ESR Studies on ^{205}Tl Hyperfine Couplings in the Radical Cations of Tl(III)Porphyrins

Chr. Mengersen *, J. Subramanian *, J.-H. Fuhrhop *, and K. M. Smith **

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The isotropic ^{205}Tl hyperfine couplings obtained from the ESR spectra of the radical cations of Tl(III) meso tetraphenyl porphyrin (TPP), octaethyl porphyrin (OEP) and octaethyl chlorin (OEC) are reported. The radical cations were generated by electrooxidation in dichloromethane as solvent. A Karplus-Fraenkel type bilinear relation is used to interpret the ^{205}Tl couplings, taking into account the sigma-pi spin polarization of Tl–N bonds by the spin density at the nitrogen atoms in the ligand as well as the direct pi interaction of the orbitals of Tl with the pi orbitals of the ligand. It is shown that for the cation radicals of Tl porphyrins, both these mechanisms contribute to the Tl couplings whereas for the cation radicals of Co- and Zn-porphyrins the sigma-pi polarization alone is sufficient to account for the metal hyperfine couplings. It is suggested that Tl-hyperfine couplings can be used to estimate the nitrogen spin densities of porphyrin radical systems when the nitrogen splittings are not resolved in the ESR spectra.

I. Introduction

The chemistry of metalloporphyrins is determined by strong sigma electron donation from the nitrogens to the metal[1]. It is this electronic interaction together with the geometric rigidity of the porphyrin ligand, which determines the chemical versatility of hemes and chlorophylls in biological redox systems. Both the pi-system of the porphyrin and the atomic orbitals of metal ions, are largely shifted in energy by mutual interaction over the sigma framework, but direct pi-bonding between metal and ligand perpendicular to the porphyrin frame seems to be of minor importance. The main body of experimental data for this statement comes from comparative electrochemical and electronic spectral measurements, from which only indirect conclusions can be drawn[1, 2].

More direct evidence for the character of metal-nitrogen bonds comes from the ESR data of metalloporphyrins with a paramagnetic central ion or a pi-radical of the porphyrin ligand. The ESR studies on the radical cations of metalloporphyrins and related systems have been pursued in great detail[3–6]. As judged from the ESR behaviour, the systems that have been investigated fall into two classes, namely, the meso (α, β, γ, δ) unsubstituted porphyrins and meso substituted porphyrins (see Fig. 1 for the topology of metalloporphyrins). For the former systems, small meso proton hyperfine couplings ($a_{\mathrm{H}}^{\mathrm{meso}} = 1.5$ G in Mg octaethyl porphyrin (OEP) radical cation) and no nitrogen hyperfine couplings are reported. In the ground state of porphyrins, the two highest occupied orbitals are nearly degenerate[4, 7]. The energy difference between these two levels designated as A_{1u} and A_{2u}, is of the order of 0.1 eV and is very sensitive to the central metal ion as well as the substituents in the macrocycle. The unpaired electron in the radical cation goes to one of these orbitals[4]. The spin density distribution as indicated by the ESR data for the meso unsubstituted porphyrin radicals can be explained by placing the unpaired electron in the A_{1u} orbital. On the other hand, for the radical cations obtained from Mg and zinc complexes of meso tetraphenyl (TPP) and meso tetra n-propyl porphyrins[4], $a_{\mathrm{N}} =$ 1.5 G. The hyperfine coupling for the α-CH$_2$ protons in the n-propyl group is 2.94 G, indicating the presence of large spin densities at the meso positions. These proton and nitrogen couplings are at best explained with the unpaired electron being in an A_{2u} orbital. Apart from the proton and nitrogen couplings, metal hyperfine couplings have also been reported for the central metal atom in some metalloporphyrin radical cations. Wolberg and Manassen[6] have observed a coupling of 5.7 G for ^{59}Co in Co(III)TPP radical dication. Fajer et al.[5] report $a_{\mathrm{Co}} = 1.2$ G for Co(III)OEP radical dication and $a_{\mathrm{Zn}} = 1.23$ G for ^{67}Zn in Zn(II)TPP cation radical[4]. The central metal hyperfine coupling has been

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Reprint requests to Doz. Dr. J.-H. Fuhrhop, *D-3301 Stöckheim über Braunschweig*, Mascheroder Weg 1, Fed. Rep. of Germany.

* Gesellschaft für Molekularbiologische Forschung mbH, 3301 Stöckheim über Braunschweig, Fed. Rep. of Germany.

** The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, England.

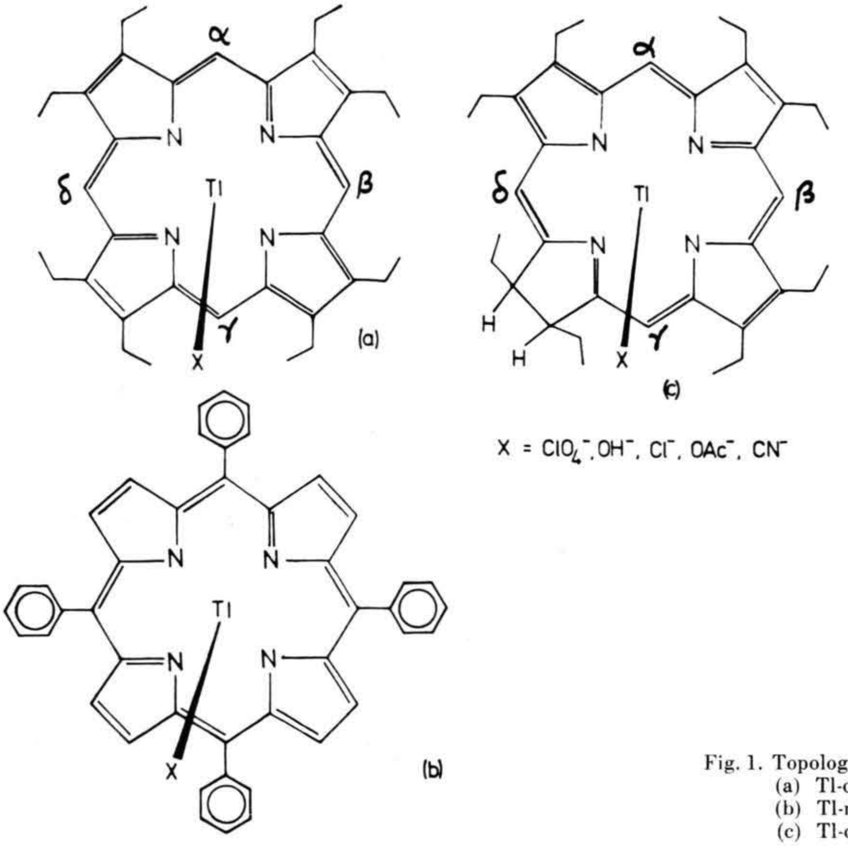

Fig. 1. Topology of the Tl porphyrins;
(a) Tl-octaethylporphyrin (OEP),
(b) Tl-mesotetraphenyl porphyrin (TPP),
(c) Tl-octaethylchlorin (OEC).

explained only in terms of the overlap of metal d orbitals with the pi orbitals of the ligand[6]. No detailed mechanism has been proposed for the delocalization of spin into the metal nucleus. Since the metal hyperfine coupling throws some light on the nature of metal-porphyrin interaction, we have investigated this aspect in the porphyrin cation radical, employing ^{205}Tl ($I = 1/2$) as the central metal. ^{205}Tl gives rise to large splitting constants[8] (the optical hyperfine coupling for ^{205}Tl in the ground state is 21310 MHz as against 1420 MHz for proton). Hence it is easy to monitor even small spin densities using ^{205}Tl nucleus. Naturally occuring Tl consists of 70% of ^{205}Tl and about 30% ^{203}Tl, the latter also having $I = 1/2$ and a magnetic moment about 1% less than that of ^{205}Tl. Since the difference between the coupling constants of ^{203}Tl and ^{205}Tl is much less than the linewidths in the ESR spectra we can safely neglect the influence of ^{203}Tl on ^{205}Tl couplings. Secondly, NMR data is available on Tl-H spin splittings in Tl alkyls and aryls[9, 10] which can be used to interpret our esr data. To our knowledge no esr studies have been made on Tl containing radical systems so far.

II. Experimental

A) Compounds

The detailed methods for the preparation and analysis of the compounds Tl(III) OEP(OH), Tl(III) OEP(CN), Tl(III) OEC(OH), Tl(III) TPP(OH) and Tl(III) TPP(CN) are presented elsewhere[11].

The general procedure consists of treating the appropriate ligand (OEP and TPP) in dichloromethane with thallium (III) acetate in tetrahydrofuran and refluxing for 16 hrs. at 40 °C. The thallium complexes were purified by column chromatography. NMR data for these compounds are also reported[11]. Only for Tl(III) TPP(CN), NMR spectrum was recorded in the present work with a Varian XL-100 NMR spectrometer and $J_{\mathrm{Tl-H}}$ (β-proton) was found to be 60 Hz.

B) Electrogeneration of the radical cations

The cation radicals were generated by electrooxidation at a platinum electrode in a vacuum electrolysis cell using dichloromethane as the solvent and tetra-n-butylammonium perchlorate as the electrolyte. A silver wire coated with AgCl was used as a reference electrode. The oxidation potentials (Table 1) were measured beforehand by cyclic voltammetry in the same medium, using a three electrode cell with a Beckmann Platinum Button (No. 3 92 73) as working electrode, a saturated calomel electrode as reference and a silver wire as auxiliary electrode. The radicals were quite stable and esr measurements could be done leisurely. Except for Tl (porphyrin) (CN)$^{+\cdot}$, both the counterions for the cation radicals are taken to be perchlorate ions since the Tl couplings were constant over a long time interval and also over a wide temperature range. In the case of Tl(TPP) CN$^{+\cdot}$ and Tl(OEP) CN$^{+\cdot}$, esr measurements were taken as quickly as possible.

Table 1. Midpoint oxidation potentials (vs. S.C.E.) measured using a platinum disc electrode for some Tl(III) porphyrins in dichlormethane [1, 2].

System [3]	$E^{\text{ox}}_{1/2}$ (V)
Tl(III) (OEC)$^+$	0.79
Tl(III) (OEP)$^+$	1.11
Tl(III (OEP) (CN)	1.05
Tl(III) TPP (CN)	1.16

[1] Base electrolyte: 0.1 M tetra n-butyl ammonium perchlorate.

[2] Estimated error in the potentials in ±0.01 V.

[3] The counterion is perchlorate unless otherwise specified. All the four systems yield reversible oxidation peaks. Deuterated [Tl(III) OEC (γ, δ, d_2)]$^+$ is also oxidized at 0.78 V.

C) Measurement of visible absorption and ESR spectra

The visible absorption spectra for the radical cations were measured using a Zeiss DMR spectrometer. ESR spectra were recorded with a Bruker BER 414 S ESR spectrometer operating at x-band with 100 kHz field modulation. The magnetic field was calibrated using an Alpha AL-675 NMR Gaussmeter and g-values were calculated using DPPH as g-marker. The microwave power was kept as low as possible to avoid saturation in all the measurements. ESR spectra at low temperatures were taken using a Bruker BST 100/700 temperature control unit.

III. Results and Discussion

A) Identification of the radical species

The visible electronic spectra of the radical cations of Tl(III) porphyrins (Fig. 2) are quite similar to the corresponding spectra of the radical cations of other metalloporphyrins reported in the literature[3, 5, 12]. The ESR spectra of the radical cations of the Tl(III) porphyrins consist of doublets with a maximum splitting of 60 – 65 G (Fig. 3) which presumably arises from the ^{205}Tl nucleus. This splitting accounts only for a spin density of 0.008 at the Tl nucleus considering its optimal hyperfine coupling constant being about 7610 G. Further we observe very little anisotropy in the g-value or a_{Tl} in the frozen solutions of the radical cations. Also the isotropic g-values are close to that of DPPH. From all these observations it is clear that one-electron oxidation in the Tl porphyrins has taken place at the ligand and not at the metal.

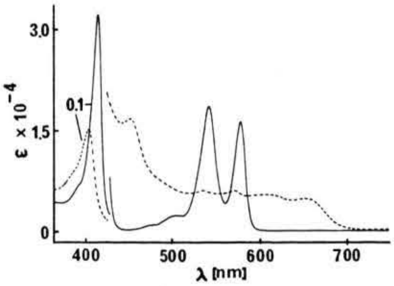

Fig. 2. Visible electronic spectra of Tl(III) OEP(OH) in CH$_2$Cl$_2$ (———) and Tl(III) OEP$^{+\cdot}$ cation radical (– – –) with perchlorate as the counterion.

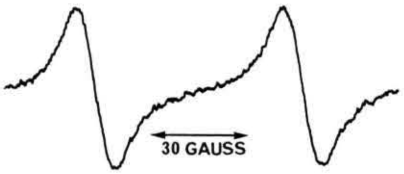

Fig. 3. ESR spectrum of the radical cation Tl(III) OEP$^{+\cdot}$ in CH$_2$Cl$_2$ with perchlorate as the counterion $\nu = 9.5$ GHz, modulation amplitude = 2.0 G, sweep = 25 G/min, T = 300 K. The magnetic field increases from left to right.

B) Radical ions with cyanide as the axial ligand

The radical ions obtained from Tl(III) TPP(CN) and Tl(III) OEP(CN) yielded Tl couplings which were quite different from those obtained from the Tl-porphyrins with OH$^-$ or ClO$_4^-$ as the axial ligands. With TPP, the introduction of CN$^-$ increased a_{Tl} from 11.8 G to 55.8 G whereas with

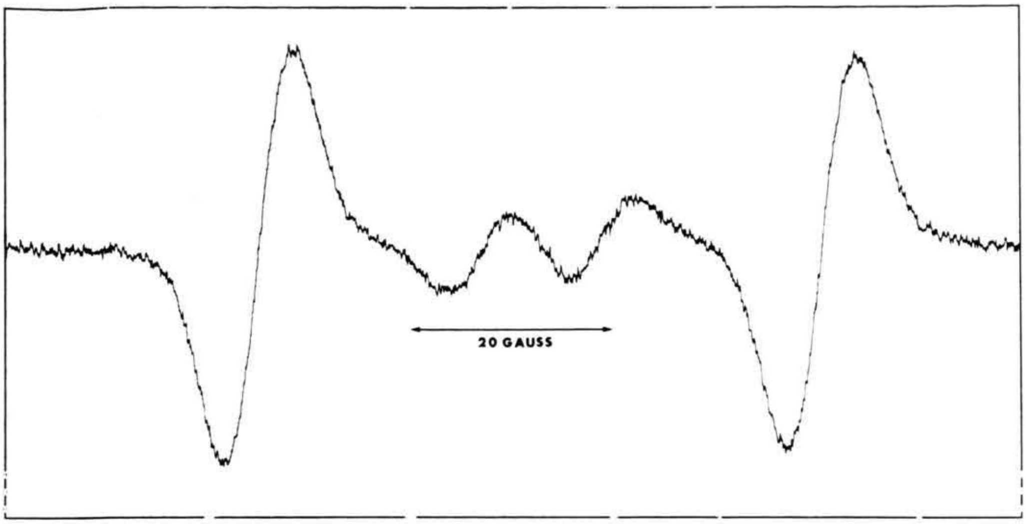

Fig. 4. ESR spectra of Tl(III) OEP$^{++\cdot}$ with perchlorate as the axial ligand (outer doublet); and Tl(III) OEP (CN)$^{+\cdot}$ (inner doublet).

OEP under the same conditions a_{Tl} decreased from 65.5 G to 19.8 G. After two to three hours the ESR spectra of the radicals with cyanide as the counterions and those with perchlorate as the counterions appeared together (Figure 4). After five hours, esr spectra of the species containing CN^- disappeared completely leaving only the species with ClO_4^- as counterions. Thus the exchange of CN^- by ClO_4^- is shown to proceed very slowly in CH_2Cl_2 indicating considerable covalency in the Tl-CN bond.

Table 2. Isotropic hyperfine coupling constants (in Gauss) and g-values for the radical cations of Tl(III) porphyrins and -chlorins at room temperature in dichloromethane.

System [1, 2]	$\lvert a_{\text{Tl}} \rvert$ [3]	$\lvert a_{\text{H}} \rvert$ [4]	$\langle g \rangle$
[Tl(III) OEP]$^{++\cdot}$	65.6	—	2.0029
[Tl(III) OEP (CN)]$^{+\cdot}$	19.8	—	2.0029
[Tl(III) TPP]$^{++\cdot}$	11.8	—	2.0020
[Tl(III) TPP (CN)]$^{+\cdot}$	55.8	—	2.0021
[Tl(III) OEC]$^{++\cdot}$	63.7	5.8 (2H)	2.0028
[Tl(III) OEC (γ, δ, d_2)]$^{++\cdot}$	62.9	5.6 (2H)	2.0031
[Zn(II) OEC$^{+\cdot}$	—	5.5 (1H)	2.0025

[1] OEP = octaethylporphyrin, OEC = octaethylchlorin, TPP = meso tetraphenyl porphyrin.

[2] The counterions are perchlorate unless otherwise specified.

[3] The estimated error in a_{H}: ±0.1 G; a_{Tl}: ±0.3 G; in the g-values: ±0.002.

[4] Assignment of the proton couplings is not unambiguous. Hückel-McLachlan calculations indicate that these couplings may arise from the β protons in the reduced pyrrole ring.

C) *Analysis of ^{205}Tl hyperfine couplings*

All the thallium porphyrin cation radicals investigated in the present work yield two line ESR spectra with linewidths in the range 5 G – 10 G. The splitting is assigned to the ^{205}Tl nucleus since no proton in the porphyrin can give rise to such a large splitting ranging from 12 – 60 G (Table 2). Attempts to get further resolution were not successful. The proton and nitrogen splittings reported so far for the cation radicals of Mg, Zn, and Cd porphyrins [4] are less than 3 G and in view of the larger linewidths in Tl porphyrins we are unable to find the effect of Tl on the spin distributions in the porphyrin system. On the other hand, in the radical cations of metallochlorins (Mg and Zn) two equivalent protons yield a coupling constant of 5.5 G (Table 2) which is larger than the linewidths we have obtained. With Tl(III) OEC cation radical we do indeed obtain the proton couplings of 5.8 G apart from a thallium coupling of 63.7 G. Thus it is clear that the presence of thallium atom has no effect on the spin distribution in the porphyrin macrocycle and we can justify the use of spin densities from other metalloporphyrin cation radicals for our discussions.

We have considered the following mechanisms for the interpretation of Tl couplings:

(i) The spin polarization of the σ-electrons in the Tl-N σ-bonds by the π-electron spin density at the nitrogen atoms leads to a spin density at the thallium nucleus which is of opposite sign to that of the spin density at the p_π orbital of the nitrogen atoms.

This is essentially an extension of McConnell relation[13] to the $\sigma-\pi$ polarization involving heavy atoms and has been successfully used to interpret the hyperfine couplings of Hg in aromatic mercury compounds[14].

(ii) The second mechanism involves the direct overlap of the orbitals of appropriate symmetry on the Tl atom with the π orbitals of the ligand, thus inducing a net spin density at the thallium nucleus. Thus we can express the thallium hyperfine couplings in terms of a Karplus-Fraenkel relation[15]:

$$a_{\mathrm{Tl}} = 4\, Q^{\mathrm{Tl}}_{\mathrm{NTl}}\, \varrho^{\mathrm{N}}_{\pi} + Q^{\mathrm{Tl}}_{\mathrm{Tl}}\, \varrho^{\mathrm{Tl}}_{\pi} . \tag{1}$$

It is difficult to interpret the term $Q^{\mathrm{Tl}}_{\mathrm{Tl}}$ in a manner similar to that employed for light atoms like ^{14}N or ^{13}C. Also it is not possible to obtain any numerical estimate for this quantity at present. We will consider the product $Q^{\mathrm{Tl}}_{\mathrm{Tl}}\ \varrho^{\mathrm{Tl}}_{\varphi}$ as a whole which gives a measure of the contributions to a_{Tl} arising from the direct overlap of the atomic orbitals of Tl with the π orbitals of the ligand.

The McConnel constant $Q^{\mathrm{Tl}}_{\mathrm{NTl}}$ in the first term has been estimated in a way similar to that followed by Dessy et al.[14] in evaluating the $\sigma-\pi$ parameter for Hg bonded to carbon. In a number of Thallium aryls, it has been shown that [9, 10] Tl-H spin-spin splittings arise essentially from Fermi contact interaction. The ratio of $J_{\mathrm{Tl-H}}$ to the corresponding $J_{\mathrm{H-H}}$ in various Tl aryls is reasonably constant and depends only on the charge density on Thallium. Thus for Tl bonded to three carbon atoms as in $\mathrm{Tl(C_6H_5)_3}$ the ratio $(J_{\mathrm{Tl-H}}/J_{\mathrm{H-H}}) = 42$ and for $\mathrm{(C_6H_5)_2Tl^+}$ type of systems the ratio is 71[10]. The $\sigma-\pi$ parameter for estimating the hyperfine coupling constant of Tl bonded to carbon can be written as

$$Q^{\mathrm{Tl}}_{\mathrm{CTl}} = (J_{\mathrm{Tl-H}}/J_{\mathrm{H-H}})\, Q^{\mathrm{H}}_{\mathrm{CH}} . \tag{2}$$

Extending the same analogy to $Q^{\mathrm{Tl}}_{\mathrm{NTl}}$, we obtain with $Q^{\mathrm{H}}_{\mathrm{NH}} = -30$ G[16], the following range for the magnitude of $Q^{\mathrm{Tl}}_{\mathrm{NTl}}$: $-1260\ \mathrm{G} \geqq Q^{\mathrm{Tl}}_{\mathrm{NTl}} \geqq -2130\ \mathrm{G}$ depending on the charge on the Thallium atom. Since we have shown earlier that the spin distribution in the porphyrin ring system is not significantly altered by the presence of Tl, we use for Eq. (1) the spin densities at the nitrogen atoms obtained from the ESR data on Mg, Zn and Cd porphyrin[3]. For the cation radicals of Zn (Cd, Mg) TPP $(\mathrm{ClO_4})$ the spin density at each nitrogen atom is $\varrho_{\pi}{}^{\mathrm{N}} = 0.05$ and for the corresponding radicals with OEP, $\varrho_{\pi}{}^{\mathrm{N}} \leqq 0.01$.

To obtain the relative signs of the Tl-couplings in the TPP and OEP system, we have studied the ESR of the radicals with cyanide bonded to Tl. Abragam et al.[11] have shown that the Tl-H spin-spin splittings (45 Hz) for meso protons in Tl(III) (OEP) $(\mathrm{OH^-, Cl^-, OAc^-})$ systems arise predominantly through direct π-interactions of Tl with the ligand. Introduction of $\mathrm{CN^-}$ as the axial ligand reduces the $J_{\mathrm{Tl-H(meso)}}$ to about 32 Hz. On the other hand in Tl(III) TPP systems, $J_{\mathrm{Tl-H(beta\ proton)}}$ values were shown to arise predominantly from the spin polarization through σ-bonds. In these latter cases introduction of a cyanide group as the axial ligand does not affect $J_{\mathrm{Tl-H}}$ values. Hence we have studied here the effect of $\mathrm{CN^-}$ as the axial ligand on the Tl couplings in the ESR spectra. We assign a negative sign to the coupling constant if it arises from the $\sigma-\pi$ interaction of Tl with the spin density at the nitrogen atoms and a positive sign for the contributions arising from direct π interaction. For $\mathrm{Tl(OEP)^{++\cdot}}$, the value of a_{Tl} decreases from 65.5 G to 19.8 G on the introduction of $\mathrm{CN^-}$ as the axial ligand (Table 2). Hence we assign tentatively a positive sign to a_{Tl} in $\mathrm{Tl(OEP)^{++\cdot}}$ $|a_{\mathrm{Tl}}|$ *decreases* considerably from 65.5 to 11.8 G when we go from OEP to TPP with perchlorate as the axial ligand. The large increase in $\varrho_{\pi}{}^{\mathrm{N}}$ raises the negative contribution to a_{Tl} thus bringing the resultant to a small value in $\mathrm{Tl\,TPP^{++\cdot}}$. In the latter situation the contribution to a_{Tl} by direct π-interaction has been reduced so much that the negative contribution from $\varrho_{\pi}{}^{\mathrm{N}}$ has increased to 55.8 G. On this basis we assign negative signs to a_{Tl} in $\mathrm{Tl(TPP)^{++\cdot}}$ with $\mathrm{CN^-}$ or perchlorate as the counterions. The results are internally consistent only when we assign opposite signs to a_{Tl} in TPP and OEP systems. (It should be mentioned that the small coupling of 11.8 G may be positive or negative since it is on the borderline).

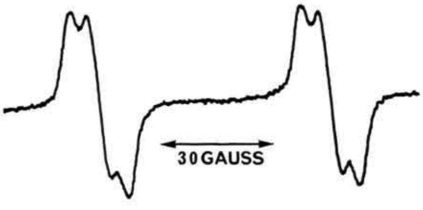

Fig. 5. ESR spectrum of Tl(III) $\mathrm{OEC^{++\cdot}}$ cation radical.

Now we can estimate the relative contributions of the first and second terms in Eq. (1) to a_{Tl} values. Using an average value of -1700 G for $Q^{\mathrm{Tl}}_{\mathrm{NTl'}}$, we get for $\mathrm{Tl(TPP)}^{+\,+\cdot}$:

$$a_{\mathrm{Tl}} = -11.8\,\mathrm{G} = -(4 \times 0.05 \times 1700) + Q^{\mathrm{Tl}}_{\mathrm{Tl}}\,\varrho^{\mathrm{Tl}}_{\pi},$$
$$Q^{\mathrm{Tl}}_{\mathrm{Tl}}\,\varrho^{\mathrm{Tl}}_{\pi} = 328\,\mathrm{G},$$

and for $\mathrm{Tl\,OEP}^{+\,+\cdot}$:

$$a_{\mathrm{Tl}} = 65.5\,\mathrm{G} = -\ (4 \times 0.01 \times 1700) + Q^{\mathrm{Tl}}_{\mathrm{Tl}}\,\varrho^{\mathrm{N}}_{\pi},$$
$$65\,\mathrm{G} < Q^{\mathrm{Tl}}_{\mathrm{Tl}}\,\varrho^{\mathrm{Tl}}_{\pi} < 133\,\mathrm{G} \ \text{for}\ 0 < \varrho^{\mathrm{N}}_{\pi} < 0.01\,.$$

Thus it is clear in the case of TPP systems both the contributions play equally significant role while for OEP systems the direct π interaction is more dominant. This conclusion, it should be emphasized, is *independent* of the choice of the $Q^{\mathrm{Tl}}_{\mathrm{NUl}}$ values.

D) Metal hyperfine couplings from other metalloporphyrin radical cations

In the light of the results on the Tl(III) porphyrins, we shall attempt to interpret the hyperfine couplings of ^{59}Co and ^{67}Zn in the cation radicals of Co and Zn porphyrins [4–6]. a_{Co} decreases from 5.7 G in Co(III) $\mathrm{(TPP)}^{+\,+\cdot}$ to 1.2 G in Co(III) $\mathrm{(OEP)}^{+\,+\cdot}$. A similar trend is observed in the Zn porphyrins: a_{Zn} in $\mathrm{Zn(OEP)}^{+\cdot} \approx 0\,\mathrm{G}$; a_{Zn} in $\mathrm{Zn(TPP)}^{+\cdot} = 1.22\,\mathrm{G}$. In both cases the trend is opposite to that observed for Tl porphyrins. The ratio $a_{\mathrm{Co}}\,\mathrm{(TPP)}/a_{\mathrm{Co}}\,\mathrm{(OEP)}$ is about the same as the corresponding ratio of the spin densities at the nitrogen atoms in TPP and OEP. Thus it is clear that in the case of the cation radicals of Zn and Co porphyrins, there is very little direct π-interaction between the metal orbitals and the ligand π-orbitals. The origin of the metal hyperfine couplings in these systems arises mainly from sigma-pi-spin polarization mechanism.

IV. Conclusion

It has been shown from the analysis of the hyperfine coupling constant of Tl in Tl-porphyrin cation radicals that both the $\sigma - \pi$ spin polarization and direct π-interaction mechanisms contribute to the Tl-hyperfine couplings. On the other hand, in other metalloporphyrins (containing Zn, Co, etc.) the nuclear hyperfine couplings from the central metal atoms arise mainly due to the $\sigma - \pi$ spin polarization mechanism. From a study of the Tl – H spin coupling on Tl(III) porphyrins, Abragam et al. [13] have also concluded that direct π-interactions exist between the orbitals of the ligand and the atomic orbitals of Tl. These authors have suggested that the metal atom is out of the plane of the porphyrin ligand. Though from our ESR results we cannot arrive at such a conclusion, they certainly support the nmr evidence. Though ESR and NMR-data indicate the presence of out-of-plane π bonding of Tl orbitals with the ligand orbitals, visible electronic spectra [11] and redox potentials [2, 12] do not indicate any abnormalities. The Tl porphyrins do not show any hemin or Mn(III) porphyrin-type of electronic spectrum wherein significant out-of-plane bonding of the metal to the ligand have been indicated [12]. But the ESR spectra of Tl porphyrin radicals indicate some anisotropy in Tl couplings measured in ESR spectra of frozen solution. For example, $A_{\parallel} = 75\,\mathrm{G}$ for Tl(III) TPP $\mathrm{(CN)}^{+\cdot}$ in dichloromethane at 100 °K and $A_{\perp}$ measured using $A_{\parallel}$ and the isotropic a_{Tl} is 46 G. It appears that the effect of the out-of-plane bonding of Tl to the ligand in these systems is not significant enough to show any abnormalities in the visible electronic spectra or the redox potentials. On the other hand these effects are reflected in the NMR and ESR spectra owing to the very large optical hyperfine coupling of the thallium nucleus which is quite sensitive to even small spin densities. The qualitative analysis of the Tl hyperfine couplings in terms of Karplus-Fraenkel type relation have indicated that these couplings are of opposite signs in Tl(III) OEP and Tl(III) TPP cation radicals. Study of Tl hyperfine couplings also offers a method of estimating the spin densities of the nitrogen atoms in the radicals of porphyrin analogs especially when the nitrogen couplings are not resolved. For example, for Tl(III) $\mathrm{OEC}^{+\,+\cdot}$ $|a_{\mathrm{Tl}}| = 61.7\,\mathrm{G}$, which is very close to the corresponding value in $\mathrm{Tl(OEP)}^{+\,+\cdot}$. Hence it appears that $\varrho_{\pi}^{\mathrm{N}}$ for both these systems is about the same. Further work on the spin distribution in the chlorin cations is in progress.

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