

Table II. IR and UV-Vis Data

compd	IR <sup>a</sup>		UV-vis <sup>b</sup>	
	$\nu_{\text{CO}}$ , cm <sup>-1</sup>	$\nu_{\text{NX}}$ , cm <sup>-1</sup>	$\lambda_{\text{max}}$ , nm	$\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup>
$(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$ (1a)	2028 <sup>c</sup>	1713 <sup>c</sup>	590 (sh)	30
	1955 <sup>c</sup>		480 (sh)	120
	2033 <sup>c</sup>		355 (sh)	720
$(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NS})$ (1b)	1962 <sup>c</sup>	1180 <sup>c</sup>	470	310
	1997	1650	480 (sh)	120
HB(3,5-Me <sub>2</sub> Pz) <sub>3</sub> Mo(CO) <sub>2</sub> (NO) (2a)	1905		435	200
	2003	1125	515	200
HB(3,5-Me <sub>2</sub> Pz) <sub>3</sub> Mo(CO) <sub>2</sub> (NS) (2b)	1924	1136	445	230
			415 (sh)	210
HB(3,5-Me <sub>2</sub> Pz) <sub>3</sub> W(CO) <sub>2</sub> (NO) (3a)	1993	1640	480 (sh)	180
	1884		425	320
HB(3,5-Me <sub>2</sub> Pz) <sub>3</sub> W(CO) <sub>2</sub> (NS) (3b)	1988	1127	510	290
	1902	1140	445	350

<sup>a</sup> KBr pellet. <sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub>; sh = shoulder. <sup>c</sup> In hexane; ref 1.

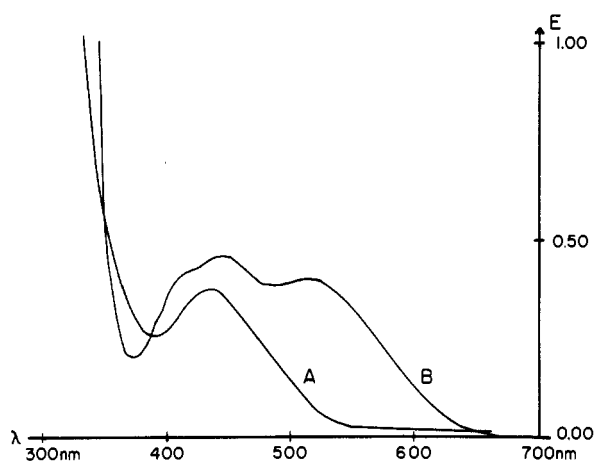


Figure 1. UV-vis spectrum: (A) HB(3,5-Me<sub>2</sub>Pz)<sub>3</sub>Mo(CO)<sub>2</sub>(NO),  $1.90 \times 10^{-3}$  M in CH<sub>2</sub>Cl<sub>2</sub>; (B) HB(3,5-Me<sub>2</sub>Pz)<sub>3</sub>Mo(CO)<sub>2</sub>(NS),  $2.0 \times 10^{-3}$  M in CH<sub>2</sub>Cl<sub>2</sub>.

The <sup>95</sup>Mo NMR results provide unique information in support of a major contribution from the paramagnetic term to the observed chemical shift differences. The <sup>95</sup>Mo chemical shift *increases* by more than 550 ppm when NO is replaced by NS. This very large increase is not expected from the relatively small charge distribution changes at the metal, which are indicated by the carbonyl stretching frequencies and the <sup>13</sup>C NMR. Equally important, *both* the <sup>95</sup>Mo and <sup>14</sup>N chemical shifts increase substantially. This deshielding of both nuclei correlates with a decrease in the energies of the low-lying excited states of the complexes as evidenced by the colors of the complexes. The nitrosyl complexes are generally yellow in solution, while the thionitrosyl complexes are more red. The bathochromic shifts of the absorptions in the UV-vis spectra are shown in Figure 1. Photoelectron spectra for the chromium complexes<sup>6,8</sup> also show that the separation between ground and excited states ( $\Delta E$ ) is less for the thionitrosyl complex. In addition, the photoelectron spectra show that the M-NX  $\sigma$ -bonding orbital is more easily ionized in the thionitrosyl complexes. A transition from this orbital to the lowest unoccupied  $\pi$ -type orbital, which is delocalized over the {MNX} triatomic fragment, will contribute to the paramagnetic terms of both the metal and nitrogen resonances. Since  $\Delta E$  occurs in the denominator of the expression for paramagnetic shielding,<sup>11</sup> the Mo and N atoms in the thionitrosyl complexes will both exhibit larger chemical shifts than in the nitrosyl complexes. It is interesting that the magnitude of the Mo chemical shift change in MoNS complexes is comparable to

that for replacement of a terminal oxo group (Mo=O) by a terminal sulfido group (Mo=S) in Mo(VI) complexes.<sup>13,14</sup>

This work shows the value of heteronuclear NMR investigation of metal complexes, which includes NMR of the metal center. It is interesting that the substantial changes in electron distribution and bonding in the M-NX portion of the molecule, as evidenced by the very large changes in the <sup>14</sup>N and <sup>95</sup>Mo chemical shifts, occur in such a way that the carbonyls experience only a small perturbation, as evidenced by the essentially unshifted <sup>13</sup>C resonances. These results provide additional justification for describing such complexes as derivatives of {MNX}<sup>6</sup> triatomic fragments.<sup>15</sup>

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### <sup>59</sup>Co NMR of a Cobalt(III) Spin-Crossover Compound

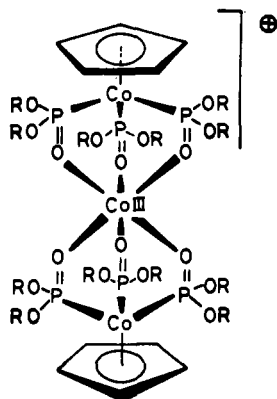
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The cobalt(III) ion has a low-spin electronic configuration in most of its octahedral coordination compounds. Only the fluoride complexes [CoF<sub>6</sub>]<sup>3-</sup> and [CoF<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>] are known to exist in the high-spin configuration.<sup>2</sup>

- (1) (a) Tel-Aviv University. (b) TH Aachen.  
 (2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 775. A few nonoctahedral Co<sup>III</sup> complexes have been reported that possess a spin-triplet groundstate or close lying excited states. See e.g.: McKenzie, E. D.; Worthington, J. M. *Inorg. Chim. Acta* **1976**, *16*, 9 and references therein.

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

A low-spin-high-spin equilibrium has been suggested to be present in  $[Co(H_2O)_6]^{3+}$  in order to explain some of its unusual properties such as high rates of electron transfer and substitution reactions.<sup>3</sup> However, it has recently been shown by  $^{59}Co$  NMR that the high-spin state is not significantly populated at room temperature.<sup>4</sup>

The first octahedral spin-crossover Co(III) compound, which has been described recently,<sup>5</sup> contains the unusual oxygen tripod ligand<sup>6</sup>  $L^- \equiv [(C_5H_5)_2Co[P(O)(OR)_2]_3]^-$ ,  $OR = OC_2H_5$ , with the spin-crossover Co(III) bound to the oxygen atoms of the phosphonate residues (See Figure 1). The low-spin-high-spin equilibrium in solution has been analyzed by using  $^{31}P$  NMR chemical shifts.<sup>7</sup> In the present work we describe the  $^{59}Co$  NMR of this crossover compound.

### Experimental Section

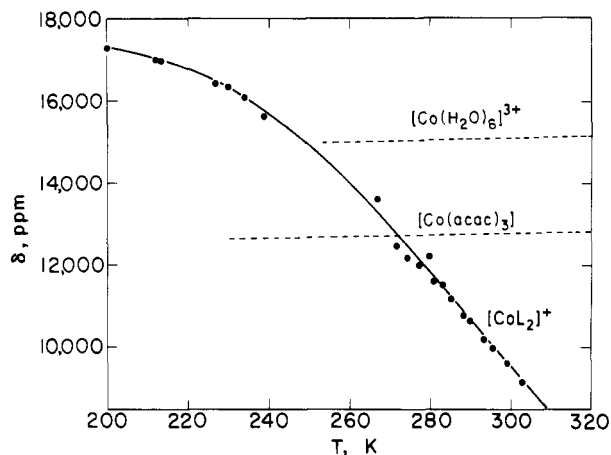
**Materials.**  $[(C_5H_5)_2Co[P(O)(OC_2H_5)_2]_3]CoSbCl_6$ , hereafter abbreviated as  $[Co^{III}L_2]SbCl_6$ , was prepared by oxidizing the corresponding  $Co^{II}$  compound  $[CoL_2]$  with an equimolar amount of  $[p-BrC_6H_4)_3N]SbCl_6$  in methylene chloride at room temperature.<sup>8</sup>

**NMR Measurements.**  $^{59}Co$  NMR data of  $[Co^{III}L_2]SbCl_6$  in  $CD_2Cl_2$  were measured with a Bruker WH-300 NMR spectrometer using 10-mm tubes. Spectral widths were chosen in the range of 20–125 kHz and a delay of 30  $\mu s$  was introduced to avoid artefacts due to the tail of the pulse. The temperature was determined by using the  $^{59}Co$  signal of  $[Co(acac)_3]$  in a 1:1 mixture of  $CH_3OH$  and  $CD_3NO_2$ , which was separately calibrated.<sup>4,9</sup>

**Spectrophotometric measurements** were performed with a Cary 17 spectrophotometer equipped with a quartz Dewar.

### Results and Discussion

Two NMR signals could be observed in  $CD_2Cl_2$  solutions of the spin-crossover compound  $[Co^{III}L_2]SbCl_6$  in the region of the  $^{59}Co$  resonance. One of them is very narrow, practically temperature independent, and appears at 71.827 MHz ( $^1H$  frequency 300.133 MHz), i.e. 8638 ppm from the  $K_3[Co(C-N)_6]$  standard at room temperature. It corresponds to the known resonance of  $^{121}Sb$  of the  $SbCl_6^-$  ion.<sup>10</sup> The other is a broad signal with a line width ranging from 3000 to 20 000



**Figure 2.**  $^{59}Co$  NMR chemical shifts of the spin-crossover cobalt(III) atom in  $[CoL_2]SbCl_6$  (0.04 M solution in  $CD_2Cl_2$ ). The continuous line is the best fit curve as explained in the text. The chemical shifts of  $[Co(H_2O)_6]^{3+}$  and  $[Co(acac)_3]$  shown for comparison are taken from ref 4.

Hz, and its position is exceptionally temperature dependent (see Figure 2). The temperature coefficient of the chemical shift is about 113 ppm  $K^{-1}$  at room temperature, corresponding to 9600 Hz  $K^{-1}$  in our experiment. Thus part of the line width is due to temperature inhomogeneity within the sample. This signal was assigned to the central spin-crossover cobalt(III) atom. Trials to detect the  $^{59}Co$  resonance of the organometallic ligand  $L^-$  were unsuccessful. Probably it is too broad to be detected in our spectrometer.  $^{59}Co$  resonances of similar organometallic compounds appear at higher fields compared to that of the  $K_3Co(CN)_6$  standard.<sup>11</sup>

The analysis of the temperature dependence of the spin-crossover  $^{59}Co$  chemical shift is based on the expressions

$$K = [hs] / [ls] \quad (1)$$

$$\delta = \delta_{ls} + (\delta_{hs} - \delta_{ls}) / (1 + K^{-1}) \quad (2)$$

The thermodynamic parameters of the spin equilibrium of the present compound have been obtained<sup>7</sup> by fitting eq 2 to the experimental temperature dependence of the  $^{31}P$  chemical shift, assuming that  $\delta_{hs} - \delta_{ls} = C/T$ , where  $C$  is a temperature-independent constant. This procedure cannot be used for the  $^{59}Co$  chemical shift since one may not take the chemical shift of the diamagnetic low-spin Co(III) compound as a reference point for the high-spin compound as could be done in the  $^{31}P$  NMR study. The  $^{59}Co$  chemical shift of the high-spin compound with the electronic configuration  $t_{2g}^4 e_g^2$  without the polarized field of the unpaired electrons is expected to be different from that of the low-spin compound with the electronic configuration  $t_{2g}^6$ . Hereafter we shall denote the difference between these two chemical shifts as  $\Delta\delta_0$ .

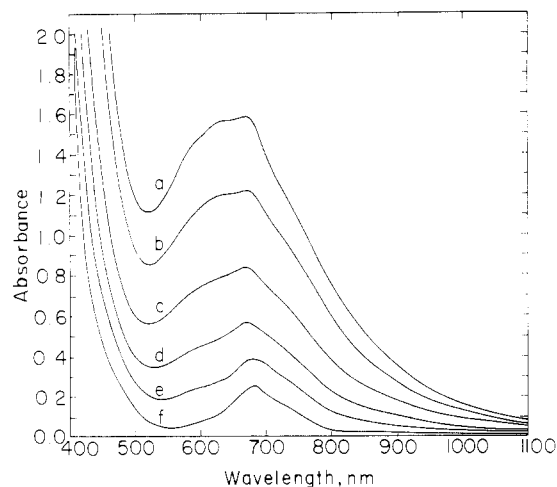
Another complication, though a minor one, is the significant temperature dependence of  $\delta_{ls}$  for low-spin Co(III) compounds.<sup>9,12</sup> Thus, one can write, as a first approximation

$$\delta_{ls} = \delta_0 + BT \quad (3)$$

$B$ , the temperature coefficient of the chemical shift, is 2.5 and 1.7 ppm  $K^{-1}$  for two diamagnetic cobalt complexes containing oxygen ligands:  $[Co(H_2O)_6]^{3+}$  and  $[Co(acac)_3]$ , respectively.<sup>4</sup> These values are very small relative to the temperature coefficient of the spin-crossover Co(III) atom (see Figure 2). In our analysis, we assume  $B = 2.0 \pm 1.0$  ppm  $K^{-1}$ . The

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**Figure 3.** Optical spectra of  $[\text{Co}^{\text{III}}\text{L}_2]\text{SbCl}_6$  in acetone at (a) 322, (b) 303, (c) 279, (d) 260, (e) 241, and (f) 204 K.

**Table I**

solvent	method	$\Delta H^\circ$ , kJ mol <sup>-1</sup>	$\Delta S^\circ$ , J mol <sup>-1</sup> K <sup>-1</sup>
$\text{CD}_3\text{COCD}_3$	<sup>31</sup> P NMR <sup>a</sup>	$24.3 \pm 1.1$	$71.5 + 8.8$ $- 4.2$
$\text{CH}_3\text{COCH}_3$	spectrophot	$24.2 \pm 0.2$	$74.3 \pm 2.7$
$\text{CD}_2\text{Cl}_2$	<sup>31</sup> P NMR <sup>a</sup>	$25.7 \pm 1.3$	$76.1 + 20.5$ $- 5.0$
$\text{CH}_2\text{Cl}_2$	spectrophot	$21.6 \pm 0.4$	$65.5 \pm 3.5$

<sup>a</sup> Reference 7.

temperature dependence of the chemical shift of the spin-crossover Co(III) was fitted to eq 1–3, with

$$\delta_{\text{hs}} = C/T + \Delta\delta_0 \quad (4)$$

$$K = e^{-\Delta H^\circ/RT + \Delta S^\circ/R} \quad (5)$$

As it was impossible to obtain unambiguous results for the five independent parameters,  $\delta_0$ ,  $C$ ,  $\Delta\delta_0$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ , we have tried to use the thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  from independent sources. The values, reported by Gütllich et al.,<sup>7</sup> include large error brackets, which result in a very large uncertainty in our fitted values of  $C$  and  $\Delta\delta_0$ . Therefore we have performed a variable-temperature spectrophotometric investigation of  $[\text{Co}^{\text{III}}\text{L}_2]^+$ . Another aim was to obtain the optical absorption spectrum of the low-spin  $[\text{Co}^{\text{III}}\text{L}_2]^+$ .

The absorbance as a function of temperature (see Figure 3) was analyzed at various wavelengths by using the expression

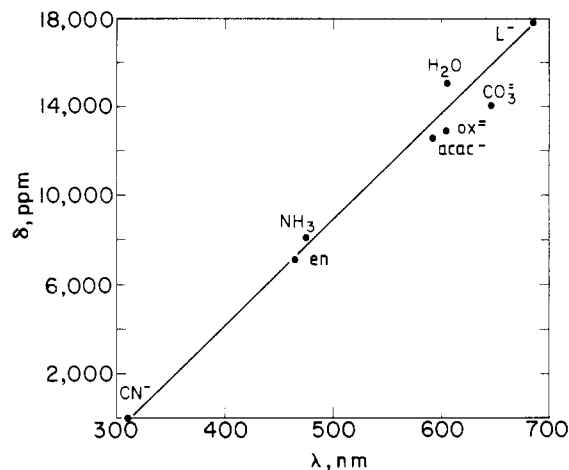
$$A = \frac{d}{d_0} \frac{A_{\text{ls}} + KA_{\text{hs}}}{1 + K} \quad (6)$$

with the equilibrium constant,  $K$ , given by eq 5, and the density of the solvent given by

$$d = d_0 + 10^{-3}\alpha T + 10^{-6}\beta T^2 + 10^{-9}\gamma T^3 \quad (7)$$

The constants  $d_0$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  for acetone and  $\text{CH}_2\text{Cl}_2$  are found in ref 13.

The results of the fitting are given in Table I. Although the random errors are rather small, it was realized that because of the limited temperature range the true values of the thermodynamic parameters may differ quite considerably from those listed in the table. The wavelength of the maximum absorption of the diamagnetic  $[\text{Co}^{\text{III}}\text{L}_2]^+$  was found to be 685 nm. Fitting eq 2–5 to our <sup>59</sup>Co experimental data by using the values of thermodynamic parameters obtained from the



**Figure 4.** Plot of chemical shifts vs. wavelength of the first spin-allowed transition of various cobalt(III) compounds. The data of  $[\text{Co}^{\text{III}}\text{L}_2]^+$  are from the present work, and those of  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Co}(\text{acac})_3]$  are from ref 4, 15, 20, and 21. All the other compounds are from ref 22.

<sup>31</sup>P NMR study in  $\text{CD}_2\text{Cl}_2$ <sup>7</sup> (see Table I) gave the results  $\delta_0 = 1.69 \times 10^4$  ppm,  $C = 4.28 \times 10^7$  ppm K, and  $\Delta\delta_0 = 1.27 \times 10^5$  ppm. The same procedure with the thermodynamic parameters taken from the spectrophotometric analysis in  $\text{CH}_2\text{Cl}_2$  gave  $\delta_0 = 1.72 \times 10^4$  ppm,  $C = 1.60 \times 10^7$  ppm K, and  $\Delta\delta_0 = 4.49 \times 10^4$  ppm. The calculated curves based on the two sets of parameters are practically indistinguishable as shown in Figure 2. These results as well as the results of other fitting trials indicated that the chemical shift of the diamagnetic  $[\text{Co}^{\text{III}}\text{L}_2]^+$ ,  $\delta_0$ , is determined quite accurately. The result corresponds to  $\delta_{\text{ls}} = 17650 \pm 200$  at room temperature. The two parameters  $C$  and  $\Delta\delta_0$  determining  $\delta_{\text{hs}}$  are too sensitive to the value of  $\Delta H^\circ$  and  $\Delta S^\circ$ , and their evaluation has to await the availability of more precise thermodynamic parameters or another independent method for their determination.

The two main contributions to the <sup>59</sup>Co chemical shifts of low-spin Co(III) compounds are (a) a diamagnetic term, which is usually assumed to be only slightly variable among the different compounds, and (b) a term due to temperature-independent paramagnetism, i.e. to a quantum-mechanical mixture of the ground state with excited states with unquenched orbital angular momentum. This contribution is expected to be inversely proportional to the energy gap between the ground state and the first spin-allowed d–d optical transition and therefore proportional to the wavelength of this transition.<sup>14,15</sup> A plot of  $\delta$  vs.  $\lambda$ , including the value  $\lambda = 685$  nm for the wavelength of the maximum absorption and  $\delta_{\text{ls}} = 17650$  ppm for the chemical shift of the diamagnetic  $[\text{Co}^{\text{III}}\text{L}_2]^+$  at room temperature, is shown in Figure 4. As was pointed out by several authors,<sup>16–20</sup> this plot is not expected to be a perfectly linear plot as corrections due to covalency and deviations from octahedral symmetry should be introduced. The linear line drawn in Figure 4 serves for an illustration only. It is seen that the point corresponding to the tripod ligand  $\text{L}^- = [(\text{C}_2\text{H}_5)_3\text{Co}(\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2)_3]^-$  extends outside the range of the other ligands. This is presumably the

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limiting case since at even lower values of the ligand field splitting the cobalt(III) is expected to cross over completely to the high-spin electronic state.

We have recently found<sup>8</sup> that it is possible to tune the position of the spin equilibrium at room temperature from completely diamagnetic to essentially paramagnetic by varying the groups *R* in  $[(C_5H_5)Co[P(O)R_2]_3]_2Co]^+$ . It is hoped that a <sup>59</sup>Co NMR study of such a series of closely related cobalt(III) compounds will give us more reliable values of the contact interaction of the unpaired electrons with the <sup>59</sup>Co nucleus, *C/T*, as well as the chemical shift of the high-spin cobalt(III) without the polarizing field of the unpaired electrons,  $\Delta\delta_0$ , and thus will allow a detailed discussion of the chemical shifts of high-spin cobalt(III).

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**Registry No.**  $[Co^{III}L_2]^+$ , 70850-84-9; Co, 7440-48-4.

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### EPR of Seven-Coordinated High-Spin Cobalt(II): Comparison with Paramagnetic Anisotropy Studies and Interpretation within the Angular-Overlap Model

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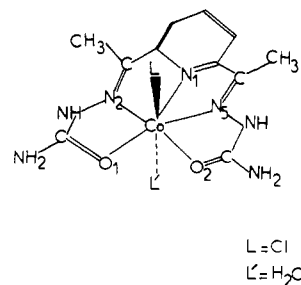
Seven-coordination is unusual for first-row transition-metal complexes. It was reviewed from the structural and stereochemical points of view by Drew.<sup>1</sup> But no magnetic or EPR studies were performed for this type of coordination. We have already reported on the magnetic and spectral properties<sup>2</sup> of the seven-coordinate high-spin cobalt(II) complex  $[Co(DAPSC)(Cl)H_2O]Cl \cdot 2H_2O$  and have reproduced them within the angular-overlap model (AOM).<sup>3</sup>

This complex is part of a series of seven-coordinate molecules characterized by Wester and Palenik.<sup>4,5</sup> The essential pentagonal-bipyramidal stereochemistry as schematized in Figure 1, around the cobalt ion, results from pentacoordination from the nearly planar ligand 2,6-diacetylpyridine bis(semicarbazone), DAPSC, and two axial ligands, one water and one chlorine atom bonding perpendicular to the equatorial plane.

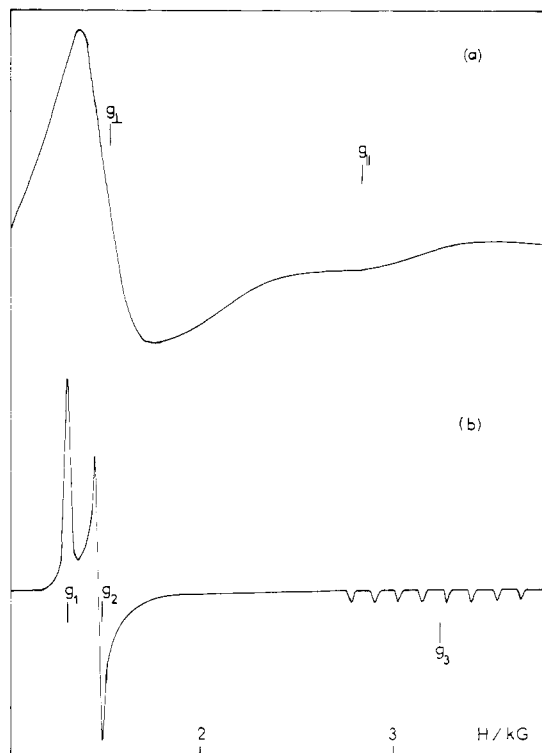
We intend here to describe the EPR properties of this complex and to compare them to results obtained from low-temperature single-crystal susceptibility measurements. We shall comment on this comparison in terms of AOM parameters and show that intermolecular interactions occur at low temperature.

#### Experimental Section

The pure complex  $[Co(DAPSC)(Cl)H_2O]Cl \cdot 2H_2O$  was obtained as previously described.<sup>2</sup> Single crystals of cobalt(II) doped into the isomorphous complex  $[Zn(DAPSC)(Cl)H_2O]Cl \cdot 2H_2O$  were grown by slow evaporation of ethanol solutions containing 10% of cobalt



**Figure 1.** Schematic seven-coordination in  $[Co(DAPSC)(Cl)H_2O]^+$  and numbering of donor atoms.



**Figure 2.** Polycrystalline powder EPR spectra recorded at X-band frequency at 4.2 K: (a)  $[Co(DAPSC)(Cl)H_2O]Cl \cdot 2H_2O$ ; (b)  $[(Co,Zn)(DAPSC)(Cl)H_2O]Cl \cdot 2H_2O$ .

chloride and 90% of zinc chloride.

The space group<sup>5</sup> of these complexes is *Ia* (nonstandard setting of *Cc*), with four molecules per unit cell. The cell dimensions are as follows: *a* = 17.968 (3) and 18.038 (11) Å; *b* = 13.139 (8) and 13.112 (5) Å; *c* = 8.052 (2) and 8.066 (3) Å with  $\beta = 99.86$  (2) and  $100.28$  (4) $^\circ$  for the Co and Zn complexes, respectively. The pseudo-*C*<sub>2</sub> axes of the DAPSC ligand for the four molecules lie nearly parallel to the *b* axis, and the metal ions are located on these *C*<sub>2</sub> pseudoaxes. The molecular equatorial planes stack over each other with a slight displacement, less than 2 $^\circ$  from being exactly parallel.

The new magnetic data, in the temperature range 4–20 K, have been obtained by using the same apparatus and method already described,<sup>2</sup> but the crystals were chosen smaller, weighing less than 1 mg, ensuring that the samples were not moving from the homogeneous zone.

EPR spectra were recorded in the temperature range 300–4 K, with a Bruker ER 200D spectrometer operating at X-band frequency and equipped with an Oxford Instruments ESR 9 continuous-flow cryostat. The crystals were oriented by Weissenberg techniques and rotated by means of a goniometer.

The AOM calculations were performed with use of the CAMMAG program written by Gerloch et al.<sup>6</sup> for the simulation of the susceptibility and *g* tensors and a program written by Gatteschi and

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