phisch untersucht. Piks traten auf, die den Methylestern der folgenden Säuren entsprachen: Hexansäure, Heptansäure, Octansäure, Nonansäure, Decansäure und Dodecansäure. (Die betreffenden Methylester waren nicht als genuine Bestandteile der Rektalampullenflüssigkeit nachweisbar.) Die eindeutige Identifizierung der Methylester erfolgte auf Grund ihrer Massenspektren, die mit Hilfe einer GC./MS.-Kombination aufgenommen wurden. Der Gas-Chromatograph der Kombination enthielt eine Glas-Trennkapillare; für die Probeneinführung wurde die Technik der Direkteinspritzung verwendet [4] [5]. Alle gefundenen Säuren erwiesen sich im S-Test nach *Hangartner* [6] als biologisch aktiv.

Eine ausführliche Abhandlung über das Spurpheromon von *L. fuliginosus* wird an anderer Stelle erscheinen.

Wir danken Herrn Dr. *H. Kutter* und Herrn Dr. *W. Hangartner* für wertvolle Ratschläge und Diskussionen, Frau *Ch. Wenk* für die geschickte Mitwirkung bei der experimentellen Arbeit und dem *Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung* für die finanzielle Unterstützung.

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90. Electron Paramagnetic Resonance Spectra of planar low-spin Complexes of Cobalt(II) with *Schiff*'s Bases.

I. N, N'-ethylene-bis(salicylideneimine)-cobalt(II)

Preliminary communication

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(28. II. 72)

Summary. The anisotropic EPR. parameters of N, N'-ethylene-bis(salicylideneimine)-cobalt(II), magnetically diluted with the corresponding nickel complex, have been determined from single-crystal measurements. From these data it is concluded that in the cobalt complex d_{yz} and d_{z^2} differ only slightly in energy, the former being the orbital accomodating the unpaired electron in the ground state.

The publication of Electron Paramagnetic Resonance (EPR.) data from *polycrystalline* samples of low-spin *Schiff*'s base complexes of cobalt(II) [1] [2] prompts us to communicate preliminary results of our investigations on magnetically dilute *single crystals* of such a compound.

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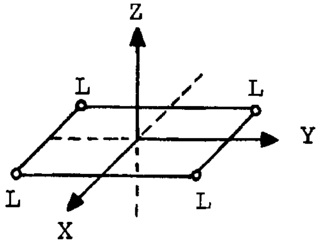
Experimental. – N, N'-ethylene-bis(salicylideneimine)-nickel(II) = Ni(salen), ^{63}Cu(salen)[2]) and Co(salen) were prepared according to methods already described [3]. Magnetically dilute crystals of ^{63}Cu(salen)/Ni(salen) and Co(salen)/Ni(salen) were grown by slow evaporation from acetone solutions containing the diamagnetic Ni(salen) in a 100-fold excess over the paramagnetic species. The pseudohexagonal plates were optically oriented on a two-circle goniometer and then transferred either into a rotating X-Band Cavity V 4533 or a cylindrical Q-Band Cavity. The EPR.-measurements were carried out on a *Varian* E-9 instrument equipped with X- and Q-Band bridges. Accurate *g*-values were measured only in the X-Band, using DPPH as a standard and a *Systron Donner* frequency counter (Modell 1017/1292) for the microwave frequency. Ni(salen)/^{63}Cu(salen) was measured at room temperature, Ni(salen)/Co(salen) at *ca.* 120°K.

A number of low-spin Co^{II} complexes with 4 N or 2 N + 2 O coordinated ligand atoms L show EPR. spectra with the general characteristics: $g_{\parallel} = g_{zz} \approx 2.0$ and $g_{\perp} = g_{xx} \approx g_{yy} \approx 2.2–2.9$ if the coordinate system is chosen as in the Figure, *e.g.* *xy* in the molecular plane. By second-order perturbation methods a ground-state configuration $(d_{xz}d_{yz}d_{x^2-y^2})^6d_{z^2}$ can be deduced unambiguously for these complexes [1]. The same configuration of the ground state is retained in most of these systems if one additional ligand is axially coordinated to the metal [4]. Recent investigations have shown, however, that EPR. spectra of Co^{II}-vitamin B$_{12}$ derivatives are very sensitive to changes in the axial coordination of the complexes [5].



A striking difference of the EPR. parameters is observed in the case of Co(salen) if the spectra are taken either in a coordinating solvent like pyridine, dimethylformamide etc., in the glassy state, or in a polycrystalline sample with the diamagnetic Ni(salen) as host lattice. For coordinating solvents the EPR. parameters indicate a normal ground state, as given above, with the unpaired electron in a d_{z^2}-orbital. The powder spectrum of a Ni(salen)/Co(salen) mixed crystal shows the pattern of nearly axially symmetric systems with $g_{\parallel} = 3.80$ and $g_{\perp} \approx 1.72$. If $g_{\parallel}$ were g_{zz} and if d_{xy} is the highest of the *d*-orbitals (which is generally assumed to be the case for planar transition-metal complexes) no configuration exists which allows for the observed values of the *g*-tensor components.

We therefore measured the EPR. spectrum of Co(salen) in a single crystal of Ni(salen) in order to locate the directions of the principal axes of the *g*-tensor with respect to the complex molecule.

Since the crystal structure of Ni(salen) is still unknown we first measured the corresponding Cu(salen) complex in this host lattice. From a very large number of experiments it is known that in planar Cu^{II}-complexes the direction of the highest *g*-value corresponds to *z* (Fig.). In particular, this has been proven to be the case in the bis-salicylaldimine-Cu^{II} [6], which is very similar to Cu(salen) except for a *trans*

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[2]) ^{63}CuO (min. 98% ^{63}Cu) was obtained from *Oak Ridge National Laboratory*.

configuration within the O_2N_2-ligand system. The measurement of the Cu(salen)/Ni(salen) complexes indicated therefore the directions of the z-axes of the complexes in the crystal.

Ni(salen) crystallizes in the orthorhombic space group *Pbca* with 8 molecules in the unit cell [7]. The molecules are in four magnetically equivalent pairs, giving rise to an EPR. spectrum composed of four sets of lines if the magnetic field is in a general direction. Experimentally, it is found that the direction of $g = 3.80$ in the case of Ni(salen)/Co(salen) is perpendicular to that of $g = g_{\|} = 2.195$ for Ni(salen)/Cu(salen). (For a compilation of the EPR. parameters, see the Table.) This means that $g = 3.80$ is obtained when the magnetic field lies *in* the molecular plane of the complex. From consideration of the possible packing arrangements of the molecules, taking into account the known structure of Co(salen), which has very similar cell dimensions (although a different space group *C2/c* [8]), it is very probable that $g = 3.80 = g_{xx}$ (x bisecting the N–Co–N angle). These findings substantiate the conjecture of *Green et al.*, based on their powder measurements [1]. The two low g-values, which we attribute to g_{yy} and g_{zz} respectively, have been determined from a least-square analysis of the angular dependence of the spectrum. They deviate slightly from the values obtained from the powder measurements [1], which were obtained in a different diamagnetic matrix, namely the chloroform containing Ni(salen)$CHCl_3$. An assignment of the EPR. signals published very recently by ***Busetto et al.*** [9] can definitly be ruled out. Their additional signals at $g_2 = 2.07$ and $g_3 = 1.97$ are most probably due to a 1:1 adduct between Co(salen) and O_2 in low concentration (see the Table).

EPR. parameter of ^{63}Cu(salen)/Ni(salen) and Co(salen)/Ni(salen). Crystals grown from acetone.

Paramagnetic compound in Ni(salen)	g_{zz}	g_{xx}	g_{yy}	A_{zz} [b]	A_{xx} [b]	A_{yy} [b]	Lit.
^{63}Cu(salen)	2.195 ± 0.001	2.043 ± 0.003	2.043 ± 0.003	202 ± 3	39 ± 1	39 ± 1	[a]
Co(salen)	1.74 ± 0.01	3.805 ± 0.005	1.66 ± 0.01	30 ± 5	291 ± 1	52 ± 26	[a]
	1.76	3.80	1.72	16	292	24	[1]
	2.07	3.80	1.97	–	284	20	[9]

[a] this work. [b] $\times 10^4$ cm^{-1}.

Since perturbation calculations are not feasible in view of the large deviation of g_{xx} from the free-electron value, we have diagonalized the spin-orbit coupling matrix directly for several assumed ground-state configurations. Together with the information obtained from the ^{59}Co ($I = 7/2$) hyperfine tensor, the only possible ground state that emerges from the calculation is $(d_{xz}d_{x^2-y^2}d_{z^2})^6 d_{yz}$. The first excited state corresponds to $(d_{xz}d_{x^2-y^2}d_{yz})^6 d_{z^2}$ and lies only at $\Delta E = 2.9 \cdot \zeta$ above the ground state (ζ = spin-orbit coupling constant of $Co^{II} \approx 0.5$ kK). The large deviation of the g-tensor components from 2.0 is due to mixing of these two close-lying states under the influence of spin-orbit coupling.

Details of the calculations, implications on the chemistry of these complexes (O_2-carrier properties) and further single-crystal investigations of Co^{II}-complexes will be published in forthcoming papers.

We thank Dr. *H. B. Bürgi*, ETH Zurich, for valuable discussions concerning the crystal structures. This work was supported by the *Swiss National Foundation for Scientific Research* (Project No. 2.466.71). We wish to thank *CIBA-GEIGY Ltd.*, Basle, for financial support.

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91. Metal Complexes of Free Radicals. Part III: Triplet State ESR. of Magnesium(glyoxal-bis-N-*t*-butylimine)$_2$

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(12. III. 73)

Summary. The preparation and the ESR. spectra of a 1:2 complex of Mg^{2+} with the radical anion of glyoxal-bis-N-*t*-butylimine (GLI) are reported. The ESR. spectrum of $Mg(GLIR)_2$ in 2-methyl-tetrahydrofuran at –165° is interpreted as due to a randomly oriented molecular triplet. The magnetic dipole-dipole interaction of the two unpaired electrons in $Mg(GLIR)_2$ can be interpreted by an axially symmetric fine structure term with $D = 0.021\ cm^{-1}$.

In previous communications we have reported on the formation of free radical complexes of closed shell metal ions of the type $M(GLIR)^+$, M(GLIR)X and $M(GLIR)X_2^-$, where GLIR is the radical anion of glyoxal-bis-N-*t*-butylimine and $X = Cl^-, Br^-, I^-, CN^-$ or NCS^- [1].

In the present paper we report on the isolation and the ESR. spectra of $Mg(GLIR)_2$, a complex with two radical ligands per metal ion, which was obtained as a crystalline solid when we attempted to prepare solid Mg(GLIR)Cl. The solution from which $Mg(GLIR)_2$ could be crystallized contained, at room temperature, only Mg(GLIR)Cl as paramagnetic species judging from its known ESR. spectrum [2]. The formation of the crystalline solid can therefore be formulated according to (1):

$$2\,Mg(GLIR)Cl \rightarrow Mg(GLIR)_2 + MgCl_2 \qquad (1)$$

Dissolution of the solid $Mg(GLIR)_2$ in dimethoxyethane (DME) or 2-methyl-tetrahydrofuran (MTHF) gave a single line ESR. spectrum ($g = 2.0036$; peak to peak

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