TABLE II. ESR Spectral Parameters.

Compound	H	g	$I_\parallel/I_\perp$	$H_{1/2}$, gauss
Cu_2(PL-DHF)Cl_2	1365 1292	4.91 5.93	6.8/10.7	104.60
Cu(PL-HIN)Cl	1365	4.92	7.0/7.8	68.25

A Dq value of 1000 cm^{-1} for the Co(II) ion and 700 cm^{-1} for the Ni(II) ion, is common for octahedral complexes, the chromophores being MON_4Cl for the HPL-DHF ligand and MO_2N_3Cl for the HPL-HIN ligand, respectively.

The parameters of the RES spectra (Table II) suggest anisotropy for the compound Cu_2(PL-DHF)-Cl_2, the spectrum of Cu(PL-HIN)Cl being approximately isotropic.

The values for $g > 2.04$ suggest an oblong octahedron.

The IR spectra of the free ligands have the characteristic band of the $\nu_{C=N}$ azomethine stretch at 1625 cm^{-1} for HPL-DHF and at 1665 cm^{-1} for HPL-HIN. The bond formation with the metal ion determined changes of the IR spectra in this region. Both the band position and their intensities varied, confirming that the azomethine group takes part in the bond with the metal ion.

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Ambiguities in the Proton NMR Studies Involving Cu(II) Ions as Paramagnetic Relaxation Centres

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The theory of nuclear spin relaxation induced by paramagnetic ions in solution has been given great relevance in delineating structural and kinetic parameters of bioinorganic reactions. Although several criticisms and corrections have been worked out, the original form of the Solomon-Bloembergen-Morgan equations [1, 2] still represents the most suitable starting point for interpreting experimental paramagnetic rates.

TABLE I. Paramagnetic Proton Relaxation Rates of Imidazole H_4, pH = 7.0; T = 300 K.

His (*M*)	Cu^{2+} (m*M*)	T_{1p}^{-1} (sec^{-1})	T_{2p}^{-1} (sec^{-1})	T_{2p}^{-1}/T_{1p}^{-1}
0.1	0.01	0.02	0.32	16
0.1	0.02	0.03	0.45	15
0.1	0.03	0.06	0.65	11
0.1	0.04	0.14	1.27	7
0.1	0.05	0.18	1.41	10

When dealing with Cu(II) ions as relaxation reagents, the scalar interaction was shown to give significant contributions to NMR line broadening, and T_1 measurements were therefore designed for getting structural information from the dipolar term.

In this report we suggest that asymmetric coordination to Cu(II) ions, resulting in large g tensor anisotropies, makes the Solomon-Bloembergen equations meaningless, since unreasonable answers are obtained in well defined Cu(II) complexes.

The $Cu(His)_2$ complex was taken as a model complex, since the X-ray structure of crystals obtained from aqueous solutions has been reported [3].

The experimental paramagnetic contributions $T_{ip}^{-1} = T_i^{-1}(obs) - T_i^{-1}(blank)$ are reported in Table I for H_4 of the imidazole moiety at different $[Cu^{++}]_{tot}/[His]_{tot}$ ratios. In these conditions CuA_2 (His = H_3A) is almost exclusively present in solution [4] and the T_{2p}^{-1}/T_{1p}^{-1} values are consistent with fast exchange of His molecules from the metal coordination sphere. The correlation time of the dipolar interaction was approximated by measuring that of water protons bound in the complex and the Cu(II)–H_4 distance was taken from crystallographic structure.

Calculations based on the Solomon-Bloembergen equations give values of the coordination number ranging between 0.039 and 0.054, which is nonsense.

Since the correlation time of the complex is not rapid enough compared with the electron spin anisotropy energy, that is

$$h\,\tau_c^{-1} \ll |g_\parallel - g_\perp|\beta B_o$$

no theoretical model is available to allow quantitative interpretation of nuclear relaxation. Combined ESR and NMR experiments are therefore suggested to build up a novel theoretical approach.

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