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Influence of Axial Coordination on the *g*-Factor Anisotropy of the Tetraimine Macrocyclic Cobalt(II) Complex $[Co(C_{10}H_{20}N_8)Cl(H_2O)]Cl \cdot H_2O$

A Ceulemans,[*,†] R. Debuyst,[‡] F. Dejehet,[‡] P. Janssen,[§] and L. G. Vanquickenborne[†]

Laboratory of Quantum Chemistry,
Katholieke Universiteit Leuven, Celestijnenlaan 200F,
B-3001 Leuven, Belgium, Laboratoire de Chimie Inorganique
et Nucléaire, Université Catholique de Louvain,
2, Chemin du Cyclotron, B-1348 Louvain-la-Neuve, Belgium,
and Laboratory for Low Temperatures and
High Magnetic Fields, Katholieke Universiteit Leuven,
Celestijnenlaan 200D, B-3001 Leuven, Belgium

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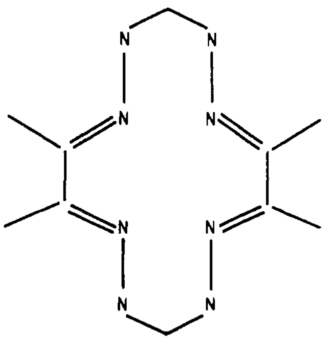
The 14-membered macrocyclic tetraimine ligand $C_{10}H_{20}N_8$ (**1**) forms complexes with the divalent ions of several first-row transition metals.[1] The specific electronic interactions between the conjugated π-system of this ligand and the metal d-orbitals give rise to an interesting phase coupling effect of the ligand field.[2] In a previous study[3] this effect was shown to control the anisotropy and spatial orientation of the molecular **g** tensor for the low-spin d^7 cobalt(II) ion, doped in $[Ni(C_{10}H_{20}N_8)Cl]Cl$. In the present note we report the measurement of the **g** tensor in the pure $Co(C_{10}H_{20}N_8)Cl_2$ compound. A reduction of the *g* anisotropy is observed which can be related to a change in coordination geometry of the Co(II) complex in going from the diluted to the pure compound.



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Experimental Section

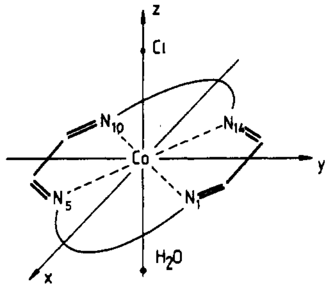
The preparation of $Co(C_{10}H_{20}N_8)Cl_2$ is similar to that of $Ni(C_{10}H_{20}N_8)Cl_2$, described by Peng et al.[1] The reaction must be carried out under a nitrogen atmosphere. The complex was found to crystallize[4] as $[Co(C_{10}H_{20}N_8)Cl(H_2O)]Cl \cdot H_2O$.

The EPR experimental procedure is identical to that described in ref 3. The particular orientation of the crystallographic axes with respect to the main faces of the single crystal (of about 1.5 mm^3) allowed the EPR measurements to be made directly in the crystallographic planes (*a*, *b*, *c**). In each plane, EPR spectra were recorded at 10-deg intervals, from 0 to 180°. These measurements were performed at ~ 295 K. Spectra of a powdered sample were taken at 77 and 295 K.

In addition some laser EPR experiments were performed on a powder. The far infrared spectrometer is based on an optically pumped FIR-laser.[5] A grating tuned CO_2-laser excites a suited molecule from its ground state to an higher vibrational level. Under favorable conditions, inversion can be obtained between rotational sublevels and laser action can follow. For the present experiment lines with wavelengths of 1899.9 and 1614.9 μm in vinyl bromide were used. Measurements were performed at 4.5 and 1.75 K. The laser radiation is guided to the sample with oversized wave guides. The sample is mounted in the center of a superconducting magnet. A carbon bolometer, mounted directly below the sample, is used to detect the transmitted radiation. A more detailed description of the spectrometer can be found in ref 6. The magnetic field is not modulated, so the direct transmission is measured rather than its derivative.

EPR of the Pure Co(II) Compound

$[Co(C_{10}H_{20}N_8)Cl(H_2O)]Cl \cdot H_2O$ crystallizes[4] in the monoclinic system (space group $P2_1/n$) with $Z = 4$, but with only two magnetically nonequivalent molecules. The coordination geometry is octahedral (**2**) with the metal ion near the center of the macrocyclic cavity and axial Cl and H_2O ligands at bond distances of 2.617 and 2.341 Å, respectively. The powder EPR spectra taken at 77 and ~ 295 K are very similar and yield the following approximate *g* values: $g_1 = 2.30$, $g_2 = 2.21$, and $g_3 = 2.04$ (see Figure 1a). Normally, in single crystals of pure compounds, only one EPR line is expected, due to exchange interactions. However in the present case, two lines, corresponding to the two magnetically nonequivalent centers, are observed for certain favorable orientations. No hyperfine structure could be resolved. These two lines overlap to some extent (see Figure 1b) depending upon their relative field positions and line widths (80–120 × 10^{-4} T). A single EPR line is actually observed in the (*a*, *c**) plane where the two centers are magnetically equivalent. In the (*b*, *a*) plane, the angular positions and the values of the g^2 extrema could be readily estimated for the two centers, the angular shift between them amounting to 45°, a value close to the angle of the two differently oriented Co–Cl bonds in the unit cell (43°). In the (*c**, *b*) plane, this shift is reduced to ~ 10° and only four data could be used to estimate the small off-diagonal element ($g_{cb}{}^2 \sim 0.1$). The diagonalization of the $\mathbf{g}^2$ tensor yields eigenvalues close to those of the powder spectrum only for a definite choice of the signs of the off-diagonal elements. The resulting molecular *g* values are given in Table 1, and the spatial orientation of the **g** tensor is shown in Figure 1c. The g_3-eigenvector is directed along



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[†] Laboratory of Quantum Chemistry, Katholieke Universiteit Leuven.

[‡] Université Catholique de Louvain.

[§] Laboratory for Low Temperatures and High Magnetic Fields, Katholieke Universiteit Leuven.

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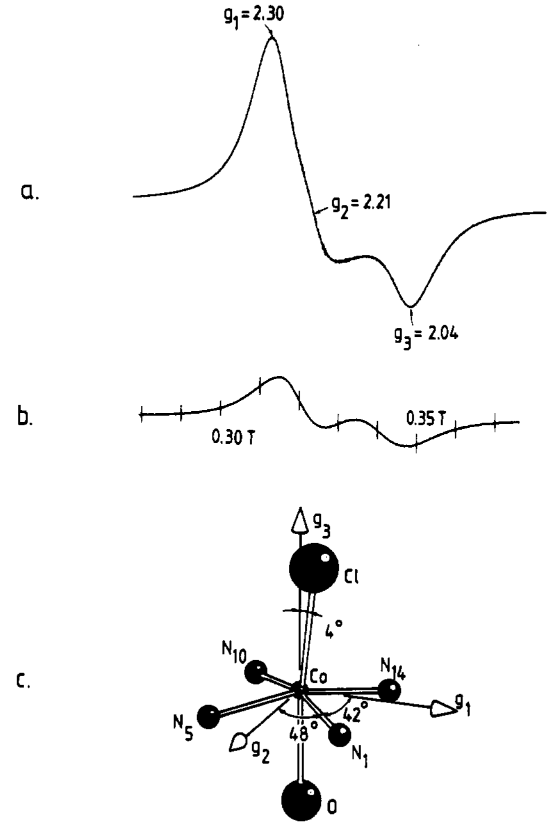


Figure 1. (a) Powder EPR spectrum of $[Co(C_{10}H_{20}N_8)Cl(H_2O)]Cl{\cdot}H_2O$ at 77 K (9.26 GHz, 0.2 mW, 0.125 mT_{pp}). (b) Single-crystal EPR spectrum at 295 K in the (*b*, *a*) crystallographic plane at 120° from *a* (9.77 GHz, 2 mW, 0.2 mT_{pp}). (c) Schematic view of the orientation of the **g** tensor, in comparison with the coordination bonds. Errors on the angles are on the order of 5°.

Table 1. Principal Values and Axes[a] for the Cobalt(II) **g** Tensor in the Pure and Doped Compounds

	$[Co(C_{10}H_{20}N_8)]Cl(H_2O)]Cl{\cdot}H_2O$			$[Ni_{0.95}Co_{0.05}(C_{10}H_{20}N_8)Cl]Cl$
	p (77 K)	lp (4.5 K)	sc (295 K)	sc (~135 K)
g_1	2.30	2.29	2.31 (g_y)	2.681 (g_y)
g_2	2.21	2.19	2.21 (g_x)	2.217 (g_x)
g_3	2.04	2.04	2.02 (g_z)	1.966 (g_z)

[a] Axes assignments in parentheses refer to the standard coordinate system of **2** and **3**; p is the EPR spectrum of the powder, shown in Figure 1a; lp refers to the laser powder experiment shown in Figure 2; sc are single-crystal measurements. The data for the doped compound were taken from ref 3. Typical errors in the values of *g* are on the order of 0.02 and 0.01 for the p and sc experiments respectively.

the CoCl bond axis, whereas g_1 and g_2 are oriented approximately along the bisectors of the bonds in the equatorial plane ($g_1 = g_y$; $g_2 = g_x$).

In spite of line broadening due to interactions between the magnetic centers, a molecular **g** tensor could thus be obtained which is consistent with the structure of the complex. This suggests that the large macrocyclic ligand reduces direct exchange interactions between the paramagnetic centers.

For a further confirmation of these results a laser EPR experiment was performed on a powder sample. The corresponding transmission spectrum at 4.5 K is shown in Figure 2. The *g* values for the two kinds of measurements almost coincide (cf. Table 1).

Comparison with the Diluted Co(II) Compound

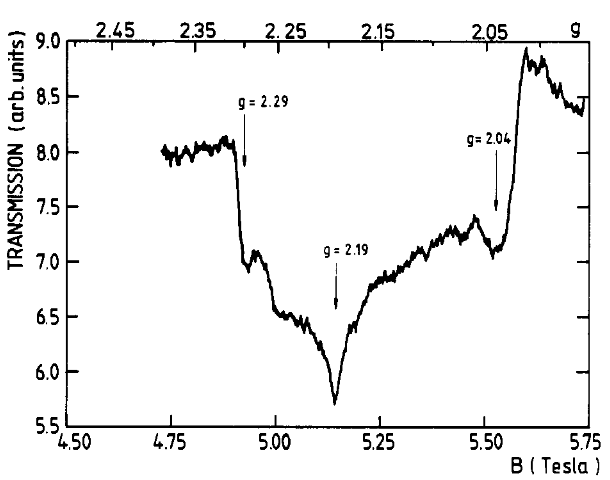
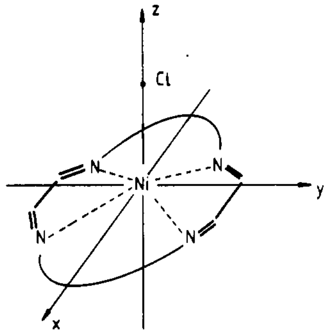


Figure 2. Laser EPR spectrum of $[Co(C_{10}H_{20}N_8)Cl(H_2O]Cl{\cdot}H_2O$ powder at 4.5 K. The irradiation wavelength is 1899.9 μm.

The final column of the table presents the *g* values obtained previously[3] for the doped compound $[Ni_{0.95}Co_{0.05}(C_{10}H_{20}N_8)Cl]Cl$. The coordination of the Ni(II) ion in the host lattice is not octahedral but square pyramidal (**3**), with the metal raised 0.28 Å above the plane of the four imine nitrogens in the direction of the apical chloride ligand. The Ni–Cl bond distance is 2.571 Å. The principal axes of the Co(II) **g** tensor in the diluted compound were found[3] to lie within 5° of the axial bond and macrocyclic bisectors. This indicates that the Co(II) ion in the diluted compound substitutes isomorphously for Ni(II). A comparison of the diluted and pure compounds thus allows to determine the influence of a change from square pyramidal to octahedral coordination. The results clearly show that the spatial orientation of the **g** tensor is not altered. However as far as the magnitude of the anisotropy is concerned a pronounced decrease is observed in going from square pyramidal to octahedral geometry. This is explained by a raise in energy of the d_{z^2} orbital upon addition of an extra axial H_2O ligand.



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The "Three-State" Model

The principal features of the **g** tensor in a low-spin d⁷-complex can conveniently be described by the "three-state" model.[7-9] In the states considered the highly energetic σ-antibonding orbital d_{xy} remains empty, while the unpaired electron is placed in d_{xz}, d_{yz}, or d_{z^2}. In the C_{2v}^z point group symmetry of the macrocyclic complexes under study these states are labeled $|^2B_1\,xz\rangle$, $|^2B_2\,yz\rangle$, and $|^2A_1\,z^2\rangle$, respectively. The three states will interact via spin–orbit coupling. The ground state eigenvector thus will be a mixture of all three. Using real and normalized coefficients *a*, *b*, and *c*

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the +1/2 component of the ground state Kramers doublet may be expressed as follows:[3]

$$|E' + 1/2\rangle = ia|^2B_2\, yz\beta\rangle + b|^2A_1\, z^2\alpha\rangle + c|^2B_1\, xz\beta\rangle \quad (1)$$

In this formalism the **g** tensor is given by

$$g_x = 2.0023\,(a^2 + b^2 - c^2) - 4(3^{1/2})ab$$

$$g_y = 2.0023\,(-a^2 + b^2 + c^2) - 4(3^{1/2})bc$$

$$g_z = 2.0023\,(-a^2 + b^2 - c^2) + 4ac \quad (2)$$

Here the squared terms denote spin contributions while the cross products refer to orbital contributions. The latter terms may be attenuated by orbital reduction factors. For the diluted compound an almost perfect fit of the **g** tensor could be obtained[3] with $a = -0.0369$, $b = 0.9944$, and $c = -0.0994$. These values point to a $|^2A_1\ d_{z^2}\rangle$ ground state with $|^2B_1\ d_{xz}\rangle$ and $|^2B_2\ d_{yz}\rangle$ excited states at approximately 3500 and 9500 cm^{-1}, respectively. In the pure compound the reduced anisotropy can be accounted for by using $a = -0.031$, $b = 0.9985$, and $c = -0.045$. The ground state thus remains $|^2A_1\ d_{z^2}\rangle$ but the $|^2B_1\ xz\rangle$ and $|^2B_2\ yz\rangle$ excited states are shifted to higher energy. According to a simplified perturbational treatment using a spin–orbit coupling value $\zeta(\mathrm{Co(II)}) = 400$ cm^{-1}, crude estimates for the $d_{xz} \rightarrow d_{z^2}$ and $d_{yz} \rightarrow d_{z^2}$ excitation energies are respectively 7700 and 11200 cm^{-1}. The latter transition may tentatively be associated with the weak shoulder ($\epsilon \approx 30$ M^{-1} cm^{-1}) which is observed[10] in the absorption spectra of a freshly prepared aqueous solution of $Co(C_{10}H_{20}N_8)Cl_2$ at 10 900 cm^{-1}.

Conclusions

It has been possible to determine the molecular **g** tensor for the $Co(C_{10}H_{20}N_8)Cl(H_2O)^+$ complex, using single-crystal EPR and powder laser EPR measurements.

The equatorial anisotropy of the *g* factor is noticeably reduced as compared to the anisotropy in the case of the Co(II) complex diluted in the anhydrous $[Ni(C_{10}H_{20}N_8)Cl]Cl$ lattice. In a "three-state" model this reduction is attributed to a raise in a energy of the d_{z^2} orbital over 2000-4000 cm^{-1} due to coordination of the H_2O ligand. Similar results may be found in the literature on low-spin Co(II) Schiff-base complexes.[8,9,11,12] As an example the square planar compound Co(salen) may add axial ligands such as dimethyl sulfoxide, pyridine, or triphenylphosphine to form square pyramidal Co(salen)L complexes. Upon addition, the *g*-factor anisotropy is found to decrease in a way which is proportional to the ligand field strength of the adduct.[13,14]

Most importantly the present data lend strong support to the earlier study[3] of the Co(II)-doped $[Ni(C_{10}H_{20}N_8)Cl]Cl$ crystal, thus confirming the presence of a pronounced phase-coupling effect in the ligand field of the $C_{10}H_{20}N_8$ macrocycle.

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