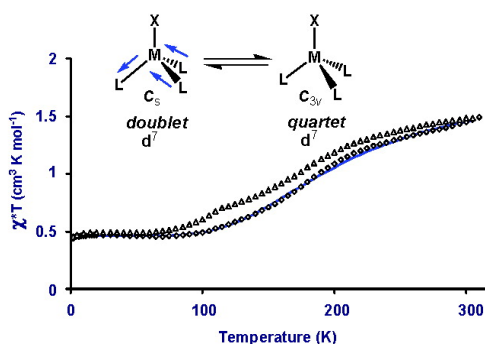
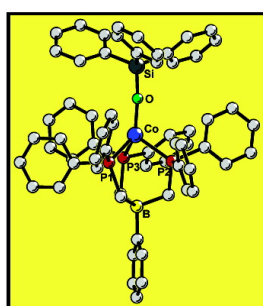


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J. Am. Chem. Soc., **2003**, 125 (37), 11162-11163 • DOI: 10.1021/ja036198f • Publication Date (Web): 22 August 2003

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Solution and Solid-State Spin-Crossover Behavior in a Pseudotetrahedral d^7 Ion

David M. Jenkins and Jonas C. Peters*

Division of Chemistry and Chemical Engineering, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Received May 16, 2003; E-mail: jpeters@caltech.edu

Molecular spin-crossover systems continue to receive widespread scrutiny due to diverse interests that range from the role of metals in biology (e.g., oxygen transport) to magnetic device applications.^{1–5} In nearly all such systems, the molecular spin-crossover platform that provides the key starting point is a pseudooctahedral, first row $d^4–d^7$ ion.^{6–8} We recently described an unusual d^7 cobalt(II) system, $[\text{PhBP}_3]\text{CoX}$ ($X = \text{I}, \text{Br}, \text{Cl}$; $[\text{PhBP}_3] = [\text{PhB}(\text{CH}_2\text{PPh}_2)_3]^-$), that exhibits a low spin ground state.⁹ The tripodal phosphine ligand appears to influence the preference for the unusual low spin state by confluence of its strong phosphine donors and by accommodating the axially distorted, pseudotetrahedral geometry.^{9,10} Encouraged by this result, we reasoned that it should be possible to observe molecular spin-crossover phenomena for complexes of related geometry given the judicious choice of a tripodal ligand auxiliary and an X-type ligand.

In this report, we describe a pseudotetrahedral d^7 complex, $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$, that exhibits thermally induced spin-crossover; to our knowledge, it is the first such complex of its type. Whereas solution spin equilibria for quadricoordinate Co(II) and Ni(II) systems were first reported nearly four decades ago,¹¹ the gross stereochemical change from tetrahedral to square planar observed in such systems is not complementary to magnetic crossover in the solid state. As depicted in Figure 1, crossover systems of the type described herein access a much gentler distortion that we suggest tracks an e -vibration under idealized three-fold symmetry. This modest structural change is compatible with gradual spin-crossover in solution and in the solid state.

The title complex, $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$, was isolated as purple crystals in 81% yield after addition of a THF solution of TiOSiPh_3 to a stirring THF solution of green $[\text{PhBP}_3]\text{CoI}$.⁹ The analytical data that are presented below were obtained from a twice recrystallized sample that was subsequently lyophilized from frozen benzene to obtain satisfactory combustion analysis (see Supporting Information).

The molecular structure of $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$ obtained at 98 K is shown in Figure 2 (left) and is consistent with a low spin ground-state configuration.^{9,10,12} Most striking is the nearly linear ($172.5(1)^\circ$) Co–O–Si bond angle and the notably short Co–O bond distance (1.799(2) Å). By comparison, a related high spin tris-(pyrazolyl)borate complex, $[\text{Tp}^{\text{ipr}}]\text{Co}(\text{OSiPh}_3)$, has been structurally characterized¹³ and exhibits a Co–O–Si bond angle that is bent (153°) and an appreciably longer Co–O bond distance of 1.846(7) Å, a distance more in accord with the high spin aryloxide complex $[\text{PhBP}_3]\text{Co}(\text{O}-2,6\text{-Me}_2\text{Ph})$ (1.851(2) Å).⁹ The low spin configuration for a pseudotetrahedral, $d^7 L_3MX$ system should exhibit a stabilizing Jahn–Teller distortion away from three-fold symmetry that lowers the energy of a singly occupied, high-lying orbital of d_{yz} (or d_{xz}) parentage.⁹ This distortion is reminiscent of that typically observed in pseudooctahedral, low spin d^7 ions,¹⁴ and is evident in the molecular structure of $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$. The Co–P(2) bond

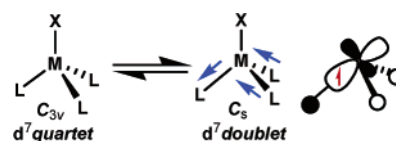


Figure 1. A pictorial representation of the gentle geometric distortion that accompanies spin-crossover in $d^7 L_3MX$ complexes. A lobal representation of the SOMO of the doublet state is also shown.

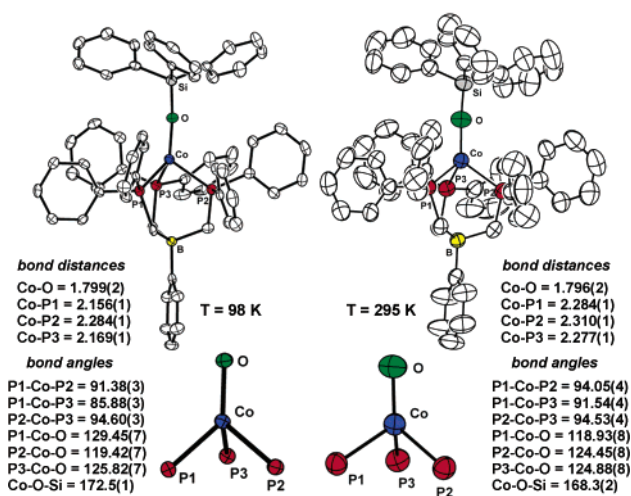


Figure 2. Displacement ellipsoid (50%) representations of $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$ at 98 and 295 K. Hydrogen atoms have been omitted for clarity. See Supporting Information for complete details.

length is appreciably elongated (2.284(1) Å) relative to the Co–P(1) and Co–P(3) bond lengths (2.156(1) and 2.169(1) Å, respectively). Elongation at Co–P(2) attenuates a σ^* antibonding interaction between a phosphine donor and the metal-based SOMO. Diffraction data for $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$ were also collected at 295 K (Figure 2, right). Despite the fact that only partial population of the quartet state is expected at this temperature (vide infra), it appears that two of the Co–P bond distances have elongated by ~ 0.1 Å and that the overall variance in the P–Co–P and O–Co–P bond angles has decreased substantially. Also, the Co–O bond distances are virtually identical between the low- and high-temperature structures. Because the metal-based orbital that lies along the Co–O bond vector is a predominantly nonbonding d_{z^2} hybrid,⁹ the Co–O bond distances are not expected to reflect the occupancy of this orbital by one versus two electrons.

Low-temperature SQUID magnetization data obtained on a powder sample establish a magnetic moment close to the $S = 1/2$ spin only value ($\mu_{\text{eff}} = 1.95 \mu_{\text{B}}$ at 50 K). The sample's magnetic moment increases as the sample is warmed above ~ 80 K (Figure 3). Crossover to the high spin population is significant but incomplete at 310 K ($\mu_{\text{eff}} = 3.46 \mu_{\text{B}}$), the highest temperature for

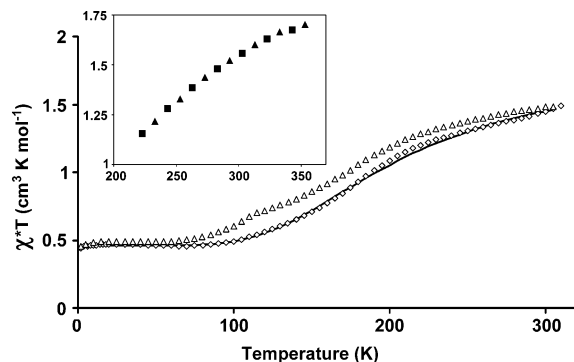


Figure 3. SQUID magnetization data plotted as χT versus T for $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$ as the temperature was raised (\diamond) and lowered (\triangle). Calculated best fit for ΔH (—) provides $\Delta H = 490 \text{ cm}^{-1}$. Inset: Variable-temperature Evans method data (χT vs T) in toluene- d_8 . \blacksquare is for T decreasing, and \blacktriangle is for T increasing.

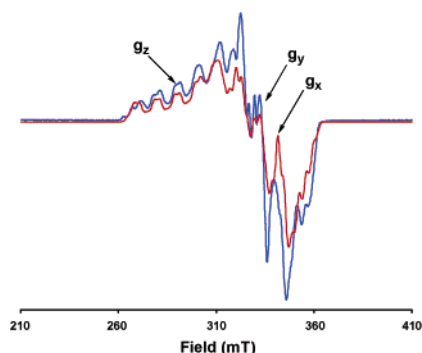


Figure 4. EPR spectrum of a glassy toluene solution of $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$ (20 K, $\nu = 9.475 \text{ GHz}$). Experimental spectrum (blue line). Simulated spectrum (red line). $g_x = 2.03$, $a_{x(\text{Co})} = 65 \text{ G}$, $a_{x(\text{P})} = 34 \text{ G}$; $g_y = 2.05$, $a_{y(\text{Co})} = 12 \text{ G}$, $a_{y(\text{P})} = 27 \text{ G}$; $g_z = 2.21$, $a_{z(\text{Co})} = 105 \text{ G}$, $a_{z(\text{P})} = 28 \text{ G}$.

which the SQUID data were recorded. Both unidirectional and bidirectional VT data were recorded,¹⁵ and Figure 3 reveals a slight variance in magnetic moment as the temperature of the powder sample is first warmed and then lowered. The gradual nature of the crossover phenomenon intimates that a simple Boltzmann model should provide a reasonable estimate of ΔH between the low and high spin forms.⁷ The data for the increasing temperature path were fit to a simple Boltzmann equation (solid line, Figure 3) to estimate ΔH . Because of the incomplete crossover at 310 K, we extrapolated an estimate for complete crossover, $\chi T_{(\text{HS})}$, at $1.87 \text{ (cm}^3 \text{ K mol}^{-1})$ and can crudely estimate $T_c \approx 220 \text{ K}$ and $\Delta H \approx 490 \text{ cm}^{-1}$.

The gradual crossover displayed by $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$ in the solid state suggests the likelihood that it might also exhibit crossover behavior in solution. To interrogate this possibility, we collected the glassy toluene EPR spectrum of $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$ at 20 K. The spectrum, shown in blue in Figure 4, exhibits well-resolved hyperfine coupling to cobalt ($I_{\text{Co}} = 7/2$) and also superhyperfine coupling to phosphorus ($3 \times \text{P}$, $I_{\text{P}} = 1/2$). The spectrum is satisfactorily simulated as an $S = 1/2$ spin system (red line). The eight-line splitting pattern in the g_z region of the spectrum is consistent with a monomeric configuration for $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$ in toluene solution.^{9,16} The EPR spectrum of $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$ was also examined as a function of temperature between 5 and 100 K. At no temperature could the EPR signal of the high spin species be discerned, a fact that is readily explained. Because of rapid relaxation rates, high spin signals for $S = 3/2$ cobalt(II) ions are typically observed by EPR spectroscopy only at temperatures

below $\sim 60 \text{ K}$.¹⁶ In the present system, we expect only the low spin species to be sufficiently populated in this lower temperature regime.

Evidence for spin-crossover in solution was provided from optical spectroscopy and magnetic measurements. For example, the optical spectrum of $[\text{PhBP}_3]\text{Co}(\text{OSiPh}_3)$ was recorded between 200 and 350 K in toluene. As the temperature of the solution was increased, a dramatic color change from deep purple (200 K) to a rich red (350 K) was observed (see Supporting Information). A broad optical band centered at 557 nm decayed as the temperature was raised, coinciding with decay of the low spin form. The solution magnetic behavior was probed by the method of Evans in toluene- d_8 (Figure 3, inset). The magnetic moment was measured to be $3.04 \mu_{\text{B}}$ at 223 K and $3.69 \mu_{\text{B}}$ at 353 K, clearly indicative of crossover behavior. Distinct from the solid-state data shown in Figure 3, the solution magnetic data proved completely reversible. The relatively narrow temperature window in which the solution data were recorded allows us to provide a rather crude estimate of ΔH in toluene solution ($\sim 770 \text{ cm}^{-1}$).

In summary, this report establishes that an equilibrium mixture of low and high spin forms for a distorted tetrahedral d^7 ion is possible. Moreover, the cobalt(II) system described underscores the close electronic structure relationship that can arise between four-coordinate, pseudotetrahedral systems and their six-coordinate, octahedral counterparts.

Acknowledgment. We thank the NSF (CHE-0132216) and the DOE (PECASE) for financial support. D.M.J. acknowledges an NSF graduate research fellowship. We are grateful to the Beckman Institute (Caltech) for use of the SQUID magnetometer, and to Mike Day and Larry Henling for crystallographic assistance.

Supporting Information Available: Complete experimental procedures and characterization data (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA036198F