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8. Metal Complexes of Free Radicals. Part II: Identification and Structures of Radical Complexes of Alkaline Earth Metals and Zinc[1]

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(4. XI. 71)

Summary. The formation of chelate complexes between free radicals and closed-shell metal ions is observed by ESR. spectroscopy. High resolution spectra of 1:1 complexes formed between the radical anion of glyoxal-bis-(N-*t*-butylimine) (GLIR) and Mg^{2+}, Ca^{2+} and Zn^{2+} are completely analysed. The complexes formed in dimethoxyethane or tetrahydrofuran solutions are $Ca(GLIR)^+$, Mg(GLIR)X, Zn (GLIR)X and $Zn(GLIR)Y_2^-$, where $X = Cl^-, Br^-, I^-$, and $Y = CN^-, NCS^-$. The formation of the heterometallic, binuclear cyanide-bridged complex $Zn(GLIR)Fe(CN)_6^{3-}$ is also described. Isotropic coupling constants are given for protons and ^{14}N in GLIR as well as for the metal nuclei and magnetic nuclei in the groups X and Y. Stabilities, structures and ESR. parameters of these radical complexes are discussed.

Complexes of chelating ligands like α,α'-dipyridyl with metals in unusually low formal oxidation states have been studied extensively by *Herzog* and his coworkers [2]. Many of these complexes can undoubtedly be considered as complexes of the radical anion ligand with the metal in a normal oxidation state [2] [3]. These complexes contain however more than one radical ligand per metal atom and their magnetic and spectroscopic behaviour is complicated by interactions between the radical ligands [4]. We have therefore attempted to prepare complex species with one radical ligand per metal ion only, in order to have the possibility of applying high resolution ESR. spectroscopy to study the structure and bonding in such complexes. Furthermore, for these studies ligands with a smaller number of non-equivalent magnetic nuclei than those of the α,α'-dipyridyl are more suitable, owing to the much simpler ESR. spectra of the radical anions.

Complex formation of closed-shell metal ions with free radicals has been observed in solution with semiquinones and nitroxides as the radical ligands. *Eaton* [5] and

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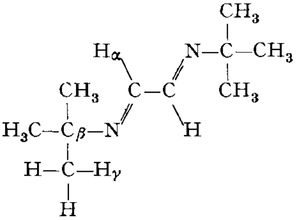
Hoffman [6] were able to demonstrate the existence of monomeric complex species with a doublet ground state, which showed a hyperfine interaction with the metal nucleus in the ESR. spectra. Complexes of Zn and Cd were further reported with a flavin radical ligand, which served as model systems for reactions of flavo-enzymes. Free radical complexes may also play an important rôle as intermediates in oxidation-reduction reactions between Cr^{2+} and certain Co^{III} complexes [7].

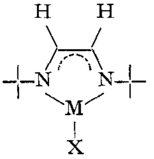
In complexes with a chelating diimine radical we have observed the occurrence of hyperfine structures of the metal and of nuclei located in ligands other than the original free radical from which the complex was formed [1]. It is this 'delocalization' of the unpaired electron over the whole complex species which yields detailed information about compositions and structures of many of these complexes. Very recently an observation of a similar hyperfine interaction of halide ions was reported with metalloporphyrin cation radicals [8].

Transition metal complexes with diimine ligands were first prepared with iron (II) by *Krumholz* [9] and were recently investigated by *tom Dieck* [10]. In most of these complexes the diimine exists in its unreduced form as a ligand. Strong π-back bonding properties have been attributed to this type of ligand.

In this paper we report on complexes containing the radical anion of glyoxal-bis-(N-*t*-butylimine) (GLIR)[3] as a chelating radical ligand. The parent neutral molecule



GLI can be reduced by potassium to the mono-anion in dimethoxyethane (DME) or tetrahydrofuran (THF). The configuration of GLIR with the lowest energy is most probably *trans, trans, trans,* in the uncomplexed ligand [10]. As will be shown, a symmetric structure is obtained upon complex formation, indicating a rotation of the ion about the central C–C bond. The configuration of the radical is therefore *trans, cis, trans,* in the complexes M(GLIR)X, where X denotes collectively other



ligands. Complex formation is accomplished by saturating dilute solutions of the potassium salt of GLIR with various binary and co-ordination compounds of d^0 and d^{10} metal ions. Under these conditions only complexes with a ratio M:GLIR = 1:1 are obtained. 1:1 complexes were also observed with the anions of α,α'-dipyridyl

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[3] The unreduced diimine will be abbreviated as GLI, and the radical anion as GLIR.

and *o*-phenanthroline. Owing to the higher number of non-equivalent magnetic nuclei, much more complicated ESR. spectra are observed than in the case of M(GLIR)X. Full analyses of these spectra are less straightforward and are not yet completed.

Experimental section

All substances were of reagent grade. Enriched isotopes were obtained from *Oak Ridge* (^{25}Mg, ^{67}Zn); Na[^{13}C]N from *Merck, Sharp & Dohme, Canada, Limited.*

Preparations. – *Glyoxal-bis-(N-t-butylimine) (GLI)*: Prepared from 5 ml 30% glyoxal aqueous solution (*Fluka*), 5 ml H_2O and 5 ml *t*-butylamine (*Fluka*). The white precipitate was filtered and recristallized from EtOH/H_2O ratio 1:1. The diimine was sublimed at 50°/10^{-2} Torr; m.p.: 52–53°; PMR. ($CDCl_3$): 1.27 (*s*, 18H), 7.95 (*s*, 2H).

$C_{10}H_{20}N_2$ Calc. C 71.62 H 11.9 N 16.66% Found C 71.12 H 12.11 N 16.50%

Anhydrous magnesium chloride, magnesium bromide, calcium chloride, calcium bromide, calcium iodide, zinc chloride, zinc bromide and zinc iodide were synthesized from commercial products by standard procedures [11].

^{25}Mg chloride: 49.5 mg ^{25}MgO (*Oak Ridge*; 99.2% ^{25}Mg) were treated with HCl-gas at 300° for $^1/_2$ h. The $^{25}MgCl_2$ was melted and then transferred directly into the ESR. tube (see Fig. 1, arm b) under a stream of argon.

^{67}Zn chloride: 37 mg ^{67}ZnO (*Oak Ridge*; 89.55% ^{67}Zn) were treated with HCl-gas at 300° for 1 h. The $^{67}ZnCl_2$ was melted and then transferred directly into the ESR. tube (see Fig. 1, arm b).

Zinc cyanide was prepared from commercial $ZnSO_4 \cdot 7\,H_2O$ and a stoechiometric amount KCN (*Merck*) [11]. The precipitate was filtered, washed and dried at 110°/10^{-2} Torr during 24 h.

Zinc cyanide, Zn([^{13}C]N)$_2$ was synthesized from $ZnSO_4 \cdot 7\,H_2O$ and a stoechiometric quantity of sodium cyanide-[^{13}C] (13 atom% ^{13}C, *Merck, Sharp & Dohme of Canada*). The precipitate was filtered, washed and dried at 110°/10^{-2} Torr during 12 h.

Sodium tetracyanozincate was prepared by adding to a suspension of $Zn(CN)_2$ in water a solution containing 2 equivalents of NaCN. Water was removed under reduced pressure and the crystals dried at 110°/10^{-2} Torr during 24 h.

Zinc thiocyanate was prepared from $Ba(NCS)_2$ [12] and $ZnSO_4 \cdot 7\,H_2O$ by the method of *Ullmann* [13]. The precipitate was filtered and dried at 50°/10^{-2} Torr during 48 h.

Zinc hexacyanoferrate(II): $K_4Fe(CN)_6$ was treated with HCl in an ethereal solution [11]. The etherate of $H_4Fe(CN)_6$ was neutralized with a solution of Na_2CO_3 in order to obtain the sodium salt [14]. With an excess of $ZnSO_4 \cdot 7\,H_2O$ the precipitate of $Zn_2Fe(CN)_6$ obtained [14] was filtered, washed and dried at 90–95°/10^{-2} Torr during 3 h.

Zinc hexacyanocobaltate(III) was prepared by neutralizing a suspension of $ZnCO_3$ with a equimolar quantity of $H_3Co(CN)_6$, both synthesized according to *Brauer* [11]. The precipitate was filtered, washed with EtOH, dried at 100°/10^{-2} Torr during 24 h.

Radical complexes. – All operations were carried out under strictly anaerobic and anhydrous conditions. Solvents were distilled over $LiAlH_4$ and stored in a vessel connected to the vacuum line. Solutions of the radical complexes were prepared in an apparatus shown in Fig. 1. First GLI was reduced to GLIR in the sealed left hand side compartment of the apparatus by freshly distilled potassium. The formation of the radical could be observed by monitoring the ESR. spectrum of its solution in tube a. The anhydrous metal compounds were transferred under a stream of argon into tube b. Solvent was distilled into the right hand side compartment after which this compartment was also sealed. A saturated solution of the metal compound was obtained by shaking the whole apparatus for several minutes. After breaking the seal at c, followed by a transfer of part of the solution containing the radical, the complex is formed immediately as shown by the change of colour of the solution. The ESR. spectrum of the solution was then recorded using tube d. Changes of concentrations were accomplished by internal distillation of solvent to suitable parts of the apparatus. Concentrations were usually lowered until no further increase in resolution was obtained. Absolute concentration determinations were not attempted.

ESR. spectra were recorded on a *Varian* E-9 instrument, equipped with a 100 kHz and a low frequency modulation unit, a standard variable temperature accessory and a *Systron Donner*

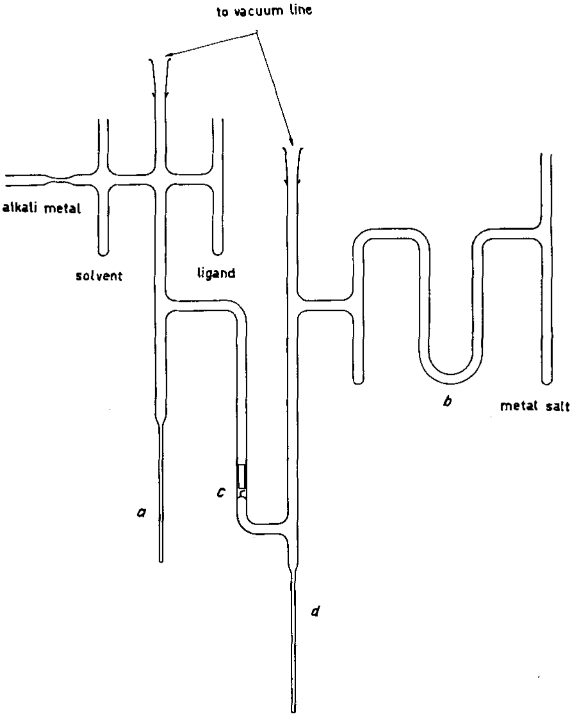

Fig. 1. *All-glass apparatus for the preparation of the radical complexes*

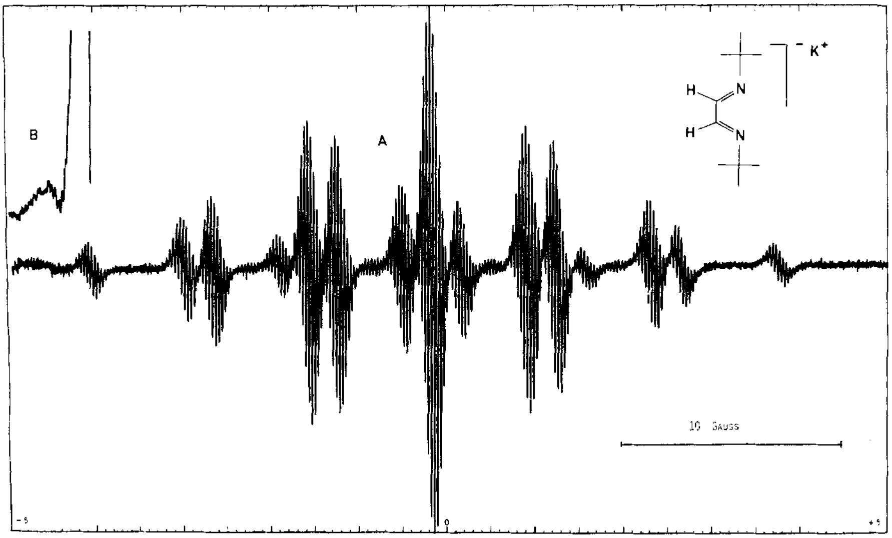

Fig. 2. *ESR. spectrum of free GLIR. Trace B shows the outermost* ^{13}C*-satellites*

frequency counter (Model 1017/1292). All spectra were recorded at X-band frequencies. g-values were measured relative to diphenylpicrylhydrazyl (DPPH) ($g = 2{,}0036$) which was attached to the sample tube by a small piece of scotch tape.

Results[4]. – *GLIR*: Upon reduction of GLI with potassium a brown-yellow solution was obtained. This solution yielded an ESR. spectrum, shown in Fig. 2.

ESR. Parameters of GLIR and its radical complexes

Coupling constants (in Gauss) ±3%, g-values ±0,0002

Complex		$a_{H\alpha}$	a_N	$a_{H\gamma}$	a_X	a_M	g
I	GLIR	4.3	5.6	0.15	–	–	2,0035
II	Mg(GLIR)Cl	5.3	5.3	0.10	Cl[a]: 0,73	u[b]	2,0033
III	^{25}Mg(GLIR)Cl	5.3	5.3	0.10	Cl[a]: 0,73	^{25}Mg: 0,96	2,0033
IV	Mg(GLIR)Br	5.4	5.4	u[b]	Br[a]: 4,6	u[b]	2,0033
V	Ca(GLIR)$^+$	5.0	5.5	0.05[c]	–	u[b]	2,0032
VI	Zn(GLIR)Cl	5.6	5.6	u[b]	Cl[a]: 0,58	^{67}Zn: 4,4	2,0024
VII	^{67}Zn(GLIR)Cl	5.6	5.6	u[b]	Cl[a]: 0,58	^{67}Zn: 4,4	2,0024
VIII	Zn(GLIR)Br	5.5	5.5	u[b]	Br[a]: 3,3	^{67}Zn: 4,3	2,0021
IX	Zn(GLIR)I	5.6	5.6	u[b]	^{127}J: 4,5	u[b]	2,0018
X	Zn(GLIR)(CN)$_2^-$	5.1	6.1	0.09	–	^{67}Zn: 4,3	2,0026
XI	Zn(GLIR)(^{13}CN)$_2^-$	5.1	6.1	0.09	^{13}C: 4,9	^{67}Zn: 4,3	2,0026
XII	Zn(GLIR)(NCS)$_2^-$	5.4	5.9	0.07	^{14}N: 1,25	^{67}Zn: 4,6	u
XIII	Zn(GLIR)NCFe(CN)$_5^{3-}$	4.3	5.6	0.15	^{14}N: 1,45	–	u

[a] Average value for the two isotopes.
[b] u: not observed.
[c] Not completely resolved.

A similar but less resolved spectrum has been reported for this radical anion [10]. Out of the theoretical 19 *hf*-components of each line, 11 have been detected with the correct intensity ratios for 18 equivalent protons. The relative intensities of the weak satellites correspond to two pairs of equivalent ^{13}C-nuclei. The absence of any further *hf*-structure, with the exception of those for the 2 equivalent protons, the two equivalent ^{14}N-nuclei, the 18 equivalent protons and the two pairs of ^{13}C-nuclei, is a strong indication that the radical anion forms no complex with potassium in this solution. Formation of the radical anion was not observed when sodium was used as a reducing agent.

Magnesium complexes. – *Mg(GLIR)Cl*: Upon mixing the solution containing the radical anion with a saturated solution of anhydrous magnesium chloride a dramatic change of the ESR. spectrum is observed [1]. The spectrum can be interpreted by assuming the formation of the neutral complex Mg(GLIR)Cl. The unambiguous proof for the existence of a magnesium complex was obtained by preparing a complex containing ^{25}Mg ($I = 5/2$) enriched to 99.2%. In this case a further splitting due to the metal nucleus is observed (Fig. 3).

The preparation of Mg(GLIR)Cl was also achieved by the direct reaction of magnesium metal with GLI in a DME solution saturated with $MgCl_2$:

$$\mathrm{Mg} + \mathrm{GLI} + \mathrm{MgCl_2} \longrightarrow 2\mathrm{Mg(GLIR)Cl}$$

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[4] All coupling constants and the g-values are given in the Table.

This heterogeneous reaction proceeds slowly at room temperature. Vibration of the reaction vessel accelerates the reaction markedly. An identical spectrum to the one obtained by the usual procedure was obtained after ca. 12 h. The presence of $MgCl_2$ is essential for this reaction, as in its absence no ESR. signal was observed, even after extended periods.

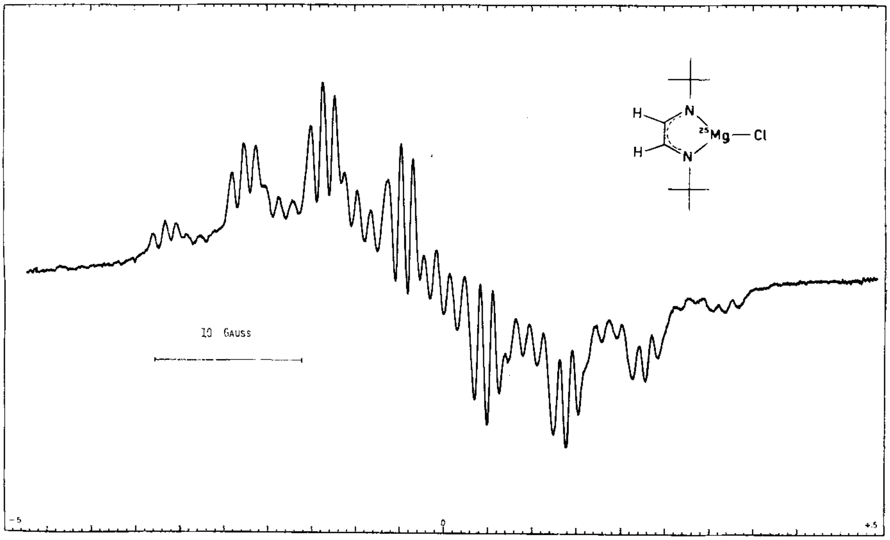

Fig. 3. *ESR. spectrum of* ^{25}*Mg(GLIR)Cl* (99,2% ^{25}Mg)

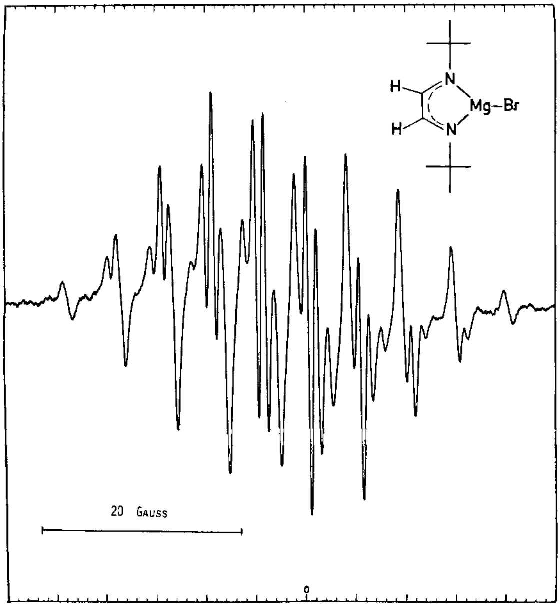

Fig. 4. *ESR. spectrum of Mg(GLIR)Br* (natural Mg)

Mg(GLIR)Br: The ESR. spectrum (Fig. 4) proves the formation of an analogous complex as in the case of the chloride. The amplitude ratio of the two outermost lines of ca. 1:2 is a result of the isotopic composition of natural Br. The superposition of the two lines yields for the two inner lines of the quartet a narrower signal with larger amplitude than for the two outer lines. This behaviour can easily be observed in the case of the analogous zinc complex, where the separation of the individual signals is better (see arrows in Fig. 8).

Calcium complexes. – Ca(GLIR)$^+$: Identical spectra (Fig. 5) were obtained from the radical complexes formed with calcium chloride, bromide and iodide. Even under high resolution conditions no splitting due to the halide nuclei was observed. We conclude therefore that the halide ions do not co-ordinate to the calcium. A remarkably small splitting of 50 mG was resolved (Fig. 5) when the low frequency modulation (10 kHz) was used. We attribute this splitting to the γ-protons of GLIR. The change of the coupling constants $a_{H\alpha}$ and a_N in these spectra compared to GLIR proves the formation of a complex species.

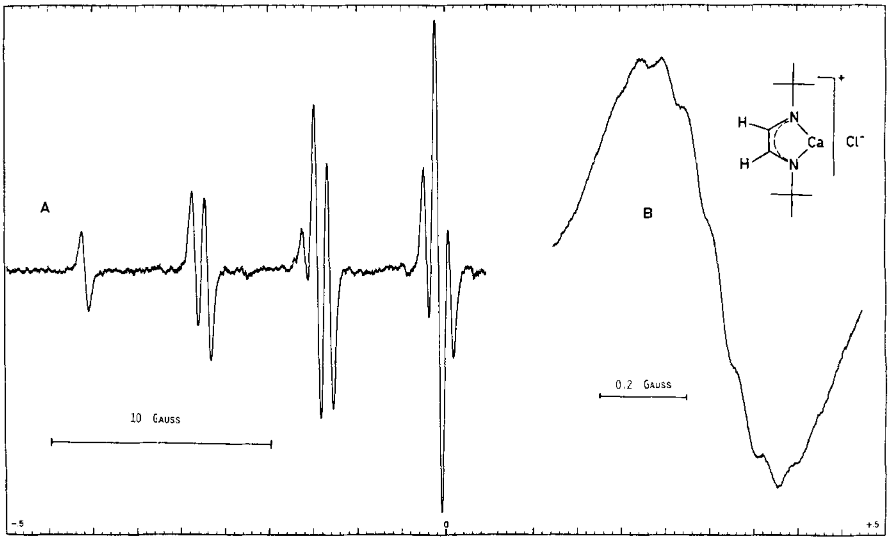

Fig. 5. *ESR. spectrum of Ca(GLIR)$^+$. Trace B shows the Hγ-splitting*

Zinc complexes. With zinc as the central metal ion an extended series of different complexes were investigated. Zinc is the most suitable of the presently investigated series of metals for this purpose, since the preparation of strictly anhydrous salts of zinc with various anions is comparatively simple.

In some cases transient spectra, which do not correspond to the complexes discussed below, have been observed immediately after mixing the solutions. These processes are presently under investigation and we report here only on the radial complexes in equilibrium solutions.

Zn(GLIR)Cl: The ESR. spectrum of the equilibrium solution (Fig. 6) consists, as in the case of the analogous magnesium complex, of seven quartets indicating clearly the co-ordination of one chloride in the radical complex. The spectrum was hardly affected by a temperature change (–60° to +30°) nor upon addition of tetra-*n*-propylammonium chloride to the solution. Weak satellites were observed and are shown in Fig. 6 with an amplification of 100 times stronger than that of the main spectrum. The origin of these satellites was attributed to the naturally abundant isotope ^{67}Zn ($I = 5/2$, 4.11%). This was verified by using enriched (89.5%) ^{67}Zn (Fig. 7), which yielded the same coupling constants as those of the weak satellites.

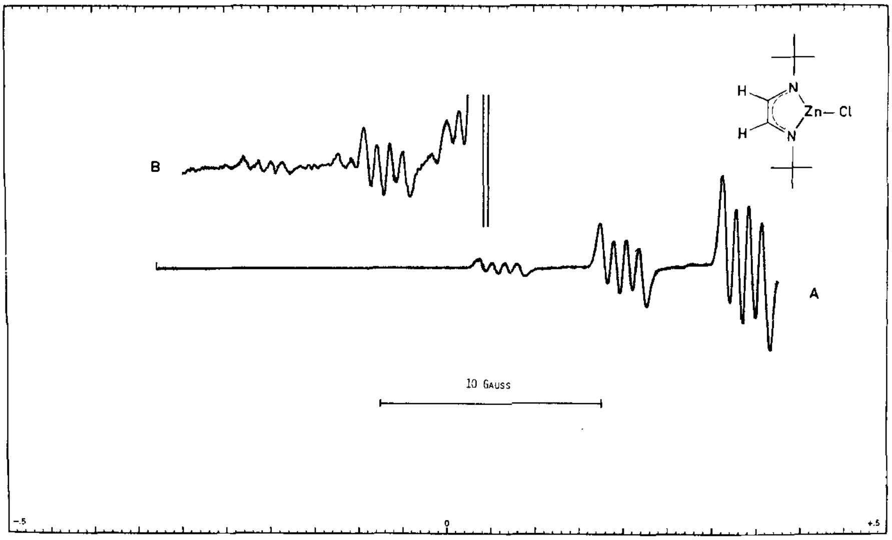

Fig. 6. *ESR. spectrum of Zn(GLIR)Cl. B:* (receiver gain × 100) ^{67}*Zn-satellites of natural Zn* ($I = 5/2$, 4,11%)

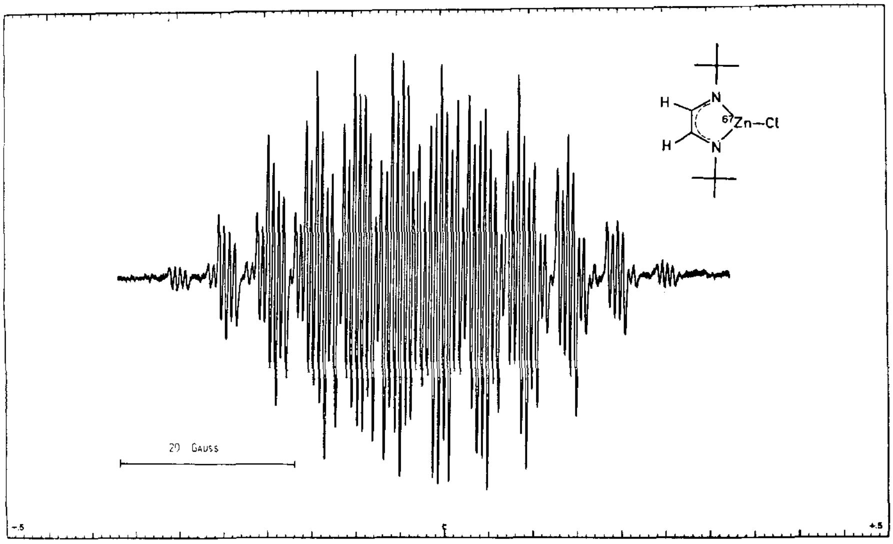

Fig. 7. *ESR. spectrum of* ^{67}*Zn(GLIR)Cl* (89,5% ^{67}Zn)

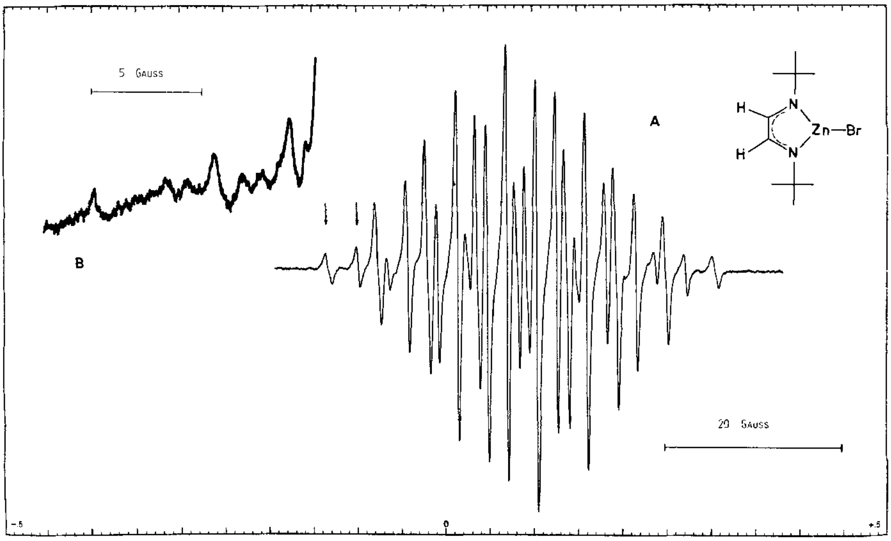

Fig. 8. *ESR. spectrum of Zn(GLIR)Br. B:* (receiver gain ca. × 100) ^{67}*Zn-satellites of natural Zn*

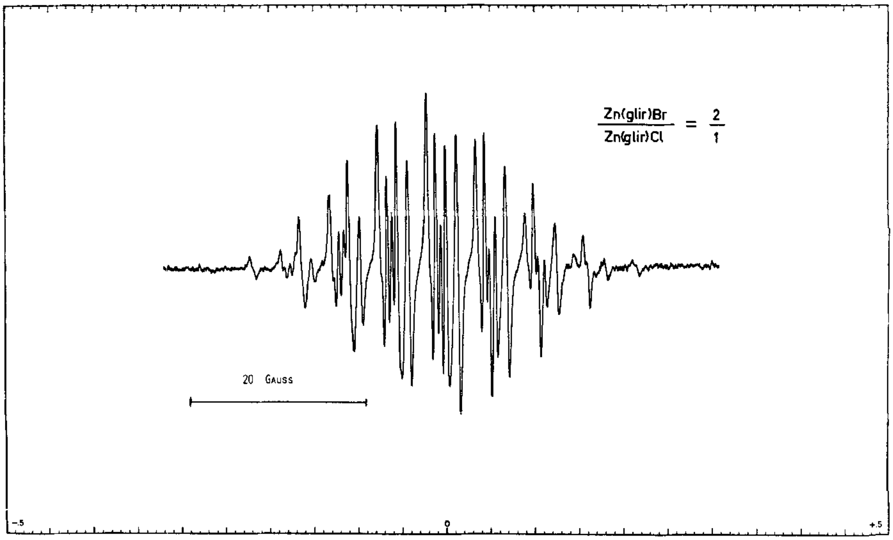

Fig. 9. *ESR. spectrum of a solution saturated with* $ZnCl_2$ *and* $ZnBr_2$

Zn(GLIR)Br: The assignment in this case (Fig. 8) follows the same lines as that for the chloro complex. The coupling constant with ^{67}Zn was in this case solely determined from the weak satellites.

An attempt was made to compare the relative stabilities of Zn(GLIR)Cl and Zn(GLIR)Br by saturating the solution simultaneously with $ZnCl_2$ and $ZnBr_2$. The observed spectrum (Fig. 9) represents a superposition of the signals of the bromo and those of the chloro complexes with an intensity ratio of ca. 2:1.

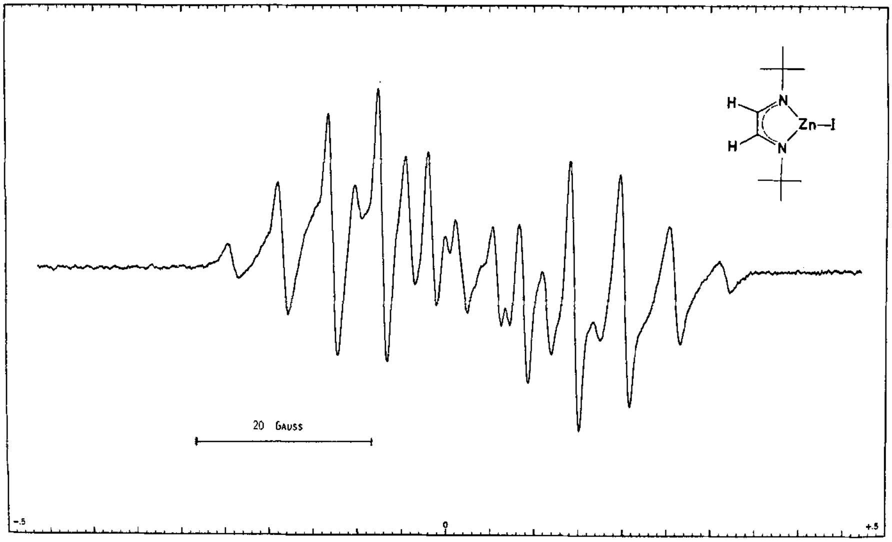

Fig. 10. *ESR. spectrum of Zn(GLIR)I*

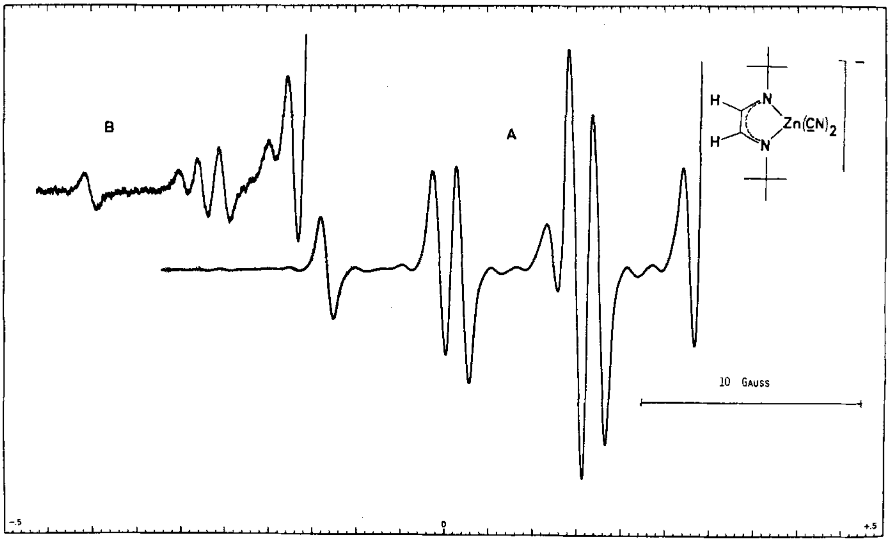

Fig. 11. *ESR. spectrum of Zn(GLIR)(CN)$_2^-$. B:* (receiver gain × 50) *^{67}Zn-satellites of natural Zn*

Zn(GLIR)I: The ESR. spectrum (Fig. 10) shows the coupling with one iodine-nucleus. The ^{67}Zn-coupling was not observable in this case, due to the larger line-widths.

Zn(GLIR) $(CN)_2^-$: The existence of a complex of this stoechiometry was proved by the use of ^{13}C-enriched cyanide. Fig. 11 and 12 show the spectra of the natural and the enriched complex. The relative intensities can only be explained if a coupling with two cyanide ions is assumed. From the line-width an upper limit of 0.1 G can be given for the coupling constants with the nitrogen of the cyanide group. The ^{67}Zn-coupling was determined from the weak satellites. The use of $Na_2Zn(CN)_4$ as starting material instead of $Zn(CN)_2$ yielded identical spectra.

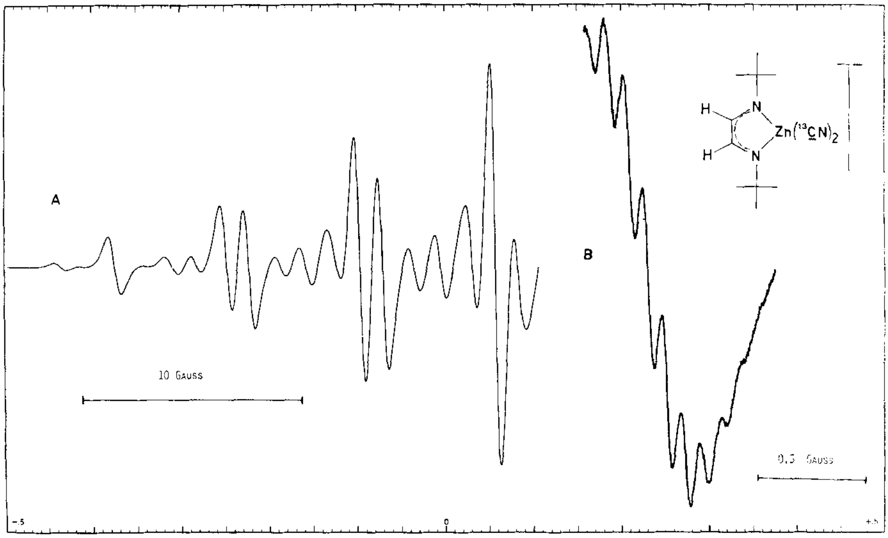

Fig. 12. *ESR. spectrum of ^{13}CN-enriched Zn(GLIR)(CN)$_2$$^-$. B: Hy-splitting*

Zn(GLIR) (NCS)$_2$$^-$: As in the case of the cyano complex, a co-ordination of two anions was found for the thiocyanate ion (Fig. 13). The quintet structure is due to the splitting of two equivalent ^{14}N-nuclei. The existence of the complex and at the same

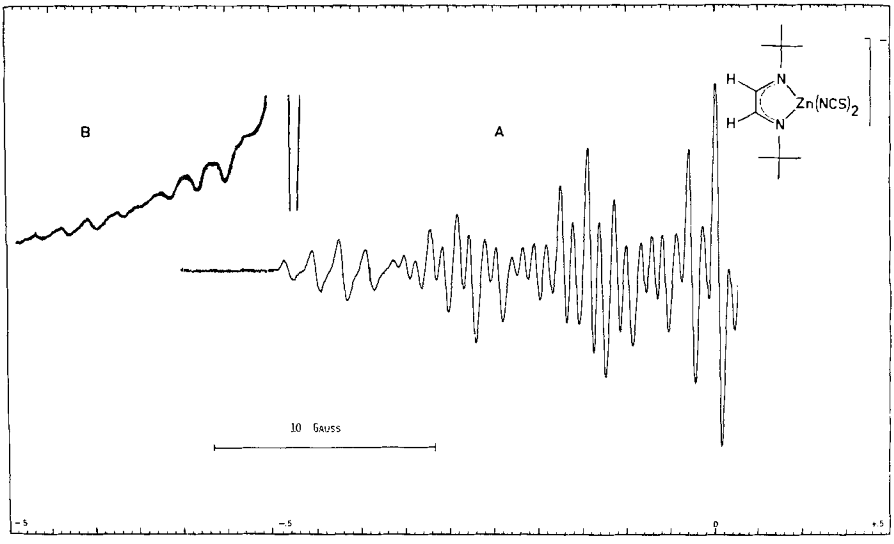

Fig. 13. *ESR. spectrum of Zn(GLIR)(NCS)$_2$$^-$. B*: (receiver gain ca. × 100) *^{67}Zn-satellites of natural Zn*

time the ^{67}Zn-coupling was established again by the observation of the weak satellites. The use of thiocyanate enriched in ^{13}C produces no additional hyperfine splitting.

Zn(GLIR)$(NCFe(CN)_5)^{3-}$: This complex was prepared from $Zn_2Fe(CN)_6$ and the radical anion. The triplet structure (Fig. 14) reveals the formation of a bridged heterometallic binuclear complex with one cyanide being co-ordinated *via* nitrogen to zinc and *via* carbon to iron. This species is not as stable as the other complexes at room temperature; the spectrum decayed completely after a few hours. An attempt to produce an analogous species with $Co(CN)_6^{3-}$ failed: Upon mixing the two solutions the colour changed immediately to black-brown and no ESR. signal was observed.

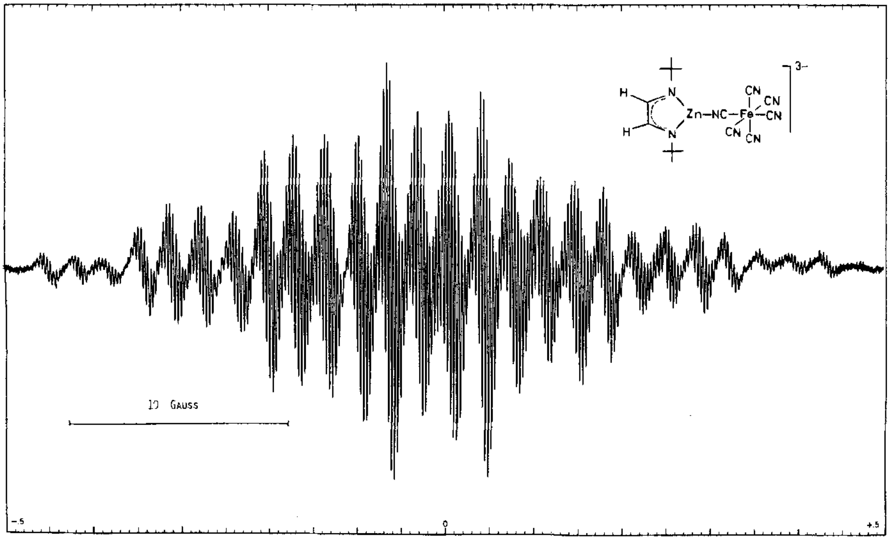

Fig. 14. *ESR. spectrum of Zn(GLIR)*$NCFe(CN)_5^{3-}$

Discussion. – a) *Stability.* Under the present conditions the complex formation (1) is always quantitative within the sensitivity limits of the applied method, *i.e.* in

$$\mathrm{GLIR} + \mathrm{MX_2} \longrightarrow \mathrm{M(GLIR)X_n} + (2\text{-}n)\mathrm{X} \qquad (1)$$

no case an ESR. signal due to free GLIR was observed in equilibrium solutions. Stability constants for the formation reaction are not yet available, since absolute concentrations are unknown. The relative stabilities of Zn(GLIR)Cl and Zn(GLIR)Br were found to be almost equal, both complexes being formed in similar amounts in the presence of $ZnCl_2$ and $ZnBr_2$.

An increase of the chloride activity by saturating the solution with tetra-*n*-propylammonium chloride did not result in the formation of a complex with two co-ordinated chloride ligands. It seems that the ionic radius of chloride is too big to allow for the formation of a complex with two co-ordinated chloride ions similar to those observed with cyanide and thiocyanate.

The reaction of magnesium metal with the unreduced diimine to the radical complex reveals the thermodynamic stability towards a possible decomposition reaction (2), indicating a considerable stabilization of the diimine radical upon complex formation. Likewise this stabilization has been observed by polarographic

$$2M(GLIR)X \longrightarrow M + GLIR + MX_2 \qquad (2)$$

reduction of co-ordinated and unco-ordinated GLI [15]. Preliminary experiments with cadmium compounds indicate however that GLIR reduces cadmium to the metal according to equation (2).

Most solutions containing the radical complexes are stable for several days in the complete absence of oxygen at room temperature and can be kept at -18°C indefinitly.

Only complex XIII decays completely at room temperature after a period of 24 h. This might be connected with a ligand exchange reaction on Fe^{II} and a subsequent formation of an unidentified iron complex.

b) *Structure.* The equivalence of the two nitrogen and the two H^{α} nuclei in all these complexes proves the formation of a chelate complex between GLIR and the metal. In the case of the calcium complex, halide ions do not co-ordinate to the $Ca(GLIR)^+$ complex unit whose co-ordination sphere is probably completed by solvent molecules. The ability of magnesium to bind chloride and bromide can be understood as a consequence of the smaller ionic radius compared to calcium, which enhances the electrostatic attraction between the metal and the halide ions. The structure of the Mg(GLIR)X and of the analogous zinc complexes is probably either planar trico-ordinated or trigonal bipyramidal with two solvent molecules occupying the axial positions. Other structures cannot be ruled out definitely, since the co-ordination of solvent molecules is not directly observable by ESR. spectroscopy. The complete identity of spectra observed in different solvents (DME or THF) shows however, that co-ordination of solvent molecules plays not an important role. The two complexes $Zn(GLIR)Y_2$ ($Y = CN$, NCS) have almost certainly tetrahedral structures, an alternative square planar or octahedral structure (with two co-ordinated solvent molecules) being excluded for steric reasons because of the bulky *t*-butyl groups. The ambidentate thiocyanate is co-ordinated through its nitrogen atom, as the coupling with this nucleus shows. The observation of the hyperfine interaction with the halides and other ligand groups co-ordinated to the metal allows for a much more detailed elucidation of the structures of the radical complexes compared to the radical complexes with semiquinones and nitroxyl radicals [5] [6]. Neither of these complexes yield additional hyperfine structure from other ligands co-ordinated to the metal. The composition of the first co-ordination sphere is therefore not known in these cases.

c) *ESR. spectra.* The ESR. spectrum of GLIR is the one expected for this 4-center π-radical. An HMO-calculation[5]), using a heteroparameter $h_N = 0{,}5$ [17] yields π-spin densities of $\varrho_{C\alpha} = 0{,}189$ and $\varrho_N = 0{,}310$, respectively. The resultant Q_{C-H} value of 22,8 G is in the usual range for a planar $>$C–H fragment. The nitrogen coupling constant cannot be represented by a single parameter equation similar to the *McConnell* equation for the proton splittings [18]. Parameters for a *Karplus-Fraenkel* type

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[5]) The calculation was done by diagonalization of the explicite *Hückel* matrix with $h_N = 0.5$ and $k_{CN} = 1.0$ [16].

equation, where spin polarization through spin density on adjacent atoms is taken into account, are not known for this particular case [19]. Of greater interest than the absolute values of the splitting constant are in the present case their variations upon complex formation.

^{13}C-coupling is clearly resolved for two pairs of equivalent carbon atoms. The coupling constants are 3,8 and 3,0 G respectively. The assignment of these coupling constants to C^{α} and C^{β} is not possible on the basis of our experimental results, since both satellites have the same intensity. In some of the radical complexes the ^{13}C satellites were also observed with coupling constants of about 3,0 G for both positions, yielding therefore one single line with a doubled intensity.

The similarity of the values observed for the coupling constants $a_{H\alpha}$ and a_N, *i.e.* the magnetic nuclei of the diimine, in the free radical and in the complexes leaves no doubt as to the existence of the diimine as radical anion in the complexes. Little variation of spin density distribution in the ligand was also reported for the flavin radical complexes [20]. A rather unexpected result is the strong variation of the coupling constant $a_{H\gamma}$ between the free ligand and its complexed form in spite of the comparatively small variation of spin density on the nitrogen-center. Molecular models of these radical complexes reveal the possibility of sufficient restriction to the free rotation of the *t*-butyl groups, thus giving raise to non-equivalent protons within these groups on the ESR. time scale. The incomplete resolution of this *hf*-structure did not allow for a precise measurement of relative intensities which could be used to proof the conjecture.

Although the coupling constants a_N and $a_{H\alpha}$ in the complexes are similar to the ones in the free ligand radical ion, in general they change significantly upon complex formation and are also influenced by the other ligands co-ordinated to the metal ion. The change of the coupling constant is much more pronounced for $a_{H\alpha}$ than for a_N. This behaviour can be understood by a transfer of electron density in the bonding π-orbitals towards the nitrogen and a corresponding transfer of electron density within the antibonding π-orbital in the opposite direction. In a HMO-calculation one can formally account for the changes in the coupling constants by using a higher value for the heteroparameter h_N (increasing the effective electronegativity of N). The spin density on C^{α} is increased by 32,3% if h_N is chosen as 1.0. It is interesting to note that the increase in spin density on the atom next to the ligand atom (C^{α} and N respectively) is roughly the same (30%) in the GLIR complexes as those in the nitroxide complexes reported by *Hoffman* & *Eames* [6].

Complex XIII with the bridging CN-group (Zn–NC–Fe) between Zn and Fe is the only one showing the same coupling constants a_N and $a_{H\alpha}$ as the free ligand. This can be interpreted as an outweighting of the σ-electron acceptor property of the metal ion by the high negative charge of the hexacyanoferrate ligand.

Metal hyperfine coupling constants are much larger for the Zn complexes than those of Mg(GLIR)Cl, being itself the only magnesium complex in which this interaction has been observed so far. ^{67}Zn and ^{25}Mg have approximately the same absolute values for the magnetic moments (0,8733 n.m. and $-0{,}8545$ n.m. respectively), so that the unpaired electron density at the nucleus is ca. 4,5 times higher in the zinc complexes than that of the magnesium complex Mg(GLIR)Cl. The spin density on the metal nucleus is approximately equal in all complexes where the ^{67}Zn interaction could be observed.

Spin-polarization of *s*-type electrons in zinc can be accomplished by polarization into σ-bonds through spin densities in the *p*- and/or *d*-orbitals of nitrogen and zinc (adjacent atom effect), and polarization of inner *s*-electrons of zinc by the *p*- or *d*-spin density on the metal. These interactions would lead to an equation for the Zn-coupling constants of the *Karplus-Fraenkel* type [21].

$$a_{\mathrm{Zn}} = \varrho_{\mathrm{Zn}} \left(S^{\mathrm{Zn}} + \Sigma\, Q^{\mathrm{Zn}}_{\mathrm{Zn\text{-}N}}\right) + 2 \cdot \varrho^{\mathrm{N}}\, Q^{\mathrm{Zn}}_{\mathrm{N\text{-}Zn}}. \tag{3}$$

The experimental results available at present are not sufficient for evaluating the parameters of (3); a preliminary discussion is possible, however: The near constancy of a_{N} in all the complexes (in complex XIII, where a_{N} is significantly different, a_{Zn} is not known) leads to a constant ϱ_{N} which in turn yields, through equation (3) and the constant a_{Zn}-value, a constant ϱ_{Zn} for all the Zn complexes studied. The values of the coupling constants $a_{\mathrm{H}\alpha}$ and a_{N} in the complexes compared to those of the free ligand suggest a total spin density near unity in GLIR if it is co-ordinated to the metal, leading necessarily to a value of $\varrho_{\mathrm{Zn}} \approx 0$. The fact that $a_{\mathrm{C}^{14}\mathrm{N}}$ and $a_{\mathrm{N}^{13}\mathrm{CS}}$ are very small can only be interpreted as very small delocalization of unpaired electron density into the antibonding π-orbitals of the CN^- and NCS^- ligands. It seems therefore that the spin polarization into σ-bonds rather than π-delocalization is responsible for hyperfine coupling with the metal- and the X-ligands. The absolute values of the parameters and a semiquantitative measure of the degree of spin delocalization in the chelate ring will only be possible after complexes with other radical ligands are fully investigated.

g-values of the calcium and magnesium complexes are equal to the ones of free GLIR within experimental error. The Zn complexes show *g*-values significantly smaller than free GLIR. Within the series of the halides a decrease in *g*-values from chloride to iodide is observed and the value for cyanide as ligand is even higher than that for chloride. This is just an opposite trend to that reported by *Fajer et al.* [8] and *Hoffman et al.* [6] for their radical complexes. Since spin-orbit coupling at all the atoms within the complex contributes to the *g*-value shift, the problem must await a more detailed elucidation of spin-density distribution in these complexes.

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9. The Stabilization of Bridged Structures of Ethanes

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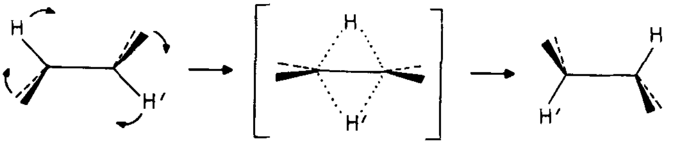
(8. XI. 71)

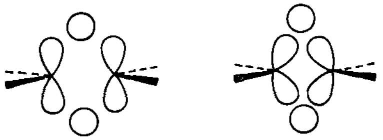
Summary. The source of the instability of D_{2h}, bridged, diborane type geometries of ethanes is traced to a single molecular orbital, b_{2g} or π^* in symmetry. The energy of this orbital can be lowered, and the barrier to bridging accordingly decreased, by appropriately placed acceptor substituents. Low bridging barriers, relative to ethane, are predicted for cyclopentenyl cation, and cyano or nitro substituted ethanes.

Ethane is much more stable in the familiar staggered D_{3d} conformation **1** than in a diborane-like bridged D_{2h} geometry **2**. We consider here the theoretical requirements for preferential stabilization of the bridged form. If sufficient stabilization could be achieved, the bridged structure might serve as an accessible transition state for a novel type of uncatalyzed intramolecular exchange: **1** $\rightleftarrows$ **1'**.



1 **2** **1'**

We first construct the molecular orbitals of **2**, to define those bonding features which cause instability. We start with a pair of in-plane sp^2 hybridized orbitals on



3 **4**