

Correspondence

Electron Spin Resonance Spectra of Low-Symmetry Pseudotetrahedral High-Spin Cobalt(II) Complexes. Tetra-*n*-butylammonium Tribromo(quinoline)cobaltate(II)

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Sir:

In recent years the interest in the spectral properties of low-symmetry cobalt(II) chromophores has largely increased¹⁻⁴ particularly as a consequence of the studies of metalloenzymes and metalloproteins. ESR spectra of high-spin cobalt(II) complexes are not numerous, and most of the studies reported up to now refer to ions diluted in continuous lattices.^{5,6} In one of the few characterizations of discrete cobalt(II) complexes in pseudotetrahedral environments,⁷ it was claimed that the only transition which could be detected was $M_S = -3/2 \leftrightarrow 3/2$, which in a high-symmetry environment is strictly forbidden. Therefore, we resolved to study some low symmetry cobalt(II) chromophores in order to investigate the nature of the transitions. The results of our analysis of the ESR spectra of $[N(n-C_4H_9)_4][CoBr_3(quinoline)]$ show that the observed absorptions can be assigned to a $M_S = -1/2 \leftrightarrow 1/2$ transition, when the effect of a large and anisotropic zero-field splitting is properly taken into account.

$[N(n-C_4H_9)_4][MBr_3(quinoline)]$, where $M = Co$ or Zn , was prepared as previously described,⁸ and prismatic crystals, containing less than 1% cobalt(II), were grown by slow evaporation of 1-butanol solutions. Diffractometric data showed that they belong to the $P\bar{1}$ space group and that the cell constants ($a = 1253$, $b = 1043$, $c = 1310$ pm; $\alpha = 101.6$, $\beta = 99.8$, $\gamma = 106.1^\circ$) compared well with those previously reported for the nickel analogue.⁸

The X-band ESR spectra were recorded at 4.2 K with the apparatus previously described.⁹ The polycrystalline powder spectra of the title compound recorded at 4.2 K are shown in Figure 1. The apparent g values are $g_1' = 6.31$, $g_2' = 2.22$, and $g_3' = 1.60$. No hyperfine splitting of the transitions was detected, and the bandwidths were found to be extremely temperature dependent, an increase of few degrees causing the disappearance of the ESR signals. The overall appearance of these spectra is not too dissimilar from the powder spectra of other pseudotetrahedral high-spin cobalt(II) complexes previously reported,⁴⁻⁷ suggesting that the nature of the transitions must be the same in every case. The line shapes suggest that all the transitions come from the same Kramers doublet.

Single-crystal spectra were recorded by rotating along three mutually orthogonal axes: they were the a crystal axis, which was labeled as the Z laboratory axis, X lying in the ab plane, and Y . Only one signal was observed in every crystal orientation, again suggesting that the three principal absorptions in the powder spectrum correspond to transitions within the same Kramers doublet.

The six independent components of the g' tensor were calculated by the method of Ayscough,¹⁰ and diagonalization yielded the principal values $g_1' = 6.51$, $g_2' = 2.33$, and $g_3' = 1.61$. Assuming that the molecular parameters in the doped compound are similar to those of the structure report,⁸ the orientation of the g' principal directions is that shown in Figure 2 and in Table I.

From Figure 2 it is apparent that the principal directions of the g' tensor are far distant from the directions one should anticipate on the basis of an idealized C_3 symmetry of the chromophore and clearly reflect the actual low symmetry of

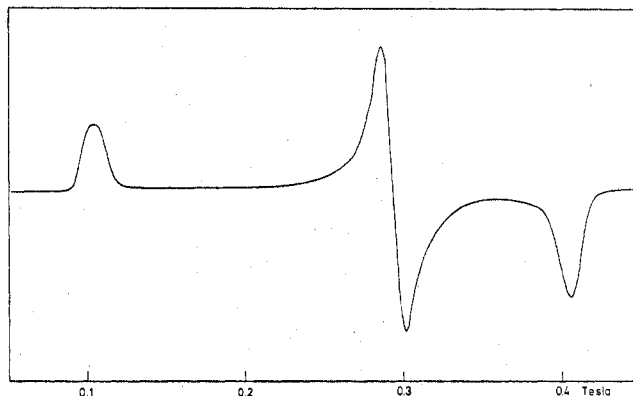


Figure 1. Polycrystalline powder spectrum of zinc-doped tetra-*n*-butylammonium tribromo(quinoline)cobaltate(II).

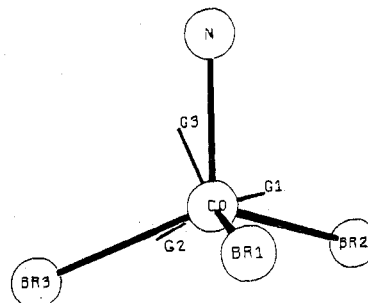


Figure 2. Orientations of the g' principal axes relative to the bond directions in tetra-*n*-butylammonium tribromo(quinoline)cobaltate(II). The g_3' vector makes an angle of $23 \pm 3^\circ$ with the Co-N bond direction.

Table I. Direction Cosines of the g' Principal Directions Relative to Crystal Axes^a

	X	Y	Z
g_1'	0.0109	-0.0112	0.9999
g_2'	-0.6090	-0.7932	-0.0022
g_3'	-0.7931	0.6089	0.0155

^a For the definition of X , Y , and Z axes see text.

the complex. Although this result is not unexpected on a symmetry basis, it must be mentioned that in the thoroughly studied low symmetry copper(II) complexes the g directions are met quite close to the pseudosymmetry axis.^{11,12} We will show below that an alternative explanation is also possible.

The spin Hamiltonian appropriate to the present system has the form

$$\mathcal{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \quad (1)$$

where \mathbf{g} and \mathbf{D} must be considered as completely anisotropic and possibly not having parallel principal axes. In the simplest case (\mathbf{g} and \mathbf{D} parallel) the number of the parameters of the above Hamiltonian is six, and they cannot be determined by the three experimentally observed transitions. However, it is possible, in our opinion, to arrive at some interesting conclusions. First of all it is possible to guess some values of g to start with by some ligand field calculations. Using the reported matrices¹³ and spectral data¹⁴ it is found that in the limit of C_3 symmetry g_{\parallel} is anticipated as 2.00 and g_{\perp} as 2.2. Of course deviations from these values are to be expected, but

Table II. Hamiltonian Matrix for a $S = 3/2$ Spin State and \mathbf{g} and \mathbf{D} Tensors Not Parallel

	$ 3/2\rangle$	$ 1/2\rangle$	$ -1/2\rangle$	$ -3/2\rangle$
$\langle 3/2 $	$(3/2)g\mu_B B$ $+ (3/2)R_1$	$3^{1/2}b^*$	$(3^{1/2}/2)a^*$	0
$\langle 1/2 $	$3^{1/2}b$	$(1/2)g\mu_B B$ $- (3/2)R_1$	0	$(3^{1/2}/2)a^*$
$\langle -1/2 $	$(3^{1/2}/2)a$	0	$(-1/2)g\mu_B B$ $- (3/2)R_1$	$-(3^{1/2}/2)b^*$
$\langle -3/2 $	0	$(3^{1/2}/2)a$	$-3^{1/2}b$	$(-3/2)g\mu_B B$ $+ (3/2)R_1$

they should not be larger than perhaps 0.1, in accord also with previous findings for tetrahedral cobalt(II) complexes.^{5,6} Second, the same ligand field calculations provide information on the sign and the value of the zero-field splitting, suggesting that the $\pm 1/2$ levels lie 4–6 cm^{-1} lower than the $\pm 3/2$ levels. In this framework our experimental data can be interpreted considering that the transitions are between the $\pm 1/2$ levels, the other transitions being in every case too high in energy. We do not consider here the $M_S = -3/2 \leftrightarrow 3/2$ transition, which must be of lower intensity because it is only partially allowed and the levels should be largely depopulated at 4.2 K. With the aim of verifying the feasibility of our assignment, we performed sample calculations on an $S = 3/2$ spin system with the Hamiltonian (eq 1). Formulas have recently been reported for the energies of the transitions in the case of nonparallel \mathbf{g} and \mathbf{D} tensors; however, they are appropriate for small zero-field splitting effects.^{16–18} If this is not the case it is necessary to diagonalize the determinant of Table II, where the symbols are defined in ref 18, and the relative rotation of the \mathbf{g} and \mathbf{D} axes is performed as in ref 17.

The first important result of these calculations is that nonparallel \mathbf{g} and \mathbf{D} tensors can determine the appearance of \mathbf{g}' principal axes which do not correspond to principal directions either of \mathbf{g} or of \mathbf{D} , and this might explain the large distance of our \mathbf{g}' principal directions from the would be C_3 axis of the molecule. However, if, for the sake of simplicity, the axes of the two tensors are kept parallel and the above values for g_{zz} , g_{xx} , and g_{yy} are considered, it is possible to reproduce the energies of the observed transitions setting D_{zz} between 1.33 and 2, D_{xx} between -0.17 and 0.00, and D_{yy} between -1.2 and -2.0 cm^{-1} . g_3' would correspond to g_{zz} , while g_1' and g_2' would correspond to g_{yy} and g_{xx} , respectively. Of course considering the nonalignment of the two tensors gives more freedom to the system and other fits can be obtained.

Our present assignment is different from that previously suggested for bis(dihydrobis(1-pyrazolyl)borato)cobalt(II),⁷ although the ESR spectra look much similar. The main advantage of our assignment is that it is not necessary to invoke any unusual relaxation mechanism in order to explain why the only observed transition should be the forbidden one.

It is worth noting that Jesson⁷ excluded the possibility of an $M_S = -1/2 \leftrightarrow 1/2$ transition on the grounds that: (i) no absorption at $g' = 2.3$, the value expected for g_{zz} , was observed; (ii) an incomplete crystal analysis showed that a $g' = 6.90$ value was observed close to a pseudo- S_4 axis, which he assumed as the Z axis. Our single-crystal data show that the observed \mathbf{g}' directions can be rotated by large angles from the idealized axes. Further there is no need to observe a \mathbf{g}' value corresponding to g_{zz} , since this is true only in the assumption that $D_{xx} = D_{yy}$, a condition which does not seem to be likely for low symmetry chromophores. Further deviations might be brought about also by nonparallel \mathbf{g} and \mathbf{D} tensors.

Concluding in our opinion it is possible to interpret the ESR spectra of low symmetry pseudotetrahedral high-spin cobalt(II) complexes assuming a large zero-field splitting which sets the $\pm 1/2$ levels lower in energy. The large variability of the apparent g values^{4–7} can be ascribed to small variations of the \mathbf{D} tensor components and to not parallel \mathbf{g} and \mathbf{D} axes, rather than to large variations of g values.

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Registry No. $[\text{N}(n\text{-C}_4\text{H}_9)_4][\text{CoBr}_3(\text{quinoline})]$, 52524-44-4; $[\text{N}(n\text{-C}_4\text{H}_9)_4][\text{ZnBr}_3(\text{quinoline})]$, 62743-75-3.

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