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ESR Studies of Paramagnetic Species Trapped in Single Crystals of Chloro(5,10,15,20-tetraphenylporphyrinato)cobalt(III)

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The ESR spectra of three paramagnetic species trapped in single crystals of chloro(5,10,15,20-tetraphenylporphyrinato)cobalt(III) (Co^{III}Cl(tpp)), have been observed at 4.2 K to room temperature. Based on the ESR parameters obtained, the paramagnetic species have been identified as two Co^{II}(tpp) with different axial ligand effects and a previously reported cation radical, [Co^{III}(tpp)]$^{2+\cdot}$(Cl$^-$)$_2$. A correlation diagram among g, A, and axial ligation made from published data of cobalt(II) complexes has been successfully used for identification of the two trapped Co^{II}(tpp) species: one is four-coordinate Co^{II}(tpp) and the other five-coordinate Co^{II}X(tpp) in which X is presumably Cl$^-$. Their electronic and molecular structures are discussed according to McGarvey's theory. Finally, the formation mechanism of the three paramagnetic species in Co^{III}Cl(tpp) is discussed, based on the results obtained from the single crystalline ESR measurements.

The functional properties of metalloenzymes can often be understood by the study of their prosthetic groups, as has been seen in the famous study of Wang.[1] On the other hand, the study on redox reactions including metalloporphyrin has become increasingly important. In the course of our investigation of chloro(5,10,15,20-tetraphenylporphyrinato)-cobalt(III) (Co^{III}Cl(tpp) (**1**), Fig. 1), we have found by ESR studies[2,3] that in solutions of **1** whose solvents are aromatic or chlorinated hydrocarbons, a π cation radical, [Co^{III}(tpp)]$^{2+\cdot}$(Cl$^-$)$_2$, is formed and that the formation of the radical occurs reversibly with small enthalpy change. Subsequent ESR measurements[4] on single crystals of **1** in which the radical is trapped have provided some information about the electronic and molecular structures of the radical and have also shown the existence of two Co^{II}(tpp) species which are influenced by axial ligation. Such co-existence of both oxidation and reduction products in the crystals prepared under ambient conditions and the reversible behavior of the cation radical in the solution are regarded as inherent properties of **1**. These facts can be closely related to the redox reaction of metalloenzyme. We have carried out detailed ESR investigations of the crystals trapping the two Co^{II}(tpp) species. The analysis of the ESR parameters obtained has given useful information for understanding the inherent properties of **1**.

In this paper, we first describe the results obtained from angular dependences of the ESR spectra due to two Co^{II}(tpp) species trapped in the single crystals of **1**. Second, the identification of the two trapped Co^{II}(tpp) species is given using a diagram of correlation among g, A, and axial ligation made from the published data of many cobalt(II) porphyrins and their related compounds. Third, their electronic and molecular structures are elucidated according to a theoretical treatment reported by McGarvey. Finally, the formation mechanism of the three paramagnetic species in **1** will be presented, based on the results obtained from the single crystalline ESR measurements and those published previously.

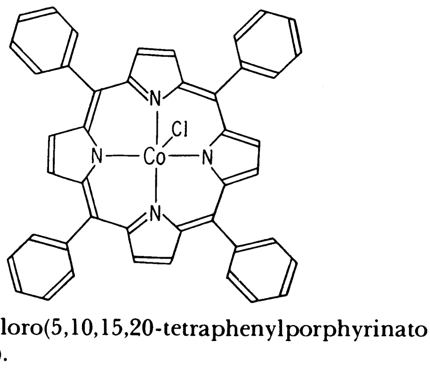
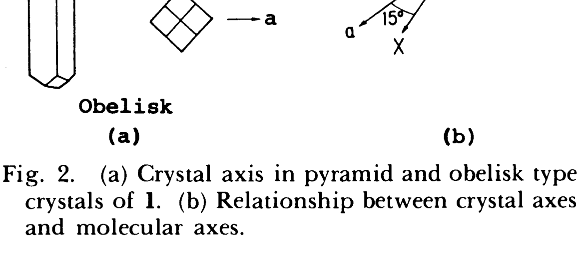


Fig. 1. Chloro(5,10,15,20-tetraphenylporphyrinato)-cobalt(III).

Experimental

Co^{III}Cl(tpp) (**1**), was prepared by using a method previously reported.[5] The spontaneous evaporation of the solvent from the solution of **1** gave crystals of various external forms: obelisk, pyramid, prism, and bulky shape. The single crystals doped with 1 mol% of pure Co^{II}(tpp) were also prepared for the comparison with the trapped paramagnetic species. Previously, the X-ray analysis of the obelisk crystals[5] has been reported: **1** is a five-coordinate cobalt(III) complex of tpp which has a square-pyramidal structure with a chlorine atom at the apex. Continuing X-ray analyses[6] for various crystals have shown that the sixth ligand position is completely or partially occupied by water contaminated from the atmosphere. The relationships between the a and b axis and the external forms are illustrated in Fig. 2. The



(a) (b)

Fig. 2. (a) Crystal axis in pyramid and obelisk type crystals of **1**. (b) Relationship between crystal axes and molecular axes.

Co–Cl bond is parallel to the c axis and the angle between the a axis and one of the Co–N bonds is 15 °. Typical sizes of the obelisk and pyramid crystals used for the measurements were $0.1\times0.1\times0.3$ and $0.2\times0.2\times0.1\,\text{cm}^3$, respectively. The ESR spectra were measured at 4.2 K to room temperature with an ESR spectrometer, JEOL FE-3X equipped with 100 kHz magnetic field modulation. The microwave frequency and the magnetic field were directly determined by using a frequency counter, Takeda Riken TR-5211, and a field measurement unit, JEOL ES-FC-4, respectively. ESR parameters were determined by simulation using a JEOL ES-9835 computer system.

Results and Discussion

(1) The ESR Spectra of Paramagnetic Species in the Obelisk and Pyramid Crystals of Co^{III}Cl(tpp). Figure 3 shows the ESR spectra of the paramagnetic species in the pyramid and obelisk type single crystals of **1** with crystal setting of $c\perp H_0$ at 77 K. As can be easily seen from the spectra, three different hyperfine (hf) patterns due to ^{59}Co with $I=7/2$ are clearly distinguished. Hereafter, we call these species α, β, and γ, as is shown in Fig. 3. The saturation behaviors of the three hf patterns were different from one another. The hf pattern due to γ was clearly observed at 4.2 K and

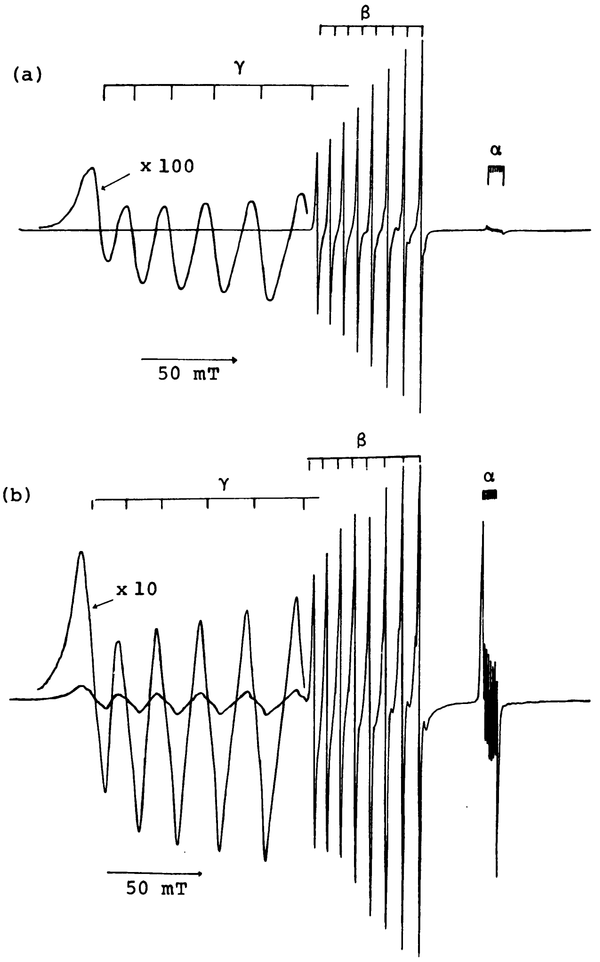


Fig. 3. The ESR spectra of paramagnetic species trapped in (a) obelisk and (b) pyramid type crystals of **1** at 77 K ($c\perp H$). Note that three species, α, β, and γ are clearly distinguished.

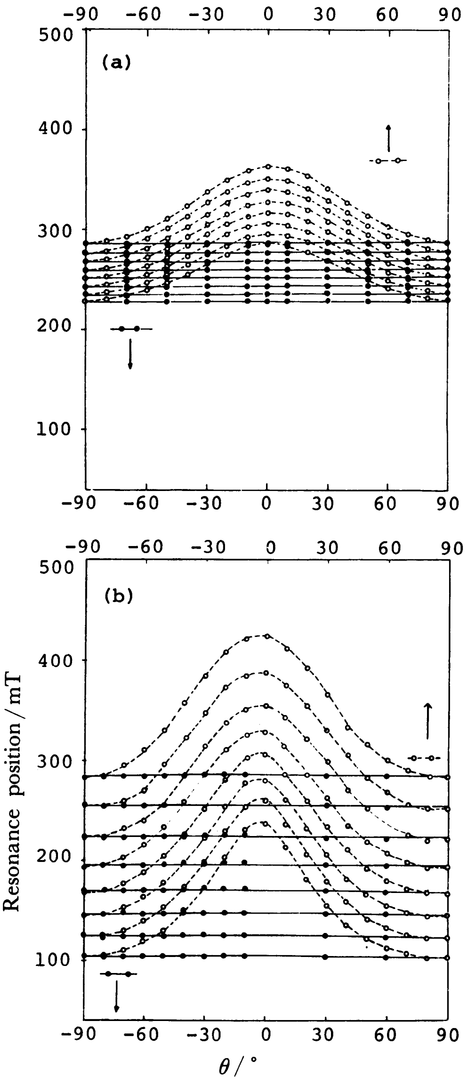


Fig. 4. Angular variations of the ESR positions of (a) β and (b) γ species trapped in **1**.
●: c axis rotation, ○: a axis (pyramid) or [110] (obelisk) rotation.

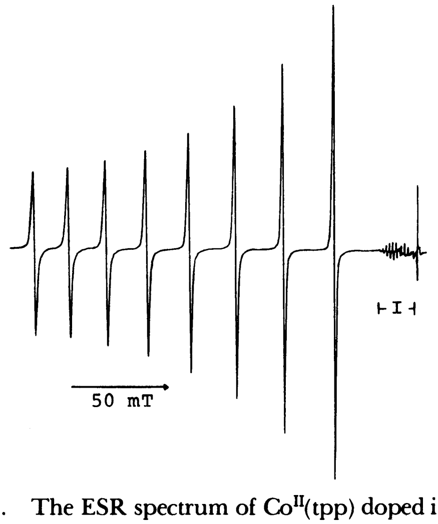


Fig. 5. The ESR spectrum of Co^{II}(tpp) doped in Co^{III}Cl(tpp) single crystal at 77 K ($c\perp H$). The position marked I in the Figure is due to Cu(tpp) paramagnetic impurity.

disappeared at above 120 K, but those due to α and β were observable even at room temperature. That is, the relaxation time of γ is considerably shorter than those of two others. α[2–4] has previously been identified as a π cation radical, $[Co^{III}(tpp)]^{2+\cdot}(Cl^-)_2$. In order to determine the electronic structures of β and γ, the angular variation of the absorption lines due to these species were measured both for the plane including the c axis and for the ab plane, which are shown in Fig. 4. The measurements show clearly that the g values of both β and γ are minimum at $\theta=0°$ ($g_\parallel$), and maximum at $\theta=90°$ ($g_\perp$). Such angular dependences are characteristic of the d_{z^2} orbital with a configuration of the z axis along the Co–Cl bond. The $g_\parallel$ of β is very close to that of free-electron predicted by first-order perturbation theory.[7] This means that the separations of excited states of β from the ground state are large enough to approximate the system with the first-order

TABLE 1. ESR PARAMETERS ESTIMATED, ENERGY SEPARATIONS ($\Delta(^2B_1)$ AND $\Delta(^4B_1)$), ISOTROPIC HYPERFINE INTERACTION (K) AND DIPOLAR SPLITTING CONSTANT (P) FOR COBALT(II) COMPLEXES OF PORPHYRINS AND THEIR RELATED COMPOUNDS

No.	System[a]	$g_\perp$	$g_\parallel$	$A_\perp$ / cm^{-1}	$A_\parallel$ / cm^{-1}	$\Delta(^2B_1)$[f] / cm^{-1}	$\Delta(^4B_1)$[f] / cm^{-1}	K[f] / 10^{-4} cm^{-1}	P[f] / 10^{-4} cm^{-1}	Ref
1	β species	2.5273 (±0.0003)	1.9964 (±0.0003)	0.0097 (±0.0003)	0.0105 (±0.0003)	4192	3867	77	62.3	This work
2	γ species[b]	3.320 (±0.002)	1.920 (±0.002)	0.0398 (±0.0003)	0.0240 (±0.0003)	1338	1322	145	195	This work
3	δ species	3.0627 (±0.0003)	1.8857 (±0.0003)	0.0306 (±0.0003)	0.0167 (±0.0003)	1773	2976	69.3	237	This work
				Four-coordinate Complex						
4	Co(tpp) in $CHCl_3$	3.330	1.848	0.0380	0.0187	1291	2992	90	243	9
5	Co(tpp) in H_2 (tpp)	3.322	1.798	0.0395	0.0197	1278	1785	122	192	9
6	Co(*p*-OCH_3 tpp) in Ni (*p*-OCH_3 tpp)	3.317	1.75	0.0403	0.0195	1263	2566	102	216	18
7	Co(*p*-OCH_3 tpp) concd polycrystal	3.285	1.79	0.0394	0.0147	1328	2316	144	267	18
8	Co(*p*-OCH_3 tpp) in H_2 (OCH_3 tpp)	3.264	1.81	0.0374	0.0171	1370	2245	52	255	18
9	Co(tpyp) in H_2 (tpyp)	3.218	1.774	0.0383	0.0213	1423	5997	110	224	10
10	Co(tpp) in $CHCl_3$	3.198	1.848	0.0358	0.0187	1585	2954	61	210	9
11	Co(*p*-OCH_3 (tpp) in H_2 (*p*-CH_3 tpp)	3.193	1.84	0.0352	0.0173	1499	2499	50	228	18
12	Co(omtbp) in (H_2 omtbp)	3.080	1.884	0.0290	0.0123	1736	2793	90	270	12
13	Co(tpp) in $CHCl_3$	3.066	1.848	0.0298	0.0187	1740	8721	90	254	9
14	Co(tbp) in H_2 (tbp)	2.901	1.949	0.0218	0.0128	2227	2713	68	236	10
15	Co(pc) in β-Zn(pc)	2.905	1.91	0.0265	0.0160	2191	6528	11	330	19
16	Co(*o*-CH_3 tpp) concd polycrystal	2.875	1.97	0.0235	0.0139	2328	2385	34.2	267.1	18
17	Co(*p*-OCH_3 tpp) in toluene	2.848	2.006	0.0228	0.0161	2450	2022	25.3	360	18
				Five-coordinate Complex						
18	Co(tpp)[c] in H_2 (tpp)	2.505	2.034	0.0092	0.0115	4517	2407	48.9	158	9
19	Co(oep)[c] in ether	2.44	2.03	0.0050	0.0095	5232	2660	50.0	211	20
20	Co(pc)[c] in α-Zn (pc)	2.422	2.007	0.0066	0.0116	5384	3879	63.5	192	19
21	Co(tpp)[c] in ether	2.395	2.024	0.0056	0.0099	5872	1190	59.1	62.7	20
22	Co(PPIX)ME[d]	2.384	2.018	0.00544	0.00932	6015	3305	32.4	133.4	14
23	Co(PPIX)MTE[d]	2.360	2.016	0.00377	0.00901	6447	3540	16.0	160.6	14
24	Co(cyt c) at pH 0.5	2.359	2.014	0.00388	0.00938	6447	3687	16.7	165.6	14
25	Co(HRP A)	2.34	2.03	0.00115	0.00739	6957	2918	−23.3	217.2	20
26	Co(HRP B, C)	2.33	2.08	0.00125	0.00748	7604	1929	−8.4	198.9	20
27	Co(Mb)[e]	2.327	2.028	0.00055	0.00834	7246	3016	−13.5	189.6	14
28	Co(*p*-OCH_3 tpp)[d] +1 pyridine	2.327	2.025	0.0012	0.00798	7118	3167	−6	185	18
29	Co(*p*-OCH_3 tpp)[d] +1 3-picoline	2.326	2.028	0.0011	0.00787	7266	3033	−7	189	18
30	Co(*p*-OCH_3 tpp)[d] +1 2-picoline	2.324	2.028	0.0011	0.00780	7303	3082	−7	162	18
31	Co(*p*-OCH_3 tpp)[d] +1 n-hexylamine	2.311	2.022	0.0010	0.00782	7604	3381	−3.3	174	18
32	Co(cyt c) at pH 12.9	2.325	2.026	0.0011	0.00757	7273	3110	−6.6	180.4	14
33	Co(tpp) (py)	2.324	2.027	0.0013	0.00789	7307	3082	−4.1	181.5	18
34	Co(Hb)[e]	2.310	2.037	0.0005	0.00790	7760	2728	−10.3	201.6	14
35	Vitamine B_{12r} +1 imidazole	2.27	2.022	—	0.00944	8844	3520	—	—	14

Table 1. (Continue)

No.	System[a)]	$g_\perp$	$g_\parallel$	$A_\perp$ / cm^{-1}	$A_\parallel$ / cm^{-1}	$\Delta(^2B_1)$[f)] / cm^{-1}	$\Delta(^4B_1)$[f)] / cm^{-1}	K[f)] / 10^{-4} cm^{-1}	P[f)] / 10^{-4} cm^{-1}	Ref
				Six-coordinate Complex						
36	Co(PPIX)2(py)[d)]	2.247	2.067	−0.00536	0.00647	10443	2147	−49.3	277.6	14
37	Co(p-COOH tpp) +2 pyridine	2.236	2.054	−0.0052	0.0053	10743	2394	−52.2	234.9	10
38	Co(p-OCH_3 tpp)[d)] +2 3-picoline	2.228	2.058	−0.00544	0.0061	11235	2319	−52.0	252.1	18
39	Co(p-OCH_3 tpp)[d)] +2 4-picoline	2.226	2.060	−0.00500	0.0061	11394	2283	−47.8	244.5	18
40	Co(p-OCH_3 tpp)[d)] at pH 4-12	2.273	2.035	−0.00517	0.0583	11086	2945	−48.1	228.1	14
41	Co(p-OCH_3 tpp)[d)] +2 pyridine	2.216	2.047	−0.00570	0.0060	11729	2577	−51.5	244.2	18
42	Co(p-OCH_3 tpp)[d)] +2 piperidine	2.214	2.054	−0.00538	0.0061	12000	2411	−48.0	241.2	18
43	Co(p-OCH_3 tpp)[d)] +2 n-hexylamine	2.208	2.067	−0.00618	0.0072	12692	2174	−54.0	284	18

a) Abbreviations: p-OCH_3tpp, tetrakis(p-methoxyphenyl)porphyrin; tpyp, tetrakis(4-pyridyl)porphyrin; p-CH_3tpp, tetrakis(p-methylphenyl)porphyrin; omtbp, octamethyltetrabenzoporphyrin; tbp, tetrabenzoporphyrin; pc, phthalocyanine; o-CH_3tpp, tetrakis(o-methylhenyl)porphyrin; oep, octaethylporphyrin; PPIX, protoporphyrin IX dimethylester; ME, 2-mercaptoethanol; MTE, 2-(methylthio)-ethanol;cyt c, cytochrome c; HPR, horseradish peroxidase; Mb, myoglobin; py, pyridine; Hb, hemoglobin; p-COOHtpp, tetrakis(p-carboxyphenyl)porphyrin. b) The valies of A, g, $\Delta(^{2,4}B_1)$, P, and K are estimated. c) Numbers of ligands are not specified in the references, but these compounds are cited for comparison. d) In toluene. e) Single crystal data. f) The values were estimated from the reported g and A data, except for those in Ref. 14.

perturbation theory. On the other hand, $g_\parallel$ of γ is very small compared with the predicted free-electron value, as will be discussed later.

The concentrations of the paramagnetic species in both pyramid and obelisk crystals were different but their ESR parameters agreed within the experimental errors, which means that the ESR parameters do not depend on the external crystal forms. The ESR parameters of β and γ were estimated by the best fit of the experimental data to an equation derived from the second-order perturbation theory,[8)] which are listed in Table 1. The ESR parameters of β and γ are very close to those of two sites of Co^{II}(tpp) diluted in H_2(tpp),[9)] respectively.

In order to obtain further information about the electronic environments of β and γ in the crystal of **1**, pure Co^{II}(tpp) (**2**) was doped in **1**. The ESR spectrum of **2** magnetically diluted in **1** is well resolved at 77 K, as is shown in Fig. 5 ($c \perp H_0$). At room temperature, no ESR signal was observed because of a short spin lattice relaxation time just as in the case of γ. It is seen in Fig. 5 that molecules of **2** are properly exchanged with those of **1**. Hereafter this paramagnetic species is called δ. The estimated ESR parameters of the species are also listed in Table 1. The angular dependence of the species also shows the d_{z^2} ground state, but the ESR parameters did not coincide with those of β or γ, nor with those in previous reports.

(2) Correlation Diagram of g, A, *and Axial Ligation.* In order to clarify the electronic and molecular structures of β and γ, correlation among g, A, and axial ligation was examined by using the data of cobalt(II) porphyrins and their related compounds. The data are also listed in Table 1 in order of $g_\perp$ value. A diagram of the correlation is shown in Fig. 6. It is seen from the figure that $g_\perp$ and $g_\parallel$ have linear relationships with $A_\perp$ and $A_\parallel$, respectively. These relationships can be simply expressed as

$$g_\perp = 2.3675 + 20.47A_\perp, \tag{1}$$

$$g_\parallel = 2.1662 - 13.70A_\parallel, \tag{2}$$

with the correlation coefficients 0.82 in Eq. 1 and 0.21 in Eq. 2, respectively. From the diagram the isotropic part of g, g_0, was estimated to be 2.233. The values of $g_\perp$ and $A_\perp$ decrease as the coordination number of Co^{II}(tpp) increases; four-, five-, and six-coordination.

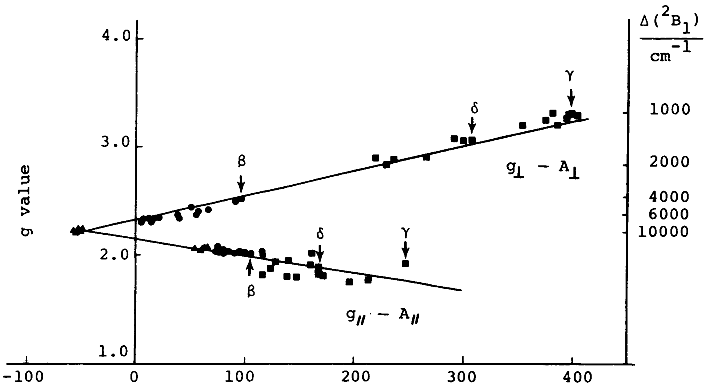


Fig. 6. A correlation diagram among g, A, and axial ligation. ■: Four-coordinate complex, ●: five-coordinate complex, and ▲: six-coordinate complex.

On the other hand, $A_{\parallel}$ decreases with the increase of the coordination number, but $g_{\parallel}$ has a reverse relation. It should be noted here that the sign of $A_{\perp}$ of six-coordinate complexes is minus. This has been already pointed out by Lin.[10] Such a linear relationship between g and A has also been observed in vanadium complexes.[11] In our diagram the relationship between ESR parameters and axial ligation is obvious. That is, the diagram is instructive for assigning the molecular environments of β, γ, and δ. As is shown in Fig. 6, γ resides on the right-end of the four-coordinate complex group and δ is, in the left-hand side of the group. On the other hand, β is on the right-end of five coordinate complex group. This means that β is fundamentally five-coordinate complex and the axial ligand is rather weak, while γ and δ are both four-coordinate complexes. Based on such procedures, γ can be assigned as the square-planar Co^{II}(tpp); on the other hand, β is square-pyramidal Co^{II}(tpp), and also δ is probably tetragonal with a weak axial ligand effect. It is not clear from the results what kind of atom is ligated in the cases of β and δ, but Cl^- in β is most probable as is discussed later.

(3) Theoretical Consideration for the Linear Relationships. The theoretical investigations of cobalt(II) complexes with planar ligands have been carried out by many authors.[12] For the interpretation of the linear relationships, we adopted McGarvey's treatment, which is analytical for the ESR parameters.

McGarvey[13] carried out the third-order perturbation treatment of low spin cobalt complexes with C_2 symmetry including the configurations with excited states $^2B_1$ and $^4B_1$. Dickinson and Chien[14] simplified the treatment and derived the theoretical g values as

$$g_{\perp}=2.0023+2c_3^2-3c_1^2, \qquad (3)$$

$$g_{\parallel}=2.0023+2/3c_3^2-6c_1^2+6c_1, \qquad (4)$$

where $c_1=\lambda/\Delta(^2B_1)$, $c_3=\lambda/\Delta(^4B_1)$, and λ is the single electron spin-orbit coupling constant, $\Delta(^{2,4}B_1)$ represents energy separation between the ground state $^2A_1$ and the excited state, $^2B_1$ or $^4B_1$. The value of λ for the Co^{2+} ion is $530\,cm^{-1}$,[9] however, as the covalency due to complex formation causes a decrease of 20—40%, we assumed as $\lambda=400\,cm^{-1}$ according to Assour.[9] Energy separations obtained for the cobalt(II) complexes are also given in Table 1. The $\Delta(^2B_1)$ is ranging from 1300 to $13000\,cm^{-1}$. Introduction of a base along the z axis destabilizes the d_{z^2} orbital relative to the d_{xz} and d_{yz} orbitals, which results in an increase of $\Delta(^2B_1)$. Thus five-coordinate complexes of N_4X type have $\Delta(^2B_1)$ values larger than those of four-coordinate complexes. Those of the N_5 complexes are of the order of 7000 cm^{-1}. Further the separation of the six-coordinate complexes having two bases should be much larger than those of five-coordinate complexes. The relation between $\Delta(^2B_1)$ and $g_{\perp}$ values is also shown in Fig. 6, from which $\Delta(^2B_1)$ can be estimated by substituting the ESR parameters, $g_{\perp}$ or $A_{\perp}$, obtained experimentally.

The principal values of the hyperfine tensor, $A_{\parallel}$ and $A_{\perp}$,[13] are also expressed as functions of c_1 and c_3:

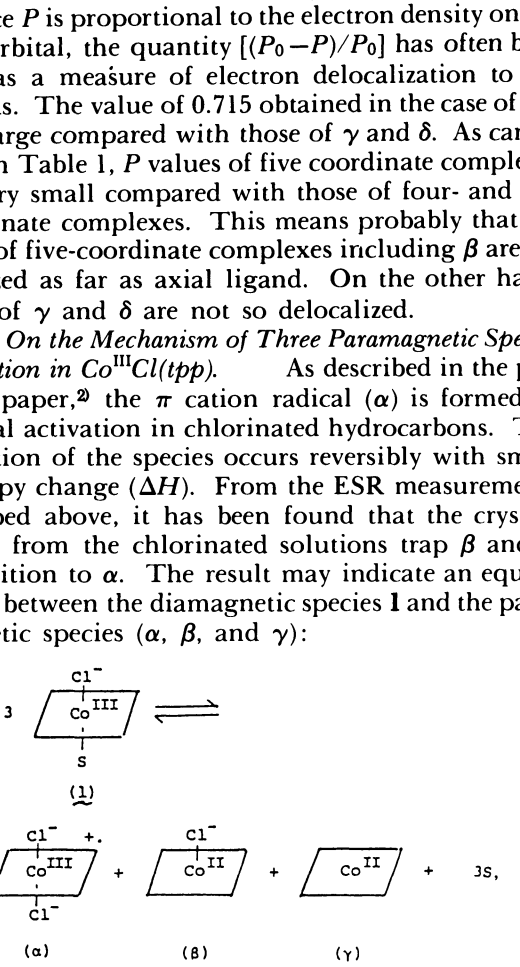
$$A_{//}=K+(P/7)[4-4c_3-6c_1+(2/9)c_3^2+15c_1^2], \qquad (5)$$

$$A_{\perp}=K+(P/7)[-2+45c_1+2c_3+(4/3)c_3^2-(57/2)c_1^2], \qquad (6)$$

where K is the isotropic Fermi hyperfine interaction parameter, $P=2\beta_e\beta_n\gamma_{Co}(d_{z^2}|r^{-3}|d_{z^2})$ is the dipolar splitting constant, and β_e and β_n are electronic and nuclear magnetons, respectively. The linear relationships of Eqs. 1 and 2 can be derived from Eqs. 3 to 6, if we assume that c_3 is constant and the square terms in Eqs. 3 to 6 are neglected compared with the other terms.[15] The average value of the dipolar splitting constants of cobalt(II) complexes listed in Table 1, P_{av}, is obtained as $0.0219\,cm^{-1}$ which nicely coincides with the value of free Co^{2+} ion ($P=0.0220\,cm^{-1}$);[16] this coincidence means that P_0 should be regarded as a standard value to measure electron density on the $3d_{z^2}$ orbital.

Since P is proportional to the electron density on the $3d_{z^2}$ orbital, the quantity $[(P_0-P)/P_0]$ has often been used as a measure of electron delocalization to the ligands. The value of 0.715 obtained in the case of β is very large compared with those of γ and δ. As can be seen in Table 1, P values of five coordinate complexes are very small compared with those of four- and six-coordinate complexes. This means probably that the spins of five-coordinate complexes including β are delocalized as far as axial ligand. On the other hand, those of γ and δ are not so delocalized.

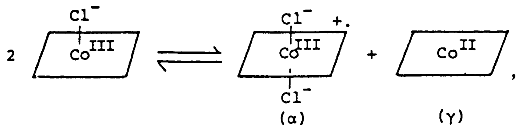
(4) On the Mechanism of Three Paramagnetic Species Formation in $Co^{III}Cl(tpp)$. As described in the previous paper,[2] the π cation radical (α) is formed by thermal activation in chlorinated hydrocarbons. The formation of the species occurs reversibly with small enthalpy change (ΔH). From the ESR measurements described above, it has been found that the crystals grown from the chlorinated solutions trap β and γ in addition to α. The result may indicate an equilibrium between the diamagnetic species **1** and the paramagnetic species (α, β, and γ):



(7)

where S means a solvent molecule or a ligand molecule such as water contaminated on crystallization. On the other hand, the crystals doping **2** showed only the formation of δ. This fact excludes the possibility that the formation of β and γ on crystallization originates from free **2**. Therefore, the formation of these species is probably inherent in the solution of **1**.

The detailed examination of Eq. 7 provides several possibilities as the elementary reaction. It was clarified by 400 MHz FT-NMR[17] that **1** in chlorinated hydrocarbons has two axial ligands, one Cl^- and the other water or solvent molecule, at low temperature as low as −60 °C. As the temperature increased, the sixth ligand is removed, which leads to the possibility of a kind of disproportionation expressed by Eq. 8.[2] The temperature dependence of the α concentration shows the appropriateness of this process.



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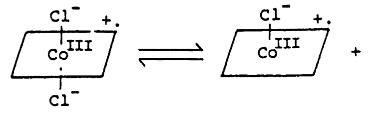

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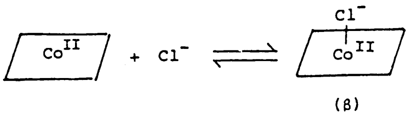

(10)

The six-coordinate cation radical formed is also labile for the dissociation into a five-coordinate cation radical and an anion,[3] as is seen in Eq.9. The existence of the five-coordinate Co^{III}(tpp) (β) in the crystal may show the possibility of a recombination reaction of Eq. 10.

In conclusion, **1** is very likely to give the three kinds of paramagnetic species. It should be understood that the observation of these species supports the apparent equilibrium described in Eq. 7 as the results of the several elementary reactions.

References

1) J. H. Wang, A. Nakahara. and E. B. Fleisher, *J. Am. Chem. Soc.*, **80**, 1109 (1958); J. H. Wang, *ibid.* **80**, 3168 (1958).

2) K. Yamamoto, M. Kohno, and H. Ohya-Nishiguchi, *Chem. Lett.*, **1981**, 255.

3) H. Ohya-Nishiguchi, M. Kohno, and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, **54**, 1923 (1981).

4) M. Kohno, H. Ohya-Nishiguchi, and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, **56**, 822 (1983).

5) T. Sakurai, K. Yamamoto, H. Naito, and N. Nakamoto, *Bull. Chem. Soc. Jpn.*, **49**, 3042 (1976).

6) T. Sakurai, Y. Iimura, K. Yamamoto, and H. Honma, Anual Meeting of Crystallographic Society of Japan, Tokyo, November (1982).

7) J. S. Grifith, *Discuss. Faraday Soc.*, **26**, 81 (1958).

8) B. Bleaney, Philos. Mag., **42**, 441 (1951).

9) J. M. Assour, *J. Chem. Phys.*, **43**, 2477 (1965).

10) W. C. Lin, *Mol. Phys.*,**31**, 657 (1976).

11) F. E. Dickson, C. J. Kunesh, E. L. McGinnis, and L. Petrakis, *Anal. Chem.*, **44**, 987 (1972).

12) W. C. Lin, "Electron Resonance and Electronic Structure of Metalloporphyrins," in "The Porphyrins," ed by D. Dolphin, Academic Press, New York and London (1974), Vol. 4, p. 335, and the other references cited therein.

13) B. R. McGarvey, *Can. J. Chem.*, **53**, 2498 (1975).

14) L. C. Dickinson and J. C. W. Chien, *Inorg. Chem.*, **15**, 1111 (1976).

15) The assumption is not so unreasonable. The fluctuation of c_3 in Table 1 is mainly because of the ambiguities encountered on the estimation of ESR parameters. On the other hand, c_1 is estimated from the $g_\perp$ value which is estimated more precisely than that of $g_{\parallel}$.

16) A. Abragam and M. L. Price, *Proc. R. Soc. London, Ser. A*, **206**, 173 (1951).

17) K. Yamamoto, M. Hoshino, T. Chijimatsu, M. Kohno, and H. Ohya-Nishiguchi, 32nd Symposium of Coordination Chemistry, Nagasaki, October, p. 152 (1982).

18) F. A. Walker, *J. Am. Chem. Soc.*, **92**, 4235 (1970).

19) J. M. Assour and W. K. Kahn, J. Am. Chem. Soc., **87**, 207 (1965).

20) G. C. Wagner, I. C. Gunsalus, M. Y. R. Wang, and B. M. Hoffman, *J. Biol. Chem.*, **256**, 6266 (1981).