Cobalt(I) Tetraphenylporphin

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Cobalt(I) tetraphenylporphin was prepared by reduction of tetraphenylporphinatocobalt(II) with sodium benzophenone ketyl in tetrahydrofuran (THF) and was purely isolated. The compound was identified as Na-[Co(I)TPP]·5THF (tetraphenylporphin is abbreviated to TPP). On the basis of electronic absorption spectrum, magnetic circular dichroism, magnetic susceptibility and NMR spectrum, the complex formed was concluded to be a complex of cobalt(I). Although some part of cobalt electron is migrated into the conjugated system of porphin, an electron furnished by the reducing reagent is mainly trapped by the central cobalt. The compound should be named sodium tetraphenylporphinatocobaltate(I).

When a metalloporphyrin is reduced, an electron given by the reducing reagent is trapped by either porphyrin π^* orbital or metal d orbital depending upon the electronic structure of the central metal. Metalloporphyrins with vacancies in $d\pi$ orbitals can capture electrons into the central metal ion, whereas metalloporphyrins with a d^8, d^9, or d^{10} dipositive metal cation accept electrons into the porphyrin conjugated system. By one-electron reduction, tetraphenylporphinatozinc(II), for example, traps an electron in the porphyrin conjugated system.[1] Thus it shows an electronic absorption spectrum of the mononegative ion of tetraphenylporphin and also an ESR signal with a g-value of almost free-spin.

If the lowest antibonding π molecular orbital of the coordinating conjugated systems is lower than the ligand field antibonding orbitals, z^2 and x^2-y^2, an electron from the reducing reagents will be trapped in the conjugated system. This gives rise to a mononegative ion of the coordinating ligand. The present authors have isolated a complex coordinated by bipyridine negative ion, $[Cr(0)(CO)_4(bipy^-)]^-$ (bipy denotes bipyridine), which was prepared by reduction of $[Cr(0)(CO)_4bipy]$.[2] Similarly $[Fe(bipy)_3]$ was a complex coordinated by bipyridine negative ions.[3] On the contrary, however, the isoelectronic $[Co(bipy)_3]^+$ was not a complex of bipyridine negative ions but a complex of Co(I) in the triplet ground state.[4] In this particular case, the lowest vacant π molecular orbital of the coordinating bipyridine must be higher than the ligand field antibonding orbitals. This arises from a rather high electron affinity of Co(II) ion. Co(I) in an octahedral ligand field should be in a triplet state with electronic configuration of $(d\pi)^6(z^2)(x^2-y^2)$, while in a planar environment it should be either in a singlet state of $(d\pi)^6(z^2)^2$ or in a triplet state of $(d\pi)^6(z^2)(x^2-y^2)$ depending upon an energy gap of z^2 and x^2-y^2 orbitals. Since z^2 and x^2-y^2 orbitals are the antibonding orbitals of the coordination binding, an electron occupation in these orbitals results in a dissociation of the coordination binding unless an electrostatic attraction between the metal ion and the ligands is present as in $[Co(bipy)_3]^+$. Although $[Co(bipy)_3]^+$ shows a trend to form $[Co(bipy)_2]^+$, it keeps two electrons with parallel spin in z^2 and x^2-y^2 orbitals, which are predominantly localized on the central metal, rather than in the lowest antibonding π molecular orbital of bipyridine. A planar cobalt(II) complex, tetraphenylporphinatocobalt(II), for example, traps an electron furnished upon reduction into a molecular orbital predominantly localized on cobalt ion. Since a gap of z^2 and x^2-y^2 orbitals in a strong planar ligand field of metalloporphyrin is appreciably large, the ground configuration of cobalt(I) at almost center of the planar ligand field turns out to be diamagnetic $(d\pi)^6(z^2)^2$. The formations of other planar diamagnetic cobalt(I) species have been established.[5]

Whitlock and Bower[6] first presumed the reduction product of tetraphenylporphinatocobalt(II) as the spin-paired cobalt(I) porphin on the basis of gram-equivalents of sodium amalgam to complete the reduction, NMR spectrum and Gouy balance experiments of the reduced species in tetrahydrofuran, and activity of catalyzing the sodium borohydride reduction of nitrobenzene.[7,8] Recently we succeeded in isolation of the cobalt(I) tetraphenylporphin. In this paper, we will present an identification of the porphin on the basis of electronic absorption spectrum, magnetic circular dichroism, magnetic susceptibility and NMR spectrum.

Experimental

Materials. $\alpha, \beta, \gamma, \delta$-Tetraphenylporphin (abbreviated to TPP) was synthesized from pyrrole and benzaldehyde by the method of Adler, *et al.*[9] Chromatographic purification was repeated on activated alumina columns using chloroform

1) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 818 (1963).

2) Y. Kaizu and H. Kobayashi, This Bulletin, **43**, 2492 (1970).

3) Y. Kaizu, T. Yazaki, Y. Torii, and H. Kobayashi, *ibid.*, **43**, 2068 (1970).

4) Y. Kaizu, Y. Torii, and H. Kobayashi, *ibid.*, **43**, 3296 (1970).

5) a) O. Müller and G. Müller, *Biochem. Z.*, **336**, 299 (1962); S. L. Tackett, J. W. Collatt, and J. C. Abott, *Biochemistry*, **2**, 919 (1963); P. K. Das, H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Biochim. Biophys. Acta*, **141**, 644 (1967). b) R. Taube, M. Zach, K. A. Stauske, and S. Heidrich, *Z. Chem.*, **3**, 392 (1963); D. H. Bush, J. H. Weber, D. H. Williams, and N. J. Rose, *J. Amer. Chem. Soc.*, **86**, 5161 (1964); P. Day, H. A. O. Hill, and M. G. Price, *J. Chem. Soc., A*, **1968**, 90; L. D. Rollman and R. T. Iwamoto, *J. Amer. Chem. Soc.*, **90**, 1455 (1968). c) G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3056 (1964); G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, **91**, 3341 (1969).

6) H. W. Whitlock, Jr. and B. K. Bower, *Tetrahedron Lett.*, **1965**, 4827.

7) A. A. Vlček and A. Rusina, *Proc. Chem. Soc.*, **1961**, 161.

8) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1963**, 3594.

9) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).

as solvent and also eluent. Cobalt(II) complex, TPPCo(II), was prepared from the metal-free base and cobalt(II) acetate by the method of Rothemund and Menotti.[10] The complex was purified by sublimation at 250—300°C under reduced pressure. Lustrous violet crystals thus obtained was identified by elemental analysis.

Found: C, 78.8; H, 3.9; N, 8.4; Co, 8.6%. Calcd for $C_{44}H_{28}N_4Co$: C, 78.7; H, 4.2; N, 8.3; Co, 8.8%.

Cobalt(III) complex, TPPCo(III)Cl·Py·C_2H_5OH, where Py denotes pyridine, was prepared from TPPCo(II) in benzene being refluxed with a mixture of pyridine, ethanol, and hydrochloric acid by the method of Yamamoto and Tonomura.[11]

Found: C, 73.4; H, 4.3; N, 8.6%. Calcd for $C_{51}H_{39}N_5$-CoCl: C, 73.6; H, 4.7; N, 8.4%.

All other reagents and solvents were commercially available. Tetrahydrofuran (THF) used for solvent was purified by careful distillation over cuprous chloride and a trace of water was removed by adding $LiAlH_4$.

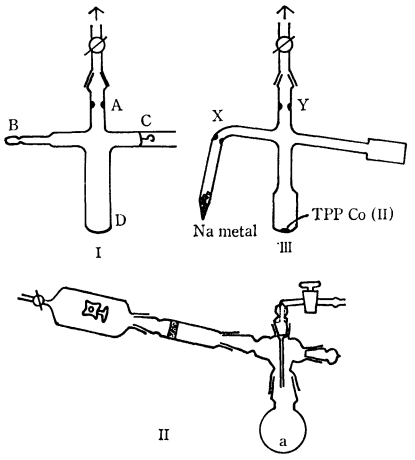

Fig. 1. Apparatus for reduction.
Benzophenone ketyl was prepared in I. The reduction of TPPCo (II) with benzophenone ketyl was carried out in II. The vessel III was used to measure absorption spectrum during the reduction process of TPPCo(II) with sodium metal in THF.

Preparation of Co(I) Complexes. Benzophenone (0.2 g) and sodium metal (0.2 g) were placed in D of the apparatus I shown in Fig. 1. The apparatus was connected to a vacuum system. After deaerated dry THF (20 m*l*) was transferred into D by distillation, the apparatus was sealed off at A and shaken for 2 hr. Thus sodium benzophenone ketyl was obtained with deep reddish violet color. TPPCo(II) (0.35 g) was placed at a under dry nitrogen in the apparatus II shown in Fig. 1. Being connected with a dry nitrogen atmosphere, the break-seal C of the apparatus I was broken, and then the tube B was cut at the top. In the nitrogen atmosphere sodium benzophenone ketyl was transferred from B onto TPPCo(II) in the apparatus II. After the mixture was stirred for 3 hr, solvent THF was removed by vacuum distillation into a trap cooled in liquid nitrogen. Then the residue was added with a mixture of deaerated dry ether (10 m*l*) and petroleum ether (10 m*l*) and then filtered. The product was dried *in vacuo*.

Found: Co, 5.4%. Calcd for $C_{64}H_{68}N_4O_5CoNa$ (Na[TPP-Co]·5THF): Co, 5.6%.

Reduction of TPPCo(II) with sodium metal in THF was also followed using the apparatus III shown in Fig. 1. After the apparatus was evacuated being connected with a vacuum system, sodium mirror was formed on the wall of the branch X and then the branch was sealed off at X. Deaerated dry THF was transferred by distillation into the container of TPPCo(II) and the apparatus was sealed off at Y. The solution was shaken being contacted with the mirror. The absorption spectrum of the solution was recorded after a period of the shaking.

Electronic Absorption Spectra and Magnetic Circular Dichroism. Measurements of the electronic absorption spectra of the air-sensitive compounds were described in a previous paper.[12] Spectra were taken on a Shimadzu automatic recording spectrophotometer Model MPS-50. Circular dichroism under an external magnetic field of 10,000 gauss was measured by a JASCO automatic recording spectropolarimeter Model ORD/UV-5 with CD attachment.[13]

Magnetic Susceptibility. Magnetic susceptibility of the complexes was measured by means of Gouy method. The measurements were carried out at room temperature. After it was calibrated for the diamagnetic term by the usual method,[14] magnetic moment of the complex was calculated.

Nuclear Magnetic Resonance. NMR spectra were recorded at room temperature on a 100 MHz Japan Electron Optics Laboratory spectrometer Model JNM 4H-100. Solvents were THF and pyridine. In the case of Co(III) complex, THF and $CDCl_3$ were used as solvent. Tetramethylsilane was used as an external reference.

Results and Discussion

Spectral change during the reduction process of TPPCo(II) with sodium metal in THF is shown in Fig. 2. The change takes place stepwise. During the first step of the reduction, remarkable isosbestic points are observed at 18.7, 19.2, 23.4, and 25.7 kK. Further reduction proceeds rather successively, therefore isosbestic points are shifted during the reaction. The complex, which has been isolated successfully in the present study, is first step product of the reduction. Absorption spectrum of the isolated complex (Fig. 3) is in good agreement with the one observed in the first step of the reduction shown in Fig. 2. The absorption maxima also coincide with those given by Whitlock and Bower.[6]

The reduced complex is extremely soluble in THF and pyridine. The spectra of the complex in benzene, THF and pyridine are actually the same in shape (Fig. 3). However the results indicate that there occurs no such axial coordination as to give a drastic change in the electronic structure, since the axial coordination by pyridine or THF may give rise to a change in the ligand field electronic structure as has been observed in Fe(II)tetraphenylporphin.[15]

10) P. Rothemund and A. R. Menotti, *J. Amer. Chem. Soc.*, **70**, 1808 (1948).

11) K. Yamamoto and S. Tonomura, *Sci. Papers Inst. Phys. Chem. Res.*, **58**, 122 (1964).

12) Y. Torii, T. Yazaki, Y. Kaizu, S. Murasato, and H. Kobayashi, This Bulletin, **42**, 2264 (1969).

13) H. Kobayashi, M. Shimizu, and I. Fujita, *ibid.*, **43**, 2335 (1970).

14) See for example, B. N. Figgis, and J. Lewis, "Modern Coordination Chemistry" ed. by J. Lewis and R. G. Wilkins, Interscience Publishers, New York, (1960), p. 415.

15) H. Kobayashi and Y. Yanagawa, This Bulletin, **45**, 450 (1972).

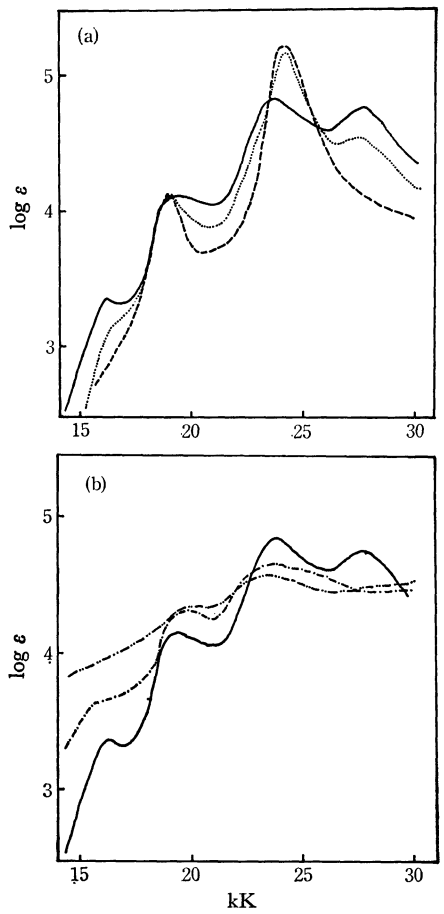

Fig. 2. Spectral change of the reduction process of TPPCo(II) with sodium metal in THF.
(a) The first step of the reduction.
------: TPPCo(II); ·····: after 1/2 hr;
——: after 1 hr
(b) Further step of the reduction.
——: after 2 hr; -·-·-: after 3 hr:
-··-··-: after 5 hr

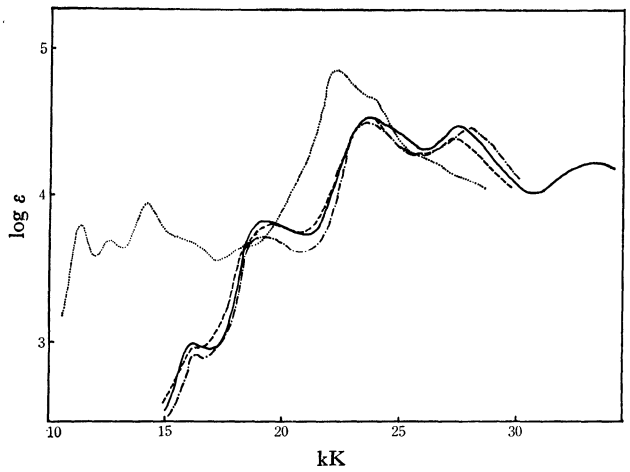

Fig. 3. Absorption spectra of Na[Co(I)TPP]·5THF.
-·-·-: in benzene
——: in THF ·····: Na[ZnTPP⁻] in THF[1,16,17]
------: in pyridine

The reduced complex in solution is very sensitive to oxygen and moisture and opening the solution to air leads to the immediate oxidation to TPPCo(II) and/or

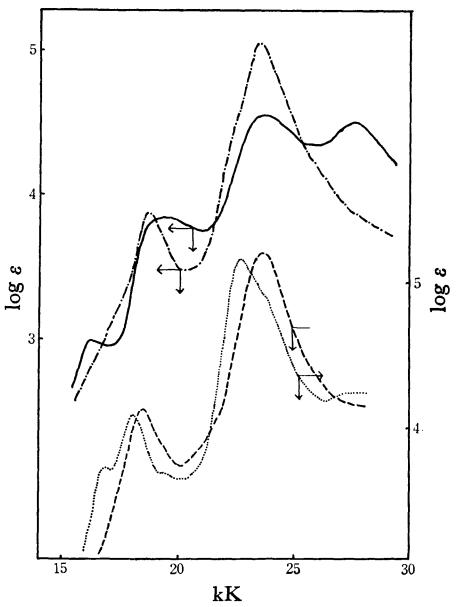

Fig. 4. Spectral change upon air-oxidation of Na[Co(I)TPP]-5THF in THF.
——: Na[Co(I)TPP]·5THF
-·-·-: after it was exposed to air
------: TPPCo(II) in THF
·····: TPPCo(III)Cl·Py·C_2H_5OH in THF
(Arrows indicate scales for the respective curves.)

TPPCo(III)X (Fig. 4). As is seen in Fig. 3, the absorption spectrum of reduced complex lacks the near-infrared bands at 11.3, 12.5, and 14.2 kK characteristic of the mononegative ion of tetraphenylporphin, which have been observed with a mononegative ion complex coordinated to Zn(II),[1,16,17] and therefore an electron furnished by the reducing reagent is much likely to localize on the central metal ion.

The first step product of the reduction was isolated in the solid state. The complex was identified by elemental analysis as Na[Co(I)TPP]·5THF. The crystal-containing THF was detected by NMR as described later. Measurements of the magnetic susceptibility reveal that the isolated first step product is diamagnetic in the solid state. Cobalt(II) ion in TPPCo(II) has an unpaired electron in the configuration $(d\pi)^6(z^2)$, whereas the observed value of the magnetic moment is larger than that expected for $S=1/2$ because of a mixing of the excited states by spin-orbit coupling perturbation.[18] Since there is no appreciable overlap between z^2 orbital and the lowest vacant π orbitals of porphin and thus there is no strong interaction between them, the ground state of the reduced complex must be triplet, $(d\pi)^6(z^2)(\pi^*)$, when an electron is trapped in one of the lowest vacant π orbitals of porphin, π^*. The observed diamagnetism of the complex prepared by one-electron reduction of TPPCo(II) should be interpreted in terms of the configuration $(d\pi)^6(z^2)^2$, where the central cobalt is

16) J. W. Dodd and N. S. Hush, *J. Chem. Soc.*, **1964**, 4607.
17) H. Kobayashi, Y. Kato, and Y. Kaizu, unpublished.
18) J. S. Griffith, "The Theory of Transition-Metal Ions" Cambridge Univ. Press, (1961), p. 370.

trapping an electron given by the reducing reagent. Whitlock and Bower have observed a diamagnetic behavior of the reduced complex present in THF solution.[6] However the fact that NMR spectrum of the complex in THF could be measured is regarded for first-order approximation as an evidence of diamagnetism of the complex in THF. As a matter of fact, opening the solution to air leads to immediate disappearance of the porphin signal and broadening of the solvent peaks.

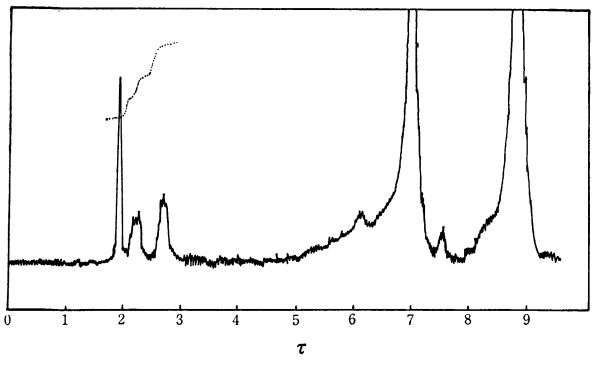

Fig. 5. NMR spectrum of Na[Co(I)TPP]·5THF in THF.

Table 1.

	a(τ)	b(τ)	c(τ)	Solvent	
TPP	1.05	1.70	2.20	$CDCl_3$	19)
TPPMg·2Py	1.05	1.70	2.20	$CDCl_3$	19)
TPPCo(III)Cl	1.03	1.98	2.35	$CDCl_3$	This work
	1.03	1.98	2.35	THF	This work
Na[Co(I)TPP]·5THF	1.95	2.10	2.55	THF	This work

TPP: tetraphenylporphin
Py: pyridine
THF: tetrahydrofuran

NMR spectrum of the complex was measured in THF and pyridine. In THF, a singlet was observed at 1.95 τ, a multiplet, at 2.10 τ and another multiplet, at 2.55 τ (Fig. 5). The singlet at 1.95 τ (band a in Table 1) is assigned to pyrrole ring protons. The multiplet at 2.10 τ (band b) is assigned to *o*-protons of phenyl groups and the one at 2.55 τ (band c), to *m*- and *p*-protons. The chemical shift values are summarized in Table 1. As is seen in the case of TPP-Co(III)Cl, the chemical shift of pyrrole protons are not influenced with the central metal ion which is less $d\pi$-donating and solvent effect of the NMR spectrum is not so appreciable. However NMR signal of the pyrrole ring protons in $[Co(I)TPP]^-$ is shifted toward higher field. This high-field shift is attributed to an increase of electron density at the pyrrole ring protons which arises from a back-donation of $d\pi$ electron to the lowest vacant π molecular orbitals of porphin.

NMR spectrum of a pyridine solution of the isolated solid sample is shown in Fig. 6. Multiplets were observed at 6.25 τ and 8.15 τ. These multiplets are very close to the ones observed with free THF. THF included in Na[Co(I)TPP]·5THF is set free in pyridine

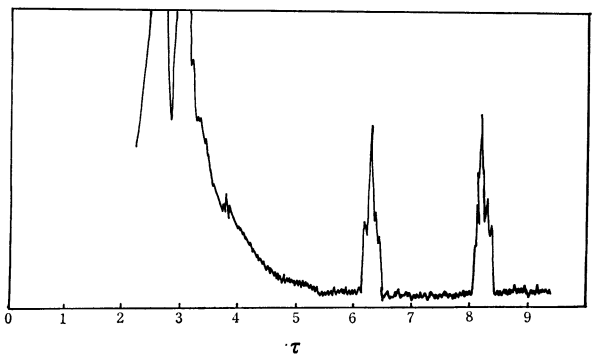

Fig. 6. NMR spectrum of Na[Co(I)TPP]·5THF in pyridine.

solution. The THF molecules are much likely to coordinate toward sodium ion in the crystal. Further studies are required concerning with the location of sodium ion in pyridine solution of the complex. However the THF molecules in the solution are present in considerably distant locations from the porphin moiety, since the THF multiplets are free from the ring current of porphin. This type of the crystal-containing THF has been found in various similar reduced metal phthalocyanines.[20]

Molecular orbital calculations on porphin yield two top filled orbitals a_{2u} and a_{1u}, and the lowest degenerate empty orbital pair e_g.[21-24] Thus the lowest excited states arise from the electronic configurations $(a_{2u})^2a_{1u}e_g$ and $(a_{1u})^2a_{2u}e_g$, whereas the ground state is $(a_{2u})^2(a_{1u})^2$. A circular box is described by a radial coordinate r and an angular coordinate θ. Orbitals are written $|\pm k)=f(r)\exp(\pm ik\theta)$, where k denotes orbital angular momentum.[25] Gouterman has pointed out that the top filled orbitals are accidentally degenerate and the orbital pair $(a_{2u}\pm ia_{1u})/\sqrt{2}$ can be identified with the degenerate pair of circular box orbitals $|\pm 4)=f(r)\exp(\pm 4i\theta)$, while the lowest empty e_g orbitals, $|\pm 5)=f(r)\exp(\pm 5i\theta)$.[26,26a]

In the ground state, the orbital pair which has z components of angular momentum $\lambda_z=\pm 4$ and angular momentum $\lambda=4$ are filled with four electrons; the configuration is denoted $(4)^4$ and has zero angular momentum $\lambda_z=0$. The first excited configurations arise by exciting a $\lambda=4$ electron to an orbital with $\lambda=5$, and are denoted $(4)^35$. This configuration gives rise to degenerate pairs of states with $\Lambda_z=\pm 1$ and with $\Lambda_z=\pm 9$. A selection rule allows a pair of transitions $\Delta\Lambda_z=\pm 1$. The allowed transition pair, $\Delta\Lambda_z=\pm 1$, is assigned to the intense Soret band of porphin

19) C. B. Storm and A. H. Corwin, *J. Org. Chem.*, **29**, 3700 (1964).

20) R. Taube, *Z. Chem.*, **6**, 8 (1966); S. Herzog and M. Schmidt, *ibid.*, **3**, 392 (1963).

21) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950); G. R. Seely, *ibid.*, **27**, 125 (1957); H. Kobayashi, *Nippon Kagaku Zasshi*, **81**, 519 (1960).

22) H. Kobayashi, *J. Chem. Phys.*, **30**, 1373 (1959).

23) C. Weiss, H. Kobayashi, and M. Gouterman, *J. Mol. Spectrosc.*, **16**, 415 (1965).

24) M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, **4**, 44 (1966).

25) $|a)$ denotes the molecular orbital a, whereas $|k^\circ>$, Slater determinantal wave function of the configuration k°. The state $|j>$ is described as a linear combination of $|k^\circ>$'s.

26) M. Gouterman, *J. Chem. Phys.*, **33**, 1523 (1960).

26a) M. Gouterman, *ibid.*, **30**, 1139 (1959).

in the near-ultraviolet denoted B band, whereas the forbidden pair, $\Delta M_z = \pm 9$, the vibronically-allowed weak visible band denoted Q band.

The measurements of magnetic circular dichroism (MCD) will give an evidence of the orbital angular momentum in the excited state.[27] As a matter of fact, an A-type dispersion of MCD observed at each of the Q and B bands of TPPZn(II) reveals an orbital angular momentum arising in the respective excited state.[13] The lowest excited states of TPPCo(II) and TPPCo(III)X can be described by pure (π, π^*) excitations. As are shown in Figs. 7 and 8, MCD spectra of these complexes preserve such a characteristics as observed with TPPZn(II).

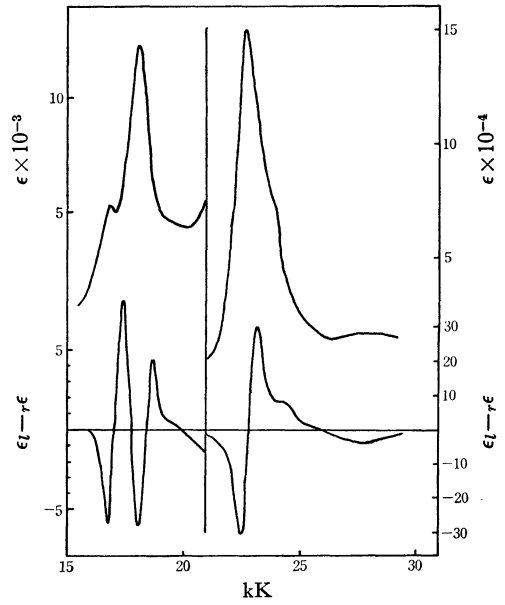

Fig. 7. Absorption spectrum and magnetic circular dichroism of TPPCo(III)Cl·Py·C_2H_5OH in THF.

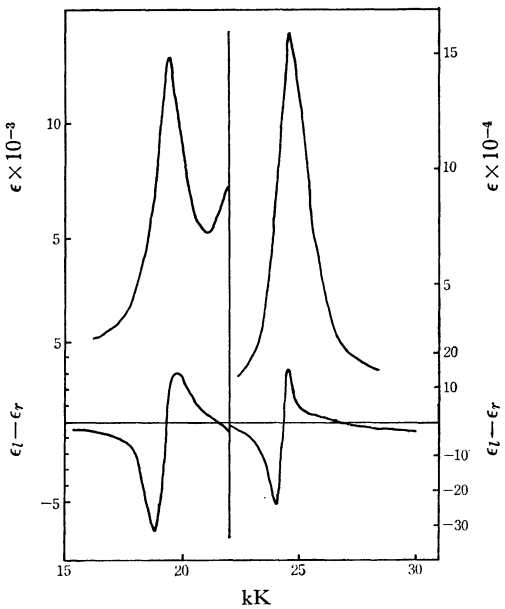

Fig. 8. Absorption spectrum and magnetic circular dichroism of TPPCo(II) in THF.

27) P. J. Stéphens, W. Suëtaka, and P. N. Schatz, *J. Chem. Phys.*, **44**, 4592 (1966).

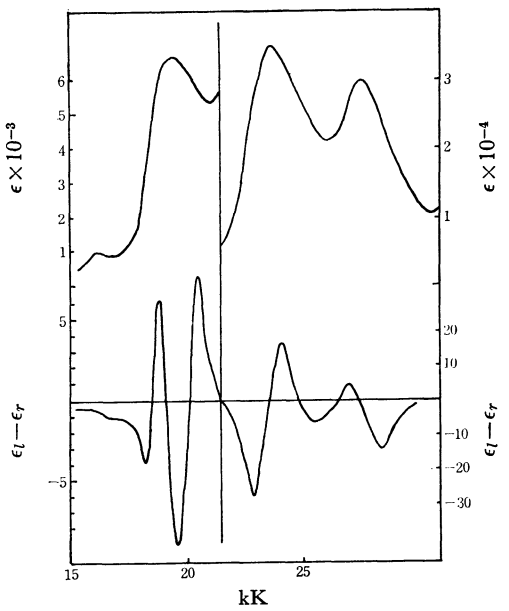

Fig. 9. Absorption spectrum and magnetic circular dichroism of Na[Co(I)TPP]·5THF in THF.

In the case of $[TPPCo(I)]^-$, back-donation of the cobalt $d\pi$ electron toward the porphin conjugated system should be appreciable in the ground state and the excited states, since an electron furnished by the reducing reagent is trapped in the cobalt z^2 orbital. Therefore the lowest excited states of $[TPPCo(I)]^-$ should be described in terms of a configuration-interaction admixture of the porphin (π, π^*) excitations and the "metal to porphin" charge-transfer excitations. Even so, as shown in Fig. 9, MCD spectrum of $[TPPCo(I)]^-$ still preserves a characteristics of the porphin Q and B bands and gives rise to A-type dispersions at 18.5, 20.0, and 23.5 kK corresponding to 0-0 and 0-1 components of Q band and B band, respectively, which are typically shown with TPPCo(III) and TPPCo(II) in Figs. 7 and 8. Two other bands were observed at 17.0 and 27.5 kK. No remarkable A-type MCD could be observed at the 17.0 kK weak band under a magnetic field of 10000 gauss. On the other hand, however, a reverse A-type dispersion was observed at 27.5 kK.

The molecular orbitals of $[TPPCo(I)]^-$ responsible to

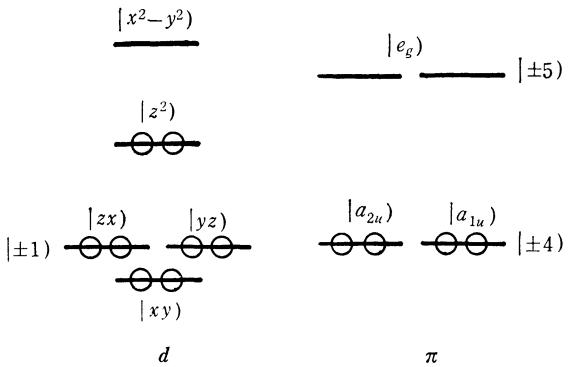

Fig. 10. The highest occupied and the lowest vacant molecular orbitals of $[TPPCo(I)]^-$.

the outer electronic configuration are schematically shown in Fig. 10. A degenerate $d\pi$ orbital pair, zx and yz, makes charge-transfer interactions with the porphin π molecular orbitals of e_g symmetry. The degenerate $d\pi$ orbital pair can be rewritten by $|\pm1)=(zx\pm iyz)/\sqrt{2}$, where ±1 denote z components of angular momentum $\lambda=1$. A one-electron term connecting the orbitals $|\pm1)$ and $|\pm5)$, $(\pm1|\hat{h}^{\text{eff}}|\pm5)\equiv\beta$, gives rise to a delocalization of the cobalt $d\pi$ electrons toward the lowest vacant porphin π orbital.

The electrons in the orbitals with $\lambda=1$, $\lambda=4$, or $\lambda=5$ (*i.e.*, the top eight electrons) are assumed to move in a one-electron effective potential set up by the nuclei and the remaining electrons. These electrons are assumed to interact with one another by two-electron term e^2/r_{ij}. There is no interaction between states with different Λ_z except the states which are connected with $(\pm1|\hat{h}^{\text{eff}}|\pm5)$. Wave functions are taken as Slater determinants which are eigenfunctions of total spin singlet.

E^0 is defined as the ground state energy, except for the electron interaction of the top eight electrons. I_1, I_4, and I_5 denote one-electron core energy of the orbitals with $\lambda=1$, $\lambda=4$, and $\lambda=5$. The Coulomb and exchange integrals over molecular orbitals are defined as

$$J_{ab}=e^2\int\frac{\phi_a^*(1)\phi_b^*(2)\phi_a(1)\phi_b(2)}{r_{12}}d\tau_1d\tau_2$$

$$K_{ab}=e^2\int\frac{\phi_a^*(1)\phi_b^*(2)\phi_b(1)\phi_a(2)}{r_{12}}d\tau_1d\tau_2$$

where 1 and 2 refer to the position of electrons 1 and 2, ϕ_a and ϕ_b, two molecular orbitals, and the star, complex conjugate. The numbers a and b refer of the λ_z value of the orbitals.

Table 2 shows the singlet states arising from the configurations $(1)^4(4)^4$, $(1)^3(4)^4(5)$, $(1)^4(4)^3(5)$, and $(1)^3(4)^3(5)^2$. Two singlets appear from a configuration of four electrons in four different orbitals. Slater determinants were then taken as follows:

$$|+5a\rangle\equiv[|1\bar{1}4\bar{4}-1-45-\bar{5}|-|1\bar{1}4\bar{4}-1-4\bar{5}-5|+|1\bar{1}4\bar{4}-\bar{1}-\bar{4}5-5|-|1\bar{1}4\bar{4}-\bar{1}-45-\bar{5}|]/2,$$

TABLE 2. EXCITED SINGLET STATES AND ENERGIES OF THE COBALT(I) PORPHIN (CIRCULAR BOX MODEL)

Configuration	Orbitals occupied	Λ_z	Wave function	Diagonal energy	Approximate diagonal energy cm^{-1}	
$(1)^4(4)^4$	$(1)^2(-1)^2(4)^2(-4)^2$	0	$\|0°\rangle$	W_0	0	0
$(1)^3(4)^4(5)$	$(1)(-1)^2(4)^2(-4)^2(5)$ $(1)^2(-1)(4)^2(-4)^2(-5)$	$\pm$ 4	$\|\pm$ 4°$\rangle$	W_2+2K_{15}	Δ_{CT}	4000
	$(1)^2(-1)(4)^2(-4)^2(5)$ $(1)(-1)^2(4)^2(-4)^2(-5)$	$\pm$ 6	$\|\pm$ 6°$\rangle$	W_2+2K_{1-5}	Δ_{CT}	4000
$(1)^4(4)^3(5)$	$(1)^2(-1)^2(4)^2(-4)(5)$ $(1)^2(-1)^2(4)(-4)^2(-5)$	$\pm$ 9	$\|\pm$ 9°$\rangle$	W_1+2K_{4-5}	$\Delta+2K$	15900
$(1)^3(4)^3(5)^2$	$(1)^2(-1)(4)^2(-4)(5)^2$ $(1)(-1)^2(4)(-4)^2(-5)^2$	$\pm$15	$|\pm$15°$\rangle$	$W_1+W_2-W_0+(J_{55}-J_{45})+(J_{14}-J_{15})+K_{14}+K_{1-5}+K_{4-5}$	$\Delta+\Delta_{CT}+K$	19100
	$(1)(-1)^2(4)^2(-4)(5)^2$ $(1)^2(-1)(4)(-4)^2(-5)^2$	$\pm$13	$|\pm$13°$\rangle$	$W_1+W_2-W_0+(J_{55}-J_{45})+(J_{14}-J_{15})+K_{1-4}+K_{15}+K_{4-5}$	$\Delta+\Delta_{CT}+K$	19100
	$(1)^2(-1)(4)^2(-4)(5)(-5)$ $(1)(-1)^2(4)(-4)^2(5)(-5)$	$\pm$ 5	$|\pm$5a°$\rangle$	$W_1+W_2-W_0+(J_{55}-J_{45})+(J_{14}-J_{15})+1/2(-K_{14}+K_{15}+4K_{1-5}+4K_{45}+K_{4-5}-K_{5-5})$	$\Delta+\Delta_{CT}+2K_1$	27700
			$|\pm$5b°$\rangle$	$W_1+W_2-W_0+(J_{55}-J_{45})+(J_{14}-J_{15})+1/2(K_{14}+3K_{15}+3K_{4-5}+K_{5-5})$	$\Delta+\Delta_{CT}+2K$	20900
$(1)^4(4)^3(5)$	$(1)^2(-1)^2(4)(-4)^2(5)$ $(1)^2(-1)^2(4)^2(-4)(-5)$	$\pm$ 1	$\|\pm$ 1°$\rangle$	W_1+2K_{45}	$\Delta+2K_1$	23700
$(1)^3(4)^3(5)^2$	$(1)^2(-1)(4)(-4)^2(5)^2$ $(1)(-1)^2(4)^2(-4)(5)^2$	$\pm$ 7	$\|\pm$ 7°$\rangle$	$W_1+W_2-W_0+(J_{55}-J_{45})+(J_{14}-J_{15})+K_{1-4}+K_{1-5}+K_{45}$	$\Delta+\Delta_{CT}+K_1$	22500
	$(1)(-1)^2(4)(-4)^2(5)^2$ $(1)^2(-1)(4)^2(-4)(5)^2$	$\pm$ 5	$\|\pm$ 5°$\rangle$	$W_1+W_2-W_0+(J_{55}-J_{45})+(J_{14}-J_{15})+K_{14}+K_{15}+K_{45}$	$\Delta+\Delta_{CT}+K_1$	22500
	$(1)^2(-1)(4)(-4)^2(5)(-5)$ $(1)(-1)^2(4)^2(-4)(5)(-5)$	$\mp$ 3	$|\mp$3a°$\rangle$	$W_1+W_2-W_0+(J_{55}-J_{45})+(J_{14}-J_{15})+1/2(-K_{1-4}+4K_{15}+K_{1-5}+4K_{45}+K_{4-5}-K_{5-5})$	$\Delta+\Delta_{CT}+2K_1$	27700
			$|\mp$3b°$\rangle$	$W_1+W_2-W_0+(J_{55}-J_{45})+(J_{14}-J_{15})+1/2(K_{1-4}+3K_{1-5}+3K_{4-5}+K_{5-5})$	$\Delta+\Delta_{CT}+2K$	20900

$W_0\equiv E^0+4I_1+4I_4+6J_{11}+16J_{14}+6J_{44}-2K_{1-1}-4K_{14}-4K_{1-4}-2K_{4-4}$
$W_1\equiv E^0+4I_1+3I_4+I_5+6J_{11}+12J_{14}+4J_{15}+3J_{44}+3J_{45}-2K_{1-1}-3K_{14}-3K_{1-4}-K_{15}-K_{1-5}-K_{4-4}-K_{45}-K_{4-5}$
$W_2\equiv E_0+3I_1+4I_4+I_5+3J_{11}+12J_{14}+3J_{15}+6J_{44}+4J_{45}-K_{1-1}-3K_{14}-3K_{1-4}-K_{15}-K_{1-5}-2K_{4-4}-K_{45}-K_{4-5}$

Mixing term	Energy	Approximate energy cm^{-1}		Mixing term	Energy	Approximate energy cm^{-1}	
$\langle0°\|\boldsymbol{H}\|\pm4°\rangle$	$\sqrt{2}\beta$	$\sqrt{2}\beta$	-5660				
$\langle\pm9°\|\boldsymbol{H}\|\pm13°\rangle$	$-\beta$	$-\beta$	4000	$\langle\pm1°\|\boldsymbol{H}\|\pm5°\rangle$	$-\beta$	$-\beta$	4000
$\langle\pm9°\|\boldsymbol{H}\|\pm5a°\rangle$	$\sqrt{2}/2\beta$	$\sqrt{2}/2\beta$	-2830	$\langle\pm1°\|\boldsymbol{H}\|\mp3a°\rangle$	$\sqrt{2}\beta$	$\sqrt{2}\beta$	-5660
$\langle\pm9°\|\boldsymbol{H}\|\pm5b°\rangle$	$-\sqrt{6}/2\beta$	$-\sqrt{6}/2\beta$	4900	$\langle\pm1°\|\boldsymbol{H}\|\mp3b°\rangle$	0	0	0
$\langle\pm5a°\|\boldsymbol{H}\|\pm5b°\rangle$	$\sqrt{3}/2(K_{14}-K_{15}+K_{5-5}-K_{4-5})$	0	0	$\langle\mp3a°\|\boldsymbol{H}\|\mp3b°\rangle$	$\sqrt{3}/2(K_{1-4}-K_{1-5}+K_{5-5}-K_{4-5})$	0	0

$$|+5b\rangle \equiv [\{|1\bar{1}4\bar{4}-\bar{1}-4\bar{5}-5|+|1\bar{1}4\bar{4}-1-\bar{4}5-\bar{5}|\}$$
$$-\frac{1}{2}\{|1\bar{1}4\bar{4}-1-4\bar{5}-\bar{5}|+|1\bar{1}4\bar{4}-1-\bar{4}\bar{5}-5|$$
$$+|1\bar{1}4\bar{4}-\bar{1}-\bar{4}5-5|+|1\bar{1}4\bar{4}-\bar{1}-45-\bar{5}|\}]/\sqrt{3};$$
$$|-3a\rangle \equiv [|1\bar{1}-4-\bar{4}-14\bar{5}-\bar{5}|-|1\bar{1}-4-\bar{4}-1\bar{4}5-\bar{5}|$$
$$+|1\bar{1}-4-\bar{4}-\bar{1}45-5|-|1\bar{1}-4-\bar{4}-\bar{1}4\bar{5}-5|]/2,$$
$$|-3b\rangle \equiv [\{|1\bar{1}-4-\bar{4}-\bar{1}45-\bar{5}|+|1\bar{1}-4-\bar{4}-1\bar{4}\bar{5}-5|\}$$
$$-\frac{1}{2}\{|1\bar{1}-4-\bar{4}-14\bar{5}-\bar{5}|+|1\bar{1}-4-\bar{4}-1\bar{4}5-\bar{5}|$$
$$+|1\bar{1}-4-\bar{4}-\bar{1}\bar{4}5-5|$$
$$+|1\bar{1}-4-\bar{4}-\bar{1}4\bar{5}-5|\}]/\sqrt{3},$$

where no bar implies spin α, a bar implies spin β and the molecular orbitals are denoted by their λ_z values. In the circular box model, $\phi_a^* \cdot \phi_a$ are identical for all the porphin molecular orbitals. It then follows that,

$$J_{44} = J_{45} = J_{55} = e^2 \int \frac{f^2(r_1) f^2(r_2)}{r_{12}} d\tau_1 d\tau_2 \equiv J$$

and

$$J_{14} = J_{15} = e^2 \int \frac{f_1^2(r_1) f^2(r_2)}{r_{12}} d\tau_1 d\tau_2 \equiv J'$$

For the K values, we set

$$K_{4-4} = K_{4-5} = K_{5-5} \equiv K$$
$$K_{45} \equiv K_1$$

as Gouterman assumed.[26] The orbitals $|\pm 1\rangle$ and $|\pm 5\rangle$ are overlapping. Therefore $(\pm 1|\hat{h}^{\text{eff}}|\pm 5)$ could be non-zero. However K_{15} and also K_{1-5} are assumed very small and are neglected. We define

$$\Delta_{CT} \equiv W_2 - W_0$$
$$\Delta \equiv W_1 - W_0.$$

For TPPZn(II), the Soret band $(\Delta + 2K_1)$ appears at 23700 cm^{-1} and the visible band $(\Delta + 2K)$, at 16900 cm^{-1}.[13] The phosphorescence of TPPCu(II) (Δ) occurs at 13300 cm^{-1}.[28] We then find

$$\Delta = 13300\ cm^{-1},\ K = 1800\ cm^{-1},\ K_1 = 5200\ cm^{-1},$$

for the tetraphenylporphins. The last column of Table 2 shows the values of the state energies in terms of Δ, Δ_{CT}, K_1, and K using the empirical values. For a variety of the values of Δ_{CT} and β, the transition energies of the cobalt(I) porphin were calculated. The singlet energy levels of the cobalt(I) porphin are shown in Fig. 11 as a function of β, assuming $\Delta_{CT}=4000\ cm^{-1}$. The excited states of $[TPPCo(I)]^-$ can be reproduced for $\Delta_{CT}=4000\ cm^{-1}$, $\beta=-4000\ cm^{-1}$. This β value is close to the value estimated from molecular orbital coefficient of the central nitrogens[23] and a similar resonance integral value as used by Hanazaki and Nagakura for a calculation of $[Fe(bipy)_3]^{2+}$.[29]

The calculation shows that the visible band of $[TPPCo(I)]^-$ arises mainly from $|\pm 9\rangle \leftarrow |0\rangle$ and the near-ultraviolet band, $|\pm 1\rangle \leftarrow |0\rangle$. A-type dispersions observed at 18.5, 20.0, and 23.5 kK reveal the orbital angular momentum expected for these porphin (π, π^*) excited states. The 17.0 kK weak band,

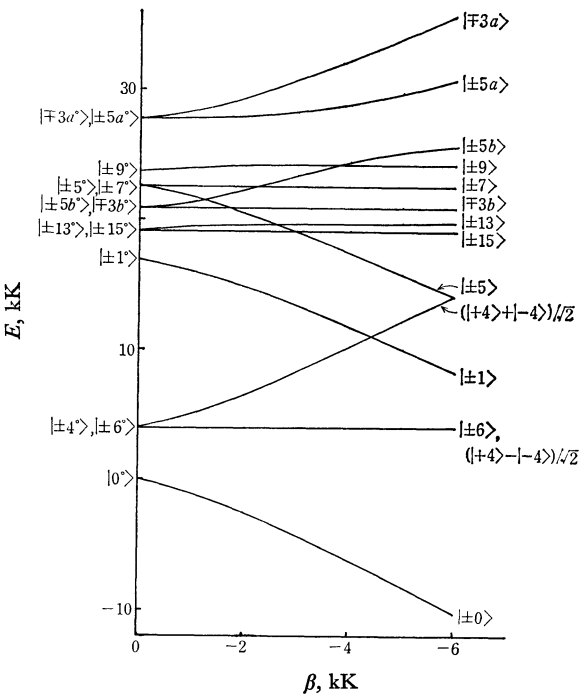

Fig. 11. The singlet energy levels of the cobalt(I) porphin as a function of β. (Δ_{CT} is assumed 4000 cm^{-1}).

however, is assigned to a "cobalt to porphin" charge-transfer transition, $(|+4\rangle + |-4\rangle)/\sqrt{2} \leftarrow |0\rangle$, which gives no orbital angular momentum in the excited state. In fact no remarkable A-type MCD could be observed at the 17.0 kK band. A reverse A-type dispersion observed at 27.5 kK may be assigned as arising from a transition mainly consisting of $|\mp 3b\rangle \leftarrow |0\rangle$. However spectral intensity of the transition $|\mp 3b\rangle \leftarrow |0\rangle$ is formally zero based on an assumption of the accidental degeneracy of a_{2u} and a_{1u} orbitals. From the same reason, the visible Q bands, $|\pm 9\rangle \leftarrow |0\rangle$, are formally prohibited. As shown in Figs. 7 and 8, intensity of the visible Q bands is appreciably high, although it is forbidden in character. Since the highest occupied a_{2u} and a_{1u} are not exactly degenerate, a term equal to half their energy difference,

$$(-4|\hat{p}|4) = 1/2[(a_{2u}|\hat{h}^{\text{eff}}|a_{2u}) - (a_{1u}|\hat{h}^{\text{eff}}|a_{1u})] \equiv \varepsilon,$$

connects two wave functions that differ by a single orbital, which is the one is $|+4\rangle$ and in the other $|-4\rangle$. This carries an spectral intensity from the allowed transition pair $|\pm 1\rangle \leftarrow |0\rangle$ to the forbidden transition apir $|\pm 9\rangle \leftarrow |0\rangle$. To reproduce the transition energies and the ratio of Q and B bands of TPPCo(II), we redetermined

$$\Delta = 14810\ cm^{-1},\ K = 2530\ cm^{-1},\ K_1 = 4600\ cm^{-1}$$
and $\varepsilon = \pm 1480\ cm^{-1}$.

As was pointed out by Gouterman on the empirical basis, the a_{1u} orbital is slightly higher than the a_{2u} orbital which is reverse to the ordering predicted by the conventional molecular orbital calculations.[26a]

From these parameters with $\Delta_{CT}=4{,}000\ cm^{-1}$ and $\beta=-4{,}000\ cm^{-1}$, we can well reproduce the excited states of $[TPPCo(I)]^-$ as shown in Fig. 12. To get a better fit of the spectral intensity of Q and B bands,

28) M. Gouterman, R. A. Mathles, and B. E. Smith, *J. Chem. Phys.*, **52**, 3795 (1970).

29) I. Hanazaki and S. Nagakura, *Inorg. Chem.*, **8**, 648 (1969); see also, I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, **50**, 265 (1969).

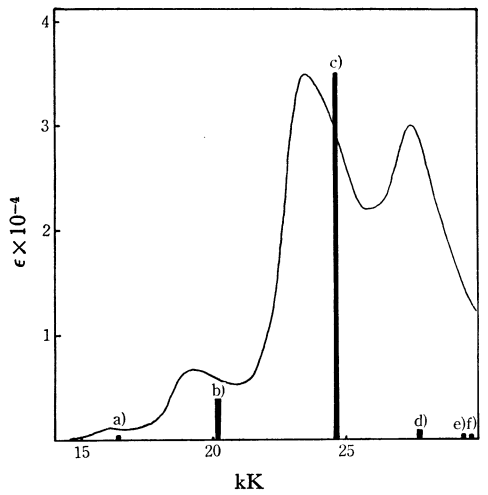

Fig. 12. Absorption spectrum of $[Co(I)TPP]^-$.
Curve: observed spectrum Vertical lines: calculated spectrum
a): $(|+4\rangle+|-4\rangle)/\sqrt{2} \leftarrow |0\rangle$, b): $|\pm 9\rangle \leftarrow |0\rangle$,
c): $|\pm 1\rangle \leftarrow |0\rangle$, d): $|\pm 13\rangle \leftarrow |0\rangle$, e): $|\mp 3b\rangle \leftarrow |0\rangle$,
f): $|\pm 15\rangle \leftarrow |0\rangle$

the parameters for $[TPPCo(I)]^-$ may be replaced by $\Delta = 14310\ cm^{-1}$ and $\varepsilon = \pm 2560\ cm^{-1}$. However the theory could not get an intensity of the band at 27.5 kK, although it could predict a reverse A-type dispersion. The (π, π^*) excited states of porphin in the ultraviolet region can not be well described without being mixed with higher energy configurations. In this context, a self-consistent molecular orbital calculation including cobalt electrons will be reported elsewhere. In a recent paper, Gouterman and his coworkers obtained $(\pm 4|\hat{\mu}_z|\pm 4) = \mp 2.27\ \beta$ and $(\pm 5|\hat{\mu}_z|\pm 5) = \mp 2.09\ \beta$ by a molecular orbital calculation.[30] If this is the case, some D_{4h} porphin should show a reverse A-type dispersion at the Soret band.[31] The circular box model predicts

$$(\pm 4|\hat{\mu}_z|\pm 4) = -\beta/\hbar(\pm 4|\hat{l}_z|\pm 4) = \mp 4\beta$$

and

$$(\pm 5|\hat{\mu}_z|\pm 5) = -\beta/\hbar(\pm 5|\hat{l}_z|\pm 5) = \mp 5\beta.$$

In a more exact treatment such as molecular orbital calculations based on a linear combination of atomic orbitals, these values are reduced. However magnetic circular dichroism of the cobalt porphin in the oxidation states, (I), (II), and (III), presented in this paper does not show any reverse A-type dispersion at B band. This indicates that $|(\pm 5|\hat{\mu}_z|\pm 5)| > |(\pm 4|\hat{\mu}_z|\pm 4)|$ even if it is treated with extensive configuration interactions.

Absorption spectrum and also magnetic circular dichroism spectrum of the cobalt(I) porphin were reproduced taking back-donation effect of the cobalt $d\pi$ electrons to porphin. To get the best fit, we assumed $\Delta_{CT} = 4000\ cm^{-1}$. However the experimental energy levels of $[TPPCo(I)]^-$ are qualitatively reproduced for $2000\ cm^{-1} < \Delta_{CT} < 8000\ cm^{-1}$. Such a positive charge-transfer energy, even if it is small, indicates an energy necessary to carry an electron from the cobalt to the porphin. Since an electron furnished by the reducing reagent is being trapped in d_{z^2} orbital of the central cobalt, a back-donation tendency of the cobalt $d\pi$ electrons to the porphin antibonding π orbital is sufficiently enhanced. The calculation predicts a transfer of the net charge $0.38\ e$ from the cobalt $d\pi$ orbitals. Felton and Linschitz have made measurements of polarographic halfwave potentials on a number of TPP complexes in dimethyl sulfoxide.[32] A gap between the first and second waves is almost constant for various systems except Co(II). Halfwave potential of the first step reduction of TPPCo(II) is appreciably lower than those of the other complexes, whereas that of the second step is rather close to those of the others. The second step reduction is assigned to an electron trapping in the porphin conjugated system, while the first step is an electron trapping in the central cobalt ion which arises from a higher electron affinity of the cobalt(II) ion in a strong planar ligand field. On the contrary, however, TPP metal free base and the metal complexes of divalent ion such as Mg(II), Ni(II), Cu(II), or Zn(II) capture an electron into the porphin conjugated system during the first step reduction process. This trend has been reproduced by an extended Hückel molecular orbital calculation.[24]

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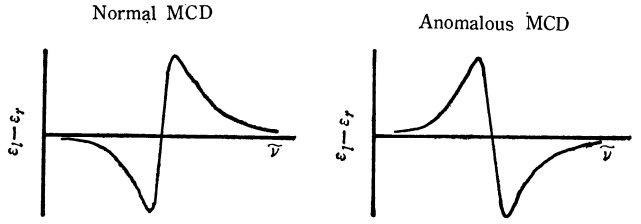
30) A. J. McHugh, M. Gouterman, and C. Weiss, Jr., *Theoret. Chim. Acta*, **24**, 346 (1972).

31) Molecular constant A of the A-term magnetic circular dichroism at the porphin degenerate transition $|j\rangle \leftarrow |0\rangle$ is defined as follows,

$$A = 3\sum_j \langle j|\mu_z|j\rangle \cdot Im\{\langle 0|\hat{m}_x|j\rangle\langle j|\hat{m}_y|0\rangle\},$$

where $\hat{\mu}$ and $\hat{m}$ are the magnetic and electric dipole operators, respectively, $\langle j|\hat{\mu}_z|j\rangle = -\beta/\hbar\langle j|\hat{l}_z|j\rangle$. Magnetic circular dichroism spectrum shows a normal dispersion when $A/D<0$, where $D=3\sum_j\{|\langle 0|\hat{m}_x|j\rangle|^2+|\langle 0|\hat{m}_y|j\rangle|^2\}$. For $A/D>0$, the spectrum shows an anomalous dispersion. "A-type dispersion" in this paper denotes the normal dispersion ($A/D<0$), whereas "reverse A-type dispersion", the anomalous dispersion ($A/D>0$).



32) R. H. Felton and H. Linschitz, *J. Amer. Chem. Soc.*, **88**, 1113 (1966).