

공액도에 따른 유기코발트 착화합물의 전자스펙트럼에 관한 연구

徐慧曠 · 李贊鏡 · 黃英愛*

상명여자대학교 자연과학대학 화학과

(1993. 9. 7 접수)

Dependence of Electronic Spectra on the Degree of Conjugation in Organocobalt(III) Complexes

Hye Kyung Seo, Chan Ah Bong, and Young-ae Whang Park*

Department of Chemistry, Sang Myung Women's University,

Seoul 110-743, Korea

(Received September 7, 1993)

요 약. 효소모델 코발트 화합물의 전자스펙트럼에서 축상의 이온성 리간드와 코발트사이의 전하전이에 해당하는 흡수띠의 위치가 용매의 극성도에 따라 변화하는 현상이 평면상의 거대고리 리간드의 공액도와 어떠한 상관관계가 있는가에 대하여 다음과 같은 여러가지의 공액도를 가진 거대고리 리간드의 유기코발트 착화합물을 사용하여 연구하였다. 완전히 공액인 CH_3CoL , $\text{C}_6\text{H}_5\text{CoL}$, CNCOL , $\text{CH}_3\text{CoL}'$, CNCOL' , 부분적으로 공액인 $\text{CH}_3(\text{py})\text{Co}(\text{DH})_2$, $\text{CH}_3\text{CoL}''$, 비공액의 이중결합을 포함하는 $[\text{CH}_3\text{Co}(1,4\text{-CT})](\text{ClO}_4)_2$ 와 고리가 완전히 닫히지 않은 $\text{CH}_3\text{Co}(\text{salen})$ 이 그들이다. 코발트와 탄소사이의 전하전이 흡수띠는 평면상의 거대고리 리간드가 완전히 공액일 때에만 용매의 극성도가 증가함에 따라 더욱 짧은 파장으로 이동하였고, 그에 해당하는 전이에너지(E_T)는 용매의 극성도(Z)와 직선의 상관관계에 있었으나, 거대고리 리간드가 불완전한 공액이거나 고리가 닫히지 않았을 때에는 전이 에너지와 용매의 극성도 사이에 상관관계를 발견할 수 없었다.

ABSTRACT. The electronic spectra of enzyme-model organocobalt(III) complexes containing completely or partially conjugated macrocyclic ligands were measured in various solvents to investigate the solvent effect on the charge transfer band for the axial cobalt-carbon bond by the extent of conjugation in the equatorial macrocyclic ring; completely conjugated, CH_3CoL , $\text{C}_6\text{H}_5\text{CoL}$, CNCOL , $\text{CH}_3\text{CoL}'$, CNCOL' , partially conjugated $\text{CH}_3(\text{py})\text{Co}(\text{DH})_2$, $\text{CH}_3\text{CoL}''$, unconjugated dienes, $[\text{CH}_3\text{Co}(1,4\text{-CT})](\text{ClO}_4)_2$, and open ring, $\text{CH}_3\text{Co}(\text{salen})$. The position of the charge transfer band which corresponds to the cobalt-carbon bond was shifted to a shorter wavelength as the polarity of solvent increased and the transition energy (E_T) had a linear relationship with solvent polarity parameter, Z -value, only in the case of completely conjugated system. However, the linear correlation between E_T and Z was not observed for partially conjugated and open ring systems.

INTRODUCTION

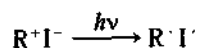
The importance of the chemistry of vitamin B_{12} has been recognized due to the effectiveness in the treatment of pernicious anaemia. Vitamin B_{12} is the cobalt(III) compound which contains 15-membered corrin ring and a benzimidazole group in

one axial position and cyanide in the other. B_{12} coenzyme is the compound which the cyanide ligand is replaced by an alkyl group. So far the known 5-coordinated organocobalt(III) compounds as the enzyme model compounds have some degree of π -conjugation¹⁻⁷. A porphyrin has $9 \times 2\pi$ -

electrons and corrin has 13π -electrons with a less π -conjugation. The cobaloxime and TIM ligands have $4 \times 2\pi$ -electrons conjugated, acacen and salen have $5 \times 2\pi$ -electrons in the inner macrocyclic ring. Thus a cobalt complex requires some degree of π -conjugation in the macrocyclic ring to form a fairly stable σ -bonded alkyl derivative.

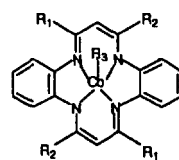
Murakami *et al.*⁸ synthesized a σ -bonded dicyanocobalt(III) complex of completely conjugated tetrapyrrolic macrocycle, dicyano (8,12-diethyl-1,2,3,7,17,18,19-octamethyl-tetradehydrocorrinate) cobalt(III), and observed that the position of a certain band in 700 nm region was sensitive to the polarity of a solvent. They assigned this band to the charge transfer band for the Co-CN bond and the transition energy (E_T , kcal mol⁻¹) was linearly correlated with a solvent polarity parameter, Z -value.

The solvent effect on electronic spectra was systematically studied in a quantitative manner by Kosower using Z -values for the first time⁹⁻¹¹. The Z -values were proposed as the charge transfer transition energies from the ionic state (R^+I^-) to the less polar state ($R \cdot I \cdot$) of the 1-ethyl-4-carbomethoxy-pyridinium iodide and utilized as standards of solvent polarity since these transition energies constitute a quantitative empirical measure of the ionizing power of the solvents. The more polar solvents have the larger Z -values.

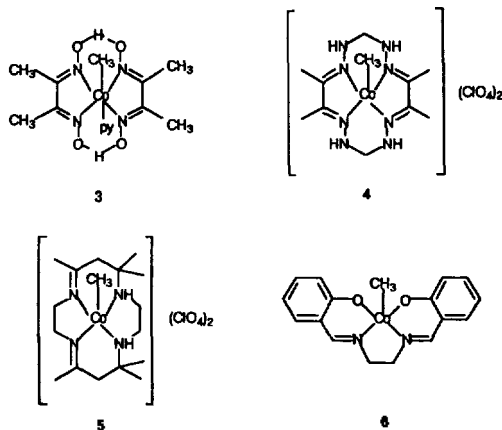


For the pyridinium iodides with various substituents on the pyridine ring the transition energies had a linear correlation with the Z -values. Therefore transition energies for any polar bond attached to aromatic rings have a linear relationship with the polarity of solvents. Sakata *et al.*¹² also observed the solvent effect for the 5-coordinate metal complex of another fully conjugated ligand, {chloro(7,17-diethyl-dibenzo[b,i][1,4,8,11] tetraazacyclotetradecinato) iron(III)}, in the 580~630 nm range of the electronic spectrum and there was also a linear relationship between the transition energies for the Fe-Cl bond and the Z -values. Although the solvent effect was observed in several fully conjugated systems as above, it has not

been clarified so far whether this phenomenon appears only in the case of complexes containing completely conjugated macrocyclic ring (more extremely, aromatic ring) or not. Due to the lack of systematic investigation on the correlation between the charge transfer of the axial polar bond, M-X, and the degree of π -conjugation in the equatorial macrocyclic ligand, it is necessary to compare and elucidate the electronic spectra of organocobalt complexes containing macrocyclic ligands with various conjugation. For that purpose, we employed square pyramidal 5-coordinate organocobalt(III) complexes of a new completely conjugated macrocyclic ligand, alkyl-5,15-dimethyl-8,17-diphenyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinatocobalt(III), [RCoL] ($R = CH_3, C_6H_5, CN, 1a \sim c$) which were synthesized in our laboratory¹³, the complexes of another macrocyclic rings with complete conjugation (14π -electrons), **2a~b**, partial conjugation, **3~4**, and unconjugated dienes, **5**, and an open ring, **6**. Thus, we wish to report the dependence of the absorption band attributable to the axial polar cobalt-carbon bond on the degree of conjugation in the equatorial macrocyclic ring of organocobalt(III) complexes.



1a ; $R_1 = CH_3, R_2 = C_6H_5, R_3 = CH_3$ 2a ; $R_1 = R_2 = CH_3, R_3 = CH_3$
 1b ; $R_1 = CH_3, R_2 = C_6H_5, R_3 = C_6H_5$ 2b ; $R_1 = R_2 = CH_3, R_3 = CN$
 1c ; $R_1 = CH_3, R_2 = C_6H_5, R_3 = CN$



EXPERIMENTAL

Reagents and Solvents. All the reagent-grade chemicals including $\text{NiAc}_2 \cdot 4\text{H}_2\text{O}$, hydrazine, potassium cyanide were purchased from Aldrich Chemical Company and were used without further purification unless stated otherwise. All the solvents were reagent-grade and were dried by distillation over appropriate drying agents under nitrogen prior to use.

Instruments. Electronic spectra were taken on a Spectronic 1201 Spectrophotometer by Milton Roy. Infrared spectra were measured on a Perkin Elmer 1310 using KBr discs or nujol mulls. Proton NMR spectra were obtained on a Varian T-60A or Jeol PMX Spectrometer. All the compounds were handled with minimal exposure to light to prevent the cleavage of cobalt-carbon bond. Standard techniques for the manipulation of air-sensitive compounds¹⁴ were used for some air-sensitive compounds and solvent were deaerated by purging them with nitrogen or by the freeze-thaw method.

Preparation of Cyano-6,15-dimethyl-diphenyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato-cobalt(III), CNC_3O_L , 1c. To a solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.31 g) in methanol (10 ml) was added LH_2 ¹⁵ (0.40 g) in acetone (30 ml) and the above solution was brought up to reflux. After an hour, KCN (0.1 g) was added and reflux was continued additional 20 minutes. Dark blue-green crystals were filtered, washed with ether and dried *in vacuo*.

mp. > 300°C

IR: $\nu_{\text{C-N}}$ 1590 cm^{-1} , $\nu_{\text{C=N}}$ 2110 cm^{-1}

¹H-NMR: 2.31(s, CH_3), 5.50(s, $-\text{CH}=\text{}$), 6.21~7.50 (m, aromatic)

Anal. Calcd for $\text{C}_{33}\text{H}_{26}\text{N}_5\text{CO}$: C, 71.9; H, 4.72; N, 12.7

Found: C, 71.3; H, 4.82; N, 12.4.

Other organocobalt(III) complexes, **1a~b**, **2a~b**, **3**, **4**, **5**, **6** were prepared by the literature method^{14,16-20}.

RESULTS AND DISCUSSION

Preparation and Characterization of CNC_3O_L . The dark blue green cyanocobalt(III) compound

was prepared by the addition of cyanide to the solution of cobalt perchlorate and the free macrocyclic ligand, LH_2 , under nitrogen atmosphere. This compound was characterized by means of IR, NMR, UV-VIS spectroscopy and elemental analysis. In the IR spectrum, the absorption band at 1590 cm^{-1} was assigned to the imine bond in the macrocyclic ring and that at 2110 cm^{-1} to the axial $\text{C}\equiv\text{N}$ stretching. The NMR spectrum shows a singlet at 2.31 ppm due to the methyl group in the macrocycle and a singlet at 5.50 ppm for the methine and a multiplet in the range of 6.21~7.50 ppm for aromatic protons. The UV-VIS spectral data show three absorptions at 17,600(ϵ , 800), 20,200(ϵ , 900), 27,800(ϵ , 6900) cm^{-1} .

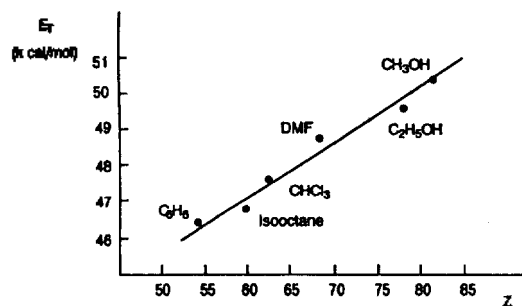
Electronic Spectra of Organocobalt(III) Complexes. The electronic spectra of the cobalt(III) complexes show intense absorption bands in the range of 15,000~40,000 cm^{-1} . The large molar extinction coefficients ($10^3\sim 10^4/\text{mol}^{-1}\text{cm}^{-1}$) are attributed to $\pi\rightarrow\pi^*$ transitions within the ligand molecules and charge transfer transitions between metal and ligand. The spectral data of the 5-coordinate organocobalt complexes of completely conjugated ligand, 6,15-dimethyl-8,17-diphenyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinate ($\text{C}_{32}\text{H}_{26}\text{N}_4$, L^{2-}), with 14 π -electrons were reported previously²⁰. An absorption band of CH_3CoL in 600 nm region can be assigned to the transition for $\text{Co}-\text{CH}_3$ bond, since the position of the band is very sensitive to the polarity of solvents as shown in Table 1: λ_{max} value being extended from 568 nm in the most polar solvent, CH_3OH , to 610 nm in the least polar one, benzene, in the series. This assignment can be supported by the fact that the electronic

Table 1. Solvent effect on CT bonds for CH_3CoL

| Solvent | Z value | λ_{max} | E_T (kcal/mol) |
|---------------------------------|---------|------------------------|------------------|
| CH_3OH | 83.6 | 568 | 50.3 |
| $\text{C}_2\text{H}_5\text{OH}$ | 79.6 | 572 | 49.9 |
| CH_3CN | 71.3 | 562 | 50.8 |
| DMF | 68.5 | 580 | 49.2 |
| CHCl_3 | 63.2 | 600 | 47.7 |
| Isocatane | 60.1 | 606 | 47.2 |
| Benzene | 54.0 | 610 | 46.9 |

Table 2. Solvent effect on CT bonds for C_6H_5CoL and $CNCoL$

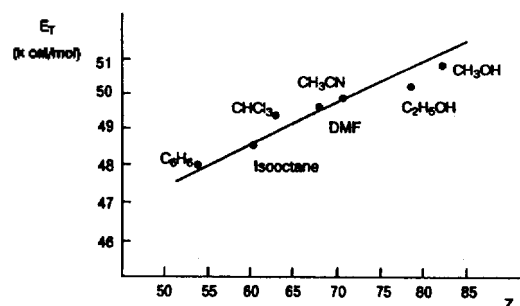
| Solvent | Complex | C_6H_5CoL | | $CNCoL$ | | |
|------------|---------|-------------|-----------------|---------|-----------------|-------|
| | | Z value | λ_{max} | E_T | λ_{max} | E_T |
| CH_3OH | | 83.6 | 572 | 49.9 | 568 | 50.3 |
| C_2H_5OH | | 79.6 | 580 | 49.2 | 576 | 49.6 |
| DMF | | 68.5 | 588 | 48.6 | 586 | 48.8 |
| $CHCl_3$ | | 63.2 | 605 | 47.3 | 602 | 47.5 |
| Isocotane | | 60.1 | 602 | 47.5 | 612 | 46.7 |
| Benzene | | 54.0 | 624 | 45.8 | 616 | 46.4 |

Fig. 1. Correlation between charge transfer transition energy (E_T) of $CNCoL$ and solvent polarity parameter (Z)

spectra of square planar 4-coordinate $Co(II)L$ and $Cu(II)L$ of this work did not have any absorption band in the same region (extinction coefficients in parentheses): $Co(II)L$; 435 nm (4,800), 360 (47,400), $Cu(II)L$; 500(1,510), 440(6,000), 395(13,500). The solvent effects on the CT (charge transfer) energies for Co-C bonds of C_6H_5CoL and $CNCoL$ are listed in Table 2. The maximum wavelengths of the CT bands were converted into transition energies by the relation, E_T (kcal/mol) = $2.859 \times 10^5 / \lambda_{max}$ (Å). The transition energies of each of the above three complexes have a linear relationship with Z -values and Fig. 1 shows this relationship for $CNCoL$. It is very interesting to note that the iodide was bonded to an aromatic system in pyridinium iodide⁹⁻¹¹, the chloride to the iron with a completely conjugated macrocyclic ligand of 14 π -electron system in the chloroiron complex¹² and the methyl to the cobalt containing a completely conjugated 14 π -electron system of $RCoL$ among

Table 3. Solvent effect on CT bonds for CH_3CoL' and $CNCoL'$

| Solvent | Complex | CH_3CoL' | | $CNCoL'$ | |
|------------|---------|-----------------|-------|-----------------|-------|
| | | λ_{max} | E_T | λ_{max} | E_T |
| CH_3OH | | 610 | 46.9 | 562 | 50.9 |
| C_2H_5OH | | 614 | 46.7 | 568 | 50.3 |
| CH_3CN | | | | 570 | 50.0 |
| DMF | | 621 | 46.0 | 576 | 49.6 |
| $CHCl_3$ | | 623 | 45.9 | 578 | 49.4 |
| Isocotane | | 626 | 45.7 | 590 | 48.5 |
| Benzene | | 628 | 45.5 | 596 | 48.0 |

Fig. 2. Correlation between charge transfer transition energy (E_T) of $CNCoL'$ and solvent polarity parameter (Z)

the reported complexes showing the solvent effect on the electronic spectra so far. Since there is neither a clear elucidation nor a systematic investigation on whether or why the solvent effect is observed only in the case of a complete conjugated system, the organocobalt complexes of various conjugation were employed in this work: the complexes of another completely conjugated ligand, CH_3CoL' (2a) and $CNCoL'$ (2b), partial conjugation, $CH_3(py)Co(DH)_2$ (3) and CH_3CoL'' (4), and unconjugated dienes, $[CH_3Co(1,4-CT)](ClO_4)_2$ (5), and an open ring, $CH_3Co(salen)$ (6). In both cases of fully conjugated systems (2a~b), there were also the solvent dependence of the absorption band at the 600 nm region for 2a and the one at the 560 nm region for 2b and the corresponding transition energies related linearly with the polarity of solvents (Table 3 and Fig. 2). Thus, the position of the absorption band for Co-C bond in the completely conjugated system is shifted to the lower wave-

Table 4. Solvent effect on CT bonds for $\text{CH}_3(\text{py})\text{Co}(\text{DH})_2$ and CH_3CoL^*

| Complex | $\text{CH}_3(\text{py})\text{Co}(\text{DH})_2$ | | | CH_3CoL^* | | |
|------------------------|--|-----|-----|---------------------------|-----|-----|
| | Wavelength (nm) | | | Wavelength (nm) | | |
| CH_3OH | 714 | 562 | 498 | 632 | 562 | 504 |
| DMF | 706 | 561 | 498 | 634 | 562 | 502 |
| Benzene | 710 | 562 | 496 | 634 | 565 | 504 |

ngth as the polarity of solvents increases and the charge transfer energies correlate linearly with the polarity of solvents. On the other hand, the absorption maxima in the electronic spectra of the complexes of partial conjugation and an open ring system in methanol are as follows (ϵ in parenthesis): compound 3; 714(620), 562(1,630), 498 nm(1,700), 4; 632(4,830), 562(6,200), 504 nm(7,820), 5; 732(1,590), 562(750), 502 nm(1,280), 6; 647(1,340), 455 (sh, 3,270), 394(sh, 3,450), 341 nm(13,300). In order to find out which band could be assigned to the cobalt-carbon bond among several bands, the electronic spectra were taken in three solvent systems; the most polar, CH_3OH , the medium, DMF, and the least polar one, benzene, among the solvents used for the completely conjugated system. It seems that all the bands have changes only within the range of experimental error as the polarity of solvents changes as shown in the Table 4 and 5. Therefore, the compounds with partially conjugated or open ring systems do not show the solvent dependence of the electronic spectra. Although the Z-value was defined as an empirical parameter of solvent polarity based on the charge transfer band of 1-ethyl-4-carbomethoxy-pyridinium iodide in various solvents as mentioned above, we might apply this concept to our metal complexes as follows. Upon excitation by light absorption, charge is transferred from the ground state, $[\text{CoL}]^+\text{R}^-$, to form $[\text{CoL}]^-\text{R}^+$ in the excited state and a large decrease in a dipole moment will result. The completely conjugated macrocycles with 14π -electrons are presumed to be similar to an electron-withdrawing aromatic system showing an absorption band within the range of $200\sim 700\text{ cm}^{-1}$. This also means that the absorption bands

Table 5. Solvent effect on CT bonds for $[\text{CH}_3\text{Co}(\text{1,4-CT})](\text{ClO}_4)_2$ and $\text{CH}_3\text{Co}(\text{salen})$

| Complex | $[\text{CH}_3\text{Co}(\text{1,4-CT})](\text{ClO}_4)_2$ | | | $\text{CH}_3\text{Co}(\text{salen})$ | | | |
|------------------------|---|-----|-----|--------------------------------------|------|-----|-----|
| | Wavelength (nm) | | | Wavelength (nm) | | | |
| CH_3OH | 732 | 562 | 502 | 647 | 455 | 394 | 341 |
| | | | | (sh) | (sh) | | |
| DMF | 734 | 562 | 502 | 649 | 454 | 392 | 340 |
| | | | | (sh) | (sh) | | |
| Benzene | 734 | 562 | 498 | 648 | 454 | 392 | 342 |
| | | | | (sh) | (sh) | | |

shown in the systems other than completely conjugated systems may not include the charge transfer bands for cobalt-carbon bond because of too large transition energies. Therefore, the reason why we observe the solvent dependence on the electronic spectrum only in the completely conjugated system is probably not because there is no charge transfer band in the partially conjugated or open ring systems but because the transition energies for the charge transfer in these systems are too high to be observed. This is the same reasoning that an organic molecule with a conjugated double bond or an aromatic ring shows a strong absorption peak due to a $\pi-\pi^*$ transition in the $200\sim 700\text{ nm}$ region of spectrum but the one with electrons of sigma bonds or simple alkenes doesn't: electrons of the latter are too tightly bound to be promoted by the radiation in this range.

In conclusion, the position of the absorption band in which the axial cobalt-carbon bond is involved is shifted to a shorter wavelength as the polarity of solvent increases and the charge transfer energies correlate linearly with the polarity of solvents only for the complexes containing completely conjugated equatorial equatorial macrocyclic ligand and the compounds with partially conjugated or open ring systems do not show the solvent dependence on the electronic spectra. Further work is now in progress to clarify also the correlation between the bonding property of an axial polar bond and the aromaticity in the equatorial macrocycle by using nonaromatic but completely conjugated $16-\pi$ systems as well as aromatic 14 - and $18-\pi$ system.

ACKNOWLEDGEMENT

The authors are grateful to the financial support of Korea Research Foundation for this work.

REFERENCE

1. R. J. Guschl and T. L. Brown, *Inorg. Chem.*, **12**, 2815 (1973).
2. G. Costa, *Pure Appl. Chem.*, **30**, 335 (1972).
3. J. Halpern, "B-12", p. 501, D. Dolphin Ed., Wiley, New York, U.S.A., 1982.
4. G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).
5. K. Farmery and D. H. Busch, *J. C. S. Chem. Commun.*, 1091 (1970).
6. G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organomet. Chem.*, **6**, 181 (1966).
7. G. Costa, *J. Organomet. Chem.*, **11**, 333 (1968).
8. Y. Murakami, Y. Aoyama, and S. Nakanishi, *Inorg. Nucl. Chem. Lett.*, **12**, 809 (1976).
9. E. M. Kosower, *J. Chem. Soc.*, **80**, 3253 (1958).
10. E. M. Kosower, *ibid.*, **80**, 3261 (1958).
11. E. M. Kosower, *ibid.*, **80**, 3267 (1958).
12. K. Sakata, M. Hoshimoto, and T. Naganawa, *Inorg. Chim. Acta*, **98**, L11~14 (1985).
13. Y. W. Park, *Bull. Korean Chem. Soc.*, **11**, 255 (1990).
14. D. F. Shriver, "The Manipulation of Air Sensitive Compounds, McGraw-Hill Inc., New York, 1969.
15. Y. W. Park and S.-S. Oh, *Bull. Korean Chem. Soc.*, **8**, 476 (1987).
16. H. K. Seo, *M. S. Thesis, Sang Myung Women's University* (1992).
17. V. L. Goedken and S.-M. Peng, and Y. Park, *J. Am. Chem. Soc.*, **96**, 284 (1974).
18. V. L. Goedken and S.-M. Peng, *J. Chem. Soc.*, **62** (1973).
19. N. F. Gurtis, *J. C. S. Chem. Commun.*, 881 (1966).
20. G. Costa, *Coord. Chem. Rev.*, **8**, 63 (1972).