209. EPR. Spectroscopic Investigations of Planar Cu(II)- and Low-Spin Co(II)-Complexes in Nematic Phases and in Single Crystals

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Summary

EPR. spectra of planar low-spin Co(II)- and Cu(II)-complexes were obtained in oriented nematic phases, and compared with single crystal measurements. Unambiguous directional information is only obtained in the case of solute molecules in which the two in-plane axes are of distinctly different length.

Introduction. - Low-spin Co(II)-complexes have been investigated for several years by various methods. One of the driving forces of these investigations has certainly been the interest in the dioxygen-binding properties of such complexes. In order to understand the oxygen-binding properties, it is necessary to elucidate the electronic structure of the complexes in depth. EPR. spectroscopy is a particularly informative tool for the investigation of the electronic structure of the Co(II)-complexes, since, in the low-spin configuration ($S = \frac{1}{2}$), detailed information on spin-orbit coupling and hyperfine fields can be obtained without the complications involved in $S > \frac{1}{2}$ ions, which show zero field splitting.

The low-spin d^7-configuration is of particular interest in the transition metal series because it would give rise to an orbitally degenerate ground state (^2E) in octahedral symmetry. This otherwise very frequently adopted coordination geometry is, in fact, never found in low-spin Co(II)-compounds. The four- and five-coordinate complexes with planar or approximate C_{4v}-symmetry are unique in their electronic structure. Most molecular compounds, including transition metal complexes, have their first electronically excited state well removed from the ground state [1]. For many planar or five-coordinate Co(II)-complexes, it was recently shown, that, within a range of 5000 cm^{-1}, two doublet- and four quartet-states occur. It is remarkable that, not only states with a spin multiplicity which is different from that of the ground state, but also states with the same multiplicity are lying so low. This property of the complexes has dramatic effects on the magnetic behavior, and especially on the EPR. spectra of such compounds.

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Due to the relatively long relaxation times at liquid nitrogen temperatures, EPR. spectra can easily be observed in glassy media and, of course, in polycrystalline samples. At higher temperatures the spectra vanish, probably because of strong relaxation in a thermally excited state (*Orbach* process). The interpretation of the frozen solution Co(II)-spectra and of the polycrystalline samples is, however, severly hampered by the fact that, contrary to most Cu(II)-complexes, no unambiguous relation between the molecular coordinate frame and the g- and A-tensor axes exists. Although the principal values of the tensors can generally be measured quite accurately in amorphous media, it is not possible to deduce any information about electronic structure without knowing the relative orientation of principal axes to the molecular coordinate system. Indeed, the first correct assignment of a low-spin Co(II) ground state could only be made from single-crystal EPR. measurements [2].

In the present paper we have investigated the possibility of obtaining directional information about the tensor-axes from measurements in magnetically and electrically ordered nematic phases. For comparison, single-crystal data are also included. Similar investigations have been carried out by *J.P. Fackler et al.* [3], *B.M. Hoffman et al.* [4] and *M.V. Rajasekharan et al.* [5] in other nematic phases.

Experimental. - The following metal complexes were synthesized according to established procedures [6] [7]: Ni(amben), Cu(amben), ^{63}Cu(amben), Co(amben) (amben = *N,N'*-bis(*o*-aminobenzyliden)ethylenediaminedianion). Co(acacen) and Cu(acacen) were kindly supplied by Dr. *C. W. Schläpfer* of our laboratory (acacen = Bis(acetylacetone)ethylenediaminedianion).

Growth of single crystals Ni(amben)/Co(amben). Small mixed crystals were obtained from solutions of 200 mg Ni(amben) and 4 mg Co(amben) in CH_2Cl_2, or in acetone, by slow evaporation of the solvent. These crystals were used as seed crystals for further growth in saturated solutions which were cooled from +60° to −20° within two days.

Nematic matrices. The nematic phases 5, 5A and 7A were purchased from *Merck*, Darmstadt [8]. These *Licristal*® products consist of eutectic mixtures of 4-methoxy-4'-butyloxy-azobenzene/4-methoxy-4-butylazoxybenzene and 4-methoxy-4-ethyloxy-azobenzene/4-methoxy-4-ethylazoxybenzene. Phase 7A contained, additionally, 10% of a nematic ester of undisclosed structure. The nematic temperature ranges are within −5° and +75° for the Phases 5 and 5A and within −10° and +80° for the Phase 7a. These matrices all exhibit a negative dielectric anisotropy ($\varepsilon_{\parallel} - \varepsilon_{\perp} < 0$).

The nematic phases were purged with argon gas. The probes for the EPR. measurements were obtained by adding 1 mg metal complex dissolved in 2 ml CH_2Cl_2 to 0.3 ml nematic phase at RT. The solvent was removed in the Ar stream. The tubes were then sealed under reduced pressure. The resulting nematic phases were probably supersaturated with respect to the metal complexes. They had to be used for EPR. measurements within a few days.

EPR. measurements. All EPR. measurements were made on a *Varian* E-9 spectrometer equipped for X- and Q-band frequencies. The field-frequency calibration was done with the aid of an *AEG*-NMR. probe and a *Systron-Donner* frequency counter. The Q-band frequencies were determined with DPPH as a reference (g = 2.0036). For the Q-band single-crystal measurements, the crystal was mounted on the cavity bottom and aligned on a goniometer. The orientation of the EPR. cavity was determined with a laser mounted on the magnet frame.

The nematic samples were oriented within the cavity at RT. by applying a magnetic field near 7000 G. While maintaining this field, the temperature was lowered quickly to −160° to produce the glass. For orienting the samples in the electric field, a pulsating field of about 50 kV/cm was applied and the samples were cooled with liquid N_2 to preserve the orientation in the glass. The orientation dependence of the EPR. spectra was obtained by rotation of the magnet.

Data treatment. The single-crystal data collected at 30 orientations were refined using the *PARA* [9] computer program. The hyperfine splitting A_x of Co(amben) in the nematic phase was numerically resolved by resolution enhancement [10] [11], using the online *Spectrosystem Varian* 620/L.

Results and Discussion. - Mainly for the purpose of comparison, the Cu(II)-complexes of the same ligands as used for Co(II) were also measured in nematic phases. *Figure 1* shows, as an example, the EPR. spectra of the differently oriented phases containing the complex Cu(acacen). For this complex, magnetic as well as electric fields were used for orientation of the nematic phases. Phase 7A, being a

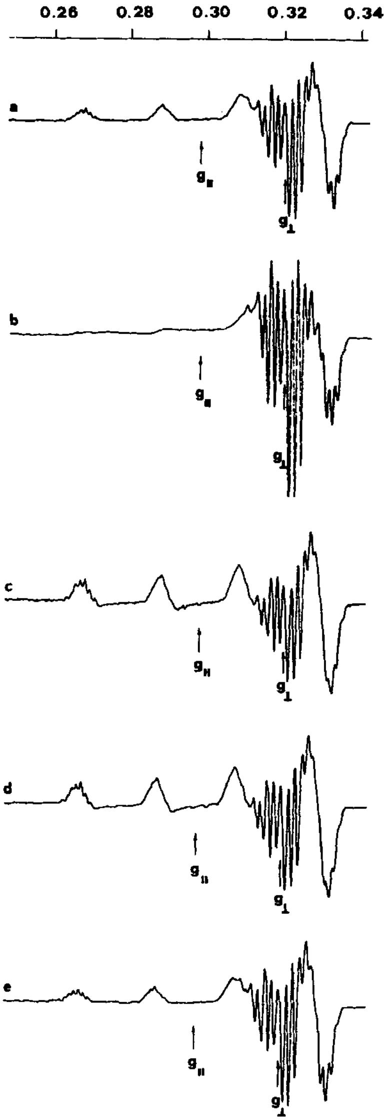

Fig. 1. *EPR. spectra of Cu(acacen) in nematic phase 7A at 77 K, X-band frequency* (a) Non-oriented sample, b) $\vec{H}_{meas}$ parallel to $\vec{H}_{orient}$, c) $\vec{H}_{meas}$ perpendicular to $\vec{H}_{orient}$, d) $\vec{H}_{meas}$ parallel to $\vec{E}_{orient}$, e) $\vec{H}_{meas}$ perpendicular to $\vec{E}_{orient}$)

Table 1. *Experimental and calculated relative intensities of the lines at lowest field for Cu(acacen) in nematic phase 5 (Fig. 1)*

Spectrum	Orientation	Experimental amplitude	Calculated amplitude
a	none	0.0796	0.0796 (Standard)
b	$\vec{H}_{meas} \parallel \vec{H}_{or}$	0.0021	0
c	$\vec{H}_{meas} \perp \vec{H}_{or}$	0.149	∞[a])
d	$\vec{H}_{meas} \parallel \vec{E}_{or}$	0.151	∞[a])
e	$\vec{H}_{meas} \perp \vec{E}_{or}$	0.0723	0.0507

[a]) δ-Line shape.

phase with negative dielectric anisotropy, shows a different pattern when oriented with an electric- as compared to a magnetic field.

Table 1 gives the relative intensities of the lines at the lowest field for differently ordered phases of the same sample. For theoretical reasons, the intensity of the line in the non-oriented sample was normalized to $1/4\pi$ [12]. The calculated values are given for a degree of order $S = 1$. It will be seen that the intensity ratio is strongly dependent on the method of orientation and on the relative orientation of orienting and measuring magnetic and electric fields respectively. The results are in qualitative agreement with what would be expected. The same is true for other Cu(II)-complexes. Resolution of the directional information is even better in the Q-band spectra.

Figure 2 gives Q-band spectra of Cu(amben) in two different orientations of nematic phases.

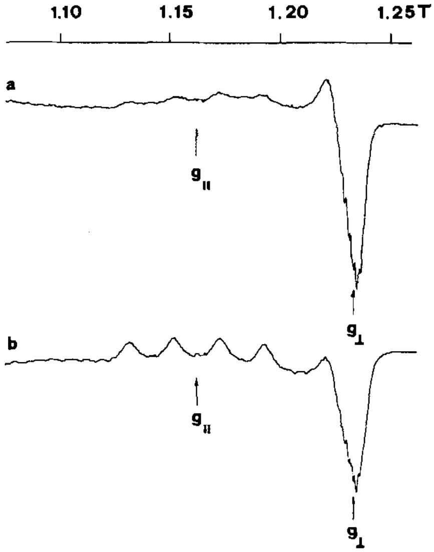

Fig. 2. *EPR. spectra of Cu(amben) in nematic phase 5 at 77 K, Q-band frequency* (a) $\vec{H}_{meas}$ parallel to $\vec{H}_{orient}$, b) $\vec{H}_{meas}$ perpendicular to $\vec{H}_{orient}$)

The EPR. spectra of Co(salen), Co(amben) and Co(acacen) are given in *Figures 3, 4* and *5*. In all cases a strong orientational effect of the nematic phases is observed. The effect of electrical ordering of these phases (negative dielectric anisotropy) is not sufficient to observe in the case Co(II)-complexes significant deviations from non-oriented samples.

In the Cu-complexes, it is obvious that the principal axis corresponding to the large value of the g-tensor ($g_{\|}$) lies perpendicular to the molecular plane. If Cu(acacen) is compared in the orientations $H \| H_{or}$ and $H \perp H_{or}$ with Co(acacen), it is seen that the intensity ratios of the low field to the high field signals change in just the opposite way. The contrary is true for Cu(salen) and Co(salen) and Cu(amben)/Co(amben). Single-crystal measurements [1] show that, for all planar low-spin Co(II)-complexes the x-axes corresponds to the tensor axis with the highest g-value. This behavior can be understood if it is assumed that the 'salen'- and the 'amben'-complexes are oriented with the y-axis along the orientation axis of the nematic phase, and that the 'acacen'-complexes are oriented with their x-axes parallel to it. Contrary to the 'salen'- and 'amben'-complexes, 'acacen'-complexes have not a 'long' molecular axis along y, and it is therefore quite comprehensible that they orient differently. Consequently, nematic phases can be useful in providing unambiguous information about the orientation of the principal

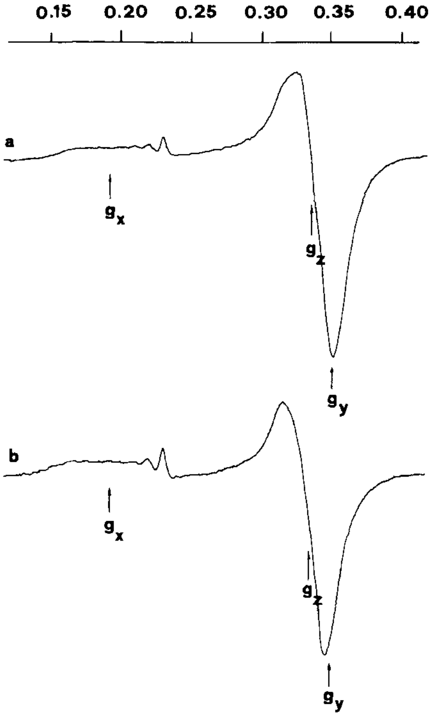

Fig. 3. *EPR. spectra of Co(salen) in nematic phase 5 at 77 K, X-band frequency* (a) $\vec{H}_{meas}$ parallel to $\vec{H}_{orient}$, b) $\vec{H}_{meas}$ perpendicular to $\vec{H}_{orient}$)

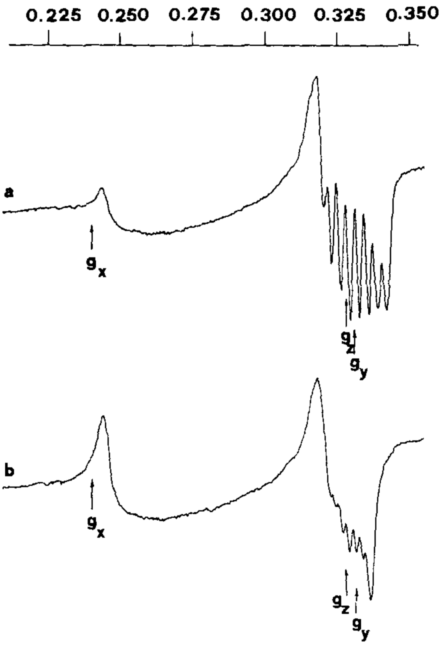

Fig. 4. *EPR. spectra of Co(amben) in nematic phase 7A at 77 K, X-band frequency* (a) $\vec{H}_{meas}$ parallel to $\vec{H}_{orient}$, b) $\vec{H}_{meas}$ perpendicular to $\vec{H}_{orient}$)

axis of the g-tensor only in cases where the moment of inertia has three distinctly different values.

The space group of Co(amben) is P_{nam}, Z=4 [13], with the dimensions a=6.94 Å, b=7.53 Å, c=26.20 Å. The structure of the host crystal Ni(amben) has not been determined by X-ray methods. However, an investigation of the Ni(amben) crystal face angles revealed only minor deviations, using the Co(amben) unit cell dimensions. The identification of the four molecular sites within the unit cell was estimated from Co(5-Cl-amben), where a complete structure is available [13]. The space group of the latter is also P_{nam} with Z=4, and dimensions a=7.097 Å, b=7.658 Å, c=28.37 Å. It seems that all these complexes pack in a very similar way. Therefore, the relation of the crystal morphology and the orientation of the complexes were assumed to be the same in all three cases. This assumption is corroborated by the fact that the g- and A-tensor main axes, as determined by diagonalization with the *PARA* program, are nearly coincident (deviations $<5°$) with the coordinates defined by the molecule. *Table 2* gives the measured EPR. parameters and some literature data.

One of the unusual features of low-spin Co(II)-complexes are their low-lying electronically excited states. It is quite generally accepted that five-coordinate species have a ground state corresponding to a configuration in which the unpaired electron is in a $d_z{}^2$-orbital. This state transforms as $^2A_1$ in C_{2v}-symmetry. In the planar complexes, however, another doublet state, $^2A_2$ with the unpaired electron

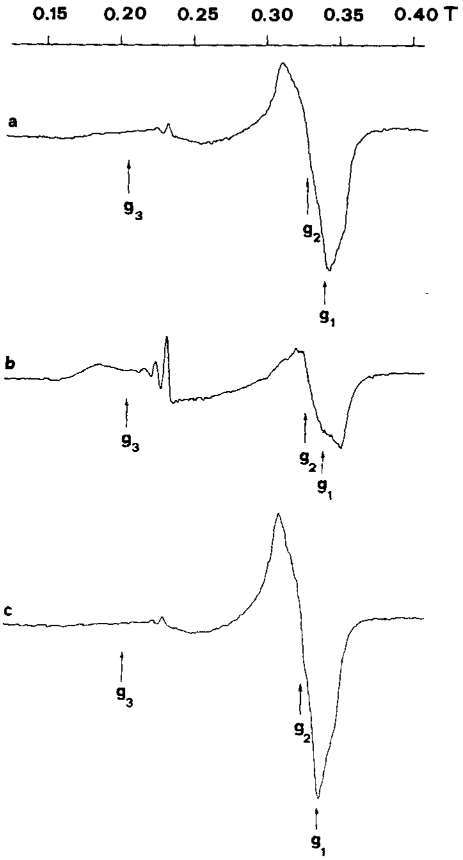

Fig. 5. *EPR. spectra of Co(acacen) in nematic phase 5A at 77 K, X-band frequency* (a) Non-oriented, b) $\vec{H}_{meas}$ parallel to $\vec{H}_{orient}$, c) $\vec{H}_{meas}$ perpendicular to $\vec{H}_{orient}$)

Table 2. *EPR. parameters of several Co(II)-complexes in various environments*

Complex	Medium	g_x	g_y	g_z	$\lvert A_x \rvert$ $10^4 cm^{-1}$	$\lvert A_y \rvert$ $10^4 cm^{-1}$	$\lvert A_z \rvert$ $10^4 cm^{-1}$	Literature
Co(Salen)	Phase 5	3.32±0.06	1.84±0.02	1.93±0.07	155±20	-	-	[a])
Co(Salen)	Ni(Salen) s.c.	3.805±0.005	1.66±0.01	1.74±0.01	291±1	52±26	30±5	[2]
Co(Amben)	Phase 7A	2.73±0.01	1.972±0.001	1.991±0.003	17±4	28±1	21±1	[a])
Co(Amben)	Ni(Amben) s.c.	2.647±0.001	1.976±0.001	2.007±0.001	3.5±1	31±3	21±3	[a])
Co(Amben)	Pyridin/Dioxane	2.65	1.97	2.01	< 10	28	28	[14]
Co(Amben)	Ni(Amben)	2.648	1.971	2.001	< 10	31	27	[14]
Co(Acacen)	Phase 7A	3.16±0.02	1.918±0.006	1.99±0.03	111±7	-	-	[a])
Co(Acacen)	Ni(Acacen)	3.16	1.93	2.01	115.8	37.5	34.5	[15]
Co(Acacen)	nematic	2.928	1.934	2.01	100.3	32.5	32.8	[4]

[a]) This work.

in the d_{yz}-orbital, may become the ground state. Since $^2A_1$ and $^2A_2$ mix under spin-orbit coupling, the EPR. parameters become particularly sensitive to small perturbations near the 'crossing point' of the two states. A complete treatment of the EPR. parameters for this situation has been given elsewhere [1]. It is seen that Co(amben) is a complex with a d_{yz}-ground-state and it has, in fact, the highest lying $^2A_1$ (d_{z^2})-state of all planar low-spin Co(II)-complexes hitherto investigated by EPR. spectroscopy. It can be estimated, that the energy separation $^2A_1/^2A_2$ amounts to $\approx 8.5\ \lambda$ (λ = spin-orbit coupling constant) which corresponds to about 3000-4000 cm^{-1}, depending on the reduction factor of λ. This relatively large separation of the two states, which corresponds to a strong stabilization of the d_{z^2}-orbital must be responsible for the reduced tendency to axial coordination. In nematic phases, where certainly some axial perturbation occurs, the g-shift, as compared to the Ni(amben) single crystal host, is only from 2.647 to 2.73 for the most sensitive parameter, namely g_x. These findings all agree with the fact, that Co(amben) has no oxygen carrying properties, in contrast to CoN_2O_2-complexes in which, through axial coordination, $^2A_1$ (d_{z^2}) can become the ground state.

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