Time-Resolved Electron Spin Resonance of Gallium and Germanium Porphyrins in the Excited Triplet State

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Gallium and germanium porphyrin complexes in the lowest excited triplet (T_1) state have been studied by time-resolved electron spin resonance (TRESR). It is found that for Ge(TPP)(OH)$_2$ (TPP = dianion of tetraphenylporphyrin) intersystem crossing (ISC) from the lowest excited singlet (S_1) state to the T_{1x} and T_{1y} sublevels is faster than that to the T_{1z} sublevel (T_{1x}, T_{1y}, and T_{1z} are sublevels of the T_1 state), while the ISC of ZnTPP and Ga(TPP)(OH) is selective to the T_{1z} sublevel. This is interpreted by a weak interaction between the d_π orbital of germanium and LUMO (e_g) of the porphyrin ligand, resulting in small spin−orbit coupling (SOC). The interpretation is supported by molecular orbital calculations. The ISC of Ge(OEP)(OH)$_2$ (OEP = dianion of octaethylporphyrin) and Ge(Pc)(OH)$_2$ (Pc = dianion of tetra-*tert*-butylphthalocyanine) is found to be selective to the T_{1z} sublevel in contrast to Ge(TPP)(OH)$_2$. This dependence on the porphyrin ligand is reasonably explained by a difference between the $^3(a_{1u}e_g)$ (the OEP and Pc complexes) and $^3(a_{2u}e_g)$ (the TPP complex) configurations. This is the first observation of a difference in selective ISC between the $^3(a_{1u}e_g)$ and $^3(a_{2u}e_g)$ configurations. The TRESR spectrum of Ge(TPP)Br$_2$ is different from those of Ge(TPP)Cl$_2$ and Ge(TPP)(OH)$_2$, and is interpreted by SOC between the T_1 and T_2 states. From ESR parameters the square of the coefficient of the e_g orbital on bromine is evaluated as 0.018 in the T_1 state.

Introduction

Photophysical properties of porphyrin complexes have been investigated, for example, in relation to photosynthesis, photonic devices, photodynamic therapy, and photocatalysis. It has been shown for *regular porphyrins* that intersystem crossing (ISC) from the lowest excited singlet (S_1) state to the lowest excited triplet (T_1) state or from the T_1 state to the singlet ground (S_0) state varies dramatically with the central atom and axial ligands.[1−3] In other words, the photophysical properties of porphyrin complexes are controlled by spin−orbit coupling (SOC) of the central atom and axial ligand, which stimulates ISC. A time-resolved electron spin resonance (TRESR) technique is a useful method for investigating SOC of porphyrin complexes in the excited states as described below.[4−8]

Selective ISC occurs from the S_1 state to three sublevels in the T_1 state (T_{1x}, T_{1y}, and T_{1z}). For regular porphyrins the S_1 and T_1 states are a (π, π*) configuration, and selectivities of ISC are divided into two groups depending on the type of the central atom. Metal-free and Mg complexes belong to the first group.[5−9] In this case, ISC to the T_{1x} and T_{1y} sublevels is faster than that to the T_{1z} sublevel because of the x and y components of SOC. This SOC is produced by orbital angular momentum between p_z and p_x (p_y) orbitals (Figure 1), since the S_1 and T_1 states are admixed with (σ, π*), (π, σ*), and (n, π*) configurations via vibronic coupling. The second group is porphyrins with a heavy central atom or axial ligands.[4−10] The LUMO of the porphyrin ligand, an e_{gx} (e_{gy}) orbital, interacts with the d_{xz} (d_{yz}) orbital of the central atom and p_x (p_y) orbital of axial ligands. Since the $^{1,3}E_{ux}$ and $^{1,3}E_{uy}$ states are degenerate in the S_1 and T_1 regions, ISC from the $^1E_{ux}$ ($^1E_{uy}$) state is selective to the z sublevel in the $^3E_{uy}$ ($^3E_{ux}$) state due to a z component of SOC between the d_{xz} and d_{yz} orbitals of the central atom or between

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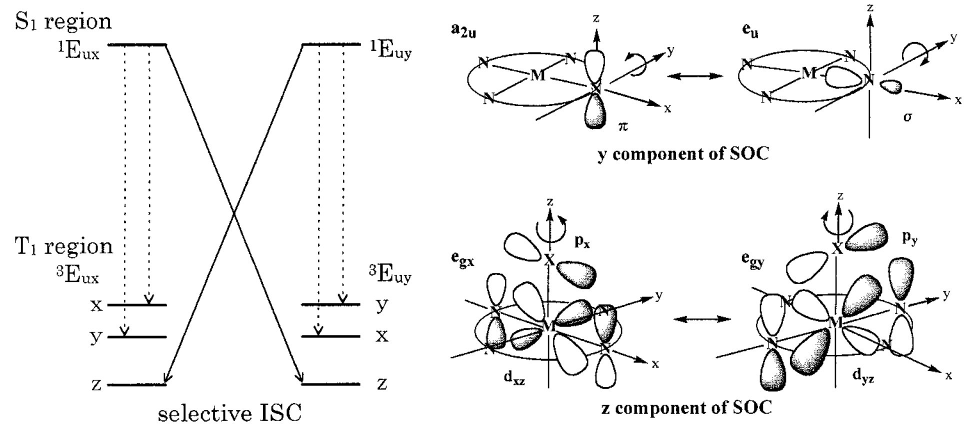
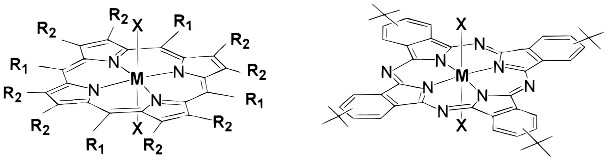


Figure 1. Selective ISC and *y* and *z* components of SOC. Full and dotted arrows indicate ISC promoted by the *z* component of SOC and by the *x* and *y* components of SOC, respectively. The *y* and *z* components of SOC originate from orbital angular momentum between the a_{2u} and e_u orbitals and between the e_{gx} and e_{gy} orbitals, respectively.

Chart 1



Compound	R1	R2	MX2
ZnTPP	C_6H_5	H	Zn
Ga(TPP)(OH)	C_6H_5	H	GaOH
Ge(TPP)(OH)$_2$	C_6H_5	H	Ge(OH)$_2$
Ge(TPP)Cl$_2$	C_6H_5	H	GeCl$_2$
Ge(TPP)Br$_2$	C_6H_5	H	GeBr$_2$
Ge(OEP)(OH)$_2$	H	CH_2CH_3	Ge(OH)$_2$

Compound	MX2
ZnPc	Zn
Ga(Pc)(OH)	GaOH
Ge(Pc)(OH)$_2$	Ge(OH)$_2$

the p_x and p_y orbitals of axial ligands (Figure 1). Since a difference among sublevel populations, which is generated by selective ISC, reflects a competition among these components of SOC, the sublevel population ratio observed by TRESR is a good parameter for evaluating SOC of the central and axial atoms.

ESR parameters in the T_1 state, i.e., *g* and zero field splitting (zfs) parameter *D* ($=-3E_z/2$) values, also reflect the SOC of porphyrin complexes. Several porphyrin complexes with a heavy central atom have negatively larger *D* and smaller g_{zz} values originating from the *z* component of SOC between the T_1 ($^3E_{uy}$) and T_2 ($^3E_{ux}$) states, which are split by the Jahn−Teller distortion.[10] Analysis of the ESR parameters provides the SOC matrix element, which is important not only for investigating the T_1−T_2 interaction but also in relation to the $^{1,3}E_{ux}$−$^{3,1}E_{uy}$ interaction.

In this paper, we describe the study of several gallium and germanium porphyrin complexes (Chart 1) using the TRESR method,[11] focusing on two areas: (1) Zinc, gallium, and germanium porphyrins are compared. For gallium and germanium porphyrins, hydroxyl groups are selected as axial ligands, since the small SOC constant of oxygen makes it easy to extract SOC of the central atom. Although the germanium ion has the heavier atomic weight and larger SOC constant than the zinc ion, the ISC of Ge(TPP)(OH)$_2$ is found to be selective to the T_{1x} and T_{1y} sublevels in contrast to ZnTPP.[5,10c] Furthermore, the ISC of Ge(Pc)(OH)$_2$ and Ge(OEP)(OH)$_2$ is shown to be selective to the T_{1z} sublevel in opposition to Ge(TPP)(OH)$_2$. These central metal and porphyrin ligand dependences are discussed from the viewpoints of the interaction between the central metal and porphyrin ligand and the difference in the electronic configurations, respectively. (2) Interactions between the porphyrin and axial ligands are investigated for Ge(TPP)X$_2$ (X = OH, Cl, and Br). It is found that a TRESR spectrum of Ge(TPP)Br$_2$ is obviously different from those of Ge(TPP)(OH)$_2$ and Ge(TPP)Cl$_2$. The ESR parameters of Ge(TPP)Br$_2$ are analyzed in terms of the SOC between the T_1 and T_2 states.

Experimental Section

All complexes were synthesized following the methods previously reported.[2,3,12] Ge(TPP)Br$_2$ was synthesized from Ge(TPP)(OH)$_2$ with reference to the synthesis of Ge(OEP)Br$_2$.[3] It exhibited absorption bands at 436, 565, and 607 nm in chloroform. A 1:1 mixture of toluene and chloroform of spectral grades was used as a solvent. The concentrations of the samples were ca. 10^{-3}−10^{-5} M.

TRESR and steady-state ESR measurements were carried out at 10−20 K on a Bruker ESP 300E spectrometer.[13] An Oxford ESR 900 cold gas flow system was used for controlling temperature. Samples were excited at 570−585 nm by a Lumonics HD 500 dye laser pumped with a Lumonics EX 500 excimer laser. The TRESR signals from the ESR unit were integrated by a LeCroy 9450A oscilloscope.

The spin Hamiltonian for the T_1 TRESR spectra is represented as follows:

$$H_{\text{spin}} = \mathbf{g}\beta\mathbf{BS} + \mathbf{SDS} = \mathbf{g}\beta\mathbf{BS} + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) \quad (1)$$

Here, the first term is the electronic Zeeman interaction, and *D* and *E* ($=|E_x - E_y|/2$) are zfs parameters. Simulations of the T_1 spectra were calculated following the procedure already reported.[14] Zero field energies of the triplet sublevels (E_x, E_y, and E_z), sublevel population ratios (P_x:P_y:P_z), *g* values (g_{xx}, g_{yy}, and g_{zz}), and line width parameters were required in the simulations, where the **g** tensor was assumed to be parallel to the **D** tensor.

Results and Interpretations

TRESR spectra of ZnTPP, Ga(TPP)(OH), and Ge(TPP)(OH)$_2$ are shown in Figure 2, and those of ZnPc, Ga(Pc)(OH), and Ge-

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(11) TPP = dianion of tetraphenylporphyrin. OEP = dianion of octaethylporphyrin. Pc = dianion of tetra-*tert*-butylphthalocyanine.

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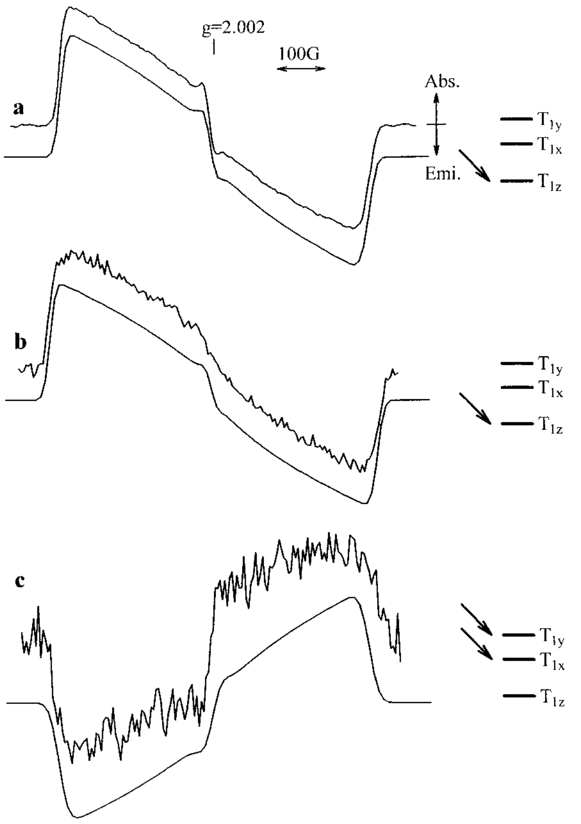

Figure 2. TRESR spectra of ZnTPP (a), Ga(TPP)(OH) (b), and Ge(TPP)(OH)$_2$ (c) together with their simulations (lower spectra). These spectra were observed at 0.5 (a), 0.9 (b), and 0.8 (c) μs after laser excitation, respectively. Simulation spectra were calculated using the parameters summarized in Table 1.

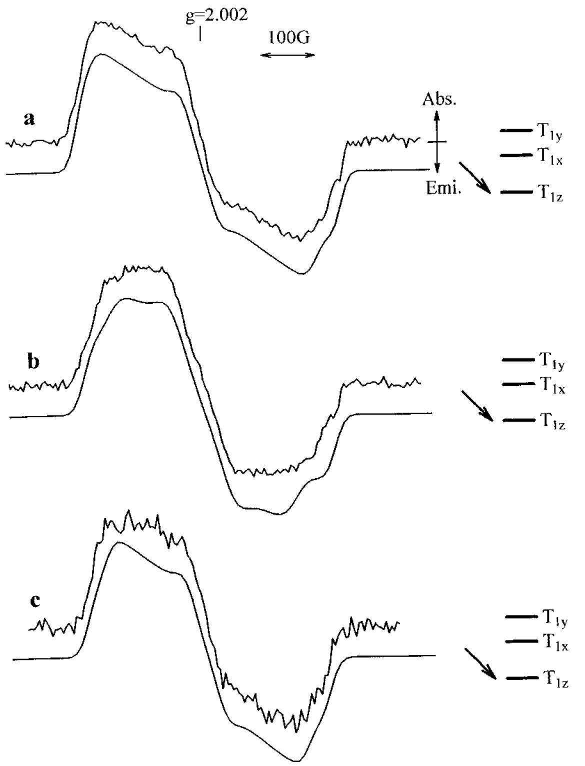

Figure 3. TRESR spectra of ZnPc (a), Ga(Pc)(OH) (b), and Ge(Pc)(OH)$_2$ (c) together with their simulations (lower spectra). These spectra were observed at 1.0 (a) and 0.8 (b, c) μs after laser excitation, respectively. Simulation spectra were calculated using the parameters summarized in Table 1.

Table 1. Zfs Parameters and Sublevel Population Ratios

compd	D^a/GHz	E^b/GHz	P_y:P_x:P_z
H_2TPP[c]	1.15	0.240	1:0.6:0.3
MgTPP[d]	0.930	0.275	0.5:0.5:0
ZnTPP	0.920	0.292	0:0:1
Ga(TPP)(OH)	0.975	0.315	0:0.1:0.9
Ge(TPP)(OH)$_2$	0.945	0.295	0.5:0.5:0
Ge(TPP)Cl$_2$	0.870	0.290	0.5:0.5:0
Ge(TPP)Br$_2$	−1.31	0.160	0:0:1
Y(TPP)(acac)[e]	0.870	0.290	0:0:1
H_2Pc[f]	0.758	0.070	0.46:0.54:0
MgPc[g]	0.713	0.168	0.46:0.54:0
Si(Pc)(OH)$_2$[h]	0.623	0.158	0:0:1
ZnPc	0.713	0.163	0:0.1:0.9
Ga(Pc)(OH)	0.660	0.110	0:0:1
Ge(Pc)(OH)$_2$	0.630	0.183	0:0.1:0.9
Y(Pc)(oac)[i]	0.650	0.140	0:0:1

[a] $D = -3E_z/2$. Errors of D values are within 0.016 GHz. [b] $E = |E_x - E_y|/2$. [c] From ref 5b. [d] From ref 6b. [e] From ref 10c. [f] From ref 8e. [g] From ref 8f. [h] From ref 8d. [i] From ref 8b.

(Pc)(OH)$_2$ are shown in Figure 3. The TRESR spectra, other than Ge(TPP)(OH)$_2$, exhibit an *AAA/EEE* polarization pattern, which is a characteristic of porphyrin complexes with a heavy central atom.[4−8,10c] Here, the *A* and *E* polarizations denote absorption and emission of the microwaves, respectively, and are due to nonequilibrium population of the triplet sublevels. The *AAA/EEE* polarization pattern is reproduced by selective ISC to the T_{1z} sublevel. On the other hand, the polarization pattern of Ge(TPP)(OH)$_2$ is *EEE/AAA*, which originates from selective ISC to the T_{1x} and T_{1y} sublevels. The selectivity of ISC for Ge(TPP)(OH)$_2$ is contrary to those for ZnTPP and Ge(Pc)(OH)$_2$, and is similar to those for metal-free and Mg complexes.[5−9] To investigate the selectivity dependence on the porphyrin ligand, a TRESR measurement was carried out for Ge(OEP)(OH)$_2$. It is found that a polarization pattern (*AAA/EEE*) of Ge(OEP)(OH)$_2$ is similar to that of Ge(Pc)(OH)$_2$ and contrary to that of Ge(TPP)(OH)$_2$.[15]

Zfs parameters, *D* and *E* values, of the TPP and Pc complexes are summarized in Table 1. The *D* values are independent of the central atom. For the TPP and Pc complexes, deviations of *D* values from ZnTPP and ZnPc are within 6% and 13% (except for metal-free compounds), respectively.[16] This indicates that the *D* values are almost due to the magnetic dipole−dipole interaction between π and π^* electrons of the porphyrin ligand.[16] The *D* values of Pc complexes are smaller than those of TPP complexes. These are interpreted as an expansion of the delocalization of unpaired π electrons in the T_1 state.

To clarify a role of axial ligands, TRESR measurements were carried out for Ge(TPP)Cl$_2$ and Ge(TPP)Br$_2$, and their spectra are shown in Figure 4. The zfs parameters and sublevel population ratios of Ge(TPP)Cl$_2$ are similar to those of Ge(TPP)(OH)$_2$ (Table 1). On the other hand, the TRESR spectrum of Ge(TPP)Br$_2$ is obviously different from those of Ge(TPP)(OH)$_2$ and Ge(TPP)Cl$_2$, indicating the heavy atom effect of bromine. The TRESR spectrum of Ge(TPP)Br$_2$ could be reproduced by two sets of parameters. First, $D = 1.31$ GHz, *E*

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(15) ESR parameters of Ge(OEP)(OH)$_2$ are evaluated as $D = 1.10$ GHz, $E = 0.103$ GHz, and P_y:P_x:P_z = 0.15:0:0.85.

(16) The *D* values of metal-free porphyrins are larger than those of corresponding metalloporphyrins. Gouterman et al. have proposed that the larger *D* values of metal-free porphyrins originate from configuration interactions between the ($a_{1u}e_g$) and ($a_{2u}e_g$) configurations for low symmetry: Langhoff, S. R.; Davidson, E. R.; Gouterman, M.; Leenstra, W. R.; Kwiram, A. L. *J. Chem. Phys.* **1975**, *62*, 169.

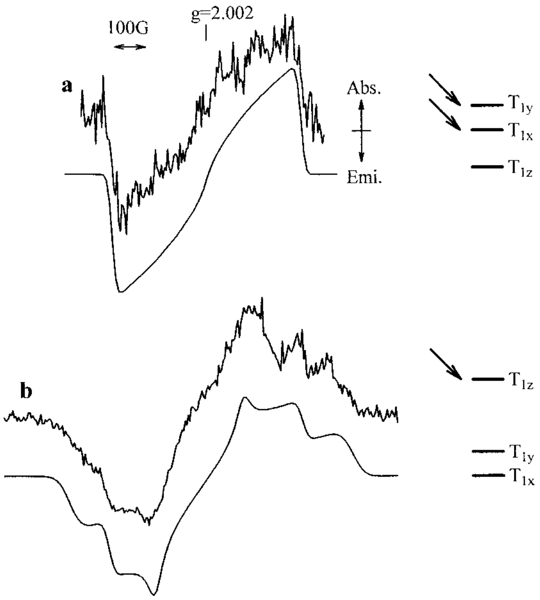

Figure 4. TRESR spectra of Ge(TPP)Cl_2 (a) and Ge(TPP)Br_2 (b) together with their simulations (lower spectra). These spectra were observed at 0.7 (a) and 0.9 (b) μs after laser excitation, respectively. Simulation spectra were calculated using the parameters summarized in Table 1.

$= 0.16$ GHz, $g_{zz} = 1.995$, and P_x, $P_y > P_z$. Second, $D = -1.31$ GHz, $E = 0.16$ GHz, $g_{zz} = 1.995$, and P_x, $P_y < P_z$. It is found that the $|D|$ value of Ge(TPP)Br_2 (=1.31 GHz) is larger than those of Ge(TPP)$(OH)_2$ (=0.945 GHz) and Ge(TPP)Cl_2 (=0.870 GHz). The D value is constituted by the magnetic dipole−dipole interaction and SOC. The only candidate for changing the magnetic dipole−dipole interaction is a charge transfer (CT) between the porphyrin and axial ligands. However, the larger $|D|$ value of Ge(TPP)Br_2 cannot be explained by the CT character, which reduces the $|D|$ value. On the other hand, a contribution of SOC is reasonable, since the SOC constant of bromine (2460 cm^{-1}) is much larger than those of oxygen (150 cm^{-1}) and chlorine (587 cm^{-1}).[3] The negatively larger D and smaller g_{zz} values are characteristic of the z component of SOC between the T_1 ($^3E_{uy}$) and T_2 ($^3E_{ux}$) states, as observed for PdP (P = dianion of porphyrin), PtP, and Y(OEP)(acac) (acac = acetylacetate).[10] Furthermore, selective ISC to the T_{1z} sublevel (P_x, $P_y < P_z$) is also interpreted by the z component of SOC between the $^{1,3}E_{ux}$ and $^{3,1}E_{uy}$ states, which is similar to that between the T_1 ($^3E_{uy}$) and T_2 ($^3E_{ux}$) states. Therefore, the ESR parameters of Ge(TPP)Br_2 are reasonably evaluated as $D = -1.31$ GHz, $E = 0.16$ GHz, $g_{zz} = 1.995$, and P_y:P_x:P_z = 0:0:1.[17]

Discussion

Central Metal and Porphyrin Ligand Dependences. As summarized in Table 1, the D and E values of Ge(TPP)$(OH)_2$ and Ga(TPP)(OH) are almost identical with those of ZnTPP, MgTPP, and Y(TPP)(acac). In a similar manner, the D values of Pc complexes are independent of the central atom. These results indicate that the zfs is almost due to the magnetic dipole−dipole interaction, and that these T_1 states are a (π, π^*) configuration localized on the porphyrin ligand.

Spectral simulations reveal that the ISC of Ge(Pc)$(OH)_2$ and Ga(Pc)(OH) is selective to the T_{1z} sublevel similar to ZnPc, Si(Pc)$(OH)_2$, and Y(Pc)(oac) (oac = acetate). In contrast, the ISC of Ge(TPP)$(OH)_2$ is selective to the T_{1x} and T_{1y} sublevels similar to H_2TPP and MgTPP, while ISC of Ga(TPP)(OH), ZnTPP, and Y(TPP)(acac) is selective to the T_{1z} sublevel. Since the germanium ion has the heavier atomic weight and larger SOC constant (1800 cm^{-1})[3a] than the zinc ion (1100 cm^{-1})[18], the difference between Ge(TPP)$(OH)_2$ and ZnTPP is unusual. Furthermore, since this type of porphyrin ligand dependence has not been observed previously,[4−10] it is interesting to note that the selectivity of ISC for Ge(TPP)$(OH)_2$ is contrary to those for Ge(Pc)$(OH)_2$ and Ge(OEP)$(OH)_2$. Therefore, a selection rule of germanium porphyrins has to be clarified.

For metalloporphyrins, origins of ISC are divided into two groups. The first is ISC to the T_{1x} and T_{1y} sublevels. This selective ISC is due to the x and y components of SOC between p_z and p_x (p_y) orbitals (Figure 1), since the S_1 and T_1 states are admixed with (σ, π^*), (π, σ^*), and (n, π^*) configurations via vibronic coupling.[1,9b] The second group is selective ISC to the T_{1z} sublevel, which originates from the z component of SOC. Since the LUMO of the porphyrin ligand, the e_{gx} (e_{gy}) orbital, is admixed with the d_{xz} (d_{yz}) orbital of the central metal and the p_x (p_y) orbital of axial ligands, selective ISC from the $^1E_{ux}$ ($^1E_{uy}$) state to the z sublevel of the $^3E_{uy}$ ($^3E_{ux}$) state is promoted by SOC between the d_{xz} and d_{yz} orbitals of the central metal or between the p_x and p_y orbitals of axial ligands (Figure 1).[1,9b] Therefore, the selectivities of ISC depend on these components of SOC.

The difference between Ge(TPP)$(OH)_2$ and ZnTPP will be explained. Gouterman discussed the origin of the x and y components of SOC.[1] It has been shown that the T_1 state of TPP complexes is an ($a_{2u}e_g$) configuration,[16] and that an ($e_u^{\sigma}e_g$) configuration (an e_u^{σ} orbital is a bonding orbital between the central atom and pyrrole nitrogens) is the best candidate of SOC in the (σ, π^*) and (π, σ^*) configurations.[1] Since both a_{2u} and e_u^{σ} orbitals have large MO coefficients on the pyrrole nitrogens, SOC between ($a_{2u}e_g$) and ($e_u^{\sigma}e_g$) is possible, and is almost produced on the porphyrin ligand.[19,20] In other words, the x and y components of SOC for Ge(TPP)$(OH)_2$ are almost the same as those for ZnTPP, and the selective ISC of Ge(TPP)$(OH)_2$ originates from a decrease in the z component of SOC.

This small SOC is interpreted by a weak interaction between the LUMO of the porphyrin ligand and the d_{π} orbital of germanium. The ionization potential (93.5 eV) of the Ge^{4+} ion, which denotes an energy of 3d orbitals, is much larger than that (39.722 eV) of the Zn^{2+} ion, indicating that the energy difference between the LUMO of the porphyrin ligand and d_{π} orbital of germanium is much larger than that of zinc. Further, the extent of the d_{π} orbital of the Ge^{4+} ion is smaller than that of the Zn^{2+} ion, since effective nuclear charge (10.85) for the d_{π} orbital of germanium is larger than that (8.85) of zinc. These differences indicate that the interaction between the LUMO of the porphyrin ligand and the d_{π} orbital of germanium is smaller

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(17) The line width of a single transition used for the simulation of Ge(TPP)Br_2 is larger than those of Ge(TPP)Cl_2 and Ge(TPP)$(OH)_2$. This larger line width is considered to originate from the distribution of the D value. The D value due to SOC is inversely proportional to the energy difference between the T_1 and T_2 states, which are split by the Jahn−Teller distortion. Since the Jahn−Teller distortion depends on the environment, the D value of Ge(TPP)Br_2 is considered to be distributed somewhat depending on the sites.

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(19) For ZnP, Ga(P)(OH), and Ge(P)$(OH)_2$, *ab initio* calculations were carried out by means of the program Hyper Chem R 5.1. These complexes were calculated on the basis of STO-3G.

(20) *Ab initio* calculations suggest that the square of the coefficient of the a_{2u} MO in the $4p_z$ orbital ($\sim 2.3 \times 10^{-2}$) of zinc is small, but larger than that ($< 10^{-4}$) of germanium. This indicates that the x and y components of SOC of zinc are small, but larger than those of germanium.

than that of zinc. This consideration is confirmed by MO calculations,[19] where the square of the coefficient of the e_g MO in the d_π orbital ($<10^{-4}$) of germanium is much smaller than that ($\sim 1.6 \times 10^{-3}$) of zinc. Using the MO coefficients and SOC constant, the z component of SOC of germanium is calculated as <0.2 cm^{-1}, and is much smaller than that (~ 1.8 cm^{-1}) of zinc.[21] Because of the smaller SOC, the ISC of Ge(TPP)(OH)$_2$ becomes selective to the T_{1x} and T_{1y} sublevels.

With respect to the dependence on the porphyrin ligand, the differences among the TPP, OEP, and Pc complexes need to be clarified. It has been shown that the T_1 state of Pc and OEP complexes is an ($a_{1u}e_g$) configuration, while that of TPP complexes is the ($a_{2u}e_g$) configuration.[16] The SOC between ($a_{1u}e_g$) and ($e_u{}^{\sigma}e_g$) configurations is impossible contrary to the ($a_{2u}e_g$) configuration, since the a_{1u} orbital has no MO coefficient on the pyrrole nitrogens. In the case of Pc complexes, an ($e_u{}^{n}e_g$) configuration (an $e_u{}^{n}$ orbital denotes a nonbonding orbital on imino nitrogens) must also be considered.[22] However, SOC with the ($e_u{}^{n}e_g$) configuration is ineffective, since the imino nitrogens are on the a_{1u} symmetry nodes. That is, the ($a_{1u}e_g$) configuration has to couple with the other (σ, π^*) and (π, σ^*) configurations. Consequently, the x and y components of SOC for the TPP complexes are larger than those for the OEP and Pc complexes. Since the z component of SOC is small, the porphyrin ligand dependence is observed for germanium porphyrins.

In the case of gallium porphyrins, ISC from the S_1 state is selective to the T_{1z} sublevel. Because of the pentacoordinated geometry, the gallium atom deviates from the porphyrin plane, promoting an interaction between the e_{gx} (e_{gy}) orbital of the porphyrin ligand and the 4p_x (4p_y) orbital of gallium. In fact, an MO calculation of Ga(P)(OH) indicates that the square of the coefficient of the e_g MO ($\sim 1.7 \times 10^{-3}$) in the p_x and p_y orbitals of gallium is much larger than that ($<10^{-4}$) in the d_π orbitals of gallium.[19] Therefore, selective ISC to the T_{1z} sublevel is mainly due to the SOC between the p_x and p_y orbitals of gallium.

Axial Ligand Dependence. It is found that the D value of Ge(TPP)Br$_2$ is negatively larger than those of Ge(TPP)(OH)$_2$ and Ge(TPP)Cl$_2$, and that the g_{zz} value of Ge(TPP)Br$_2$ is smaller than that of a free electron. These D and g_{zz} values of Ge(TPP)Br$_2$ are explained by the contribution of SOC between the T_1 ($^3(a_{2u}e_{gy})$) and T_2 ($^3(a_{2u}e_{gx})$) states. In this case, the D value is expressed as follows:

$$D = D_{SS} - D_{SO} \tag{2}$$

Here, D_{SS} denotes the magnetic dipole−dipole interaction between the triplet spins. We assume that D_{SO} originates from the SOC between the T_1 and T_2 states, and that the one-center terms on heavy atoms, germanium and bromine, are important for the SOC. Under the second-order perturbation theory, the D_{SO} is represented as follows:

$$D_{SO} = Z'^2/4\Delta E_{TT} \tag{3a}$$

$$iZ' = iqZ = (C_{Ge}{}^2\langle d_{yz}|\xi_{Ge}l_z|d_{xz}\rangle + 2C_{Br}{}^2\langle p_y|\xi_{Br}l_z|p_x\rangle)\langle\phi(T_1)|\phi(T_2)\rangle \tag{3b}$$

$$\Delta E_{TT} = E(T_2) - E(T_1) \tag{3c}$$

Here, q ($=\langle\phi(T_1)|\phi(T_2)\rangle$) is the vibrational overlap between the T_1 and T_2 states. Z is a matrix element of SOC. C_{Ge} and C_{Br} are the e_g orbital coefficients of germanium and bromine, respectively. In a similar manner, the change in the g_{zz} value, Δg_{zz}, is expressed as follows:

$$\Delta g_{zz} = Z'\Lambda'/\Delta E_{TT} \tag{4a}$$

$$i\Lambda' = iq\Lambda = \langle\Phi(T_1)|l_z|\Phi(T_2)\rangle\langle\phi(T_1)|\phi(T_2)\rangle \tag{4b}$$

Λ is a matrix element of an orbital Zeeman interaction. In eq 3b, the SOC of germanium is negligibly small, since the D ($=0.945$ GHz) and g_{zz} ($=2.002$) values of Ge(TPP)(OH)$_2$ are almost the same as the D value of MTPP (M = Mg, Zn) and g value of a free electron, respectively. In this case, the Z value is represented as follows:

$$Z = 4\Lambda D_{SO}/\Delta g_{zz} = 2C_{Br}{}^2\langle p_y|\xi_{Br}l_z|p_x\rangle \tag{5}$$

The D_{SO} is estimated as 2.26 GHz from a difference between Ge(TPP)Br$_2$ and Ge(TPP)(OH)$_2$. Using Δg_{zz} ($=0.007$) and Λ ($=2.1$), which was calculated for the T_1 state,[23] the Z value is evaluated as 88 cm^{-1}, being much larger than those calculated for zinc (~ 1.8 cm^{-1}) and germanium (<0.2 cm^{-1}). Using $\xi_{Br} = 2460$ cm^{-1}, the $C_{Br}{}^2$ is estimated as 0.018 in the T_1 state, and is similar to that ($=0.022$) calculated for Sn(P)Br$_2$.[3a]

Conclusions

In this study, gallium and germanium porphyrin complexes have been investigated by TRESR. It is found that the ISC of Ge(TPP)(OH)$_2$ is selective to the T_{1x} and T_{1y} sublevels, while that of ZnTPP and Ga(TPP)(OH) is selective to the T_{1z} sublevel. This is interpreted by a weak interaction between the d_π orbital of germanium and the LUMO of the porphyrin ligand. The ISC of Ge(Pc)(OH)$_2$ and Ge(OEP)(OH)$_2$ is shown to be selective to the T_{1z} sublevel in good contrast to Ge(TPP)(OH)$_2$. This selectivity dependence on the porphyrin ligand is interpreted by the difference in the electronic configurations. This is the first observation of the difference in selective ISC between the $^3(a_{1u}e_g)$ and $^3(a_{2u}e_g)$ configurations. The TRESR spectrum of Ge(TPP)Br$_2$ is obviously different from those of Ge(TPP)(OH)$_2$ and Ge(TPP)Cl$_2$, and is explained by the z component of SOC between the T_1 and T_2 states. From the g_{zz} and D values, the square of the coefficient of the e_g MO on bromine can be estimated as 0.018 in the T_1 state.

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(21) The SOC is calculated by multiplying the square of the coefficient of the e_g MO on the central atom by the SOC constant.[3,10]

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