.; Hendrickson, D. N. Manuscript in preparation.

temperature is increased? It is entropy which drives this interconversion.

There is a good analogy with spin-crossover complexes[12] which change in a certain temperature region from low-spin to high-spin as the temperature is increased. Fe^{II} spin-crossover complexes change from low-spin $^1A_1$ ground-state complexes to high-spin $^5T_2$ ground-state complexes, for example. Most Fe^{II} spin-crossover complexes are complexes with a FeN_6 ligand structure. The Fe–N bond length decreases 0.15–0.20 Å in the conversion from the $^5T_2$ high-temperature form to the $^1A_1$ form at lower temperatures.[12b] Heat capacity studies[20] of complexes undergoing the spin-crossover transformation either in a phase transition or in a gradual manner show that there is an appreciable entropy gain which drives the conversion. In the classic heat capacity study[20a] of [Fe(phen)$_2$-(NCS)$_2$], the enthalpy and entropy changes were evaluated to be $\Delta H = 8.60 \pm 0.14$ kJ/mol and $\Delta S = 48.78 \pm 0.71$ J/(mol K). It was concluded that there are two major factors contributing to the relatively large entropy gain. The $^5T_2$ high-spin complex has a greater electronic entropy than the $^1A_1$ low-spin complex. The 5-fold spin degeneracy ($2S + 1 = 5$) of the $^5T_2$ complex contributes an entropy gain of $\Delta S = R \ln 5 = 13.38$ J/(mol K). The other major contribution to ΔS arises from changes in the phonon modes. Of these, it is changes in the metal–ligand atom vibrational normal modes which contribute the most. The frequencies of the metal–ligand normal modes are less for the high-spin complex compared to the low-spin complex. Thus, changes in electronic degeneracies and in frequencies of metal–ligand vibrations lead to an appreciable change in entropy. This dominates the free energy at the temperature where the spin-crossover complex converts from low to high spin.

In the case of the valence-tautomeric cobalt complexes, both of these factors are present and contribute to ΔS. The Co^{III} complex has one unpaired electron ($S = {}^1/_2$; $2S + 1 = 2$) localized on its one semiquinonate ligand. The metal ion is high-spin in the Co^{II} tautomer and has an $S = {}^3/_2$ state; there are also two $S = {}^1/_2$ semiquinonate ligands. Very weak magnetic exchange interactions[17] between the Co^{II} ion and two semiquinonate ligands

lead to one $S = {}^5/_2$, one $S = {}^1/_2$, and two $S = {}^3/_2$ states. These four states are very close in energy. Thus, when a Co^{III} tautomer converts to the Co^{II} form, there is an electronic entropy gain. Also, the Co^{II} tautomer has larger Co–ligand atom bond lengths than does the Co^{III} tautomer. The frequencies of the metal–ligand vibrations will be less for the Co^{II} tautomer. There will also be a vibrational contribution to ΔS for the valence-tautomeric transformation.

Finally, there may even be a contribution to ΔS for the valence-tautomeric conversion from the onset of motion associated with solvate molecules in the solid state. Thus, if the solvate molecule begins to jump between two or more positions which are distinguishable in the crystal, then it may also contribute to ΔS and help drive the valence-tautomeric transformation.

Concluding Comments

A new series of valence-tautomeric complexes with the composition [Co(N⌒N)(3,5-DTBSQ)("3,5-DTBQ")] have been prepared and characterized. Depending on the diiminium ligand N⌒N and/or the temperature of a solution, it has been shown that a complex can be either in the Co^{II} tautomeric form where "3,5-DTBQ" is a semiquinonate(1–) ligand or in the Co^{III} tautomeric form where "3,5-DTBQ" is a catecholate(2–) ligand. The two [Co(phen)(3,5-DTBSQ)$_2$]·S complexes, where S is either toluene or chlorobenzene, have been shown to undergo the valence-tautomeric transformation in the solid state. A phase transition is involved where the transformation from the low-spin Co^{III} tautomer at low temperatures to the high-spin Co^{II} tautomer at higher temperature is entropy driven. Electronic and vibrational entropy contributions are present.

Supplementary Material Available: Tables of crystallographic data, bond distances and angles, positional parameters, isotropic and anisotropic displacement coefficients, and calculated hydrogen atom coordinates for [Co(bpyz)(3,5-DTBSQ)$_2$] at 296 K and for [Co(phen)(3,5-DTBSQ)$_2$] at 295, 238, and 173 K (32 pages); tables of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

(20) (a) Sorai, M.; Seki, S. *J. Phys. Chem. Solids* **1974**, *35*, 555. (b) Kaji, K.; Sorai, M. *Thermochim. Acta* **1985**, *88*, 185. (c) Sorai, M.; Maeda, Y.; Oshio, H. *J. Phys. Chem. Solids* **1990**, *51*, 941.