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Effect of Substituents in the Chelate Ring on the Electronic State of Tetraazamacrocyclic Complexes of Cobalt(II), Nickel(II) and Copper(II)

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*The ESR and electronic spectral studies were performed for the square planar copper(II), nickel(II) and cobalt(II) complexes with Jager's N_4-macrocyclic ligands (*cf. *Fig. 1). From the results, it was shown that the introduction of the electron withdrawing group ($-COCH_3$, $-COOC_2H_5$) in the N_4-macrocycles causes a significant change in the π-systems of the ligands, that is, the lowering of the energies of π-orbitals and/or the decreasing of the π-electron delocalization.*

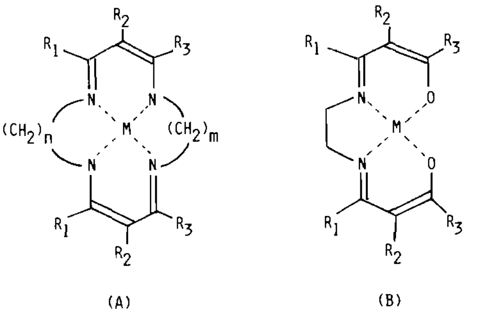

Fig. 1. N_4-macrocyclic metal complexes ((A)-group) cited in this paper (*cf.* Table I).

Introduction

It is known that the effect of substituents in a chelate ring is remarkable in tetraazamacrocyclic complexes. For example, pK_a values, redox potential and reactivity with molecular oxygen are much affected by the substituents in iron(II) porphyrins [1–3]. Similar effects were also observed for some metal complexes of synthetic tetraazamacrocyclic ligands [4–8].

In this study the attention has been focussed on the substituent effect upon the electronic state of the macrocyclic metal complexes as shown in Fig. 1 and Table I. For comparison, N_2O_2-coordinating quadridentate ligands with similar substituents (see Fig. 1 and Table I) were also studied. The electronic spectra of these compounds were discussed in relation to the effect of electron withdrawing groups such as $-COCH_3$ and $-COOC_2H_5$ at the γ-position of the six-membered chelate ring.

TABLE I. Abbreviations of the Metal Complexes (*cf.* Fig. 1).

Group	Abbreviation	R_1	R_2	R_3
A	$[M(x\text{-}R_1\text{-}R_2\text{-}R_3)]$[a]	CH_3	H	CH_3
		H	H	CH_3
		H	C_6H_5	H
		H	$COCH_3$	CH_3
		H	$COOC_2H_5$	CH_3
B	$[M(N_2O_2\text{-}R_1\text{-}R_2\text{-}R_3)]$	CH_3	H	CH_3
		CH_3	H	C_6H_5
		H	$COCH_3$	CH_3
		H	$COOC_2H_5$	CH_3

[a] x represents the ring size of macrocyclic ligands. x = 14, n = m = 2; x = 15, n = 2, m = 3; x = 16, n = m = 3 (*cf.* Fig. 1).

TABLE II. ESR Parameters of Cobalt(II) Complexes.[a]

Complex	g_1	g_2	g_3	$\lvert A_1 \rvert$ ($\times 10^{-4}$ cm^{-1})	$\lvert A_2 \rvert$	$\lvert A_3 \rvert$
[Co(N_2O_2-H-$COOC_2H_5$-CH_3)]	3.80	1.73	1.72	297	36	58
[Co(14-H-$COCH_3$-CH_3)]	2.929	2.00	1.92	60	29	29
[Co(14-H-$COOC_2H_5$-CH_3)]	2.947	2.00	1.94	66	27	34

[a] For the interpretation of these parameters, see ref. 13.

Experimental

Preparations

The copper(II) and nickel(II) complexes with Jager's N_4-macrocycles were prepared according to the methods described in the literature [9]. In this paper, new cobalt(II) complexes described below were prepared.

[Co(14-H-$COOC_2H_5$-CH_3)]

To a hot ethanol solution of H_4(14-H-$COOC_2H_5$-CH_3)$^{2+}$(PF_6)$_2$ [10] and cobalt(II) acetate, was added a calculated amount of $NaOC_2H_5$ under an atmosphere of nitrogen. After the solution was kept at 60 °C for an hour, deposited yellow crystals were filtered, and recrystallized from a hot ethanol–acetonitrile solution. Found: C 50.99%, H 6.18%, N 13.35%; calcd. for [Co(14-H-$COOC_2H_5$-CH_3)], C 51.13%, H 6.22%, N 13.30%.

[Co(N_2O_2-H-$COOC_2H_5$-CH_3)]

To a hot dmf solution (200 ml) of H_2(N_2O_2-H-$COOC_2H_5$-CH_3) [9], was added a methanol solution (20 ml) of cobalt(II) acetate (0.003 mol) under an atmosphere of nitrogen. Deposited orange crystals were recrystallized from 1,2-dichloroethane. Found: C 47.92%, H 5.48%, N 7.09%; calcd. for [Co(N_2O_2-H-$COOC_2H_5$-CH_3)], C 48.37%, H 5.58%, N 7.05%.

Measurements

In this study, the ESR spectra of [Co(14-H-$COCH_3$-CH_3)], [Co(14-H-$COOC_2H_5$-CH_3)] and [Co(N_2O_2-H-$COOC_2H_5$-CH_3)] were measured (*cf.* Table II). For the ESR measurements, all the cobalt(II) complexes were diluted in the corresponding nickel(II) complexes. ESR spectra were obtained with a JEOL ESR apparatus model MEX-3X at liquid nitrogen temperature. Absorption spectra were measured with a Shimadzu Multipurpose model PMS-5000 at room temperature.

Results and Discussion

Cobalt(II) Complexes

In our previous papers, it was shown that the ground state electronic configuration of low-spin square planar cobalt(II) complexes can be assessed from the powder or frozen solution ESR spectra [11–15]. Inspection of the ESR spectra has revealed that all the cobalt(II) complexes of the ligands of (B) group (*cf.* Fig. 1) [28], [Co(14-H-$COCH_3$-CH_3)] and [Co(14-H-$COOC_2H_5$-CH_3)] are of the $(d_{xy})^2$-$(d_{yz})^1$ ground state electronic configuration (for the ESR spectra of [Co(x-H-C_6H_5-H)] series, see ref. [14]). A typical example of the ESR spectra is shown in Fig. 2. On this basis and considering the 6π–6π system of the ligand, the molecular orbitals of the complex are described in Table III and schematically illustrated in Fig. 3.

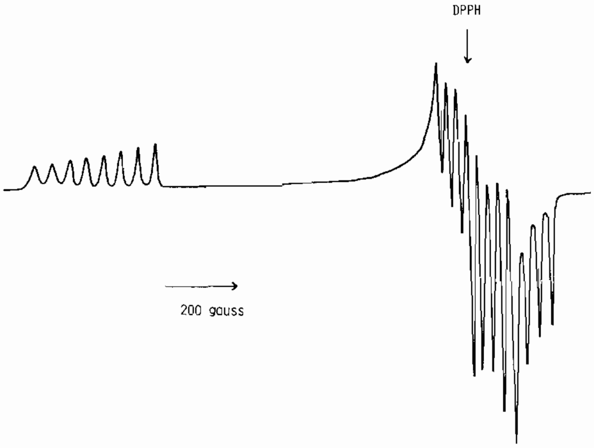

Fig. 2. ESR spectrum of [Co(14-H-$COOC_2H_5$-CH_3)] (77 K, in nickel(II) complex).

Examples of electronic spectra of the cobalt(II) complexes are shown in Fig. 4, and positions and intensities of absorption bands in the lower energy region ($<25 \times 10^3$ cm^{-1}) are summarized in Table IV. It is seen that the electronic spectra are remarkably affected by substituents in the chelate ring. All of them show a band in the near-infrared region (8000–12000 cm^{-1}). This is certainly assigned to the $d_{x^2-y^2} \rightarrow d_{yz}$ ($a_g \rightarrow b_{3g}$ in Fig. 3) transition [11–16]. As seen in Table III, this band shifts to a lower frequency region, when the electron-withdrawing group such as –$COCH_3$ and –$COOC_2H_5$ is introduced

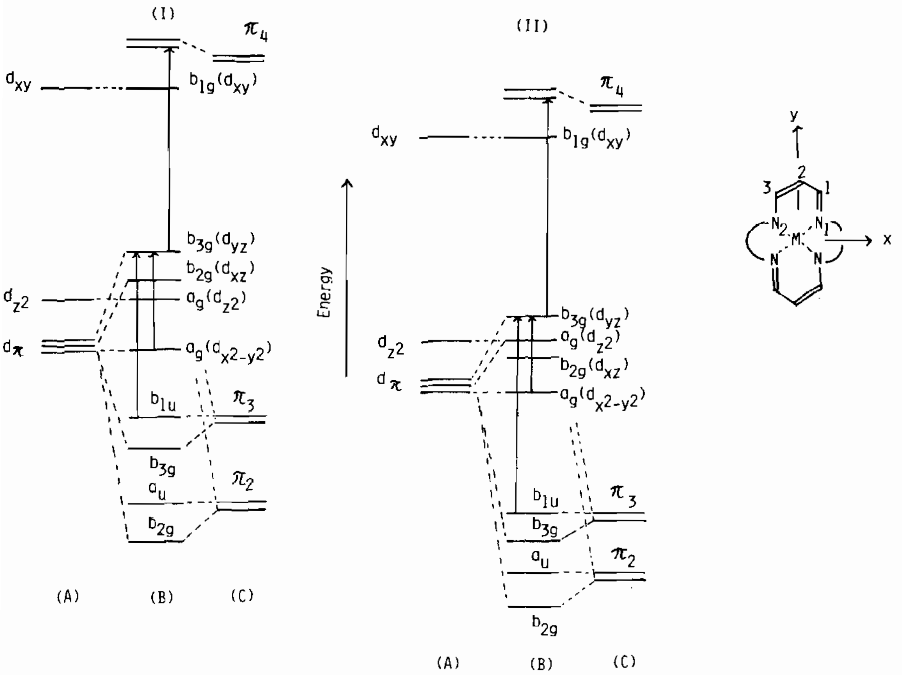

Fig. 3. Schematic illustration of π-interaction between metal and ligand (D_{2h} symmetry is assumed). The interaction between metal orbital and π_1, π_5 is neglected in this figure, because the large energy separation between them. (A) metal orbitals (σ-interaction only); (B) M.O. of the complexes (σ- and π-interaction); (C) ligand orbitals; (I) for [Co(x-H-C_6H_5-H)] series; (II) for [Co(x-H-$COCH_3$-CH_3)] series.

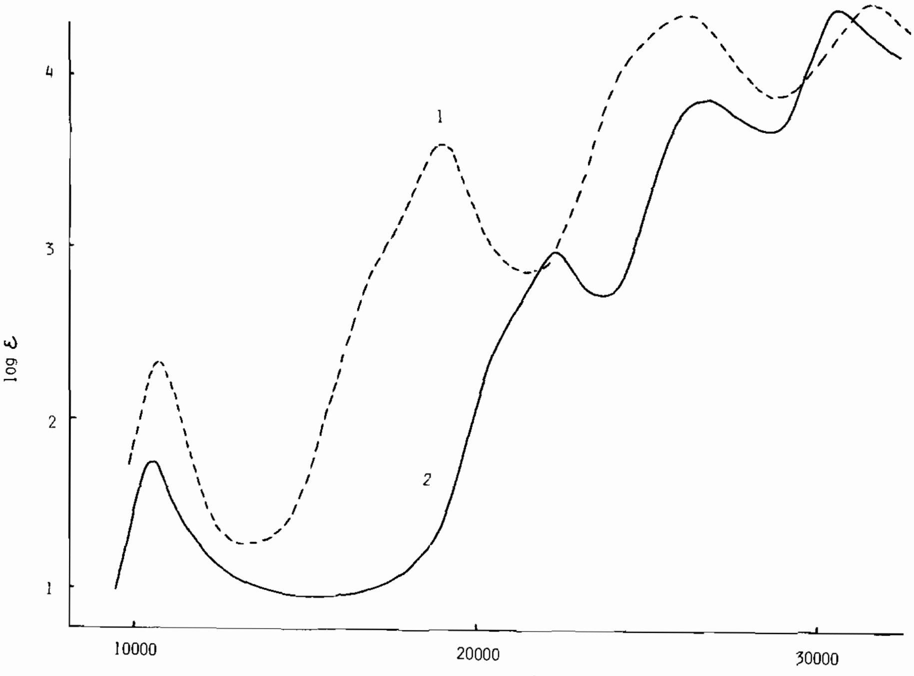

Fig. 4. Absorption spectra of cobalt(II) complexes. 1 (------) [Co(14-H-C_6H_5-H)] (in 1,2-dichloroethane); 2 (———) [Co(14-H-$COOC_2H_5$-CH_3)] (in acetonitrile).

at R_2 (*cf.* Fig. 1). This effect must be due to the lowering of the d_{yz} level effected by the electron-withdrawing group, since $d_{x^2-y^2}$ is practically nonbonding in tetraazamacrocyclic metal complexes [14, 17, 18]. The lowering of the π-antibonding energy of d_{yz} orbital should be due to the decreased ligand

TABLE III. Ligand π-orbitals in the Metal Complexes Illustrated in Fig. 3.

$\pi(1)^{a} = (\pi N_1 + \pi N_2) + c_1(\pi_1 + \pi_3) + d_1\pi_2{}^{b}$

$\pi(2) = (\pi N_1 - \pi N_2) + c_2(\pi_1 - \pi_3)$

$\pi(3) = (\pi N_1 + \pi N_2) - c_3(\pi_1 + \pi_3) - d_3\pi_2$

$\pi(4) = (\pi N_1 + \pi N_2) - c_4(\pi_1 + \pi_3)$

$\pi(5) = (\pi N_1 - \pi N_2) - c_5(\pi_1 - \pi_3)$

[a] All normalization constants are omitted for simplicity. Numbering of atoms (and orbitals) is illustrated in Fig. 3. In the metal complexes, ligand M.O. are constructed by the linear combination of two sets of 6 π-systems [29]. Representations of ligand orbitals in D_{2h} symmetry are a_u, b_{1u}, b_{1g} and b_{3g}. [b] c_1, c_2, ~c_5, d_1 and d_3 are the coefficients in the linear combinations.

π-basicity effected by $-COCH_3$ and $-COOC_2H_5$ group.

Low-spin cobalt(II) complexes with N_4-macrocycles, to which we assigned the $(d_{xy})^2(d_{yz})^1$ ground electronic configuration, generally show a band in the 19–23 × 10^3 cm^{-1} region (*cf.* Fig. 4) with log ϵ = 3.0–3.7. On the other hand, no band with an ϵ larger than 1000 has ever been observed in this region for analogous copper(II) and nickel(II) complexes (*cf.* ref. 19 and Fig's 5, 6 and 7). Therefore, this band should be attributed to a transition from ligand π to metal d_{yz} ($b_{1u}(3) \rightarrow b_{3g}$ (d_{yz}) in Fig. 3). On this basis, the absence of this band in nickel(II) and copper(II) analogues is well explained, because the metal d_{yz} orbital is filled with electrons in d^8 and d^9 systems. As seen in Table IV, this band

TABLE IV. Spectral Data of Cobalt(II) Complexes.

Complexes	$\tilde{\nu}$ (10^3 cm^{-1}) (log ϵ)		Ref.
$[Co(N_2O_2\text{-}CH_3\text{-}H\text{-}CH_3)]$	8.58 (1.8)	a	25
$[Co(N_2O_2\text{-}CH_3\text{-}H\text{-}C_6H_5)]$	8.60 (1.8)	a	25
$[Co(N_2O_2\text{-}H\text{-}COOC_2H_5\text{-}CH_3)]^{c}$	8.50 (1.8)	a	b
$[Co(14\text{-}H\text{-}C_6H_5\text{-}H)]^{c}$	11.7 (2.3)	19.0 (3.6)	b
$[Co(14\text{-}H\text{-}COCH_3\text{-}CH_3)]$	10.6 (1.2)	21.8 (3.4)	26
$[Co(14\text{-}H\text{-}COOC_2H_5\text{-}CH_3)]^{c}$	10.5 (1.8)	22.3 (3.0)	b

[a] For $[CoN_2O_2]$ type complexes, a clear peak was not observed below 23000 cm^{-1}. [b] This work. [c] In CH_2ClCH_2Cl.

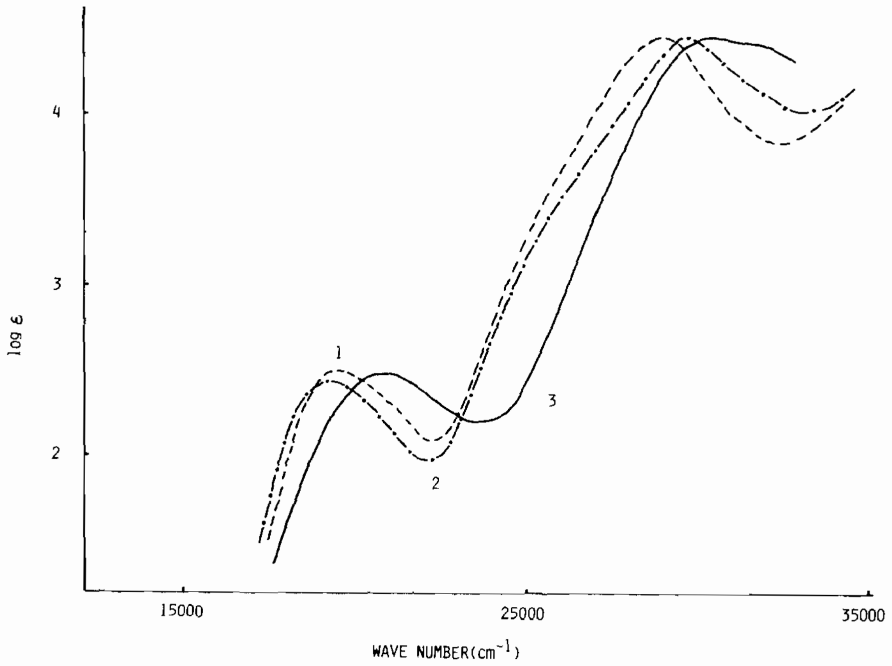

Fig. 5. Absorption spectra of nickel(II) complexes (in 1,2-dichloroethane). 1 (-------) $[Ni(14\text{-}H\text{-}COCH_3\text{-}CH_3)]$; 2 (–·–·–) $[Ni(15\text{-}H\text{-}COCH_3\text{-}CH_3)]$; 3 (———) $[Ni(16\text{-}H\text{-}COCH_3\text{-}CH_3)]$.

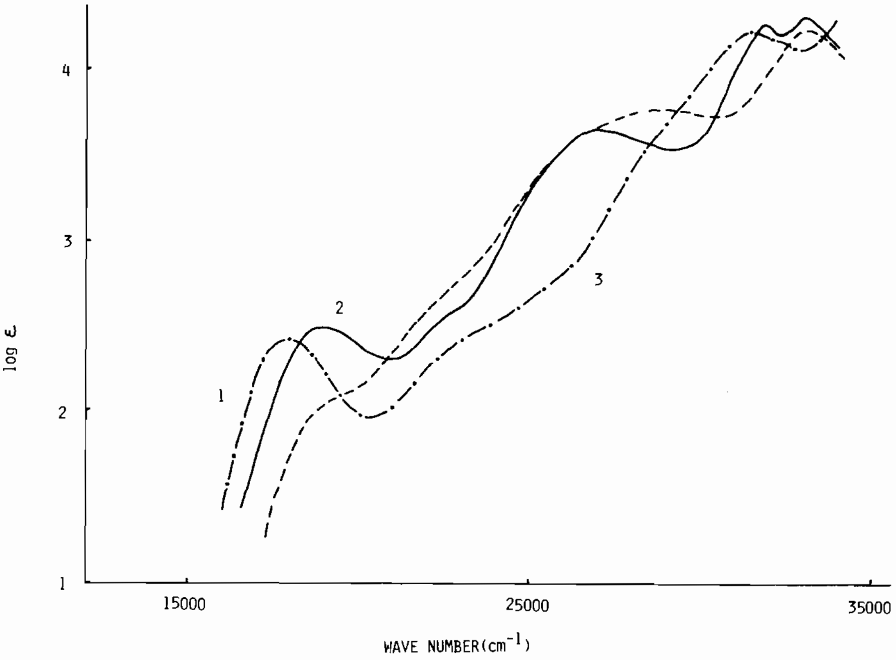

Fig. 6. Absorption spectra of [M(x-H-COOC$_2$H$_5$-CH$_3$)] series (in 1,2-dichloroethane). 1(— · — · —) [Cu(14-H-COOC$_2$H$_5$-CH$_3$)]; 2 (————) [Ni(14-H-COOC$_2$H$_5$-CH$_3$)]; 3 (-------) [Ni(15-H-COOC$_2$H$_5$-CH$_3$)].

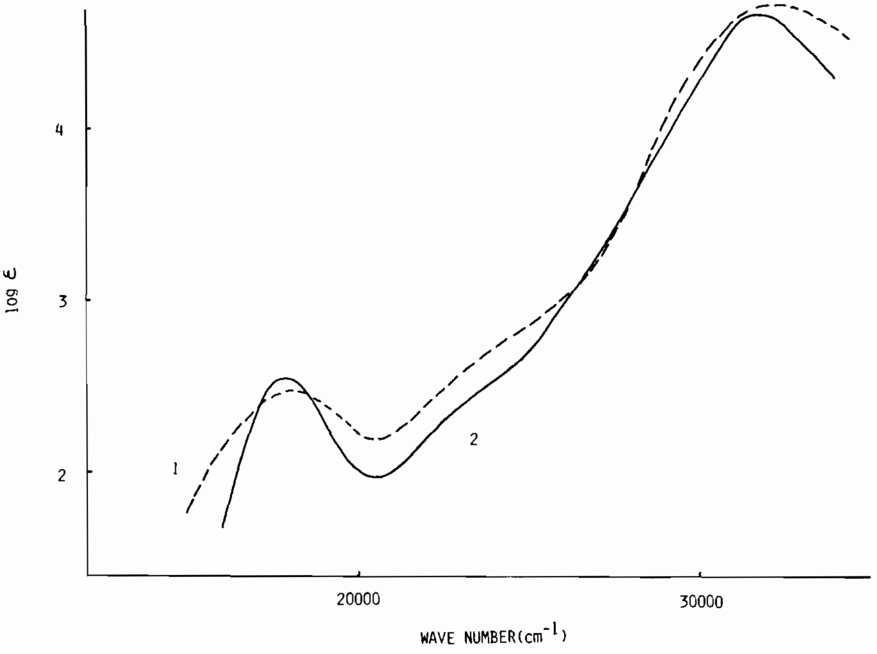

Fig. 7. Absorption spectra of [Cu(x-H-COCH$_3$-CH$_3$)] complexes (in 1,2-dichloroethane). 1 (------) x = 14; 2 (————) x = 15.

is shifted by the electron-withdrawing group to a higher energy region, which is a direction opposite to that of the shift of the near-infrared band. This result can also be well interpreted in terms of lowering of the ligand π level relative to the metal d_{yz} orbital due to the electron-withdrawing ability of the substituents.

The above discussion seems to be consistent with the result obtained from the d–d band in the near-infrared region, because a larger energy gap between

TABLE V. Lowest Energy d–d Band in Nickel(II) and Copper(II) Complexes.

Complex	$\tilde{\nu}$ (10^3 cm^{-1})	
[M(14-H-$COCH_3$-CH_3)][a]	19.6 (M = Ni)	17.8 (M = Cu)
[M(14-H-$COOC_2H_5$-CH_3)][a]	19.0 (M = Ni)	18.0 (M = Cu)
[M(14-H-C_6H_5-H)][b]	16.5sh (M = Ni)	16.5 (M = Cu)
[M(14-CH_3-H-CH_3)] [23]	17.9 (M = Ni)	16.2 (M = Cu)
[Ni(15-H-NO_2-CH_3)] [5]	19.8	
[M(15-H-$COCH_3$-CH_3)][a]	19.3 (M = Ni)	18.0 (M = Cu)
[Ni(15-H-$COOC_2H_5$-CH_3)][a]	18.0	
[M(15-H-C_6H_5-H)][b]	15.0sh (M = Ni)	13.0 (M = Cu)
[Ni(15-H-H-CH_3)] [5]	17.2	
[Ni(16-H-$COCH_3$-CH_3)][a]	20.7	

[a] In $CHCl_3$. [b] In CH_2ClCH_2Cl.

the π and d_π orbitals causes a weaker interaction between them, which leads to the decrease of $d_{x^2-y^2} \rightarrow d_{yz}$ transition energy.

Nickel(II) and Copper(II) Complexes

In Table V, the lowest-energy bands of the nickel(II) and copper(II) complexes are summarized. These bands are undoubtedly attributed to a d–d transition judging from their position and intensity. Nishida *et al.* assigned this band to the $d_\pi(d_{xz}, d_{yz}) \rightarrow d_{xy}$ transition [14, 17]. It is seen in Table V that the band is blue-shifted by the introduction of an electron-withdrawing group such as $-COCH_3$, $-COOC_2H_5$ and $-NO_2$. Here, it should be noted that the present result is an unexceptional case of the generally accepted view that an electron-withdrawing group in the ligand reduces the electron density of the donor atom, thereby making the splitting of d-orbitals to be small. For the present complexes, it was shown that the d_π orbitals are raised by the antibonding interaction with the bonding ligand π-orbitals [14]. Thus, the spectral data in Table V can be elucidated in terms of our assignment and on the assumption that when an electron-withdrawing group is introduced in the γ-position of the six-membered chelate ring, electrons are drifted mainly by π-path so that π-antibonding effect upon the d_π orbitals is reduced, whereas the metal–ligand σ-bond is affected only indirectly. The lowering of the d_π orbital energy was already verified for the analogous cobalt(II) complexes, as shown in the previous section. It was demonstrated [20] that the $g_\parallel$ value is the most reliable measure of σ-bonding strength for square planar N_4-macrocyclic copper(II) complexes. According to the results, $g_\parallel$-values for [Cu(14-H-C_6H_5-H)], [Cu(14-H-$COCH_3$-CH_3)] and [Cu(14-H-$COOC_2H_5$-CH_3)] are 2.123, 2.136 and 2.126, respectively. As their differences are small, these ESR data seem to support the above assumption.

TABLE VI. Proton NMR Chemical Shifts.

Complex	X[a]	δ(ppm)[b]
[Ni(x-H-C_6H_5-H)] [22]	14	7.12
	15	6.91
	16	6.92
[Ni(x-H-$COCH_3$-CH_3)]	14	7.80
	15	7.62
	16	7.38

[a] x represents the macrocyclic ring size. [b] Proton chemical shift of proton attached at β-carbon atom (R_1 = H).

Thus, it is concluded that the introduction of electron withdrawing groups in the chelate rings causes no significant effect on the σ-donor ability, whereas it causes a remarkable change in the π-systems of the ligands, that is, the lowering of the energies of the π-orbitals, and/or decreasing of π-electron delocalization.

It is expected that an expansion of macrocyclic ring size brings about the lowering of the ligand field strength, giving rise to a red-shift of d–d transition. This is in practice for almost cases. In the present study, however, we have found that the energy order of the lowest d–d bands is [Ni(16-H-$COCH_3$-CH_3)] > [Ni(14-H-$COCH_3$-CH_3)] > [Ni(15-H-$COCH_3$-CH_3)] as shown in Fig. 5, whereas the band shift of the [Ni(x-H-C_6H_5-H)] (x = 14, 15, 16) is of the normal order [14]. Appearance of such unusual order may be explained in terms of the distortion of the macrocyclic ring from the coordination plane, and the distortion should be strongly affected by substituents in the chelate ring of [Ni(x-H-$COCH_3$-CH_3)] series. In order to examine the above discussion, we have measured the ^{1}H NMR spectra of [Ni(x-H-$COCH_3$-CH_3)] series, the results being given in Table VI (we will compare the chemical shifts of protons attached at the β-carbon atom in both series). It is difficult to compare the absolute chemical shift values of the two series complexes, because the influence due to the magnetic anisotropy by acetyl group [21] may be remarkable in the [Ni(x-H-COCH$_3$-CH$_3$)] series. In the case of [Ni(x-H-C$_6$H$_5$-H)] series, it was found [22] that ^{1}H chemical shifts of β-carbon atoms change to a higher field with increasing macrocyclic ring size; however, their changes are very small, and the chemical shift in [Ni(15-H-C$_6$H$_5$-H)] is almost the same as that of [Ni(16-H-C$_6$H$_5$-H)]. On the other hand, the chemical shift in [Ni(15-H-COCH$_3$-CH$_3$)] is greatly different from that in [Ni(16-H-COCH$_3$-CH$_3$)]. These ^{1}H NMR results suggest that a structural difference between [Ni(15-H-COCH$_3$-CH$_3$)] and [Ni(16-H-COCH$_3$-CH$_3$)] is more serious, than that between [Ni(15-H-C$_6$H$_5$-H) and [Ni(16-H-C$_6$-H$_5$-H)]. However, no further discussion can be made at present, and thus X-ray crystal analyses for those complexes are desirable.

As shown in Fig's 5 and 6 and ref. [19], some peaks are always observed in the region 28000–33000 cm^{-1} in these nickel(II) and copper(II) complexes. These bands can be assigned to the $\pi \rightarrow \pi^*$ transitions, on the basis of spectral studies on the free ligands [23, 24] and its large molar extinction coefficients ($\epsilon > 20000$). It should be noted that other bands are observed in the range 23000–25000 cm^{-1} (ϵ = 3000–5000) in [Ni(x-H-C$_6$H$_5$-H)] series [19, 23], whereas no band was observed in this region for [Ni(x-H-COCH$_3$-CH$_3$)] series, and in the case of [Ni(x-H-COOC$_2$H$_5$-CH$_3$)] series, similar bands were observed in the region 25000–27000 cm^{-1}.

For these bands, three possible assignments may be considered:

1) $d_\pi(d_{xz}, d_{yz}) \rightarrow \pi^*$

2) $\pi \rightarrow d_\sigma(d_{xy})$

3) $N(\sigma) \rightarrow d_\sigma(d_{xy})$

Because the molar extinction coefficients of these bands are 4000–6000, possibility 3) can be excluded. Although a definite assignment cannot be given for these bands from only our experimental data, we tentatively assign these bands to the $d_\pi(d_{xz}, d_{yz}) \rightarrow \pi^*(b_{3g} \rightarrow \pi_4)$, because the higher the energies of these bands, the less oxidizable the metal ion is [27]. Thus, it has become apparent in this study that significant changes are observed in the energies of the charge-transfer (between metal and ligand) bands due to changes in the ring substituents. These spectral changes seem to be consistent with our previous conclusion that a change of ring substituents at R$_2$ has a significant effect on the energies of the π-orbitals of the ligands.

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27 Although the redox potentials of [Ni(x-H-C$_6$H$_5$-H)] series have not yet been reported, it is expected that these complexes are more oxidizable than [Ni(x-H-COCH$_3$-CH$_3$)] and [Ni(x-H-COOC$_2$H$_5$-CH$_3$)] series on the basis of the results in ref. 5.
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