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Temperature-Dependent $^5T_2(O_h) \rightleftharpoons {}^1A_1(O_h)$ Spin Equilibrium in a Six-Coordinate Cobalt(III) Complex. Investigation by ^{31}P NMR in Solution

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Received January 3, 1980

The temperature-dependent $^5T_2(O_h) \rightleftharpoons {}^1A_1(O_h)$ spin equilibrium in a six-coordinate cobalt(III) complex $[Co^{III}L_2]PF_6$, with L being the tridentate oxygen tripod ligand $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}^-$, has been studied in solution by ^{31}P NMR spectroscopy. The use of four different solvents shows very little difference in the transition behavior. The enthalpy change $\Delta H°$ and the entropy change $\Delta S°$ of the spin transition have been evaluated from the temperature dependence of the paramagnetic shifts. Average values of ca. 24 kJ mol^{-1} for $\Delta H°$ and ca. 70 J mol^{-1} K^{-1} for $\Delta S°$ have been found, which are practically constant for all the solvents used. It is concluded that the spin multiplicity change in the $[Co^{III}L_2]^+$ complex ion is basically an intramolecular electron-transfer process involving predominantly inner-sphere effects. Spin change induced outer-sphere reorganization involving solute–solvent interaction appparently plays no significant role.

Introduction

The phenomenon of temperature-dependent spin crossover (otherwise called spin transition, spin equilibrium, magnetic crossover) may occur in octahedral transition-metal complexes with d^4–d^7 electron configuration, provided the difference between the ligand field strength Δ and the mean spin pairing energy, $|\Delta - P|$, is on the order of kT.[2a]

Particularly numerous examples of temperature-dependent spin crossover have become known in the complex chemistry of iron(II)[2b] and iron(III).[3] A good number of spin crossover systems of cobalt(II)[4] and, to a lesser extent, of nickel(II)[4] have also been described. Recently, W.K. has communicated the first example of a cobalt(III) complex compound exhibiting a temperature-dependent spin transition.[5] In this compound, abbreviated here as $[Co^{III}L_2]PF_6$, two tridentate ligands L = $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}^-$ are coordinated octahedrally to the central cobalt(III) ion (see Figure 1). The ligand L itself is a *diamagnetic* anionic half-sandwich complex,[6] which can act as a weak and hard oxygen tripod ligand in a variety of metal complexes.[7] The spin transition in $[Co^{III}L_2]PF_6$ is very gradual in solution as well as in the solid state, as has been evidenced by magnetic susceptibility measurements.[5]

The present ^{31}P NMR study has been undertaken to confirm the existence of the spin equilibrium in solution by using a different method. It was also necessary to find if the spin-transition behavior (transition temperature T_c and the slope of the spin-transition curve at T_c) depends on the nature of the solvent. Finally, it is intended to determine the thermodynamic parameters such as the changes in enthalpy (ΔH) and entropy (ΔS) for the spin crossover in this unique molecule when in solution. The NMR method seems to be a suitable method of determining these thermodynamic parameters, as was first shown in studies of the Ni(II) (planar, $S = 0$) $\rightleftharpoons$ Ni(II) (tetrahedral, $S = 1$) system.[8] The NMR method has also been used to study the $^6A_1(O_h) \rightleftharpoons {}^2T_2(O_h)$ spin equilibrium in dithiocarbamates of iron(III).[9]

Table I. Measured ^{31}P NMR Shifts ($\Delta\nu/\nu_0$) of the Cation of $[Co^{III}L_2]PF_6$, Relative to That of the PF_6^- Anion as an Internal Standard, as a Function of Temperature in Various Solvents

CD_2Cl_2		CD_3COCD_3		DMF		3-heptanone	
T, K	$\Delta\nu/\nu_0$, ppm	T, K	$\Delta\nu/\nu_0$, ppm	T, K	$\Delta\nu/\nu_0$, ppm	T, K	$\Delta\nu/\nu_0$, ppm
190	274.5	185	274.3	300	423.0	246	307.0
210	278.3	205	277.5	313	463.8	267	335.3
231	285.9	226	284.7	327	516.3	290	389.6
251	308.7	246	299.7	339	568.2	303	433.6
271	352.4	267	333.4				
287	400.0	282	373.3				
300	454.1	291	401.9				
		298	427.3				
		308	456.8				
		317	491.3				

For the compound studied here one could use either ^1H or ^{31}P NMR methods. We have chosen to use ^{31}P NMR spectroscopy because the paramagnetic shifts will be larger, and only one single resonance will be observed from the cation.

Experimental Section

(a) Preparation of the Compound. Bis[cyclopentadienyltris(diethyl phosphito-*P*)cobalt-*O*,*O*′,*O*″]cobalt(III) hexafluorophosphate, $[Co^{III}L_2]PF_6$, has been prepared by electrochemical oxidation of the corresponding complex $[Co^{II}L_2]$[10] at +1.3 V at a carbon gauze in methylene chloride.[11]

(b) ^{31}P NMR Measurements. ^{31}P NMR data were measured with a Bruker CXP-100 HRFT spectrometer operating at a frequency of $\nu_0 = 36.44$ MHz. The shifts were measured relative to that of the PF_6^- anion, which served as an internal standard. To obtain these shifts relative to H_3PO_4, the conventional ^{31}P NMR standard, subtract 145 ppm from the values shown in Figure 4 and Table I. Solvents used in the study were deuterated dichloromethane, CD_2Cl_2 (mp −97 °C, bp 41 °C), deuterated acetone, CD_3COCD_3 (mp −95.4 °C, bp 56.2 °C), *N*,*N*-dimethylformamide, abbreviated as DMF (mp −61 °C, bp 153 °C), and 3-heptanone (mp −39 °C, bp 150 °C). The temperature of the sample was determined by using a copper/constantan thermocouple. The error of the temperature is estimated to be ±1 K.

Results and Discussion

Spectra for $[Co^{III}L_2]PF_6$ in CD_2Cl_2 (concentration 0.102 mol L^{-1}) for temperatures between 190 and 300 K were obtained and are shown in Figure 2. Similar spectra were obtained by using deuterated acetone as a solvent (concentration 0.046 mol L^{-1}) between 185 and 317 K (Figure 3). In an attempt to extend the study to higher temperatures the

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(2) (a) More precisely speaking, the energy gap between the spin singlet level and the lowest energy level of the 15 $^5T_2(O_h)$ states, split and shifted by low-symmetry crystal field and spin–orbit interaction, should be on the order of kT for both spin states to become thermally populated. (b) H. A. Goodwin, *Coord. Chem. Rev.*, **18**, 293 (1976).

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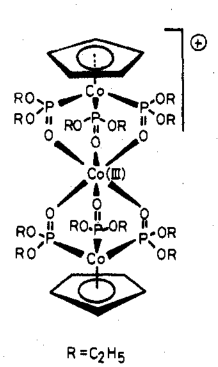

Figure 1. Molecular structure of $[\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}_2Co]PF_6$, $[Co^{III}L_2]PF_6$.

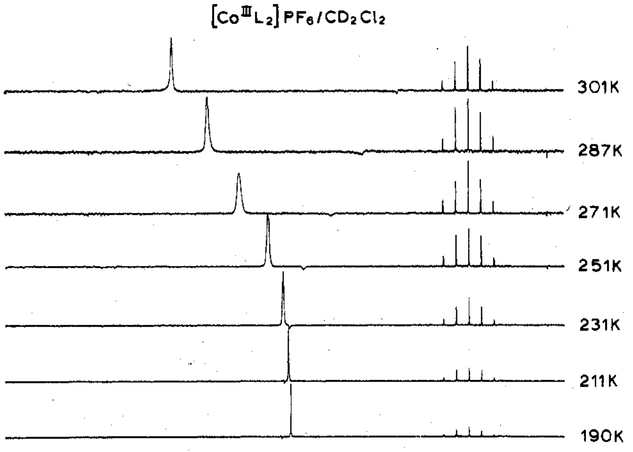

Figure 2. ^{31}P NMR spectra of $[Co^{III}L_2]PF_6$ in deuterated dichloromethane at various temperatures.

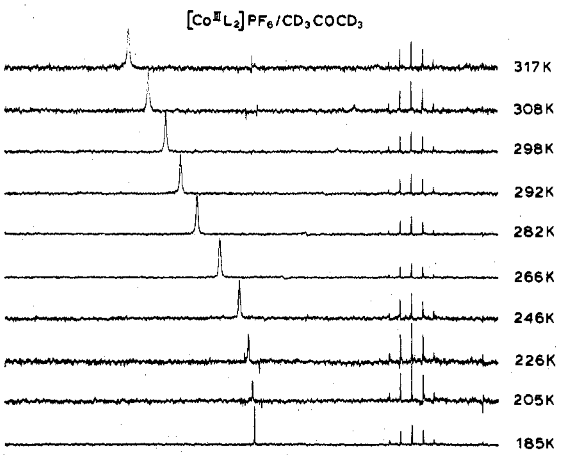

Figure 3. ^{31}P NMR spectra of $[Co^{III}L_2]PF_6$ in deuterated acetone at various temperatures.

solvents *N*,*N*-dimethylformamide and 3-heptanone (both nondeuterated) were used, but it was found that rapid decomposition occurred in both solvents at higher temperatures (≳350 K).

In Figures 2 and 3, the septet resonance at high field is due to the PF_6^- anion, for which the spin–spin splitting is 710.7 Hz, and the lower resonance (single line) is from the cation. The shift of this cation resonance has been measured relative to the center of the PF_6^- resonance as the internal standard for this system. Values of this shift at each temperature for all four solvents used here are given in Table I. To be sure that ion pairing effects on the shift of the PF_6^- anion were not significant, the position of this resonance was checked against another resonance. For CD_2Cl_2 and CD_3COCD_3 this was done relative to the solvent's deuterium resonance since an internal lock was used. For DMF and 3-heptanone an external deuterium resonance was used. In no case did any measurable change in the resonance position of PF_6^- occur. It was not necessary in the case of an external reference to make susceptibility corrections because calculations revealed that it would be no more than 0.5 ppm even at the highest temperatures used.

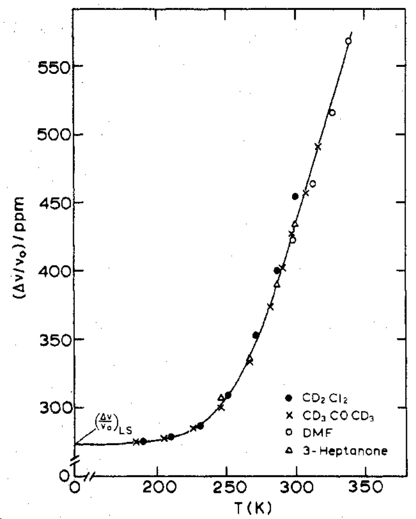

Figure 4. ^{31}P NMR shift $(\Delta\nu/\nu_0)$ of the cation of $[Co^{III}L_2]PF_6$, relative to that of the PF_6^- anion as an internal standard, as a function of temperature for various solvents. The solid curve has been calculated by adjusting eq 1 to acetone data with use of the parameters as listed in Table II.

The line width of the cation resonance did not increase steadily with rising temperature. At ca. 190 K it was fairly narrow (~20 Hz), as would be expected for a nearly diamagnetic substance. It increased with temperature to ~270 K where it maximized (~140 Hz for CD_3COCD_3, ~240 Hz for CD_2Cl_2). Above this temperature the line narrowed, becoming ~110 Hz at 300 K. Above 300 K it was observed to broaden rapidly with increasing temperature. The samples heated up to ca. 340 K were subsequently remeasured at room temperature to make sure that the results were not blurred by decomposition products. The shifts $\Delta\nu/\nu_0$ are plotted as a function of temperature in Figure 4. Below 185 K the shift is practically independent of temperature, indicating that the cation is nearly completely in the $^1A_1(O_h)$ low-spin state. The rapid change in $\Delta\nu/\nu_0$ at the highest temperatures measured indicates that the conversion to the paramagnetic state is far from complete. There is a very small solvent effect on the spin equilibrium; only the data for CD_2Cl_2 deviate slightly from those of the other solvents in the higher temperature range.

The values of $\Delta H°$ and $\Delta S°$, the changes of enthalpy and entropy associated with the transition of 1 mol of complex molecules from the low-spin (LS) to the high-spin (HS) state, are obtained by fitting eq 1[8] to the experimental points.

$$\frac{\Delta\nu}{\nu_0} = \frac{C}{T(1 + e^{\Delta G°/RT})} + \left(\frac{\Delta\nu}{\Delta_0}\right)_{LS} \tag{1}$$

$(\Delta\nu/\nu_0)_{LS}$ is the shift for the low-spin state. In our analysis $(\Delta\nu/\nu_0)_{LS}$ was taken from Figure 4 to be 273 ppm. C/T is the shift for the high-spin state, and $\Delta G° = \Delta H° - T\Delta S°$ is the molar free energy change on going from low spin to high spin. The best-fit values obtained for $\Delta H°$, $\Delta S°$, and C are given in Table II. Insufficient data were taken for the solvent DMF and 3-heptanone for a least-squares analysis. However, a least-squares analysis was done on the combined data from the DMF and acetone experiments, because from Figure 4 it appeared that the DMF curve was just an extension of the

Table II. Best-Fit Values for ΔH°, ΔS°, and C from a Least-Squares Adjustment of Eq 1 to the Observed ^{31}P NMR Shifts ($\Delta\nu/\nu_0$)

solvent	temp range, K	ΔH°, kJ mol^{-1}	ΔS°, J mol^{-1} K^{-1}	C, K
CD_3COCD_3	185-317	24.3 ± 1.1	71.5 (+8.8, −4.2)	200 200 ± 32 600
CD_2Cl_2	190–300	25.7 ± 1.3	76.1 (+20.5, −5.0)	220 000 ± 66 110
DMF/ CD_3COCD_3[a]	180–317	22.4 ± 1.4	62.3 (+13.4, −5.0)	260 000 ± 53 480

[a] A least-squares fit was carried out for the combined data from DMF and acetone, because DMF data were available only for the temperatures 300-339 K.

acetone curve. The results from this analysis are also included in Table II.

The values of ΔH°, ΔS°, and C are very similar for the various solvents used. Thus the influence of the solvent on the spin crossover behavior is very small. This is not unexpected since the central cobalt atom, where the spin transition takes place, is probably very well shielded from the solvent by the 12 ethoxy groups of the two ligands (see Figure 1). The crystal structure analysis of the analogous copper(II) complex $[CuL_2]$ supports this.[12]

The observed entropy change ΔS° for the spin transition is very much larger than the contribution from the change in spin degeneracy, which is in the present case $R \ln 5 = 13.4$ J mol^{-1} K^{-1}. If the distortion of the $^5T_2(O_h)$ state of this complex is small compared to kT, the total electronic contribution to ΔS° from both orbital and spin degeneracy would be $R \ln 15 = 22.5$ J mol^{-1} K^{-1}. This is still much smaller than the observed value of ca. 70 J mol^{-1} K^{-1}. It seems very likely that the additional contributions, and thus the major part of ΔS°, originate from changes in the vibrational characteristics of both intramolecular and intermolecular vibrations. Since, however, there is little solvent effect, we consider the intermolecular part to be small. Furthermore, the absence of a noticeable solvent effect suggests that contributions to ΔS° from outer-sphere reorganization between the $[Co^{III}L_2]^+$ cations and solvent molecules be negligibly small. These conclusions are supported by investigations made by Sorai and Seki.[13] They determined the entropy change ΔS° associated with the spin transition in the isoelectronic $[Fe^{II}(phen)_2(NCS)_2]$ and $[Fe^{II}(phen)_2(NCSe)_2]$ crossover systems (phen = 1,10-phenanthroline) from heat capacity measurements. They found ΔS° values of 48.8 and 51.2 J mol^{-1} K^{-1}, respectively. About 75% of the total entropy change ΔS° was attributed by these authors to vibrational contributions with the major portion originating from the intramolecular part. In the present case it seems justified also to consider the contribution to ΔS° from changes in the intramolecular vibrational characteristics (metal–donor atom stretching and deformation modes) on going from the low-spin to the high-spin state to be most important in accounting for the excess entropy change. The relatively large entropy changes in our case may be rationalized in terms of the complex molecule under study being considerably larger and probably more flexible than the systems investigated by Sorai and Seki. Both the greater size and greater flexibility of L offer more vibrational degrees of freedom accessible upon spin conversion. Other factors like differences in bonding properties may also be significant. It is hoped that data from similar studies on analogous $[Co^{III}L_2]^+$ complexes containing different OR substituents on the phosphorus atom (Figure 1) will soon be available and eventually enable us to give a more definitive interpretation of the entropy change ΔS°. It should be noted that the kinetics of intersystem crossing in a number of isoelectronic spin crossover systems of iron(II) have been studied in solution by the laser Raman temperature jump technique; the derived entropy changes span a surprisingly wide range from ca. 33[14] to ca. 110 J mol^{-1} K^{-1}.[15] It has been suggested that the very lage ΔS° values may be due to hydrogen-bonding interaction with the solvent molecules.[15] A significant solvent effect has been observed in such cases.[15] Systems with no hydrogen bonding have yielded considerably smaller ΔS° values, some of which compare well with the present data.

The ΔH° values range from 22.4 to 25.7 kJ mol^{-1} and seem to reflect predominantly the enthalpic change associated with the intramolecular reorganization induced by the spin change. It is well established that the metal–donor atom distance may increase by as much as 0.1–0.2 Å on passing from the low-spin state to the high-spin state in d^6 and d^5 systems with $\Delta S = 2$ changes.[14,16-19] It is also well documented that the intramolecular vibrational frequencies change accordingly, with the low-spin state possessing the higher wavenumbers; see, e.g., ref 13. For the present case of a $^1A_{1g}(O_h) \rightleftharpoons {}^5T_{2g}(O_h)$ spin state equilibrium the change in metal–ligand bond length is a direct consequence of the intramolecular electron transfer between the $t_{2g}^6(O_h$, low spin) $\rightleftharpoons$ $t_{2g}^4e_g^{*2}(O_h$, high spin) electron configurations. In view of the net change by two electrons in the antibonding e_g^* orbitals we expect that the change in metal–ligand bond length is close to 0.2 Å as in isoelectronic iron(II) systems.[18,19] Stynes and Ibers[20] have estimated qualitatively the inner-sphere reorganization energy. For a spin-change-induced variation of the bond length in the range 0.11–0.17 Å one finds reorganization energies of 2.0–6.2 kcal mol^{-1} (8.2–25.9 kJ mol^{-1}). We notice that for bond length changes close to 0.2 Å, as anticipated for the present system, the estimated inner-sphere reorganization energy agrees very well with the observed ΔH° values.

From the observed data for ΔS° and ΔH° we conclude that the spin multiplicity change in the $[Co^{III}L_2]^+$ complex in the solutions under study should be treated as an intramolecular electron-transfer process, followed by predominantly inner-sphere effects. These findings parallel results from earlier studies on iron(II), iron(III), and cobalt(II) crossover systems in solution.[14]

Acknowledgment. This work was supported by The National Science and Engineering Research Council of Canada, the Deutsche Forschungsgemeinschaft, and NATO Research Grant No. 1372.

Registry No. $[Co^{III}L_2]PF_6$, 70850-85-0.

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