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[8] 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 ^{59}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 ^{59}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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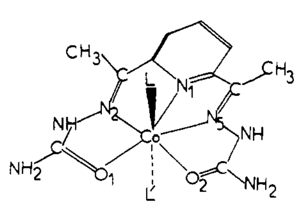
Seven-coordination is unusual for first-row transition-metal complexes. It was reviewed from the structural and stereochemical points of view by Drew.[1] But no magnetic or EPR studies were performed for this type of coordination. We have already reported on the magnetic and spectral properties[2] of 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).[3]

This complex is part of a series of seven-coordinate molecules characterized by Wester and Palenik.[4,5] 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.[2] 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 chloride and 90% of zinc chloride.



L = Cl
L' = H$_2$O

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

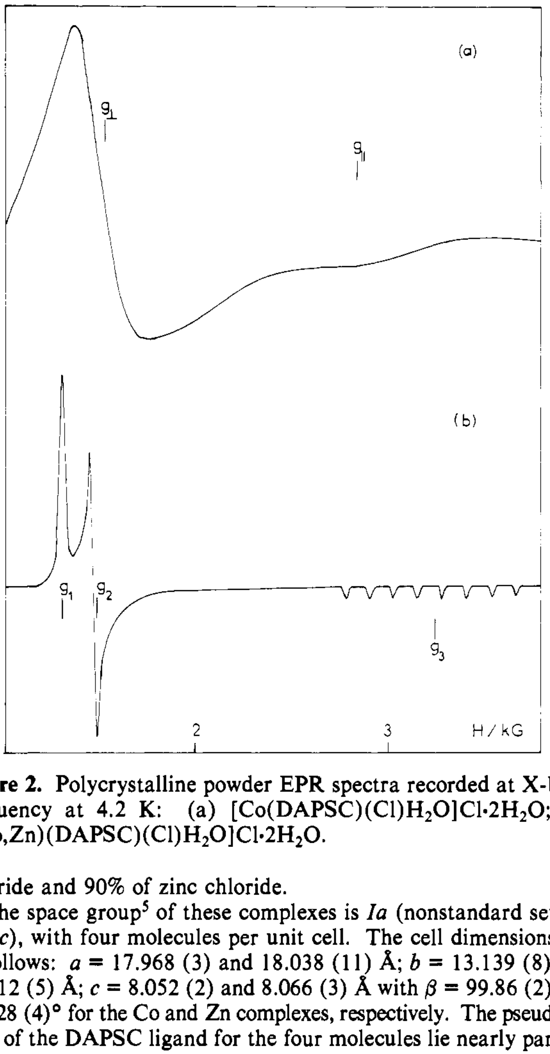


Figure 2. Polycrystalline powder EPR spectra recorded at X-band frequency at 4.2 K: (a) $[Co(DAPSC)(Cl)H_2O]Cl\cdot 2H_2O$; (b) $[(Co,Zn)(DAPSC)(Cl)H_2O]Cl\cdot 2H_2O$.

The space group[5] 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 β = 99.86 (2) and 100.28 (4)° for the Co and Zn complexes, respectively. The pseudo-C_2 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_2 pseudoaxes. The molecular equatorial planes stack over each other with a slight displacement, less than 2° 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,[2] 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.[6] for the simulation of the susceptibility and **g** tensors and a program written by Gatteschi and

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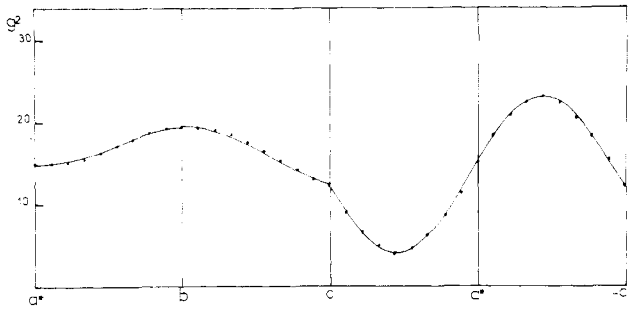

Figure 3. Angular dependence of g^2 on the static magnetic field in three orthogonal planes, for the complex [Co(DAPSC)(Cl)H_2O]Cl·$2H_2O$. The solid lines are the least-squares fits to the experimental points.

Table I. Principal Values and Directions of the g Tensor

	a^*	b	c
$g_1 = 4.41_3$	0	1	0
$g_2 = 4.80_4$	−0.7541	0	0.6541
$g_3 = 2.02$	−0.6568	0	−0.7564

Bencini[7] for the simulation of the hyperfine coupling.

Results and Discussion

The polycrystalline powder spectrum recorded at 4 K for the pure complex shows a broad band at low field and a small feature at higher field. The powder spectrum of the Co-doped Zn complex at 4 K is much better resolved as shown in Figure 2. It is typical of a rhombic pattern associated with an effective spin $S = {}^1/_2$. With use of the spin Hamiltonian formalism with an anisotropic **g** tensor for the transition observed within a Kramers doublet, the g values, for the pure complex, are approximately $g_\perp \simeq 4.4$ and $g_\parallel \simeq 2.0$ and for the doped complex are $g_1 = 4.87_4$, $g_2 = 4.32_7$, and $g_3 = 1.99_5$. The differences in g values are due to the bad resolution of the pure complex spectrum and probably also to some distortions of the chromophore when passing to a different lattice. The hyperfine structure observed in the g_3 region due to the coupling of the spin of the electronic ground state with the ^{59}Co nuclear spin is resolved into eight lines equally spaced with a splitting of 120 G. The single-crystal spectra of the pure complex confirm that the three features seen in the powder spectra are associated with the same transition, within a Kramers doublet. In all the orientations of the crystal in the static magnetic field, one signal is recorded. The fact that no evidence of the presence of two magnetically nonequivalent sites, as expected for a monoclinic cell, is found may be due either to intermolecular exchange, which averages the two signals, or to the fact that the difference in the resonance fields is smaller than the line width. Since it is not conceivable that intermolecular forces are very large, due to the long cobalt–cobalt distance, and since small disorientations of the two molecules would yield large differences in the resonance fields, the effective g values ranging from 2 to 4.4, it can be safely concluded that the two above interpretations converge to give the image of two quasi-parallel sites. In fact the crystal structure data show that the equatorial planes of the molecules are very nearly parallel to each other. Therefore, the crystal g values must be very nearly the molecular g values. In Figure 3 is shown the angular dependence of the g^2 tensor with the orientation of the magnetic field, for three orthogonal planes, by rotating about the a^*, b, c crystal axes. The principal g values and directions are given in Table I. One of the principal directions lies along the b axis of the monoclinic cell. The largest anisotropy is observed in the a^*c plane. The orientation of the **g** tensor with respect to the molecular bonds is given in Figure 4. The lowest g value, g_3, can be considered as a "unique" value lying nearly parallel to the axial Cl–Co–H_2O direction while g_1 and g_2, of the same order of magnitude, lie in the equatorial plane with g_1 nearly along the Co–N(pyridine) bond. The line width is orientation and temperature dependent (Figure 5). At 4 K, it varies from 1550 to 200 G, for the orientation of the magnetic field corresponding to the minimum and maximum principal g directions, respectively. When the sample is warmed up, the line width remains constant up to 50 K, except along the minimum direction, where a very striking narrowing from 1550 to 1040 G occurs in the temperature range 4–10 K. At temperatures higher than 50 K, the line width increases smoothly for all the directions and the lines disappear above 120 K, according to the spin–lattice relaxation phenomenon. This important broadening observed for the minimum principal g direction is partly due to an unresolved hyperfine structure characterized by an anisotropic **A** tensor with its maximum principal value along this direction. Indeed, the line width of 1040 G measured at 10 K closely corresponds to the overall width of eight hyperfine components related to the observed hyperfine splitting of 120 G along the same principal direction, from the diluted powder spectrum (Figure 2b). But the overall broadening of 1550 G observed when the sample is cooled to 4 K could be due to both effects, hyperfine and intermolecular interactions. The single-crystal spectra of the Co-doped Zn complex were recorded by performing experimental rotations in the same crystallographic planes as for the pure complex. In the a^*b and bc planes, the two sets of signals arising from the two magnetically nonequivalent molecules are quite undistinguishable: in the best resolved spectrum, the centers of the two sets are separated by less than 150 G. This clearly indicates that the two molecules have quite parallel **g** tensors. We were not able to

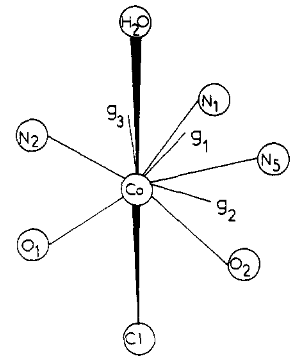

Figure 4. Orientation of the **g** tensor for the complex [Co(DAPSC)(Cl)H_2O]Cl·$2H_2O$: $\theta[g_3,\text{Cl–Co–}H_2O] = 5°$; $\theta[g_1,\text{Co–}N_1\text{(pyridine)}] = 8°$.

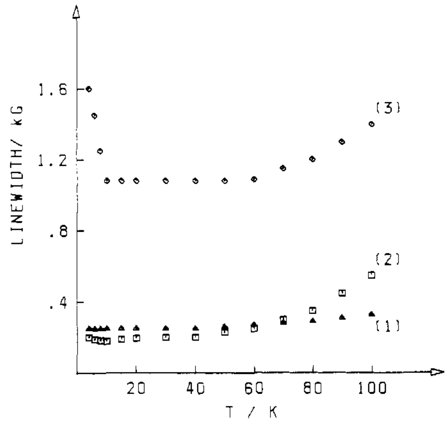

Figure 5. Temperature dependence of the EPR line width. [1], [2], and [3] respectively refer to the principal directions of the **g** tensor, as specified in Table I.

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Table II. AOM Parameters[a]

	N_1	$N_{2,5}$	$O_{1,2}$	$Cl + H_2O$
e_σ	4500	3500	2500	4000
$e_{\pi\parallel}$	0	0	400	800
$e_{\pi\perp}$	200	1000	2000	

$B = 800$; $\xi = 500$; $k = 0.5$

[a] All energies in cm^{-1}.

Table III. Principal Values and Directions of the g Tensor[a]

exptl				calcd			
	X	Y	Z		X	Y	Z
$g_1 = 4.41_3$	8	82	93	$g_1 = 4.46$	9	82	94
$g_2 = 4.80_4$	82	171	85	$g_2 = 4.71$	81	171	86
$g_3 = 2.02$	89	85	5	$g_3 = 2.01$	87	85	5
$\bar{g} = 3.94$				$\bar{g} = 3.92$			

[a] Comparison of experimental and calculated data with parameters given in Table II. All angles in degrees. The X, Y, Z molecular axes are defined with X parallel to the Co-N(pyridine) bond and Z along the axial $Cl-Co-H_2O$ direction.

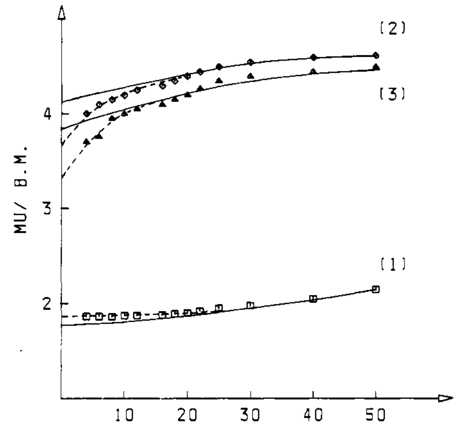

Figure 6. Temperature dependence of the single-crystal magnetic moments. μ_3 lies along the b axis of the monoclinic cell, and μ_1 and μ_2 are in the ac plane, with μ_1 near the axial $Cl-Co-H_2O$ direction. Solid lines correspond to the calculated moments with the parameter set of Table II (all values in Bohr magnetons).

fully analyze the hyperfine ^{59}Co structure. Only one direction is well resolved: this direction is along the minimum g leading to the maximum A hyperfine parameter. The data in this direction yield

$$g_{min} = g_3 = 1.99 \qquad A_{max} = 115 \times 10^{-4}\ cm^{-1}$$

A_{min} can be evaluated to be less than 20×10^{-4} cm^{-1} in the g_2 or g_1 region direction. To ensure the reliability of the ligand field analysis previously performed,[2] the new magnetic data and the EPR properties have been calculated by using the same AOM parameter set, summarized in Table II, which we derived from the interpretation of the spectra and single-crystal susceptibilities. The computed g tensor, which is defined by the first-order Zeeman splitting of a degenerate manifold, reproduces the experimental tensor in magnitude and orientation (Table III). The temperature dependence of the effective moments μ_1, μ_2, μ_3 associated with the principal susceptibilities down to 4 K is shown in Figure 6. The solid lines represent the temperature dependence of the calculated moments; the limits when T tends to 0 K agree quite well with the experimental limits obtained by extrapolation from the higher temperature range. This additional result corroborates the existence of intermolecular interactions, since the AOM does not take into account any intermolecular properties. Finally, the reproducibility of another observable, the hyperfine coupling, has been obtained within the same parameter set. The calculated hyperfine parameters are as follows (in 10^{-4} cm^{-1}): $A_1 = 18$; $A_2 = 17$; $A_3 = 106$. They closely agree with the experimental values of $A_{max} = 115 \times 10^{-4}$ cm^{-1} and $A_{min} < 20 \times 10^{-4}$ cm^{-1}. For this fit, the other two parameters involved are $P = g_e g_n \mu_B \mu_n \langle r^{-3} \rangle_{av} = 0.025$ cm^{-1} and κ (the isotropic Fermi interaction constant) = 0.35, which are nearly the calculated values for the free ion.[8]

The consistency of the agreement between experimental and calculated data for quite different observables reinforces the efficiency of this overparametrized model and makes sense to the deduced parameters, which reflect the essential pentagonal-bipyramidal ligand field.

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Registry No. $[Co(DAPSC)(Cl)H_2O]Cl\cdot 2H_2O$, 43010-81-7; $[Zn(DAPSC)(Cl)H_2O]Cl\cdot 2H_2O$, 42936-39-0; Co, 7440-48-4.

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