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Linear Tricobalt Compounds with Di-(2-pyridyl)amide (dpa) Ligands: Studies of the Paramagnetic Compound $Co_3(dpa)_4Cl_2$ in Solution

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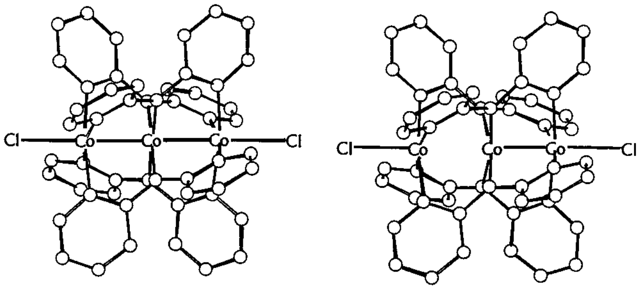
Solutions of $Co_3(dpa)_4Cl_2$, where dpa = di(2-pyridyl)amide ion, in CD_2Cl_2 were studied by NMR in the temperature range 183−303 K. The spectra show only four ^1H and five ^{13}C resonance signals, consistent with the D_4 symmetry of the molecules found in the solid. The magnetic susceptibility in solution was determined by the Evans method from 193 to 308 K. These observations can be modeled as an $S = 1/2$ to $S = 5/2$ spin-transition process with $\Delta H = 7.7(2)$ kJ mol^{-1} and $\Delta S = 20.8(8)$ J K^{-1} mol^{-1}.

Introduction

Previous structural studies have shown that $Co_3(dpa)_4Cl_2$ (**1**) consists of a linear array of three cobalt atoms surrounded by four dpa ligands and two axial chlorine atoms.[1] Two structural motifs (see Chart 1) have been shown to exist: type **I** has symmetrical Co−Co distances of 2.32 Å, while type **II** possesses unequal distances of 2.29 and 2.47 Å. To a first approximation, the metal−metal bonding can be visualized as delocalized over the three Co atoms for type **I**, but a single Co−Co bond must be localized between only two Co atoms in molecules of type **II**; the third Co^{II} atom resides in an isolated square pyramidal coordination environment. The existence of such “bond stretch isomers” of **1** in the solid state suggests that the difference in energy between the symmetrical and unsymmetrical molecules is small.[2] Thus, small changes in the crystallization conditions or the composition of the crystal[1a] may lead to a significant variation of metal-to-metal distances.

If such bond stretch isomers exist in solution, more than one species might be observable by spectroscopic methods. NMR spectroscopy is one of the techniques that may provide structural information even for paramagnetic compounds containing transition metal centers.[3] We have now found that when dissolved in CD_2Cl_2, both symmetrical and unsymmetrical forms give the same ^1H and ^{13}C NMR spectra. The following questions are addressed in the NMR work: (1) Which form does the molecule adopt in solution? (2) How does the magnetism of **1** change with temperature?

Chart 1



I **II**

Experimental Section

Manipulations were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were purified by conventional methods and were freshly distilled under nitrogen prior to use. Anhydrous $CoCl_2$ was purchased from Strem Chemicals, Inc. Di(2-pyridyl)amine was purchased from Aldrich and sublimed prior to use; $Co_3(dpa)_4Cl_2$ (**1**) was prepared as published.[1] ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Plus 300 spectrometer at 300 and 75.4 MHz, separately. Chemical shifts are referenced to CD_2Cl_2 (5.32 ppm for ^1H and 53.8 ppm for ^{13}C spectra). Magnetic susceptibility measurements in CH_2Cl_2 solution were performed by the Evans method.[4] The concentration of **1** at each temperature was corrected by the CH_2Cl_2 density change.[5] X-band EPR spectra in frozen dichloromethane solution were recorded on a Bruker model ESP 300 spectrometer.

Results and Discussion

NMR Spectroscopy. Figure 1 shows the ^1H NMR spectrum of $Co_3(dpa)_4Cl_2$ in CD_2Cl_2 solution with four peaks spanning

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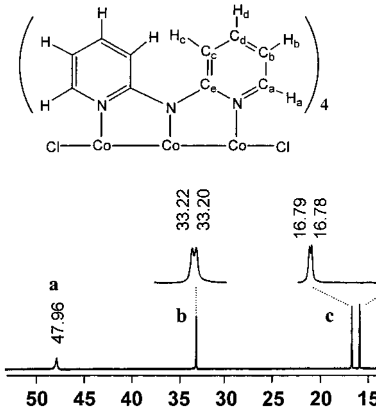

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Figure 1. Room temperature ^{1}H NMR spectrum of **1** in CD_2Cl_2. Signals **a**−**d** are assigned to the corresponding H atoms as shown at the top.

the range from 47 to 15 ppm. As in the previously reported case of $Ni_3(dpa)_4Cl_2$,[6] the paramagnetism of the molecule has not obliterated the spectrum, but simply caused abnormal chemical shifts, broadened the lines, and caused intensity ratios to deviate from those expected (i.e., 1:1:1:1). This spectrum admits of two interpretations: (a) the molecule in solution is symmetrical, or (b) the molecule in solution is unsymmetrical, but the two equivalent forms are interconverting rapidly on the ^{1}H NMR time scale (ca. 10^{-3} s). For the symmetrical structure with idealized D_4 symmetry there should be only four signals, whereas if the molecule were to have lower symmetry in solution, as it would if the middle Co atom were to move off center, at least twice as many signals would appear. Clearly, the NMR spectrum tells us, that in solution, all eight pyridyl rings are equivalent on the NMR time scale. We believe, but cannot prove, that interpretation (a) is correct. By employing a spectroscopic technique with an even shorter time scale (say vibrational spectroscopy), this point could be settled conclusively. Unfortunately, we cannot carry out such studies at this time. As an alternative, the temperature dependence of the NMR spectrum of $Co_3(dpa)_4Cl_2$ was studied, with the hope that line shape changes might reveal a dynamic process, should one exist. In fact, the line shapes or widths did not change over the available temperature range of 183−303 K, thus supporting interpretation (a). However, as shown in Figure 2, and discussed below, the line positions showed great sensitivity to temperature. This can be attributed to variation of the molecular magnetic moment with temperature, and we shall later provide direct evidence for this.

Let us now return to further details of the NMR study. Despite the short relaxation time of the paramagnetic molecule and the broad spectral window required, we were able to obtain a 2-D COSY spectrum, shown in Figure 3. For convenience in discussion we shall designate the observed signals in Figures 1 and 3 as **a** (singlet at 47.96 ppm), **b** (doublet at 33.21 ppm), **d** (triplet at 15.96 ppm), and **c** (doublet at 16.78 ppm). It is clear from Figure 3 that **d** is coupled to both **b** and **c**, with $^2J_{H-H}$ values of 7.88 and 6.70 Hz, respectively. The very short T_1 for **a** leads to a broad peak, considerably wider than the scalar coupling constants between the pyridyl protons. We assign the signals **a**−**d** to the protons H_a−H_d, as shown in Figure 1, since this is consistent with their relative distances from the paramagnetic Co_3 chain, with the observed $^2J_{H-H}$ values, with the multiplet structures, and with the couplings shown in the COSY spectrum.

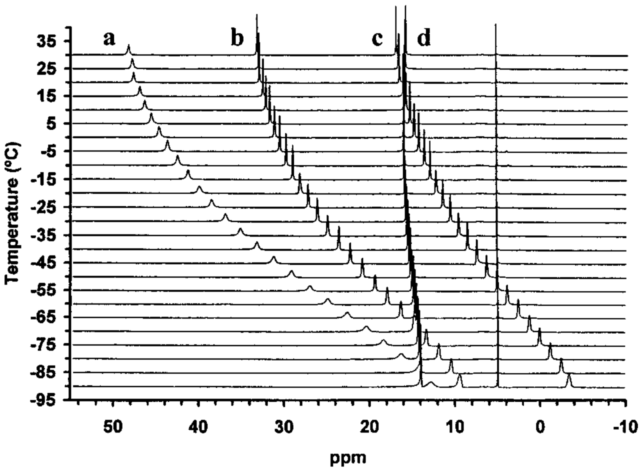

Figure 2. ^{1}H NMR spectra of **1** in the temperature range 183−303 K. Solvent signal at 5.32 ppm.

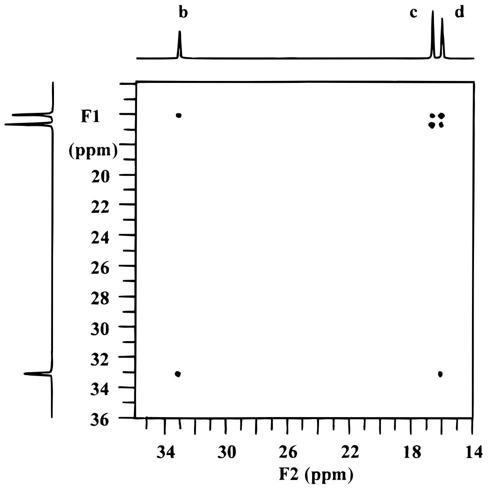

Figure 3. ^{1}H 2-D COSY spectrum of **1** in CD_2Cl_2 at room temperature.

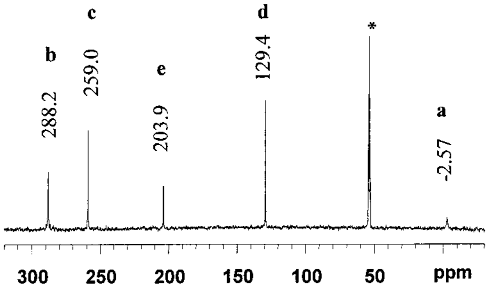

Figure 4. ^{13}C NMR spectrum of **1** in CD_2Cl_2 at room temperature. For the assignment of signals **a**−**e** to the corresponding C atoms, see Figure 1. Starred signal due to solvent.

The ^{13}C NMR spectrum of **1**, shown in Figure 4, was assigned by a heteronuclear proton decoupling experiment. The presence of only five signals also supports the conclusion that all eight pyridyl groups are equivalent. The resulting chemical shifts (ppm) and J_{C-H} coupling constants (Hz), in parentheses, for the four carbon atoms labeled as C_a−C_d (see Figure 1) are −2.57 (162.2), 288.2 (166.2), 259.0 (166.2), and 129.4 (159.0), respectively. The fifth carbon atom C_e that is connected to the amide N atom instead of an H atom shows a resonance signal at 203.9 ppm.

The variation of the ^{1}H NMR spectra of **1** as a function of temperature is shown in Figure 2. Resonance **d** is essentially temperature-independent, while **a**, **b**, and **c** move upfield as the

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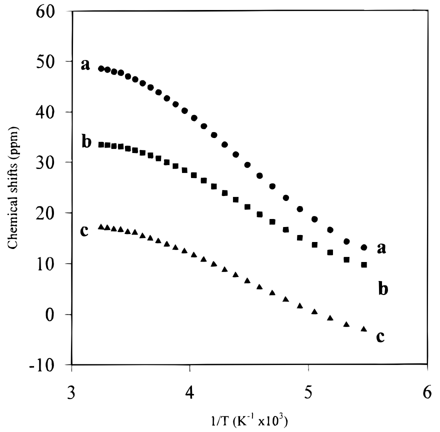

Figure 5. Temperature dependence of ^{1}H NMR chemical shifts for **1** in CD_2Cl_2.

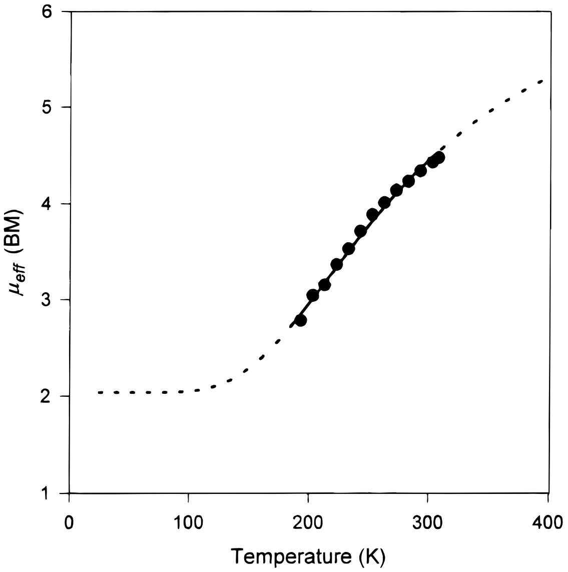

Figure 6. Temperature dependence of the magnetic susceptibility measured in solution for **1**. (●, experimental data; —, fitted results; ···, extension of the fitted results beyond the solution temperature range). The fits were obtained by procedures described in the text.

temperature is lowered, and the total width of the spectrum decreases markedly (~36 to ~14 ppm). A plot of chemical shifts vs 1/*T* (Figure 5) is not linear; thus, there is no adherence to the Curie law as would have been expected for a process based on pseudocontact shifts with a temperature-independent magnetic moment. Instead, the system is complicated by temperature dependence of the magnetic moment of the Co_3 group, indicating the existence of a spin-state equilibrium in solution. Because these two factors (i.e., the pseudocontact shifts and temperature dependence of μ_{eff}) are involved, we have been unable to model the spectrum quantitatively. It was more useful to seek information on the temperature dependence of the magnetic properties of **1** directly on the basis of solution magnetic susceptibility measurements by the Evans method.[4]

Solution Magnetic Properties. The magnetic moment of **1** was measured in CH_2Cl_2 solution by the Evans method[4] in the temperature range 193−308 K, and the results are shown in Figure 6. As temperature increases, the μ_{eff} changes from 2.78 to 4.48 μ_B. This increase in magnetic moments for the tricobalt compound, at higher temperature, is consistent with a spin transition taking place in solution. The ground state for three linearly and symmetrically distributed Co^{2+} ions in the molecule

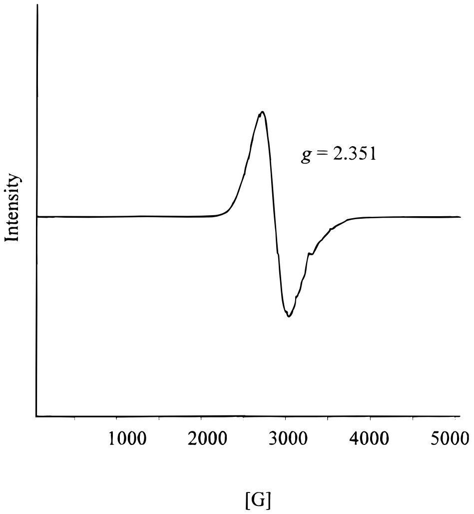

Figure 7. X-band EPR spectrum of **1** in frozen CH_2Cl_2 at 5 K.

of **1** has been proposed[2] as a doublet, $S = 1/2$. The spin doublet ground state is supported by a frozen-glass EPR measurement.

Figure 7 shows the X-band EPR spectrum of compound **1** in CH_2Cl_2 glass at 5 K. It has one isotropic resonance with a *g* value of 2.351, which is consistent with the expected $S = 1/2$ ground state. This *g* value is also in agreement with those obtained from SQUID measurements of the solid[7] in which a doublet ground state was found to give the best fit to the experimental data. The broadness (~450 G) of these signals is probably due to the unresolved hyperfine interactions of the unpaired electron with the three ^{59}Co ($I = 7/2$) nuclei present in these molecules. The measured *g* value of 2.351 at 5 K by EPR gives a calculated effective moment (μ_{eff}) of 2.04 μ_B for the low-spin (LS) $S = 1/2$ ground state. While the solution data do not cover the temperature range below 193 K due to the freezing of solvent, an increase of μ_{eff} at higher temperature is clearly observed in Figure 6. Also the effective magnetic moment measured by the Evans method reaches the value of 4.48 μ_B at 308 K. We attribute this to a spin-state equilibrium, which is larger than the spin-only value for a high-spin ($S = 3/2$) Co_3 entity, $[3(3 + 2)]^{1/2} = 3.87\ \mu_B$, but smaller than that for a high-spin $S = 5/2$ species, $[5(5 + 2)]^{1/2} = 5.92\ \mu_B$. However, the limiting magnetic moment for the high-spin state becomes 4.55 μ_B for $S = 3/2$ or 6.95 μ_B for $S = 5/2$ if the experimental *g* value of 2.351 is employed. Both values are larger than the experimental value of 4.48 μ_B at 308 K, which indicates that the thermally populated high-spin state for **1** could possibly be either 3/2 or 5/2.

The temperature dependence of an equilibrium of spin states in solution can be analyzed by employing the following expression:[8]

$$K = \frac{C_H}{C_L} = \frac{\chi - \chi_L}{\chi_H - \chi} = \frac{{\mu_{eff}}^2 - {\mu_L}^2}{{\mu_H}^2 - {\mu_{eff}}^2} \qquad (1)$$

where C_H and C_L are concentrations of the different spin species in solution, χ, χ_H, and χ_L are the susceptibilities of the mixture and of the individual high (H) and low (L) spin states, separately, μ_{eff} is the measured effective magnetic moment, μ_L (2.04 μ_B) is the limiting magnetic moment for the low-spin state, and μ_H is the limiting magnetic moment for the high-spin state, and it

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could be either 4.55 μ_B ($S = 3/2$) or 6.95 μ_B ($S = 5/2$), but the latter value gives a better fit of the experiment data (vide infra).

A least-squares fit of the experimental data was made using the equation

$$-R \ln K = \Delta H/T - \Delta S \qquad (2)$$

yielding $\Delta H = 7.7(2)$ kJ mol^{-1} and $\Delta S = 20.8(8)$ J K^{-1} mol^{-1} for the $S = 1/2 \leftrightarrow S = 5/2$ spin-transition process. The critical temperature, T_c, of 370 K, for which there are equal populations of high- and low-spin molecules and $\Delta G = 0$, is obtained from $T_c = \Delta H/\Delta S$. The amount of high-spin species is found to be 35% at 300 K. The spin transition proceeds further above room temperature as indicated by both the experimental data and the fitted curve in Figure 6.

The changes of entropy and enthalpy for **1** in solution are consistent with a spin-transition process in which there are species with spin states $S = 1/2$ and $S = 5/2$. To a first approximation, the ΔS term consists of the following contributions:[8]

$$\Delta S = \Delta S_{\text{spin}} + \Delta S_{\text{vib}} + \Delta S_{\text{solv}}$$

where ΔS_{spin} donates the spin-only entropy component due to the change in electronic degeneracy, ΔS_{vib} is the change of vibrational entropy, and ΔS_{solv} is the change of solvation entropy. The ΔS_{spin} contribution is usually assumed to be equal to $R \ln[(2S + 1)_{\text{LS}}/(2S + 1)_{\text{LS}}]$. Thus, the value of ΔS_{spin} would be $R \ln 3 = 9.1$ J mol^{-1} K^{-1} for the change of one unit in spin states, and $R \ln 5 = 13.4$ J K^{-1} mol^{-1} for the change of two units in spin states.[8] In the present system the entropy increase of 20.8(8) J K^{-1} mol^{-1} is dominated by an electronic contribution as the result of an $S = 1/2 \leftrightarrow S = 5/2$ spin transition. A change of two units for such a spin-transition process is well-known for mononuclear Fe(II) complexes;[9] the entropy and enthalpy changes are found in the ranges 37−65 J K^{-1} mol^{-1} and 6−15 kJ mol^{-1}, respectively.[9a] The much larger entropy changes for the iron compounds come from the dominant vibrational contributions as the result of significant variations of the iron coordination sphere.

The ΔH values are positive because of the endothermic nature of the spin-transition process. The enthalpy changes are due primarily to the weakening of metal−ligand bond on going from the low-spin to the high-spin state. The ΔH value of 7.7(2) kJ mol^{-1} for **1** is also larger than those of 1−7 kJ mol^{-1} found in the cobalt compounds known to undergo $S = 1/2$ to $S = 3/2$ spin transitions.[10] However, the change of enthalpy is smaller than the values of 14−21 kJ mol^{-1} found in compounds associated with ligand dissociations.[11] The intermediate ΔH and relatively large ΔS values for **1** are in agreement with a nondissociative process involving multiple spin changes. This is the first example of an $S = 1/2$ to $S = 5/2$ spin-transition process that has been observed for a complex containing trinuclear Co(II) ions.

Concluding Remarks

From solution NMR spectroscopy and magnetic studies, we draw the following conclusions: (a) The D_4 symmetry of the molecule of **1** is maintained in solution at all temperatures. (b) The magnetic moment of the Co_3 unit increases with increasing temperature. (c) An $S = 1/2$ to $S = 5/2$ spin-transition process fits the data and is consistent with the enthalpy and entropy changes in solution.

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