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Electron Spin Resonance Spectra of Low-Symmetry Rare-Earth Complexes: Tetraphenylarsonium Pentakis(nitrato)ytterbate(III)

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The single-crystal ESR and electronic spectra of the title compound $[(C_6H_5)_4As]_2Yb(NO_3)_5$ have been recorded. The absolute g values have been found to be highly anisotropic, with $g_1 = 5.48$, $g_2 = 2.45$, and $g_3 = 1.76$. Angular-overlap calculations reproduce fairly well the low-symmetry **g** tensor, the energies of the electronic transitions, and the previously measured susceptibility values. The derived angular-overlap parameters are related to the bonding abilities of the nitrate ligands.

Introduction

Rare-earth ions can form complexes with high coordination numbers, when they are bonded to multidentate ligands or to small bidentate ions. The resulting coordination polyhedra usually possess low symmetry. A close scrutiny of these polyhedra very often reveals, however, that they arise from a slight distortion of a more symmetrical entity.

The pentanitrate ion is an example for 10-coordination. The most stable arrangement for coordination number 10 is the bicapped square antiprism.[1] However, when bidentate ligands having a small "bite" are involved, a tentative way of discussing the structure is to use the suggestion of Bergman and Cotton[2] and to consider that these ligands occupy only one coordination site. Actually, the arrangement of the five nitrogen atoms in $[Ce(NO_3)_5]^{2-}$ (C_2 symmetry) of $[(C_6H_5)_3C_2H_5P]_2Ce(NO_3)_5$ comes close to a trigonal bipyramid (D_{3h} symmetry).[3] Thus, it seems that in the low-symmetry pentanitrate complexes a higher symmetry can be assumed. To clarify this point ESR studies on single crystals of the title compound have been performed, as ESR spectra have been shown to be extremely sensitive to low-symmetry components of the crystal field.[4]

Besides the experimental difficulties, due to the necessity of obtaining very low temperatures in order to have reasonably narrow signals, problems arise in the interpretation of the spectra by applying theoretical models that have to consider low-symmetry crystal fields. The appropriate approach here should be the angular-overlap model (AOM), which has been established for f^n-electron systems with linear as well as nonlinear ligators.[5] This model, taking σ and π bonding into account, has been applied to crystal field parameters $R_k c_{kq}$ of numerous rare-earth systems.[6] The parameters $R_k c_{kq}$ with $k > 2$ could be reproduced by the model, and values for the angular-overlap parameters e_σ and e_π, which are transferable from one complex to another,[7] were deduced. The crystal field parameter $R_2 c_{20}$ was found too low by the model. Here, electrostatic contributions from noncoordinated ions also have to be taken into account. If we consider a complex compound with a well-isolated complex, electrostatic contributions from noncoordinated ions should be negligible, and the AOM should reproduce all crystal field parameters reasonably well. In a previous paper[8] a method employing the AOM has been suggested that allows calculation of the anisotropic magnetic susceptibilities of low-symmetry complexes, without making any use of idealized symmetries. This model should be of great help in the interpretation of the ESR spectra of the title

compound. The model has already been applied to explain the powder susceptibilities of numerous rare-earth compounds with the elpasolite structure.[9]

The complex compound $[(C_6H_5)_4As]_2Yb(NO_3)_5$ can be doped into the isotypic lutetium analogue, which is prepared by a recently given method.[10,11] The C_2 symmetry[10] of the complex anion $[Yb(NO_3)_5]^{2-}$ implies that one direction of the **g** and **A** tensors is fixed, while the other two are to be determined. In this paper we report the single-crystal ESR and electronic spectra of $[(C_6H_5)_4As]_2Yb(NO_3)_5$ as well as the single-crystal ESR spectra of the doped lutetium analogue, together with their interpretations based on the angular-overlap model.

Experimental Section

Single crystals of $[(C_6H_5)_4As]_2Yb(NO_3)_5$ and of Yb^{3+} (2%) doped into $[(C_6H_5)_4As]_2Lu(NO_3)_5$[11] ($[(C_6H_5)_4As]_2(Yb,Lu)(NO_3)_5$) were grown as recently described.[10] The crystals show well-developed (021) and (100) faces.

The single-crystal electronic spectra were recorded with a Cary 17 spectrophotometer equipped with an Oxford Instruments liquid-helium continuous-flow cryostat. The ESR spectra were recorded with a Varian E-line spectrometer operating at 9.3 GHz (X band) and equipped with an Oxford Instruments continuous-flow cryostat. The crystals were mounted on a quartz rod by using the geometrical features for the orientation.

Results

ESR Spectra. The single-crystal spectra were recorded by rotating around the b and c^* (perpendicular to a and b) axes. Figure 1 shows a typical single-crystal ESR spectrum of $[(C_6H_5)_4As]_2Yb(NO_3)_5$ at 4.2 K at X-band frequency. The central line corresponds to the Yb isotopes with nuclear spin $I = 0$. The satellites arise from ^{171}Yb ($I = \frac{1}{2}$; natural abundance $\approx 14.3\%$) and ^{173}Yb ($I = \frac{5}{2}$; natural abundance $\approx 16.1\%$). The spectrum of the diluted pentanitrate $[(C_6H_5)_4As]_2(Yb,Lu)(NO_3)_5$ differs from that of the concentrated nitrate by the line width, which here is more than 1 magnitude smaller (typically ≈ 5 G).

The spectra with the static magnetic field in the ab and ac planes were analyzed. The angular dependence of the g^2 values in the ac plane is shown in Figure 2. Since the metal ions have C_2 site symmetry in the lattice, one principal direction of the **g** tensor is fixed by the C_2 axis, which lies parallel to the b axis. The corresponding absolute g value for $[(C_6H_5)_4As]_2Yb(NO_3)_5$ ($[(C_6H_5)_4As]_2(Yb,Lu)(NO_3)_5$) was found to be $g_2 = 2.45 \pm 0.03$ (2.46 ± 0.03). The principal g_3 value was found at $25 \pm 5°$ ($27 \pm 5°$) from a, with $g_3 = 1.76 \pm 0.02$ (1.740 ± 0.005), and the g_1 value was found orthogonal to g_3 with $g_1 = 5.48 \pm 0.03$ (5.46 ± 0.03). The principal g values are compiled in Table I. The orientation of the principal axes

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Table I. Representative Fit of the Principal g Values and Directions for $[(C_6H_5)_4As]_2Yb(NO_3)_5$ and $[(C_6H_5)_4As]_2(Yb,Lu)(NO_3)_5$[a]

	g values		$\Delta\phi$[b]	
	calcd	obsd	calcd	obsd
g_1	5.33 ± 0.04	5.48 ± 0.03 (5.46 ± 0.03)	121 ± 1	115 ± 5 (117 ± 5)
g_2	2.27 ± 0.08	2.45 ± 0.03 (2.46 ± 0.03)		
g_3	1.61 ± 0.01	1.76 ± 0.02 (1.740 ± 0.005)	31 ± 1	25 ± 5 (27 ± 5)

[a] The values for $[(C_6H_5)_4As]_2(Yb,Lu)(NO_3)_5$ are given in parentheses. [b] $\Delta\phi$ is the angle between the indicated g direction and the a crystal axis in the ac plane (cf. Figure 2).
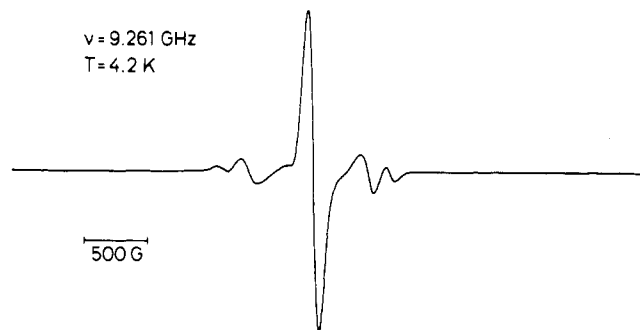

Figure 1. Typical single-crystal ESR spectrum of $[(C_6H_5)_4As]_2Yb$-$(NO_3)_5$. The static magnetic field is parallel to the a axis. The satellites belong to odd isotopes of Yb.
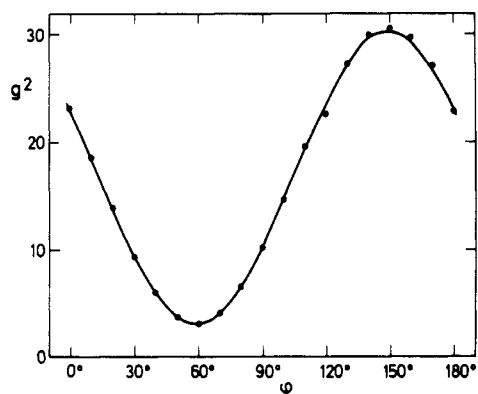

Figure 2. Angular dependence of g^2 in the ac plane for $[(C_6H_5)_4$-As]$_2$Yb(NO$_3$)$_5$. The curve corresponds to the least-squares fit of the experimental points. The crystal has been rotated around the b axis. For $\phi = 34°$ the static magnetic field is parallel to the a axis.

of **g** within the complex anion is illustrated in Figure 3. The angle between the normal on the $N_1N_1'N_2$ plane (pseudotrigonal axis) and the g_3 direction is 37°.

The spectra show resolved hyperfine splitting (cf. Figure 1). The corresponding hyperfine constants for ^{171}Yb have been determined to be $|A_1^{171}| = (1384 ± 46) × 10^{-4}$ cm^{-1} ((1456 ± 11) × 10^{-4} cm^{-1}), $|A_2^{171}| = (669 ± 38) × 10^{-4}$ cm^{-1} ((651 ± 19) × 10^{-4} cm^{-1}), and $|A_3^{171}| = (477 ± 26) × 10^{-4}$ cm^{-1} ((448 ± 5) × 10^{-4} cm^{-1}). The ratio $|A_i^{171}|/g_i$ comes close to the one obtained for other systems with Yb^{3+}; e.g., it was found for Yb^{3+} doped into CaF$_2$ ($g = 3.426 ± 0.001$, $|A^{171}| = (886.5 ± 1.5) × 10^{-4}$ cm^{-1}).[12,13]

Electronic Spectra. The electronic spectrum of a crystal (thickness 1 mm) of $[(C_6H_5)_4As]_2Yb(NO_3)_5$, recorded at liquid-helium temperature, is displayed in Figure 4. The corresponding spectrum of the diamagnetic f^{14} lutetium analogue is featureless in the region shown.

Discussion

From the principal g values and directions shown in Table I and Figure 3, we clearly see that a higher symmetry for
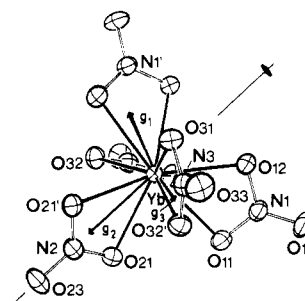
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Figure 3. Orientation of the principal axes of **g** within [Yb(NO$_3$)$_5$]$^{2-}$.
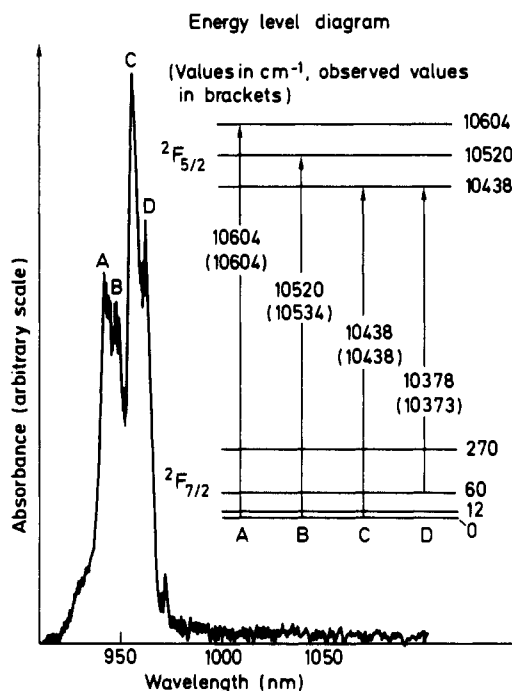

Figure 4. Single-crystal electronic spectrum and energy level diagram of Yb^{3+} in $[(C_6H_5)_4As]_2Yb(NO_3)_5$.

[Yb(NO$_3$)$_5$]$^{2-}$ than C_2, possibly D_{3h}, cannot be assumed. Calculations have to take the actual low symmetry into account.

In a previous paper[8] a general model for the calculation of the energies of the electronic transitions and of the magnetic susceptibilities of low-symmetry complexes has been suggested. This approach allows calculation of the principal values and directions of the susceptibility tensor without the assumption of any idealized symmetry. In order to interpret our ESR data, a corresponding treatment for the symmetric **g**^{2} tensor is necessary. Assuming the presence of isolated multiplets and given a laboratory axis frame, the nondiagonal **g**^{2} tensor is calculated according to the relation

$$g_{\alpha\beta}{}^2 = p\sum_i\sum_k \langle i|\mu_\alpha|k\rangle\langle k|\mu_\beta|i\rangle \qquad (1)$$

where α and β are arbitrary Cartesian components, μ_α and μ_β are the αth and βth components of the Zeeman operator, the sums are taken over all functions that are degenerate in the

Table II. Angular-Overlap Parameters (cm^{-1}) for
$[(C_6H_5)_4As]_2Yb(NO_3)_5$ and $[(C_6H_5)_4As]_2(Yb,Lu)(NO_3)_5$

$$e_\sigma{}^a = 217, 200, 183, 181$$
$$e_\sigma/e_{\pi\perp} = 2.00 \pm 0.01$$
$$e_{\pi\parallel} = 9$$

^{a} Accuracy ± 0.5 cm^{-1}.

absence of a magnetic field, and p is a number that depends on the degeneracy of the multiplet in the absence of a magnetic field.[14] The functions are computed as described in ref 8.

In our calculations we use all 14 $|LSJM_J\rangle$ wave functions of the ^2F term for Yb^{3+} (f^{13} configuration). The spin–orbit coupling and the C_2 crystal field splits the ^2F term into seven Kramers pairs, where the ground-state $^2F_{7/2}$ gives four doublets and the excited-state $^2F_{5/2}$ three doublets. All pairs are characterized by the representation ($\Gamma_3 + \Gamma_4$).[15]

The program requires the spin–orbit coupling constant ζ, the position coordinates of the atoms of the complex [Yb(NO$_3$)$_5$]$^{2-}$, and the angular-overlap parameters e_λ ($\lambda = \sigma, \pi$) as an input. The coupling constant was taken to be $\zeta = 2980$ cm^{-1}, as derived from the interpretation of the electronic spectra. The position coordinates of the 10 coordinated oxygen atoms were the ones for the isostructural [Er(NO$_3$)$_5$]$^{2-}$. Calculations show that no reasonable fit for the g^2 tensor is possible if only one e_σ and one e_π parameter is varied. Hence, the detailed structure of the complex anion has to be considered. From susceptibility measurements on [(C$_6$H$_5$)$_4$As]$_2$M(NO$_3$)$_5$ (M = Pr, Nd, Yb) we know that nonequivalent π bonding for the coordinated oxygen atoms has to be taken into account.[16] As the rare-earth ion and the atoms of the NO$_3^-$ group practically lie in one plane,[10] one can differentiate between a π bonding perpendicular to this plane ($e_{\pi\perp}$) and a π bonding in this plane ($e_{\pi\parallel}$). In order to consider that the 10 Er–O distances (R_i) in [Er(NO$_3$)$_5$]$^{2-}$ are essentially represented by just four different values, four e_σ parameters have to be introduced in this case. It has now been assumed that this will also be valid for [Yb(NO$_3$)$_5$]$^{2-}$.

For the calculation we thus varied successively the parameters $e_\sigma(R_1)$, $e_\sigma(R_2)$, $e_\sigma(R_3)$, $e_\sigma(R_4)$, $e_\sigma/e_{\pi\perp}$, and $e_{\pi\parallel}$. As starting values we have taken the ones that were obtained from the interpretation of the susceptibility data of [(C$_6$H$_5$)$_4$As]$_2$Yb(NO$_3$)$_5$: $e_\sigma = 256$ cm^{-1}, $e_\sigma/e_{\pi\perp} = 2.4$, $e_{\pi\parallel} = 30$ cm^{-1}.[16] A representative fit of the g values and directions are given in Table I. The parameter values on which this fit is based are grouped in Table II. Though this set may not be unique, it shows a not surprising approximate R^{-4} dependence of the e_σ values. Figure 4 shows the electronic spectrum of [(C$_6$H$_5$)$_4$As]$_2$Yb(NO$_3$)$_5$ and the energy level diagram for Yb^{3+}. The energy levels have been calculated with the parameter values of Table II and the spin–orbit coupling constant $\zeta = 2980$ cm^{-1}. The strongest bands can be interpreted by the energy level diagram; e.g., band A can be assigned to transitions from the lowest levels of the $^2F_{7/2}$ state (0, 12 cm^{-1}) to the highest level of the $^2F_{5/2}$ state (10 604 cm^{-1}). The assignment of the strongest bands is depicted in Figure 4.

With the above quoted parameter values a good fit for the magnetic susceptibility data of the title compound[16] has also been obtained as shown in Figure 5.

The value found for the spin–orbit coupling constant $\zeta = 2980$ cm^{-1} is slightly larger than the free-ion value calculated in the relativistic Hartree–Fock approximation $\zeta = 2948$ cm^{-1}, quoted in ref 17. This is somewhat unexpected. Normally,
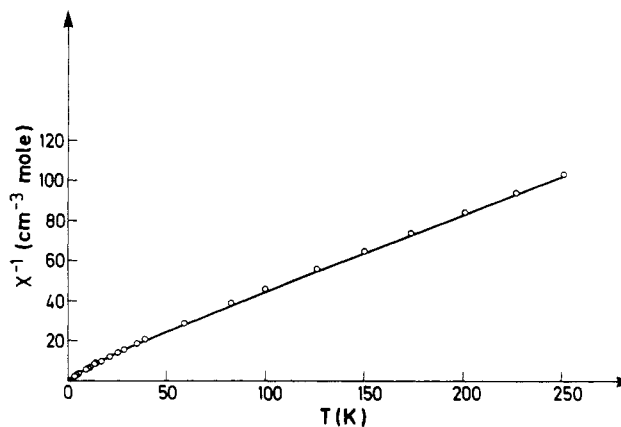
Figure 5. Inverse magnetic susceptibility vs. temperature for [(C$_6$-H$_5$)$_4$As]$_2$Yb(NO$_3$)$_5$. The line represents calculated values.

Table III. Angular-Overlap Parameters e_σ (cm^{-1}) and Overlap Integrals $S_\sigma{}^2(R)$ for Cs$_2$NaYbF$_6$, Cs$_2$NaYbCl$_6$, $[(C_6H_5)_4As]_2Yb(NO_3)_5$, and Cs$_2$NaYbBr$_6$

compd	e_σ	$10^4 [S_\sigma{}^2(R)]$	ref
Cs$_2$NaYbF$_6$	360 ± 30	2.11	9
Cs$_2$NaYbCl$_6$	236	1.01^a	9
$[(C_6H_5)_4As]_2Yb(NO_3)_5$	256 ± 28	0.99^b	16
	200.0 ± 0.5		this work
Cs$_2$NaYbBr$_6$	160 ± 10	0.59	9

^{a} Here the parameter for the position of the Cl$^-$ ion has been assumed to be $x = 0.24$. ^{b} This value has been calculated by employing the O$^-$ wave function of ref 20 and taking the estimated value $R = 241$ pm for the mean Yb–O distance.

a reduction from the free-ion value is observed and is accounted for by an orbital reduction factor. In our case an orbital expansion factor is required, and, indeed, the measured g values are better reproduced by inserting an expansion factor that is greater than 1 (cf. Table I).

The obtained values for the angular-overlap parameters can be explained by a simple concept for the bonding between the ytterbium ion and the coordinated oxygen atoms in [Yb(NO$_3$)$_5$]$^{2-}$. The following relation can be assumed for the angular-overlap parameters:

$$e_\lambda(R) = k[S_\lambda{}^2(R)] \qquad \lambda = \sigma, \pi_\perp, \pi_\parallel \qquad (2)$$

where k is a proportionality constant and $S_\lambda(R)$ represents the overlap integral for λ bonding between Yb^{3+} and oxygen and a given bond length R.[5,18]

Thus, by referring to eq 2 we have to investigate the possibilities for overlap of the occupied 2p orbitals 2p$_z$, 2p$_\perp$, and 2p$_\parallel$[19] of the coordinated oxygen atoms (e.g., O$_{21}$ in Figure 3). Whereas the 2p$_z$ and 2p$_\parallel$ orbitals are involved in σ bonding to the ytterbium ion and nitrogen atom (the N–O–Yb angle is about 95°), the 2p$_\perp$ orbital is involved in delocalized π bonding perpendicular to the NO$_3^-$ plane. Therefore, π bonding within the NO$_3^-$ plane should not be possible. Indeed, the e_σ and the $e_{\pi\perp}$ values are found larger than zero whereas $e_{\pi\parallel}$ is close to zero. The delocalization of the π bonding is not restricted to the NO$_3^-$ group but also involves the ytterbium ion. This might explain why the atoms of the NO$_3^-$ group and Yb^{3+} practically lie in one plane,[10] similar to the case of benzene.

Table III displays e_σ values for different ytterbium compounds, which have been obtained previously. Besides the

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angular-overlap parameter, the angular-overlap integral $S_\sigma^2(R)$ over the 4f Yb^{3+} function and np ligand function is given. The e_σ values for $[(C_6H_5)_4As]_2Yb(NO_3)_5$ correspond reasonably well to the $S_\sigma^2(R)$ value as is shown in Table III.

Conclusions

The analysis of ESR spectra of low-symmetrical $[(C_6H_5)_4As]_2Yb(NO_3)_5$ have clearly demonstrated that it is not justified to assume idealized high symmetry. The angular-overlap model has been shown to be a valuable tool for the interpretation of the spectral and magnetic properties of low-symmetry rare-earth complexes. The obtained values for the angular-overlap parameters give some insight into chemical bonding between rare-earth ions and ligand ions.

Registry No. $[(C_6H_5)_4As]_2Yb(NO_3)_5$, 85584-68-5.

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Investigation of Complex Equilibria in Solution by EPR Spectroscopy

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The pH-dependent equilibria between copper(II) and 3,7-diazanonanedioic acid diamide (DANA, L) have been studied in aqueous solution by EPR spectroscopy. Data of high quality were obtained by designing a specific titration system using a flow cell. Representation of the digitized spectra in their eigenvector basis significantly reduces the number of data to be handled in the subsequent numerical treatment and also gives the number of complexes present in solution. Stability constants ($\log K^{Cu}_{CuL} = 12.06$, $\log K^{H}_{CuL} = 7.05$, $\log K^{H}_{CuLH_{-1}} = 8.41$) and solution EPR spectra of the different complexes ($g_{CuL} = 2.125$, $g_{CuLH_{-1}} = 2.111$, $g_{CuLH_{-2}} = 2.100$) were calculated by using a program based on Marquardt's modification of the Newton–Gauss nonlinear least-squares method. No information with respect to the EPR spectra of the species is needed, which makes the mathematical technique especially useful if several complexes are formed simultaneously and if their spectra are unknown and/or strongly overlapping. The results of this study show that EPR titration offers an alternative both to potentiometry and to spectrophotometry for the investigation of solution equilibria.

Introduction

The EPR spectra of paramagnetic ions strongly depend on the ligand environment.[1] EPR spectroscopy therefore should be a valuable tool for investigating complex equilibria in solution. However, solution EPR[2,3] plays only a minor role among the methods used for determining equilibrium constants and moreover is mostly restricted to the simplest systems, which can be described by a single constant.[2–4] Examples are the association of iodide with organic radical anions,[5] inner- and outer-sphere complexes of Mn^{2+} and simple anions,[6,7] and ion-pair formation between organic radical anions and alkali metal ions.[8,9]

EPR parameters used in the determination of stability constants are (i) coupling constants,[5] (ii) line widths,[6,7] (iii) g values,[9] and (iv) line intensities, i.e. spin concentrations.[8] Methods i–iii can be used, where the complexation kinetics are fast on the EPR time scale and where only one time-averaged signal is found. In cases where the different species in a mixture give rise to separate signals, only method iv can be applied.

In the EPR spectra obtained from a mixture of organic radicals, the observed lines are readily assigned to the individual species because the spectrum of a pure component consists of a set of rather sharp and narrow lines.[1] The concentrations of the different species are obtained by simply integrating over the respective lines.[10] Computer programs exist for this purpose.[11] The situation is quite different for many transition-metal complexes due to the much broader spectra.[1] E.g. for cupric complexes, where the dependence of the EPR parameters on coordinating atoms, geometry, and charge is well understood,[12,13] the spectra of the species present in an equilibrium system are strongly overlapping.[14,15] Therefore, for species that occur only to a minor extent, the spectra cannot be obtained straightforwardly and the problems in determining stability constants from EPR data are the same as in spectrophotometry.[16,17]

Only recently a paper appeared that dealt with the determination of equilibrium constants for a number of Cu^{2+}-peptide complexes from EPR data.[18] The calculation was done on a mainframe computer using a grid search, which is easy to apply but converges slowly and is thus expensive in computer time.[19] The procedure used[18] has the disadvantage that for n simultaneously occurring complexes $n - 1$ spectra have to be known, which limits its practical use to systems with only two species occurring in a certain mixture.

In the present work the complexation of Cu^{2+} by 3,7-diazanonanedioic acid diamide (DANA, L) in aqueous solution was studied by EPR spectroscopy. The main difficulties related to the use of EPR data in the determination of stability

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