

250. Stabilities and Structures of Cu(II) Complexes with Linear Pentadentate Ligands by EPR Spectroscopy

by Harald Gampp

Institut für Anorganische Chemie der Universität, Spitalstrasse 51, CH-4056 Basel

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Summary

The pH-dependent equilibria between Cu(II) and the potentially pentadentate ligands 4,7,10-triazatridecane-1,13-diamine (**1**) and 1,9-bis(2-hydroxyphenyl)-2,5,8-triazanonane (**2**) have been studied in aq. solution at 298 K by EPR titration. Each ligand forms complexes CuLH_x ($x = 1,2,3$) with strongly overlapping spectra. By using a recently developed algorithm, which does not need any information with regard to the spectra of the species, stability constants and spectra were calculated from the EPR titration data. The anisotropic EPR spectra of the complexes were measured at 153 K and display axial or nearly axial symmetry ($g_{\parallel} > g_{\perp}$) in each case. Based on the spectral parameters the assignment of the structures of the complexes was possible. With **1** and **2** the protonated complexes are equatorially coordinated, whereas in the fully deprotonated complexes an additional axial interaction occurs which is stronger with **2** than with **1**.

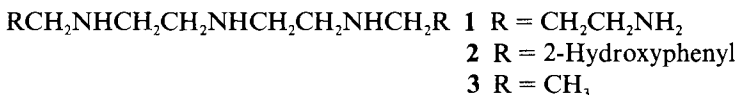
The results of this study show that EPR spectroscopy is a useful method for investigating equilibrium systems of Cu^{2+} even in complicated cases where minor species occur and where the individual spectra are unknown and strongly overlapping.

Introduction. – Recently, we showed that solution EPR is a useful method for the investigation of equilibria [1] and kinetics [2] of paramagnetic complexes. Stability or kinetic constants as well as spectra of the different species can be calculated in a straightforward manner. Contrary to the method described in [3], only initial estimates for the stability or rate constants are required, while no information with regard to the spectra of the complexes is needed. Matrix rank analysis not only gives the number of species in the respective chemical system but also greatly reduces the number of data to be handled in the numerical treatment without any loss of significant information [4]. The different mathematical methods incorporated [4] [5] make the algorithm especially useful if several complexes are formed simultaneously and if their spectra are unknown and strongly overlapping.

The method in equilibrium studies was demonstrated for the pH-dependent complexation of Cu(II) by 3,7-diazanonanedioic acid diamide (DANA) [1]. In this system, which has already been investigated potentiometrically [6] and spectrophotometrically [7], three different complexes occur each of which is formed to more than 70% in a certain pH region. Because DANA cannot be more than tetradentate, the assignment

of the structures of the complexes can be achieved straightforwardly using either ligand-field [6] [7] or EPR spectra [1].

A different situation is encountered with potentially pentadentate ligands (L) like 4,7,10-triazatridecane-1,13-diamine (**1**) and 1,9-bis(2-hydroxyphenyl)-2,5,8-triazanonane (**2**). The complexation of Cu(II) by **1** and **2** and by the tridentate ligand 3,6,9-triazaundecane (**3**) were subject of a combined potentiometric and spectrophotometric study [8]. With **1** and **2** three different complexes were found, namely $\text{CuLH}_2^{(n+2)+}$, $\text{CuLH}^{(n+1)+}$, and CuL^{n+} (L = **1**: n = 2; L = **2**: n = 0; charges omitted in the following).



For CuLH_2 , which is formed to not more than 30% (**1**) or 55% (**2**), two structures are possible: one with the three nitrogen atoms of the central diethylenetriamine (dien) unit coordinating, the other where only two of these together with one of the donors in the side arms are in the equatorial positions (in both cases a water molecule occupies the fourth position). Neither stabilities nor VIS spectra allowed to distinguish between the two possibilities.

For CuLH a quasi-planar structure with one protonated and thus non-coordinating side arm could be safely assumed since the d-d* transitions are shifted to shorter wavelengths relative to a corresponding 3N-coordinated species indicating additional equatorial coordination.

For CuL the VIS band is shifted to longer wavelengths relative to CuLH . The red shift is only small with **1**, which is explained by a weak additional apical interaction in an essentially still tetragonal complex. With **2** the corresponding red shift is almost 100 nm and, therefore, it was concluded in [8] that a substantial reorganisation occurs upon deprotonation of CuLH . It was, however, not possible to decide from the VIS spectra if the structure of the pentacoordinate complex is square pyramidal or trigonal bipyramidal.

In the present paper, the pH-dependent complexation of Cu(II) by the pentadentate ligands **1** and **2** is studied by EPR spectroscopy. Since in both equilibrium systems several complexes are simultaneously present in solution, spectra and stability constants are determined from EPR titrations. Room temperature and frozen glass EPR spectra are used in order to assign the structures of the complexes. For the sake of comparison the EPR spectrum of $\text{Cu}(\mathbf{3})^{2+}$, the Cu(II) complex of the tridentate ligand **3**, is included. Moreover, this study is considered as a further test of the possibility of analyzing solution EPR data from complicated systems, especially since with **2** the complex present at low pH is only formed to a minor extent.

Experimental. - *Materials.* NaOH (Merck, titrisol), KCl and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck, p.a. grade) were used without further purification. 4,7,10-Triazatridecane-1,13-diamine (**1**) used as pentahydrobromide, 1,9-bis(2-hydroxyphenyl)-2,5,8-triazanonane (**2**) used as trihydrochloride, and 3,6,9-triazaundecane (**3**) used as trihydrobromide were synthesized as described in [8]. Doubly distilled H_2O was used throughout. Buffers of pH 4.00 and 7.00 (Metrohm) were used for calibrating the potentiometer.

Apparatus. The flow system used in the titration experiments has been described in [1]. EPR spectrometer was a Varian E3 using 100-kHz field modulation and equipped with a 9.5-GHz microwave bridge. Glass spectra were obtained at 153 K using a Varian E9 (100-kHz, 9.5-GHz) equipped with a Varian Variable Temperature Controller.

Measurement. The titrations both with **1** and **2** were done at 298 K in aq. soln. of constant ionic strength ($I = 0.5M$ (KCl)) under N_2 . To 12 ml of a soln., which was 0.0204M in **1**, 0.020M in HCl and 0.0194M in Cu^{2+} , was added 3.1 ml of a 0.5M NaOH in increments of 0.1 ml. To 10 ml of a soln., which was 0.0134M in **2** and 0.0116M in Cu^{2+} 0.5M NaOH was added. A precipitate formed at pH 3.0, which did not dissolve until pH 7.9 (1.25 ml base added). To this solution 0.6 ml base was added in 18 increments. The EPR spectrum of the Cu^{2+} complex of **3** was obtained from 0.02M solution.

The EPR spectra were measured between 2750 and 3450 G and recorded on chart paper. Instrument settings were: 4-mW microwave power, 1-G modulation amplitude, 1-s time constant, and 1-Gs⁻¹ scan rate. Pentaphenyl allyl ($g = 2.0026$) [9] was used as a standard and displayed a signal at 3290 G. Glass spectra were measured between 2500 and 4000 G in 2 mm soln. either in 33% EtOH/H₂O or in 50% DMSO/H₂O at 153 K. The pH was measured prior to the addition of the org. solvent. Instrument settings were: 4-mW microwave power, 4-G modulation amplitude, 0.3-s time constant and 4-Gs⁻¹ scan rate. The spectral parameters (g_{\parallel} , A_{\parallel} , and g_{\perp}) were determined by using a simulation program ESR2 [10].

Data Reduction. The first-derivative spectra from the titrations were digitized and stored on diskette as described recently [1]. With **1** each of the 31 spectra was resolved into 50 digital points at equidistant intervals of 10 G between 2830 and 3320 G. With **2** each of the 18 spectra was resolved into 46 digital points at equidistant intervals between 2900 and 3350 G. The data were multiplied by appropriate factors to make them all correspond to the same receiver gain, are expressed in arbitrary units (au) and range from 0 to 75 au.

The digitized spectra are first represented in their eigenvector space, which gives the number of complexes present in soln. and significantly reduces the number of data to be handled in the subsequent numerical treatment [1] [2] [4]. Stability constants and spectra of the different species were calculated by using a *Newton-Gauss-Marquardt* program [5] [11]. No information with respect to the complex spectra is needed and the whole data set is used in the calculation (*cf.* [1] for the mathematical methods used and a detailed description of the data treatment).

With **2** the spectrum of $CuLH_2$ was obtained from a solution of pH 2.9, *i.e.* under conditions where precipitation did not yet occur and where the complex is formed to about 5%. The spectrum showed the broad and unstructured signal of aq. $Cu(II)$, on the high-field flank of which the spectrum of $CuLH_2$ was superimposed. Subtracting the contribution of free $Cu(II)$ yielded the spectrum of the pure complex.

Results and Discussion. – Eigenvector Analysis. Matrix rank analysis shows that the experimental data obtained with **1** (Fig. 1a) can be represented by four eigenvectors. This is to be expected since three complexes (and free Cu^{2+}) were found both spectrophotometrically and potentiometrically [8]. The overall standard deviation between the experimental data and their eigenvector representation of 0.34 au (Table 1) corresponds to about 0.5% of the average measured signal (first derivative of the intensity with respect to the magnetic field strength) and equals the error introduced by digitizing the spectra.

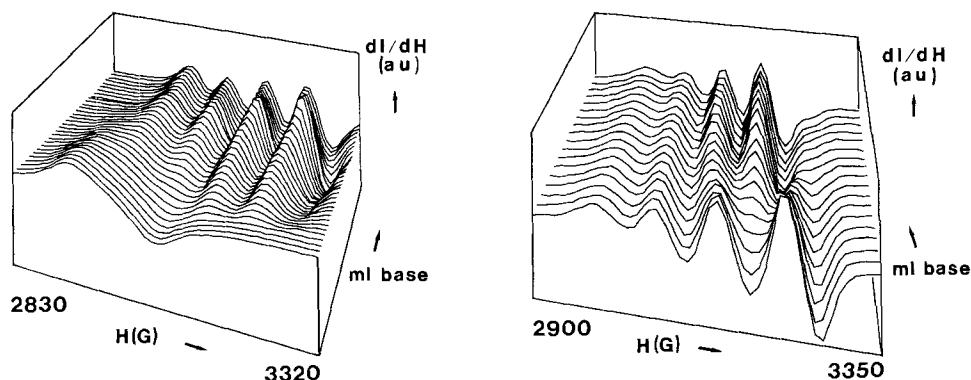


Fig. 1. Three-dimensional plot of the EPR titration data. a) **1**; $[Cu^{2+}]_{tot} = 19.4$ mM, $[HCl]_{tot} = 20.0$ mM, $[1]_{tot} = 20.4$ mM. b) **2**; $[Cu^{2+}] = 13.4$ mM, $[2] = 11.6$ mM ($I = 0.5M$ (KCl); 298 K).

Table 1. Stability Constants and Standard Errors of the Cu(II) Complexes with **1** and **2** at 298 K and $I = 0.5M$

Ligand	Method ^{a)}	No. of species	σ_{ev} ^{b)} [au]	σ_{cal} ^{c)} [au]	$\log K_{CuLH_2}^H$ ^{d)}	$\log K_{CuLH}^H$	$\log K_{CuL}^{Cu}$
1	E	4	0.34	0.37	3.20 (0.01)	8.95 (0.01)	21.63 (0.01)
	S				3.27 (0.02)	8.97 (0.02)	22.11 (0.09)
	P				3.31 (0.03)	8.99 (0.01)	21.65 (0.05)
2	E	2 ^{e)}	0.78	0.82	–	8.53 (0.01)	–
	S				3.99 (0.01)	8.65 (0.01)	22.60 (0.04)
	P				4.08 (0.01)	8.49 (0.01)	22.53 (0.02)

^{a)} E: EPR, this work; S: spectrophotometry and P: potentiometry from [8].

^{b)} Standard error between experimental data and their eigenvector representation [1] [3].

^{c)} Standard error between experimental data and their calculated analogues obtained from the least-squares refinement [1] [5].

^{d)} $K_{CuLH_x}^H = [CuLH_x]/([CuLH_{x-1}] \cdot [H^+])$; $K_{CuL}^{Cu} = [CuL]/([Cu] \cdot [L])$.

^{e)} Due to precipitation at low pH (*cf. Experimental*) only the equilibrium $CuLH \rightleftharpoons CuL + H^+$ could be studied.

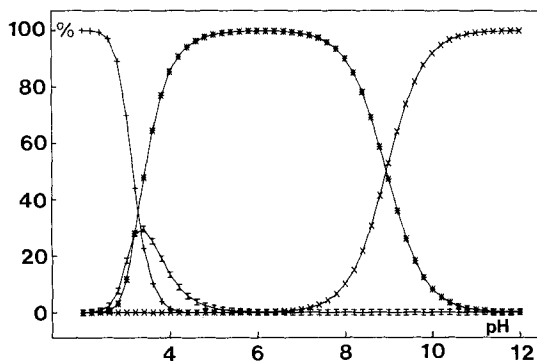


Fig. 2. Species distribution of the copper(II)-1 system as a function of pH. The results are given as the percentage of total copper present. +, Cu^{2+} ; x, CuL^{2+} ; *, $CuLH^{3+}$; I, $CuLH_2^{4+}$. (Conditions as in Fig. 1a.)

With **2** only two eigenvectors are needed to represent the data (*Fig. 1b*). Due to the low solubility of $CuLH_2$ only the complexes $CuLH$ and CuL were present over the pH-range studied (*vide supra*). The eigenvector representation yields a standard error of 0.78 au (*Table 1*), *i.e.* about twice the value obtained with **1**. This is explained by the fact that in the titration of **2** the total concentrations were only half of those used with **1**, which results in an increased instrumental noise.

Stability Constants. The stability constants were calculated by using the potentiometrically determined ligand protonation constants [8] and agree well with the values obtained by other methods (*cf. Table 1*). The species distribution for the equilibria of **1** (*Fig. 2*) shows that $CuLH_2$ is present to not more than 30% over a rather narrow pH-range only. For both ligands the standard error between the experimental data and the corresponding points calculated by the non-linear least-squares method is only slightly larger than the standard error obtained from the eigenvector representation (*Table 1*).

EPR titration curves with **1** are given in *Fig. 3* and show that the calculated curves nicely fit the experimental points. This clearly demonstrates that EPR titration is a useful method for studying solution equilibria of Cu^{2+} even in cases, where some complexes are only formed to a minor extent.

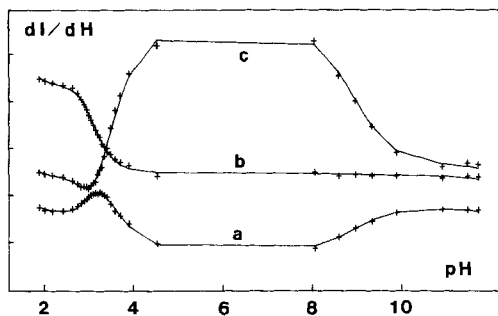


Fig. 3. EPR titration curves for the copper(II)-I system. The magnetic field strengths are a) 3120 G, b) 2920 G, and c) 3240 G. Experimental points: +. Calculated curves: —. (Conditions as in Fig. 1a.)

EPR Spectra. The calculated solution spectra show four lines each (Fig. 4) consistent with the interaction of an unpaired electron with a Cu nucleus of nuclear spin $I = 3/2$ [13]. Each spectrum has an asymmetrical shape with peak heights increasing with the magnetic field. Such a presence of anisotropic terms in the *Hamiltonian* indicates a restricted rotation of the complexes and is frequently observed for room temperature spectra of Cu(II) complexes in solution [1] [3] [14]. As the individual spectra

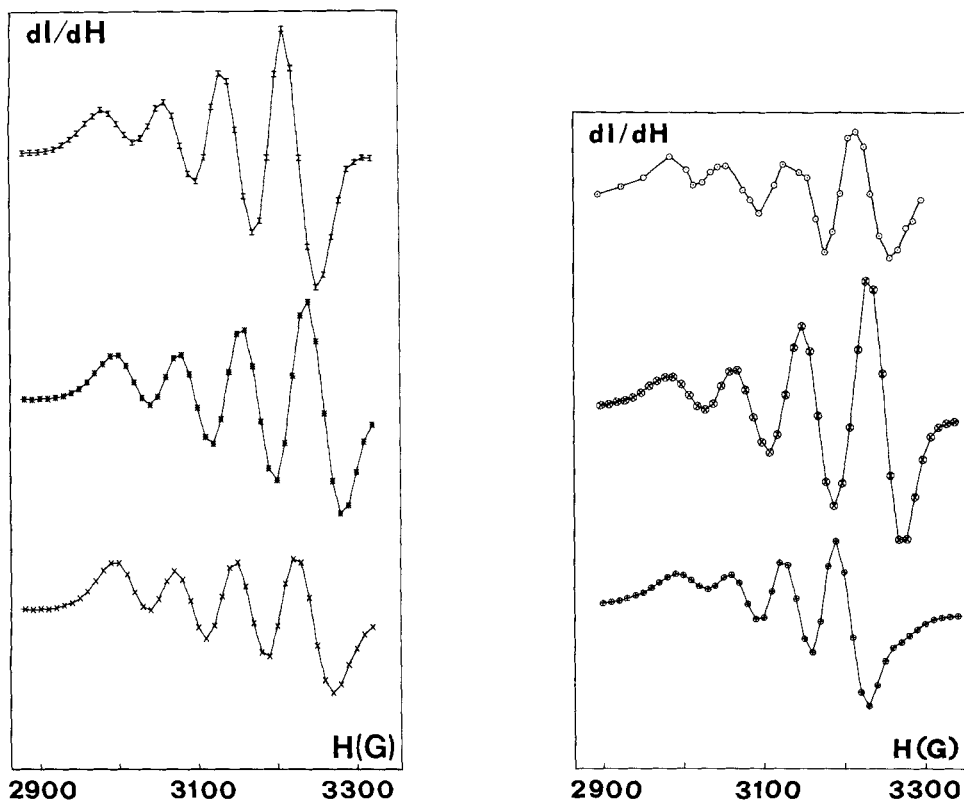


Fig. 4. Calculated EPR spectra of the Cu(II) complexes with 1 and 2 at 298 K. a) I, Cu(1)H₂²⁺; *, Cu(1)H³⁺; x, Cu(1)²⁺. b) ⊙, Cu(2)H₂²⁺; ⊗, Cu(2)H⁺; ⊕, Cu(2).

Table 2. *Isotropic EPR Spectral Parameters of the Cu(II) Complexes with 1–3 from EPR Titration at 298 K and I = 0.5 M*

Species	g_{av} ^{a)b)}	A_{av} [mK]	Int [au] ^{c)}
Cu_{aq}^{2+}	2.193	–	8.1 ^{d)}
$Cu(1)H_2^{4+}$	2.112	7.49	10.5
$Cu(1)H^{3+}$	2.102	7.95	9.2
$Cu(1)^{2+}$	2.106	7.77	9.7
$Cu(2)H_2^{2+}$	2.112	7.96	
$Cu(2)H^+$	2.106	8.16	
$Cu(2)$	2.121	6.54	
$Cu(3)^{2+e)}$	2.114	7.65	

a) The values g_{av} and A_{av} were determined graphically.

b) The magnetic field was calibrated by using the signal of pentaphenyl allyl [9] as standard.

c) Double integral calculated between 2900 and 3300 G by numerical integration.

d) Part of the low-field signal has been cut off.

e) Obtained from a soln. of pH 8.30.

are relatively broad and as the spectral parameters are also rather close (*Table 2*) the measured spectra overlap strongly. This is illustrated by *Fig. 1a* for the Cu(II) complexes of **1**. Only the initial and final spectra can be clearly attributed to aq. Cu and CuL, respectively, whereas this is not possible for the intermediate ones. Thus, contrary to the case of mixtures of organic radicals, where overlapping is no major problem [13] and where accordingly the spectra of the different species are readily assigned (their concentrations are simply obtained by integrating over the respective lines [15]) rather sophisticated mathematical methods are needed for our systems.

The calculated spectra were checked against experimental spectra obtained under conditions where only one species is present. No significant difference is found between initial and final spectra from the titration of **1** and **2** and the calculated spectra of Cu, CuLH (L = **2**), and CuL (L = **1**, **2**), respectively.

For the complexes of **1** the results of the calculation were independently tested by doubly integrating the calculated spectra. This should give the same value (*i.e.* spin concentration) for each species. The calculated values for the three complexes are indeed reasonably close ($\pm 7\%$) and only the result for Cu^{2+} is too small because a part of the low-field signal has been cut off (*Table 2*).

Thus, without making any assumptions with regard to the shape of the spectra of the complexes our mathematical method allows one to calculate the correct spectra even if they strongly overlap and if minor species occur.

The anisotropic EPR spectral parameters of the different Cu^{2+} species were obtained by using a simulation program [10] and are summarized in *Table 3*. The frozen-glass spectra (*Fig. 5*) all display axial or nearly axial symmetry ($g_{\parallel} > g_{\perp}$) and have the usual line shape for mononuclear Cu(II) complexes with a $d_{x^2-y^2}$ ground state. The high-field region in the spectrum of CuL (L = **2**) is more spread out than in the case of the other complexes and three g values are necessary for a satisfactory description.

With **1** the complexes CuLH₂ (maximum concentration = 30%) and CuLH are formed simultaneously, (*cf. Fig. 2*). The spectra observed at low pH were always a superposition of the two spectra and showed a single g_{\parallel} pattern only. Consequently,

Table 3. Anisotropic EPR Spectral Parameters at 153 K and VIS Absorptions at 298 K of the Cu(II) Complexes with 1–3

Species	pH ^{a)}	g_{\parallel} ^{b)}	A_{\parallel} [mK]	g_{\perp}	λ_{\max} ^{c)} [nm]	ϵ^c [$M^{-1}cm^{-1}$]
Cu_{aq}^{2+}	–	2.411	–	2.080	–	–
$Cu(1)H_2^{2+d)}$	–	–	–	–	631	146
$Cu(1)H^{3+}$	7.75	2.207	21.64	2.040	573	187
$Cu(1)^{2+}$	11.34	2.224	19.73	2.050	585	214
$Cu(2)H_2^{2+}$	3.42	2.236	19.83	2.045	633	155
$Cu(2)H^+$	7.42	2.213	20.15	2.045	595	202
$Cu(2)$	10.30	2.227	18.19	– ^{e)}	680	160
$Cu(3)^{2+}$	8.30	2.235	19.30	2.050	631	158

^{a)} pH of the aq. soln. prior to the addition of the org. solvent and freezing. ^{b)} The EPR spectral parameters were obtained by using a simulation program [10]. ^{c)} From [8]. ^{d)} The EPR spectrum of this minor species was not obtained. ^{e)} Best fit of the spectrum with $g_x = 2.020$ and $g_y = 2.055$.

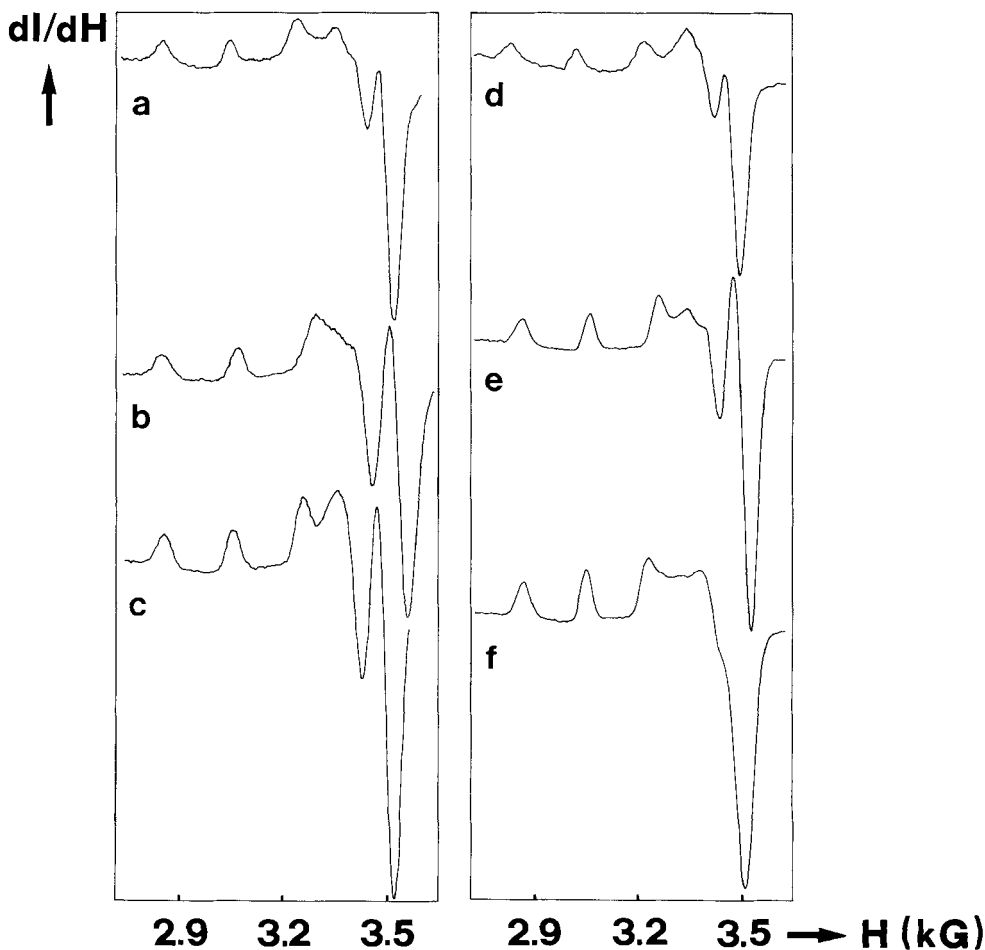


Fig. 5. Anisotropic EPR spectra of the Cu(II) complexes with 1–3 at 153 K. a) Cu(3); b) Cu(1)H; c) Cu(1); d) Cu(2)H₂; e) Cu(2)H; f) Cu(2).

the spectrum of CuLH_2 ($L = 1$) could not be obtained. With **2** the spectrum of CuLH_2 was measured in a solution of pH 3.42, *i.e.* under conditions where at room temperature most of the metal remains uncomplexed and only 30% are present as CuLH_2 . The observed spectrum, however, is that of a pure axial complex and does not show the presence of free metal ion (*Fig. 5*). The g_{\parallel} values of Cu^{2+} and of CuLH_2 ($L = 2$) are markedly different (*Table 3*). If a mixture of the two species were present in the frozen glass two different g_{\parallel} patterns would show up in the EPR spectrum as was demonstrated for related Cu(II) systems [18] [19]. This means that the room-temperature equilibria are not simply 'frozen' upon cooling but are affected by decreasing the temperature. (A possible effect of the cosolvent can be excluded in the present case since the same spectra are observed in $\text{H}_2\text{O}/\text{DMSO}$ and in $\text{H}_2\text{O}/\text{EtOH}$ glasses.) Before any conclusions regarding the solution structure of the complexes can be drawn on the basis of the anisotropic EPR spectra, we have to make sure that the structures of the different species are the same in fluid solution and in the frozen glass. For square planar Cu(II) complexes it was shown that only a weak temperature dependence of g_{av} exists due to solvent interactions at the vacant positions if the structures do not change otherwise [20]. From the anisotropic spectra (*Table 3*) values for g_{av} were calculated by using the first-order approximation $g_{\text{av}} = 2/3 g_{\perp} + 1/3 g_{\parallel}$ [21]. In the average these values were by 0.003 smaller than those obtained at room temperature (*Table 2*). This leads to a temperature dependence similar to the one given in [20] and we therefore can assume that the structures of the complexes are the same in aq. solution and in the frozen glass.

Structure of the Copper(II) Complexes. For the complexes CuLH_2 the isotropic EPR spectra are very close and almost the same as found for Cu(**3**) (*Table 2*). An equally good agreement between Cu(**2**) H_2 and Cu(**3**) is evident from the frozen glass spectra (*Table 3*, *Fig. 5*). As the VIS spectra are also almost identical (*Table 3*), we can safely assume the same structure for all three complexes: three nitrogen donors of the central dien moiety are equatorially coordinated and the protonated side chains of **1** and **2** are dangling freely in solution. For Cu(**3**) a slightly distorted coordination sphere was suggested by the VIS spectra [8] and the same will be true for the complexes CuLH_2 . A major distortion, however, can be excluded on the basis of both VIS and EPR spectra.

For CuLH a quasi-planar structure with the three nitrogen atoms of the dien moiety and the donor group of one side chain coordinating equatorially was found with **1** and **2** [8]. Deprotonation of CuLH_2 results in a decrease of g_{av} (**1**, **2**) and of g_{\parallel} (**2**), in a less pronounced increase of A_{av} and of A_{\parallel} , and in a shift of the d-d* band to shorter wavelengths (*Tables 2* and *3*). As has been shown for a great number of square planar Cu(II) complexes, the values for g and A depend on the equatorial donor atoms and on the charge of the complexes [22] [23]. Increasing donor strength and increasing negative charge both result in an increase of the cubic ligand field and lead to smaller values for g , larger ones for A [22] [23] and to a shift of the d-d* band to higher energies [24] [25]. If the ligand field is not strictly square planar the relatively large changes in g and A resulting from distortions will dominate the rather small changes due to differences in charge [23]. For the complexes CuLH_2 no effect of charge is seen whereas the g values for Cu(**1**) H^{3+} are even smaller than those for Cu(**2**) H^+ (*Tables 2*

and 3). It would be interesting to know, whether this reflects the different donor strengths of the ligands or a different degree of distortion of the square planar symmetry. The spectral data available for monomeric phenolate complexes of known square planar structure are of no help in this context, since strongly electron-withdrawing substituents at the phenols had to be used in order to prevent oxidation [26–28]. An estimation of the donor strength of a phenolate relative to an amine can be made by comparing the tetradentate ligands 1,6-bis(2-hydroxyphenyl)-2,5-diazahexane [29] and 4,7-diazadecane-1,10-diamine [30]. The cupric complexes of these ligands have the same sequence of chelate rings (6-5-6) and absorb at 588 [29] and 543 nm [30], respectively. This suggests a weaker donor strength of a phenolate relative to an amine and thus explains the small differences observed between the g values of the complexes CuLH .

With both ligands **1** and **2** deprotonation of CuLH is accompanied by an increase of g_{av} and g_{\parallel} and a decrease of A_{av} and A_{\parallel} (Tables 2 and 3). The red shift of the ligand-field transition was explained by an apical interaction of the donor in the remaining side chain [8]. Similar shifts of the $d-d^*$ band in going from a CuN_4 to a CuN_5 chromophore are known for a long time for ammonia complexes [31–33] and are well-documented for chelate complexes [34–36].

Tetrahedral distortion of a planar CuX_4 moiety which would also result in a red shift of the ligand-field transition [37] can be excluded in our case. The ratio $g_{\parallel}/A_{\parallel}$ can be used as an empirical index of tetrahedral distortion of a regular square planar symmetry [38]. The range of the values calculated for our complexes, 102–122 cm, indicates no such distortion since this would lead to ratios of about 200 cm [38].

The change of the EPR spectral parameters due to axial interaction can be explained by simple crystal-field arguments. If a fifth ligand coordinates apically the energy of the $d_{x^2-y^2}$ level and the separation between $d_{x^2-y^2}$ and d_{xy} decrease [39] [40]. This leads to an increase of g_{\parallel} (and g_{av}) and to a decrease of A_{\parallel} (and A_{av}) as has been shown for adduct formation of square planar acetylacetonate complexes of Cu(II) [39] [40]. As the same spectral changes occur upon deprotonation of CuLH this clearly indicates an axial interaction in the fully deprotonated complexes. For Cu(1) the values of g_{av} , A_{av} , and λ_{max} range between those found for CuLH_2 and CuLH . The anisotropic EPR spectrum is that of an axial Cu(II) complex and can be described by only two g values. Therefore, this complex will be essentially tetragonal with a fifth donor weakly coordinating in the apical position. For Cu(2) , too, the isotropic spectral parameters are different from those of the respective protonated complexes, the differences being much larger as in the case of **1**. A stronger axial interaction in Cu(2) is further evident from the high-field region in the anisotropic EPR spectrum, which is considerably more spread out than in the case of the other complexes. For square pyramidal Cu(II) complexes the low-field part of the anisotropic EPR spectrum resembles the normal tetragonal Cu(II) spectra, whereas the high-field part is rather broad and contains two g values, one of which is smaller than 2.04 [41] [42]. In our case the high-field region is less spread out as found in regular square pyramidal symmetry, which therefore can be excluded for Cu(2) . Hence, an axial interaction of the fifth donor group occurs in both complexes CuL , but even in the case of the phenol this interaction is not strong enough that all coordinating atoms are bound with equal strength to the metal.

Conclusions. – The results of this study show that EPR spectroscopy is a useful method for investigating complex equilibria of Cu^{2+} even in complicated cases where several complexes are simultaneously present and where certain species are formed to a minor extend only.

By using an algorithm, which is especially designed for the common situation that the spectra of the complexes are unknown and strongly overlapping, the evaluation of EPR titration data is straightforward [1]. No care has to be taken to select the data since the calculation of stability constants and spectra of the species is simultaneously done on the whole data set (*i.e.*, a set of spectra measured over a certain pH range).

The EPR spectra of paramagnetic metal ions are strongly dependent on the ligand field, and the calculated solution EPR spectra can be used to derive the structures of the complexes.

The possibilities offered by the EPR method have been demonstrated in the present paper for the equilibria between Cu(II) and the potentially pentadentate ligands **1** and **2**: stability constants (comparing favorably with those obtained potentiometrically and spectrophotometrically [8]) and solution spectra have been calculated. From these isotropic EPR-spectral parameters (and with additional information from anisotropic EPR and ligand-field spectra) a structural picture of the complexes could be derived, which is much more detailed than the one obtained from spectrophotometric results alone [8].

Hence, EPR titration offers an alternative both to potentiometric and to spectrophotometric titrations. It should be used whenever possible especially in cases where the solution structures of complexes are to be established.

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