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ESR Spectra of Low-Symmetry High-Spin Cobalt(II) Complexes. 3. Square-Pyramidal Nitratotetrakis(methyldiphenylarsine oxide)cobalt(II) Nitrate[1]

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Nitratotetrakis(methyldiphenylarsine oxide)cobalt(II) nitrate has been described as a square-pyramidal complex with the cobalt ion in a C_4 site symmetry. Despite this, the observed g values are highly anisotropic; $g_1 = 8.6$, $g_2 = 1.3$, and $g_3 = 0.9$. The smallest g value is found to make an angle of 12 ± 5° to the perpendicular to the basal plane. The anisotropic g values are justified by the off-axis position of the Co–O bond. A completely symmetry independent ligand field model allowed us to rationalize the data in a simple and effective way.

Introduction

The interest in the characterization of low-symmetry cobalt(II) complexes has greatly increased in the last years.[2-6] In particular the ESR spectra of high-spin complexes are attracting the interest of many researchers.[7-10] Since low-symmetry components play a major role in determining the features of the spectra,[11,12] it appeared interesting to us to characterize some complexes which are not cubic but possess still enough symmetry to keep the interpretation as simple as possible.

$[Co(MePh_2AsO)_4X]X$, where X = ClO_4 or NO_3, were reported to be five-coordinate square-pyramidal complexes with the four arsine oxide ligands in the basal positions and an oxygen atom of the anion in the axial position.[13] Preliminary crystal structure data were reported, which showed that the nitrate and perchlorate salts are isomorphous and that the site symmetry of the metal ion is C_4. A previous analysis[15] of single-crystal polarized electronic spectra and of bulk magnetic anisotropy provides important additional information on the electronic levels. We wish to report here the single-crystal ESR spectra of $[Co(MePh_2AsO)_4NO_3]NO_3$.

Experimental Section

The zinc and cobalt complexes were prepared as previously reported.[13] Single crystals suitable for ESR study were grown by slow evaporation of acetone–ethyl alcohol solutions. The crystals were found to conform to the reported structure[14] by the Weissenberg technique and the crystal faces were identified by the same technique. The nitrate complex was preferred since it formed crystals easily.

Single-crystal ESR spectra down to 4.2 K were recorded with the apparatus previously described.[1]

Results

The polycrystalline-powder ESR spectrum of $[(Co,Zn)(MePh_2AsO)_4NO_3]NO_3$ is shown in Figure 1. The spectrum can be interpreted with an anisotropic spin Hamiltonian,[16] with $S = {}^1/_2$ effective spin, yielding $g_1 = 8.6 \pm 0.1$, $g_2 = 1.3 \pm 0.1$, and $g_3 = 0.9 \pm 0.1$. The line width is small in the region of g_1 and very broad in the region of g_2 and g_3. The low-field region shows a ^{59}Co hyperfine splitting of 115 ± 5 G. These results are surprising if one considers the site C_4 of the cobalt atom seen in the structure. The analogous copper(II) complex, doped into the zinc lattice, does not show any low-symmetry effect and yields axial ESR spectra with $g_\parallel = 2.35$, $g_\perp = 2.05$, and a parallel hyperfine splitting of 125 G. The spectra are substantially independent of temperature in the range 300–4.2 K, suggesting that dramatic phase transitions are not operative in the zinc lattice. We also recorded the powder ESR spectra of the undiluted cobalt complex and found them practically identical with the spectra of the doped powders, except for the hyperfine splitting, which was no longer resolved. Also the single-crystal spectra of the diluted and undiluted complexes are quite similar to each other, but the undiluted spectra are easier to interpret since they show fewer bands. Furthermore, they give signals, which can be easily followed notwithstanding the large bandwidth. The single-crystal spectra were recorded by rotating around the *a*, *b*, and *c* crystal axes.

In the (001) plane, where only one resonance signal corresponding to $g_\perp$ would be expected on the basis of tetragonal symmetry, two magnetically inequivalent sites related by the tetragonal axis are present, as shown in Figure 2. The two sites become equivalent when the field is parallel to the bisectors of the *a* and *b* axes. It is apparent from Figure 2 that the two sites possess identical extremes, within experimental errors, in this plane, with $g = 8.4 \pm 0.1$ and $g = 1.3 \pm 0.1$ parallel to *a* and *b*. In the low-field region hyperfine splitting is resolved in the doped crystals, while the line shape of the undiluted complex can be considered as the sum of eight Gaussian components which are partially overlapping. The resulting peak-to-peak width corresponds well to the overall width of the hyperfine components. The lines at high field are in every case featureless, with a peak-to-peak width of the order of 750 G.

The spectra recorded with the static magnetic field in the (010) and (100) planes have been found to be practically identical. Three magnetically inequivalent sites were detected as shown in Figure 3. Two of the sites have been found to be symmetrical with respect to the *c* axis. The extremes were found at ±12 ± 5° from the *c* axis with $g = 8.6 \pm 0.1$ and $g = 0.91 \pm 0.05$. To the third site corresponds a signal which has twice the intensity of each of the two previous ones. One extreme *g* value was found parallel to *a* (or *b*), $g = 1.3 \pm 0.1$, the other being $g = 2.1 \pm 0.1$.

Discussion

Assignment of the Spectra. The results of the previous section show that the actual symmetry of the cobalt(II) ion is distinctly lower than C_4. As a matter of fact in the original structure report[14] of $[Co(MePh_2AsO)_4ClO_4]ClO_4$ it was observed that the axial perchlorate is disordered, with the chlorine atom lying on the perpendicular to the basal plane and the oxygen atom bound to cobalt displaced to one side. It seems reasonable to assume that the isomorphous nitrate has a similar behavior. Therefore the cobalt ion may possess C_4 symmetry either on a time-average basis, if the axial ligand is rotating, or on a statistical basis, if the axial ligand is fixed. In either case at 4.2 K the symmetry of the cobalt environment cannot be C_4, therefore justifying the low-symmetry spectra. If the axial ligand is disordered on four positions, four magnetically independent sites can be formed, related by the tetragonal axis. According to this view, the direction cosines of a principal g_i direction with the *a*, *b*, and *c* crystal axes for the four sites should be of the type: $l_i, m_i, n_i; \bar{l}_i, \bar{m}_i, n_i; m_i, \bar{l}_i, n_i; \bar{m}_i, l_i, n_i$. With these symmetry relations, two magnetically inequivalent sites are anticipated in the (001) plane while four sites are expected in both the (100) and the (010) planes. Since, however, one principal *g* value is observed parallel to

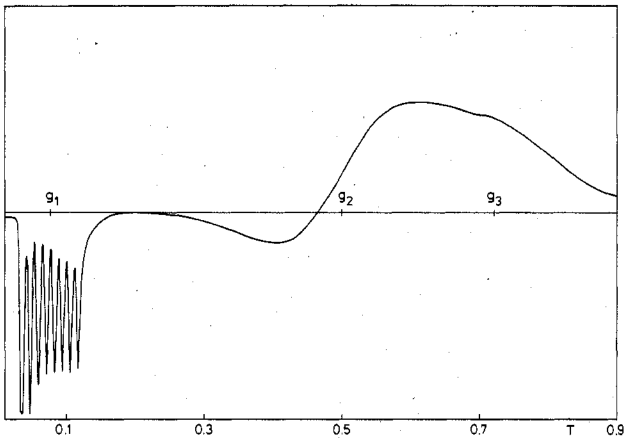

Figure 1. Polycrystalline powder ESR spectrum of $[(Co,Zn)(MePh_2AsO)_4NO_3]NO_3$ recorded at X-band frequency at 4.2 K.

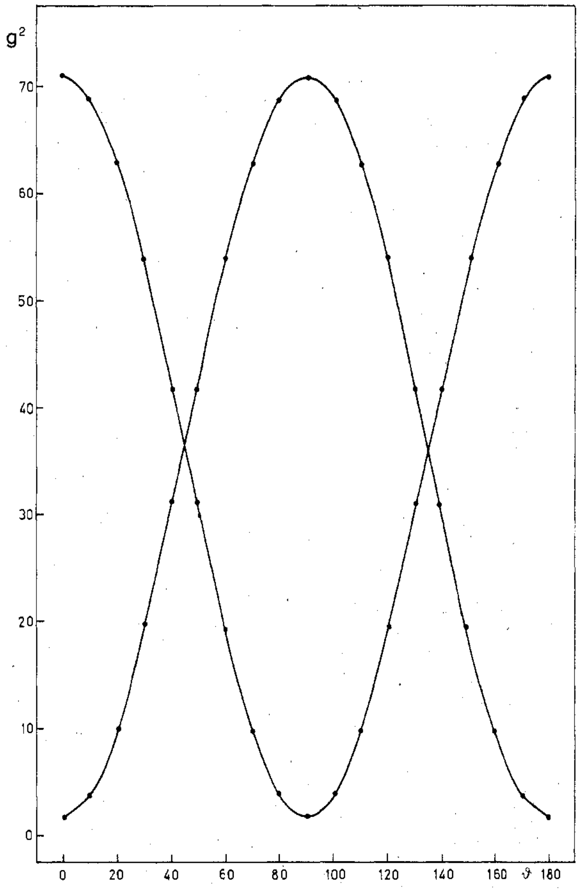

Figure 2. Angular dependence of g^2 with the static magnetic field in the (001) plane. The full lines are the least-squares fits to the experimental points. $\theta = 0°$ and $\theta = 90°$ correspond to the static magnetic field parallel to a and b, respectively.

a (and correspondingly another is parallel to *b*), two of the four sites become equivalent in the (100) and (010) planes, so that in these planes three signals are expected with intensity ratios 1:1:2. The experimental data can be reconciled to these expectations if the direction cosines of one site are as shown in Table I.

The *g* values have quasi-axial symmetry, but the g_3 value, which is close to g_2 and might be anticipated to be the split component of $g_\perp$, is actually associated with a direction which is close to the pseudo-C_4 axis. It is apparent that low-symmetry effects must play a relevant role in the spin Hamiltonian.

It is interesting at this point to compare the present ESR results with the magnetic anisotropy data previously reported.[15]

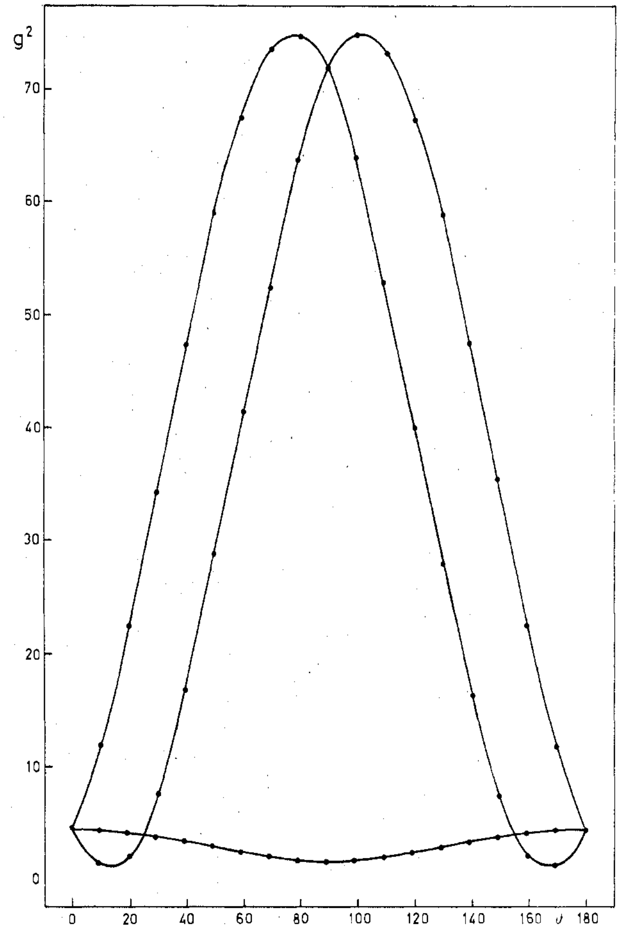

Figure 3. Angular dependence of g^2 with the static magnetic field in the (100) plane. The full lines are the least-squares fits to the experimental points. $\theta = 0°$ and $\theta = 90°$ correspond to the static magnetic field parallel to b and a, respectively.

Table I. Direction Cosines of the Principal *g* Directions of One Magnetic Site Referred to the Tetragonal Crystal Axes

	a	*b*	*c*
g_1	0.98	0.00	0.22
g_2	0.00	1.00	0.00
g_3	−0.22	0.00	0.98

Since the tetragonal symmetry is preserved in the bulk of the crystal, the actual low symmetry of the complex could not be detected by the susceptibility measurements. The magnetic moments associated with our observed *g* values are $\mu_\parallel = 1.82$ μ_B and $\mu_\perp = 5.27$ μ_B. These values cannot be compared directly to the values reported for the magnetic measurements, since the latter are relative to higher temperatures, and the contributions of excited Kramers doublets are important. However $\mu_\perp$ was found to be almost insensitive to temperature in the range 80–300 K, and its value (5.54–5.60 μ_B) compares well with that calculated by us. The $\mu_\parallel$ value was found to be more sensitive to temperature, varying from 3.95 to 2.85 μ_B in the same temperature range, and this might be the origin of the discrepancy with our calculated value.

Fitting of the Spectra. The results of the previous section demand a theoretical justification. The principal question is how it is possible that the low-symmetry components can split $g_\perp$ by ~7 *g* units. In our opinion this can be justified only through the low-symmetry ligand field model[17] shown also in the preceding paper.[1] In order to apply it to the present case it is necessary to make a choice of geometrical parameters. Unfortunately the full structure report has never been published; therefore, it is necessary to use the sparse data which

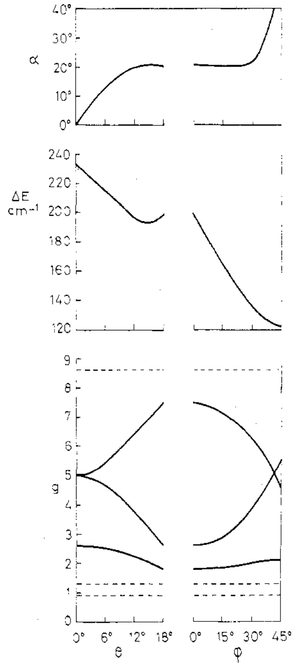

Figure 4. The calculated g, ΔE (zero-field splitting), and α (angle of g_3 to the perpendicular to the basal plane), for the lowest Kramers doublet of $[Co(MePh_2AsO)_4NO_3]NO_3$. θ and ϕ are the polar angles of the axial oxygen, with the equatorial oxygens lying on the x and y axes. Left: the effect of varying θ with $\phi = 0°$, $e_\sigma^{basal} = 6000\ cm^{-1}$, $e_\pi^{basal} = 1200\ cm^{-1}$, $e_\sigma^{axial} = 4000\ cm^{-1}$, $e_\pi^{axial} = 960$, $k = 0.8$, $\zeta = 533\ cm^{-1}$, and $B = 850\ cm^{-1}$. Right: the effect of varying ϕ with $\theta = 18°$. The dotted lines correspond to the experimental values.

Table II. A Representative Fit of the Principal g Values and Directions of $Co(MePh_2AsO)_4(NO_3)_2$[a]

g	value		α[b]	value, deg	
	exptl	calcd		exptl	calcd
g_1	8.6 ± 0.1	8.6	α_1	78	83
g_2	1.3 ± 0.1	1.2	α_2		
g_3	0.9 ± 0.1	0.9	α_3	12	7

[a] The parameters in this calculation are $e_\sigma{}^{axial} = 6015\ cm^{-1}$, $e_{\pi_s}{}^{axial} = 1580\ cm^{-1}$, $e_{\pi_c}{}^{axial} = 3950\ cm^{-1}$, $e_\sigma{}^{basal} = 6685\ cm^{-1}$, $e_\pi{}^{basal} = 2765\ cm^{-1}$, $B = 760\ cm^{-1}$, $k = 0.9$, and $\zeta = 533$. [b] α is the angle between the indicated directions and the tetragonal axis in the ac plane. $\alpha_1 = \cos^{-1}(\sin\theta\cos\phi)$; $\alpha_3 = 90° - \alpha_1$.

are available.[14] The cobalt atom is reported to be 32 pm above the basal plane, which, for a bond distance of about 200 pm, corresponds to an angle of ~100° of the basal bond with the perpendicular to the plane. The axial oxygen in the perchlorate derivative was reported to be 210 pm from the cobalt atom and to be displaced 72 pm to one side of the fourfold axis. If these values are used for the nitrate derivative, the angle of the Co–O bond to the perpendicular to the basal plane can be calculated as ~19°. However nothing is said about the direction along which the axial oxygen is distorted; therefore, we used as parameters the θ and ϕ angles of this bond to the perpendicular. For $\phi = 0°$ the axial bond projection on the basal plane is parallel to a Co–O bond. Figure 4 shows the effect of varying these angles for fixed values of e_σ and e_π for the axial and equatorial ligands. For $\theta = 0°$ the system has the required axial symmetry, while the splitting of the $g_\perp$ values increases dramatically as θ increases. Further, the lowest g value becomes smaller, and its principal direction moves away from the perpendicular to the basal plane. If the position of the axial bond is rotated around the perpendicular to the basal plane by varying the ϕ angle, the two highest g values tend to cross. In order to arrive at a reasonable fit we performed many calculations, varying the values of the parameters and taking into consideration the energies of the electronic transitions as determined from a single-crystal spectrum.[14] Reasonable fits of the transitions, as well as the g values, were found for the sets of parameters $e_\sigma{}^{axial} = 5800–6200\ cm^{-1}$, $e_{\pi_s}{}^{axial} = 1500–1700\ cm^{-1}$, $e_{\pi_c}{}^{axial} = 3900–4100\ cm^{-1}$, $e_\sigma{}^{basal} = 6400–6800\ cm^{-1}$, $e_\pi{}^{basal} = 2600–2800\ cm^{-1}$, $k = 0.8$, and ζ at the free-ion value. A typical fit is shown in Table II. All the electronic transitions were reproduced within $1500\ cm^{-1}$. It can be observed that the e_σ and e_π values for the arsine oxide ligands compare well with the values reported for hexakis(pyridine N-oxide)cobalt(II) diperchlorate[12] and for dichlorobis(triphenylphosphine oxide)cobalt(II),[1] confirming that the ligand field model we used has a reasonable physical foundation.

Conclusions

The results of the previous section have given a dramatic example of the extreme sensitivity of the ESR spectra of high-spin cobalt(II) to low-symmetry components. As a matter of fact, while the spectra of the copper(II) analogue are axial within experimental error, the g values of cobalt(II) are completely anisotropic.[18] The suggested ligand field model has been able to rationalize the experimental spectra, showing in particular the extreme sensitivity of the g values to the angle of the axial oxygen to the perpendicular to the basal plane. The values of the parameters compare well with those determined for other complexes with similar ligands, giving a reasonable hope that the use of the suggested model can rationalize the ESR spectra of low-symmetry high-spin cobalt(II).

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Registry No. $[Co(MePh_2AsO)_4NO_3]NO_3$, 18712-88-4; $[Zn(MePh_2AsO)_4NO_3]NO_3$, 70891-76-8.

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