J. Am. Chem. Soc. **1994,** *116,* 2229–2230

Photomechanical Polymers. Synthesis and Characterization of a Polymeric Pyrazine-Bridged Cobalt Semiquinonate–Catecholate Complex

Ok-Sang Jung† and Cortlandt G. Pierpont*

Department of Chemistry and Biochemistry
University of Colorado, Boulder, Colorado 80309

Received October 28, 1993

The unique photomechanical property observed for Rh(CO)$_2$(3,6-DBSQ) has stimulated interest in the development of rational synthetic routes to stable, polymeric complexes that may show high sensitivity to low-energy excitation.[1,2] Photomechanical behavior has been observed for a few solid-state materials,[3,4] and origins of the effect remain poorly understood. An empirical model for the "bending crystal" effect of Rh(CO)$_2$(3,6-DBSQ) has been described that is based on the expansion and contraction of the metal core of columnar stacks of complex molecules in the solid state.[2] Light-induced intramolecular metal–quinone electron transfer is responsible for a change in column length as charge is transferred from the Rh(I) core to the electron-deficient semiquinone ligands at low energy. Complexes that undergo light-induced spin transitions show crystal-shattering effects that are associated with changes in molecular volume.[5] Gutlich has described this behavior in terms of an "elastic interaction and lattice expansion" model.[6]

Quinone complexes of cobalt of composition Co^{III}(N–N)(DBSQ)(DBCat), where DBSQ and DBCat are semiquinonate and catecholate forms of 3,5- and 3,6-di-*tert*-butylbenzoquinone and N–N is a nitrogen-donor coligand, exhibit equilibria between Co(III) and Co(II) species (1)in solution and in the solid state.[7-10]

$$\mathrm{Co^{III}(N{-}N)(DBSQ)(DBCat) \rightleftarrows Co^{II}(N{-}N)(DBSQ)_2} \quad (1)$$

The metal ion of Co^{III}(N–N)(DBSQ)(DBCat) is in the form of low-spin Co(III), Co^{II}(N–N)DBSQ)$_2$ contains high-spin Co(II), and the equilibrium between forms of the complex differing in charge distribution occurs in separate steps involving Cat → Co(III) electron transfer and Co(II) spin transition. Electron transfer from the DBCat ligand to Co(III) gives a low-spin Co(II)* species (2). Optical charge transfer occurs at an unusually

$$\mathrm{Co^{III}(N{-}N)(DBSQ)(DBCat) \rightleftarrows Co^{II*}(N{-}N)(DBSQ)_2} \quad (2)$$

low energy, transitions in the 2500-nm region appear characteristically for the Co^{III}(N–N)(DBSQ)(DBCat) complexes, and thermal electron transfer occurs at energies further into the infrared.[10] Spin transition gives the high-spin Co(II) form of the complex (3)that may be observed in spectral and magnetic

$$\mathrm{Co^{II*}(N{-}N)(DBSQ)_2 \rightleftarrows Co^{II}(N{-}N)(DBSQ)_2} \quad (3)$$

measurements recorded on complex samples in solution or in the solid state. Both steps of the equilibrium are sensitive to the balance of quinone and metal orbital energies, and coligand donation effects have been investigated for a series of bidentate N-donor ligands.[9,10]

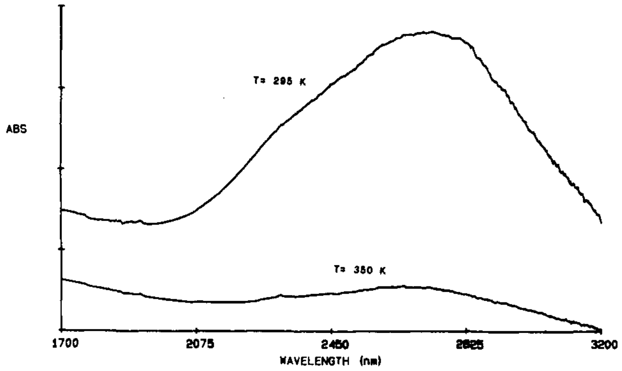

Figure 1. Temperature-dependent changes in the low-energy Cat → Co(III) charge-transfer transition of [Co^{III}(pyz)(3,6-DBSQ)(3,6-DBCat)]$_n$ in the solid state (KBr pellet).

Structural characterizations on Co^{III}(N–N)(DBSQ)(DBCat) and Co^{II}(N–N)DBSQ)$_2$ forms of the complexes show the expected increase of approximately 0.2 Å in Co–O and Co–N bond lengths with the transition from low-spin Co(III) to high-spin Co(II).[7-10] The equilibrium described in eq 1 would have an accompanying change in complex volume of roughly 100 Å^3. Polymeric complexes formed from linked monomeric cobalt quinone units may show photomechanical properties that result from photoinduced changes in metal ion radius amplified along the linear polymer axis. Indeed, a recent report has indicated that Co(bpy)(3,6-DBSQ)(3,6-DBCat) shows a photomechanical effect upon irradiation with light in the near-IR.[8] In the solid-state structure of this complex, bipyridine ligands of adjacent molecules stack to form a one-dimensional lattice.[10b] In contrast, Co(bpy)(3,5-DBSQ)(3,5-DBCat), which crystallizes with dimeric pairs of molecules linked by interacting bpy ligands, fails to show the photomechanical property.[7] From the properties of Rh(CO)$_2$(3,6-DBSQ) and Co(bpy)(3,6-DBSQ)(3,6-DBCat) it can be concluded that photomechanical activity may be observed in cases where the complex crystallizes in a one-dimensional lattice and there is a structural distortion associated with a light-induced change in charge distribution. To test this model, studies have been carried out on polymeric quinone complexes of cobalt.

The reaction between Co$_2$(CO)$_8$ and 3,6-di-*tert*-butyl-1,2-benzoquinone carried out in the presence of a stoichiometric equivalent of pyrazine results in formation of the [Co(pyz)(3,6-DBQ)$_2$]$_n$ polymer.[11] Shifts in the Co(III)/Co(II) equilibrium that occur in the solid state have been studied by monitoring temperature-dependent changes in magnetism and optical spectrum. At 350 K, complex units are nearly completely in the Co^{II}(pyz)(3,6-DBSQ)$_2$ charge distribution. Spin alignment results in a magnetic moment of 5.86 μ_B at this temperature, and the 2700-nm transition that appears characteristically for the

---

† Permanent address: Korea Institute of Science and Technology, Cheongryang, Seoul, Korea.

[1] Abakumov, G. A.; Nevodchikov, V. I. *Dokl. Akad. Nauk SSSR* **1982,** *266,* 1407.

[2] Lange, C. W.; Foldeaki, M.; Nevodchikov, V. I.; Cherkasov, V. K.; Abakumov, G. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1992,** *114,* 4220.

[3] Nagabhooshanam, M.; Veerender, C.; Dumke, V. R. *J. Alloys Compd.* **1991,** *176,* 247.

[4] (a) Suski, J.; Largeau, D.; Steyer, A.; Van de Pol, F. C. M.; Blom, F. R. *Sens. Actuators A* **1990,** *A24,* 221. (b) Royer, M.; Midavaine, T. In *Sensors*; Goepel, W., Hesse, J., Zemel, J. N., Eds.; VCH: Weinheim, Germany, 1992; pp 201–232.

[5] Decurtins, S.; Gutlich, P.; Hasselbach, K. M.; Hauser, A.; Spiering, H. *Inorg. Chem.* **1985,** *24,* 2174.

[6] Spiering, H.; Meissner, E.; Koppen, H.; Muller, E. W.; Gutlich, P. *Chem. Phys.* **1982,** *68,* 65.

[7] Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980,** *102,* 4951.

[8] Abakumov, G. A.; Cherkasov, V. K.; Bubnov, M. P.; Ellert, O. G.; Dobrokhotova, Z. B.; Zakharov, L. N.; Struchkov, Y. T. *Dokl. Akad. Nauk SSSR* **1993,** *328,* 12.

[9] Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993,** *115,* 8221.

[10] (a) Jung, O.-S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994,** *116,* in press. (b) Jung, O.-S.; Pierpont, C. G. *Inorg. Chem.*, in press.

[11] For the synthesis of Co(pyz)(3,6-DBSQ)(3,6-DBCat), Co$_2$(CO)$_8$ (86 mg, 0.25 mmol) and pyrazine (40 mg, 0.50 mmol) were combined in 30 mL of hexane. The mixture was stirred for 5 min, and 3,6-DBBQ (220 mg, 1.0 mmol) in 30 mL of hexane was added. The mixture was stirred under Ar for 2 h at room temperature. Slow evaporation of the solvent produced dark blue crystals of the complex in 70% yield as the hexane solvate, Co(pyz)(3,6-DBSQ)(3,6-DBCat)·C$_6$H$_{14}$. Optical spectra were recorded on a Perkin-Elmer Lamda 9 spectrophotometer, and magnetic measurements were made on a Quantum Design MPMS-5 SQUID magnetometer.

0002-7863/94/1516-2229$04.50/0

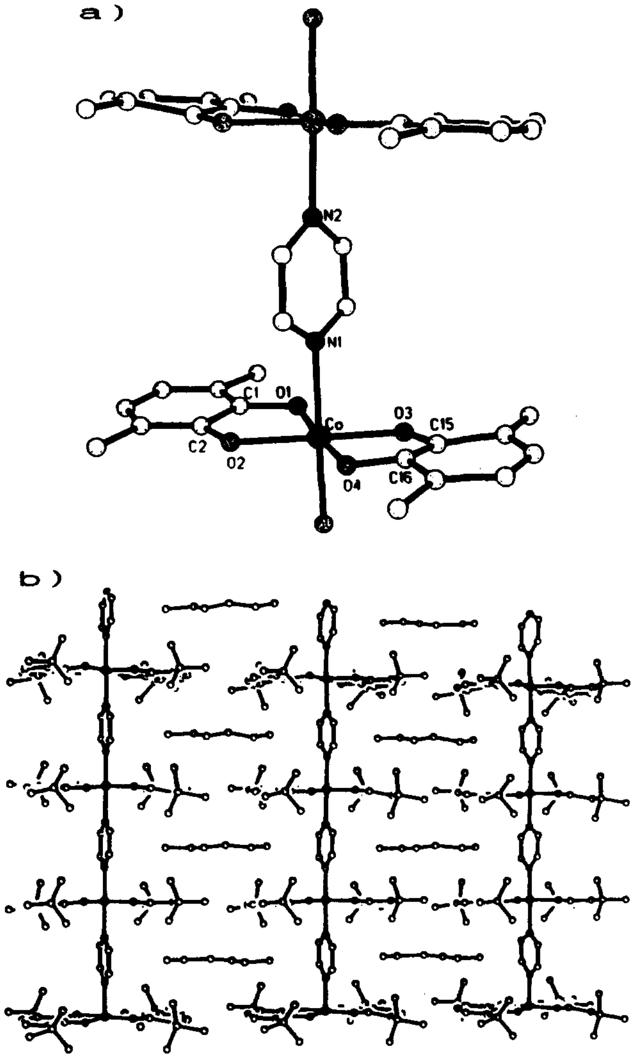

Figure 2. View of one complex unit of the $[Co(pyz)(3,6\text{-}DBQ)_2]_n$ polymer (a) and one plane of polymer strands including hexane solvate molecules viewed down the crystallographic *c* axis (b).

Co(III) form of the complex is barely visible (Figure 1). This transition grows in intensity with decreasing temperature. Magnetic moment decreases to a value of 2.32 μ_B at 150 K and decreases further to the $S = {}^1/_2$ value (1.71 μ_B) of Co^{III}(pyz)(3,6-DBSQ)(3,6-DBCat) at 5 K. Corresponding shifts in the intensity of transitions at 500 nm (Co^{III}(pyz)(3,6-DBSQ)(3,6-DBCat)) and 800 nm ($Co^{II}(pyz)(3,6\text{-}DBSQ)_2$) occur reversibly with changes in temperature for solid samples of the polymer.

Crystals of $[Co(pyz)(3,6\text{-}DBSQ)(3,6\text{-}DBCat)]_n$ obtained from hexane solution have been used for a crystallographic molecular structure determination at 296 K.[12] A view of the repeating Co(pyz)(3,6-DBSQ)(3,6-DBCat) unit is shown in Figure 2 with a view of the crystal packing arrangement including the hexane solvate molecules located in voids between adjacent columns of polymeric strands. In this solvated form, the complex crystallizes in a tetragonal space group with the length of the polymer chains aligned along the crystallographic *a* and *b* axes. The resulting crystal structure consists of layered planes containing perpendicular polymeric strands stacked along the *c* axis. The light-induced transition from Co^{III}(pyz)(3,6-DBSQ)(3,6-DBCat) to $Co^{II}(pyz)(3,6\text{-}DBSQ)_2$ for complex units along the polymer chain would have an associated change of approximately 0.2 Å in Co–N bond length. Propagated along the length of the polymer, the micromechanical change in Co–N bond length would correspond to a change of 0.06 mm per millimeter of polymer length. Crystals form as thin plates with the surface of the plate corresponding to the crystallographic *ab* plane and with polymer strands oriented at right angles within the plane. Light-induced changes in polymer length would occur within the surface of the plate. Thin crystals show a reversible distortion upon irradiation with a tungsten–halogen lamp.[13] As for crystals of $Rh(CO)_2(3,6\text{-}DBSQ)$, response is greatest for thin crystals; thick crystals either show only slight deformation or shatter under intense irradiation.[1] The magnitude of the effect is not as great as that observed for the Rh complex due to the difference in crystal morphology, and crystals of the cobalt polymer used in this investigation deteriorate due to solvent loss over the period of several minutes of irradiation if the crystal is not kept at reduced temperature.

The dramatic crystal oscillation experiments described by Abakumov for $Rh(CO)_2(3,6\text{-}DBSQ)$ are not possible with the cobalt polymer. Nevertheless, this system is significant as the first material to show the photomechanical effect as a product of rational design.

Acknowledgment. We would like to thank Brenda Conklin for recording magnetic susceptibility measurements. Support for this research was provided by the National Science Foundation through Grant CHE 90-23636.

Supplementary Material Available: Tables of crystal data and details of the structure determination, atomic coordinates, anisotropic thermal parameters, hydrogen atom locations, and bond lengths and angles for Co(pyz)(3,6-DBSQ)(3,6-DBCat) (12 pages); listing of observed and calculated structure factors (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(12) Crystals of the Co(pyz)(3,6-DBSQ)(3,6-DBCat) polymer were obtained from hexane solution as thin tetragonal plates. Axial photographs indicated a marked tendency for twinning along the tetragonal *c* axis, the thin axis of the crystals. A thin single crystal was found and used for X-ray data collection. The small volume of the crystal gave few observed reflections, allowing only anisotropic refinement of the Co atom. X-ray analysis of $Co(pyz)(3,6\text{-}DBSQ)(3,6\text{-}DBCat)\cdot C_6H_{14}$: tetragonal, space group $P4_32_12$, $a = 14.364(1)$ Å, $c = 37.611(5)$ Å, $V = 7760(1)$ Å^3, $Z = 8$, $R = 0.073$ for 1289 unique observed reflections. Details of the structure determination are given with the supplementary material.

(13) Photomechanical measurements were carried out on a thin single crystal. Experiments were carried out using an apparatus similar to that described by Abakumov.[1] A tungsten–halogen lamp was used as the incident light source. The crystal was maintained at reduced temperature (–35 ± 5 °C) with a slow flow of cooled dry N_2 gas.