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

by **Peter Clopath** and **Alexander v. Zelewsky**[1])

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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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1) Author, to whom correspondence should be addressed.

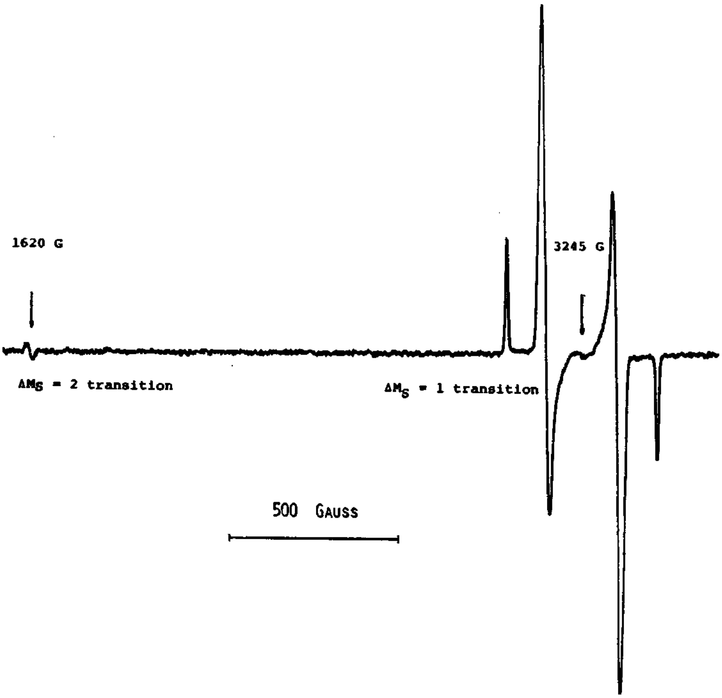
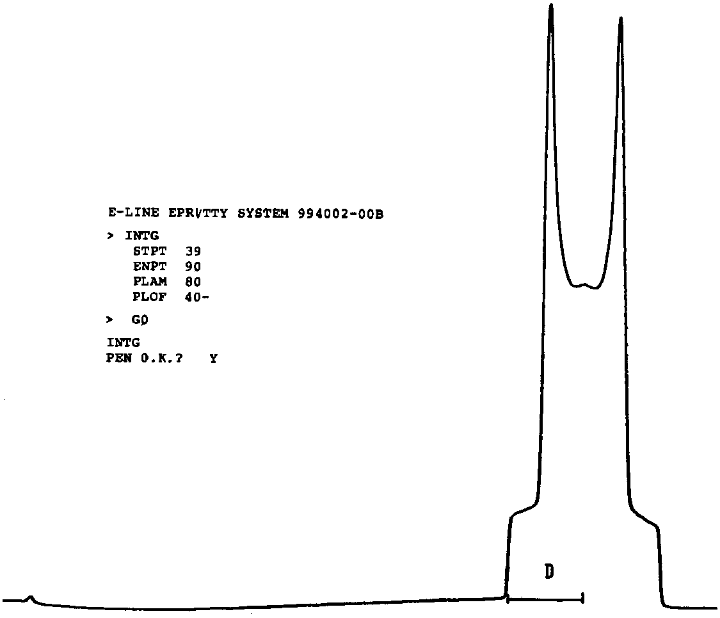


Fig. 1a. *Observed spectrum of* $Mg(GLIR)_2$ *in MTHF at* $-165°$ (first derivative).



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   ENPT  90
   PLAM  80
   PLOF  40-
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PEN O.K.?    Y
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Fig. 1b. *Observed absorption spectrum of* $Mg(GLIR)_2$. $D = 0{,}0210\ \mathrm{cm}^{-1}$; $E = 0$.

width ~ 15 Gauss). In frozen solutions in MTHF (which forms a homogeneous glass at low temperatures) the spectrum shown in Fig. 1a is obtained. The integrated spectrum is shown in Fig. 1b. The observation of the half field (1620 Gauss) $\Delta M_S = 2$ transition and the four lines in the high field region is typical for the ESR. spectra of randomly oriented systems in the triplet state [3]. The appropriate spin hamiltonian is given by (2), where D and E

$$\hat{\mathscr{H}} = g\beta \cdot H \cdot \hat{S} + D(\hat{S}_z - {}^1/_3\,\hat{S}^2) + E(\hat{S}_x^2 - \hat{S}_y^2) \qquad (2)$$

are the zero field splitting parameters, and x, y, z the principal axis coordinate system [4]. The almost perfect symmetry of the high field lines (Fig. 1b) is in agreement with the theoretical expectation for a system with a vanishingly small value of E [4]. This line shape also justifies the assumption made in (2) that the g-value is isotropic. The Table shows the ESR. parameter of $Mg(GLIR)_2$ (for the determination of D see Fig. 1).

Table. *ESR. parameter of* $Mg(GLIR)_2$ *in MTHF at 108°K*

g	D(cm^{-1})	E(cm^{-1})
2.0036 ± 0.0003	0.0210 ± 0.0001	0

No hyperfine splitting could be detected. The vanishingly small value of E indicates axial symmetry of the spin-spin interaction which is expected for a complex where the two GLIR radicals form two chelate rings perpendicular to each other, giving rise to a tetrahedral coordination of the metal ion, the symmetry of the complex being D_{2d}.

These findings are in agreement with the properties of a similar bis-chelate complex $Mg(dipy)_2$ which was investigated by *Brown & Weissmann* [5]. From D a value of $< r^{-3} >^{-1/3} = 3.96$ Å is obtained for $Mg(GLIR)_2$, whereas $< r^{-3} >^{-1/3} \sim 5$ Å for $Mg(dipy)_2$. Since dipy has a more extended electronic π-system, the mean distance between the two unpaired electrons localized mainly on the ligands is larger in $Mg(dipy)_2$ than in $Mg(GLIR)_2$, and in the latter the spin-spin interaction is therefore stronger.

Experimental Part. – All substances were of reagent grade. The operations were carried out under strictly anaerobic and anhydrous conditions. Solvents (DME and MTHF) were distilled over $LiAlH_4$ and stored in a vessel connected to the vacuum line.

ESR. spectra were recorded on a *Varian* E-9 instrument, equipped with a standard variable temperature accessory and a *Systron Donner* frequency counter (Model 1017/1292). All spectra were recorded at X-band frequencies. The g-value is measured relative to DPPH ($g = 2.0036$), which was attached to the sample tube by a small piece of scotch tape. The integrated spectrum was calculated with an on-line *Varian* 620 L computer.

Preparation of $Mg(GLIR)_2$. Anhydrous magnesium chloride and glyoxal-bis-N-*t*-butylimine (GLI) were synthesized by standard procedures [1]. Mg-metal was activated with 10% HCl, washed with H_2O, EtOH and Et-O-Et.

14,1 g GLI (84 mmol), 4,0 g $MgCl_2$ (42 mmol) and 1,01 g Mg (42 mmol) were transferred into a vessel connected to the vacuum line under a stream of dry argon. Through the vacuum line about 150 ml DME were distilled. The heterogeneous mixture was stirred for 24 h. At 4°, black crystals could be collected by filtration.

$C_{20}H_{40}MgN_4$		C	H	Mg	N
	Calc.	C 66.60	H 11.17	Mg 6.74	N 15.52%
	Found	,, 66.81	,, 11.36	,, 7.0	,, 15.82%

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92. Über die Wirkung von Auxochromen in Flavyliumsalzen, I

7-Hydroxy-flavyliumsalze

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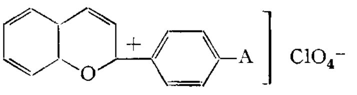
Institut für Farbenchemie der Universität Basel

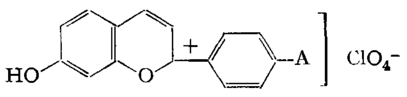
(21. II. 73)

Summary. 7-Hydroxy-flavylium salts absorb at longer wave lengths than the corresponding flavylium salts, yet auxochromes in 4′-position have a less bathochromic effect in the 7-hydroxy-flavylium series than in the flavylium series. As a result the absorption maxima converge. 4′-Dimethylamino derivatives show a convergence of 22 nm.

Auxochromhaltige Flavyliumsalze sind zwar schon in grosser Zahl bekannt – es sei nur erinnert an die Anthocyanidine und deren Methyläther –, doch sind umfassende Regeln über die Wirkungsweise der Auxochrome bisher nicht ermittelt worden. Wir haben nun mit der einigermassen systematischen Bearbeitung dieses umfangreichen Gebiets begonnen. Als Erstes wählen wir den Vergleich von Flavyliumsalzen mit einem Auxochrom in 4′-Stellung mit den analogen 7-Hydroxy-flavyliumsalzen.

Zum Ausmessen der Spektren wurde einheitlich Eisessig als Lösungsmittel benutzt. Im sichtbaren Gebiet zeigen sämtliche Farbsalze nur eine Bande. In der folgenden Tabelle sind unter a und a′ die Lösungsfarben, unter b und b′ die Maxima





A	a	b	c	a′	b′	c′	b′–b
H—	I blassgelb	397	–	VI gelb	435	–	38
CH_3—	II gelb	410	13	VII gelb	446	11	36
CH_3O—	III gelb	444	47	VIII gelb	467	32	23
HO—	IV gelb	447	50	IX orange	468	33	21
$(CH_3)_2N$—	V karminrot	534	137	X rotviolett	550	115	16

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1) Am 1. IV. 73, während der Drucklegung dieser Mitt., verschieden (*Red.*).