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SPLITTING OF *d*-ORBITALS IN SQUARE PLANAR COMPLEXES OF COPPER(II), NICKEL(II) AND COBALT(II)

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CONTENTS

A. INTRODUCTION

The electronic states of transition metal complexes have been studied extensively in the last two decades, and detailed knowledge has been accumulated for octahedral and tetrahedral complexes [1—5].

However, for complexes of tetragonal or lower symmetry electronic states, even the energy sequence of *d*-orbitals, have not yet been thoroughly elucidated. Since the majority of the biologically important metal complexes are of tetragonal symmetry, it is desired to obtain accurate knowledge on the electronic states of those complexes in order to understand various properties such as stabilities, reactions and structures of the biologically important metal complexes.

At the beginning of this article we will briefly review the recent development of the studies on the splitting of *d*-orbitals of Cu(II) and Ni(II) complexes (mainly of Cu(II)). Later we will describe the recent progress of the studies on Co(II) complexes, and then demonstrate our latest results so that we can consistently elucidate the optical and ESR spectra of square planar complexes of Cu(II), Ni(II) and Co(II) in terms of our model of ligand field splitting derived from the studies of Co(II) complexes.

B. THEORETICAL APPROACH

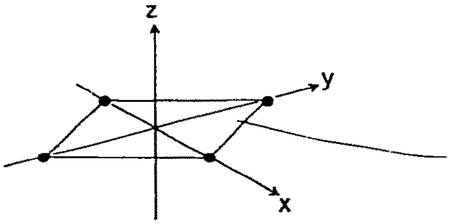
(i) Electrostatic crystal field approach

Crystal field theory has been quite successful for the elucidation of various properties of transition metal complexes, in spite of its daring assumption that a metal ion is surrounded by point charges or point dipoles so that no covalency is allowed for [1—5]. This is due to the fact that the theory has been applied mainly to octahedral and tetrahedral complexes, in which the magnitude of the *d*-orbital splitting is only dependent on one parameter, *Dq*; thus one may obtain a satisfactory result in the case of octahedral complexes, the error due to neglecting the covalency being almost eliminated in the process of adjusting *Dq* to fit experimental data. On the other hand, non-empirical calculations of *d—d* splitting based on $D(=\overline{r^4}/6R^5)$ (where R and r denote the distance between the metal and a point charge and between the metal and the *d*-electron, respectively) and q so far attempted have not yet given satisfactory results [6—9].

When the symmetry of a complex descends from O_h to D_{4h} or lower, the *d*-orbitals further split, so that more parameters other than *Dq* become necessary to describe the splitting, e.g., in the case of D_{4h} three parameters are to be determined [5,10]. Therefore, in such cases it is not easy to determine those necessary parameters from experimental data. In principle, the three parameters can be determined when three energy differences between the orbitals are known. However, even in such a fortuitous case, the values obtained as the parameters cannot be expected to be correct, because the orbital energies described in terms of *Ds*, *Dt* and *Dq*, as shown in Fig. 2 [5], should contain a considerable error due to the neglect of the overlapping between ligand and metal orbitals. In addition, the presence of π-interaction between metal and ligand orbitals makes the situation much more complex, and the electrostatic crystal field approach becomes completely inadequate for such systems.

(ii) Molecular orbital or angular overlap approach

In the molecular orbital theory, the splitting of *d*-orbitals is expressed as an antibonding effect of ligand orbitals. Hence, the magnitude of the splitting can be readily calculated, if the Coulomb integrals (H_{ii}), overlap integrals (S_{ij}) and exchange integrals (H_{ij}) are evaluated, and once three parameters have been determined, there are no difficulties for descent in symmetry [11]. Therefore the molecular orbital approach is much more advantageous than the



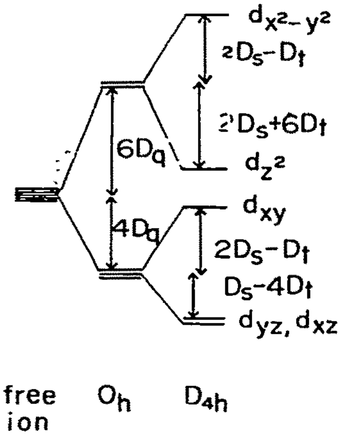


Fig. 1. The molecular axes adopted in this paper.

Fig. 2. Splitting of *d*-orbitals based on the electrostatic crystal field model.

electrostatic crystal field approach for the study of *d*—*d* splitting of complexes of lower symmetry.

The MO treatment of metal complexes is more simplified in the angular overlap approach [12—15]. This approach is based on the assumption that the square of the group overlap integral S_{MX} between metal(M) *d*- and ligand(X) orbitals is proportional to the splitting energy of the *d*-orbital. On this basis, the *d*-orbital energies can be evaluated in units of e_σ and e_π (which are only dependent on radial parts of ligand and metal orbitals), when the positions of coordinating atoms are given. As an example the result of the angular overlap approach for a square planar complex involving π-bonding is shown in Fig. 3. As seen in the figure, the *d*-orbital energies are dependent on three independent parameters, e_σ, e_π and e_π^*. Since nonempirical calculation of those para-

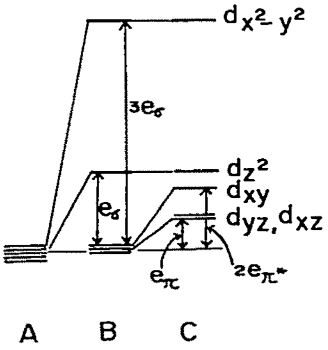


Fig. 3. Splitting of *d*-orbitals of a square planar complex based on the angular overlap model. A, free ion; B, square planar complexes with no π-interaction; C, square planar complex with π-interaction.

meters is very difficult, it is practically impossible to theoretically predict the splitting of *d*-orbitals, even qualitatively. Thus, a number of studies have been carried out making use of various experimental techniques in order to clarify the splitting of the *d*-orbitals.

C. STUDIES ON COPPER(II) AND NICKEL(II) COMPLEXES

(i) Spectroscopic studies on copper(II) and nickel(II) complexes

It is well known that cobalt(II), nickel(II) and copper(II) ions often form square planar complexes, among which copper(II) complexes are the most extensively studied by the spectroscopic method. In the square planar or elongated octahedral complexes, the highest energy orbital is undoubtedly $d_{x^2-y^2}$, (where x, y and z axes are adopted as shown in Fig. 1; this coordinate system will be used throughout this article). Therefore, three transitions, $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ are possible for the d^9 system. However, the spectra of copper(II) complexes generally show only one broad band, (frequently with shoulder(s)), in the visible region. It is difficult to resolve it into three bands. This is due to the fact that the four *d*-orbitals, d_{z^2}, d_{xy}, d_{xz} and d_{yz} lie close together. Even when one can resolve the band into three bands, it is not easy to make a precise assignment to each *d—d* transition, because the energy order of the *d*-orbitals is still controversial among numerous investigators.

The simplest way to resolve a superposed band into each component is by Gaussian analysis of the spectrum [16]. Although this method has been conventionally used for many years, its accuracy is far from convincing, except for the case where distinct shoulders are observed. A number of theoretical and experimental approaches have been made for the assignment of the resolved bands. However, the conclusions reported by different authors are frequently inconsistent [16].

Recently, an extensive number of studies of single-crystal spectra of Cu(II) complexes have been reported using polarized light [17—32]. Among these the studies of Hathaway and co-workers are the most extensive and conspicuous [24—32]. The normal modes of vibration of a square planar complex which make the Laporte forbidden *d—d* transitions observable are listed in Table 1. It was found that the *x*,*y*-polarized spectra always show only one band with a considerable intensity and this was attributed to the $^2B_{1g} \rightarrow {}^2E_g$ transition activated by B_{2u} and/or A_{2u} mode(s) of vibration(s) both of which are out-of-plane deformation vibrations. Hathaway and co-workers [25] thought that if E_u mode had been the most active vibration to make the *d—d* transitions allowed, two bands, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2A_{1g}$, with considerable intensities should have been observed in the *x*, *y*-polarized spectra (see Table 1). On this basis, Table 1 leads to the conclusion that the strongest band observed in the *z*-polarized spectrum can be assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition which is activated by the out-of-plane deformation mode, B_{2u}. In

TABLE 1

Normal modes of vibrations to make parity-forbidden transitions observable in a square planar complex [73]

Electronic transition	Normal mode of vibration [a]	
	(x,y)	(z)
$^2B_{1g} \rightarrow {}^2A_{1g}$	E_u	
$^2B_{1g} \rightarrow {}^2B_{2g}$	E_u	B_{2u}
$^2B_{1g} \rightarrow {}^2E_g$	B_{2u}, A_{2u}	E_u

[a] A_{2u}, out of plane; B_{2u}, out of plane; E_u, in-plane stretch; E_u, in-plane deformation.

this way, Hathaway and co-workers have made assignments of the *d*—*d* bands of numerous copper(II) complexes of tetragonal symmetry, and concluded that the energy order of the *d*-orbitals for elongated octahedron and tetragonal pyramid is generally $d_{x^2-y^2} >> d_{z^2} > d_{xy} \geqslant d_{xz}, d_{yz}$, although some exceptions were observed where the order of d_{z^2} and d_{xy} is reversed [6,27], when the Cu(II) is bonded with strongly π-donating ligands.

The results of the analysis of single-crystal spectra by polarized light on the square planar copper(II) complexes [20,23,30], in which we are most interested at present, are summarized in Table 2, where $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2] \cdot H_2O$ [30], $CaCuSi_4O_{10}$ [20] and $[(CH_3)(C_6H_5)NH_2]_2[CuCl_4]$ [33] were demonstrated by X-ray analysis to have square planar $[CuN_4]$, $[CuO_4]$ and $[CuCl_4]$ units, respectively. As seen in the table, the lowest energy orbital is d_{xz} (or d_{yz}) in $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2 \cdot H_2O$, but d_{z^2} is the lowest in the other three complexes. This fact is explainable in terms of π-antibonding effect of the donating negative charged oxygen and chlorine atoms, which lift the energies of d_{xy}, d_{xz} and d_{yz} orbitals.

Single-crystal polarized spectra of various β-diketonato copper(II) complexes have been reported. However, only the data of $Cu(3\text{-meaca})_2$ [31] are

TABLE 2

Ligand field bands of square planar copper(II) complexes determined by single-crystal polarized spectra

Complex	$d_{z^2} \rightarrow d_{x^2-y^2}$	$d_{xy} \rightarrow d_{x^2-y^2}$ (10^3 cm^{-1})	$d_{xz} \rightarrow d_{x^2-y^2}$	Ref.
$Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2 \cdot H_2O$	18.4	(19.2)	19.2	30
$Ca_2CuSi_4O_{10}$	18.8	12.9	15.8	32
$[(CH_3)(C_6H_5)NH_2]_2[CuCl_4]$	16.1	11.8	13.7	33
$[Cu(3\text{-meaca})_2]$ [a]	19.2	15.5	15.8	31

[a] H(3-meaca) represents 3-methylacetylacetone.

reliable among these, because the compound contains one molecule in each unit cell, whereas the other β-diketonato complexes studied so far generally contain molecules with different orientations in each unit cell. Hence, different conclusions were reported by several authors for the energy order of *d*-orbitals of β-diketonato complexes [18,20,22]. The results for quadridentate Schiff base copper(II) complexes are in a similar situation.

Such difficulties displayed above show the limit of the approach making use of single-crystal polarized spectra. Furthermore, there remains the problem of determining which mode of vibration is most effective in making Laporte forbidden transitions observable, even though Hathaway's discussion [25] seems to be plausible. It appears to the authors that more convincing evidence is necessary to achieve definite assignments of the bands. In conclusion, studies by single-crystal polarized spectra have brought much progress in the resolution of superposed bands into individual components and in the assignment of each band to a *d—d* transition. However, the reliability of the results is not totally satisfactory. In order to obtain definite conclusions we have to accumulate more experimental data by other techniques, and finally to obtain a theory consistent with all the data.

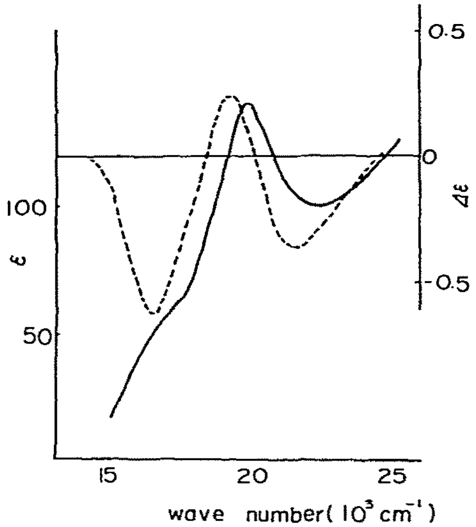
Circular dichroism spectra can often resolve a broad absorption band into several components. Making use of the advantage of CD spectra, Nishida and Kida [34] studied the *d—d* spectra of some square planar copper(II) and nickel(II) complexes with optically active ligands, and found that the three distinct CD bands are observable in the $15—25 \times 10^3$ cm^{-1} region for the copper(II) and nickel(II) complexes with quadridentate amides and Schiff bases, whereas in ordinary absorption spectra only one band is observed in this region (see for example, Fig. 4). The disadvantage of the CD method is that it is applicable only to optically active complexes. In MCD (magnetic circular dichroism) spectra it is not necessary for the compounds to be optically active. There have been a few MCD studies [35,93]. An example is shown in Fig. 5, where the MCD at 15×10^3 cm^{-1} is of *A*-type, and hence it was concluded that this is due to the transition to the degenerate level, that is $^1A_{1g} \rightarrow {}^1E_g$. However, good MCD spectra have been obtained only in exceptional cases due to the weak intensity of the *d—d* bands in the complexes. Therefore, at the present stage, it appears that an extensive application of the MCD technique can not be expected, until improvement of the instrument has been achieved.

(ii) Approach by ESR to copper(II) complexes

According to ligand field theory [36], *g*-values of copper(II) complexes of axial symmetry may be approximated by the equations

$$g_{\parallel} = 2\left(1 - \frac{4\lambda K_{\parallel}}{\Delta E(d_{x^2-y^2} - d_{xy})}\right) \tag{1}$$

$$g_{\perp} = 2\left(1 - \frac{\lambda K_{\perp}}{\Delta E(d_{x^2-y^2} - d_{xz})}\right) \tag{2}$$



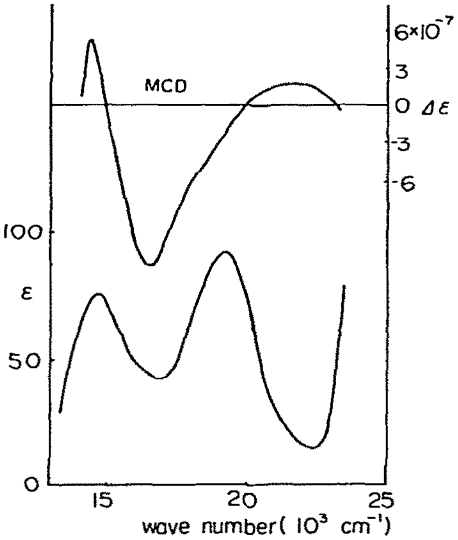


Fig. 4. Absorption and circular dichroism spectra of $[Cu(sad(-)pn]^{2-}$ complex [34].

Fig. 5. Magnetic circular dichroism spectrum of $[Ni(dtp)_2]$ [35].

where λ is the spin—orbit coupling constant of the copper ion, and $K_{\parallel}$ and $K_{\perp}$ are the orbital reduction factors for $\parallel$ and $\perp$ components, respectively. ($K_{\parallel}$ and $K_{\perp}$ may be substituted by the relations, $K_{\parallel} = \alpha^2\beta_1^2$, and $K_{\perp} = \alpha^2\beta^2$, where α, β and β_1 are the coefficients of $d_{x^2-y^2}$, d_{xz} and d_{xy} in the molecular orbitals [37,38].) If one could obtain the correct $g_{\parallel}$ and $g_{\perp}$ values experimentally and estimate the $K_{\parallel}$ and $K_{\perp}$ values, the energy separations $\Delta E(d_{x^2-y^2} - d_{xy})$ and $\Delta E(d_{x^2-y^2} - d_{xz})$ are readily calculated by using the relations (1) and (2). In practice, however, it is difficult to estimate the correct $K_{\parallel}$ and $K_{\perp}$ values from other experimental data. Hence it is rather conventional that the relations (1) and (2) are utilized in order to estimate $K_{\parallel}$ and $K_{\perp}$ values by using the spectroscopically obtained $\Delta E(d_{x^2-y^2} - d_{xy})$ and $\Delta E(d_{x^2-y^2} - d_{xz})$ values [23, 24,27—30,32,39].

In this treatment one can to some extent assess the validity of the ΔE values on the grounds of whether one obtains reasonable $K_{\parallel}$ and $K_{\perp}$ values by using these values, e.g., the ΔE values which make $K > 1$ or $K < 0.5$ would not be accepted as reasonable values. However, this approach has so far rarely been successful for the absolute determination of energy separations between *d*-orbitals. Smith proposed equations a little more complicated than those shown here, allowing for the contribution from charge transfer states [40]. Using these equations, Cassidy and Hitchman made assignments of the visible bands of the planar $[CuCl_4]^{2-}$ complex [23]. At any rate, it is essentially important in this approach to obtain accurate *g*-values. It is generally dangerous to develop a detailed discussion, using the $g_i(i=x,y,z)$ values obtained from a powder or frozen solution sample.

D. GENERAL FEATURES OF LOW-SPIN COBALT(II) COMPLEXES

Since cobalt(II) has a d^7 electronic configuration, it is susceptible to strong Jahn—Teller distortion in the case of low-spin type configuration, and assumes an elongated octahedral, tetragonal pyramidal or square planar geometry. Accordingly, low-spin cobalt(II) is somewhat similar to copper(II) in coordination geometry and d-orbital splitting scheme.

However, magnetism, ESR and electronic spectra of copper(II) and low-spin cobalt(II) complexes are quite different from each other, because of the different numbers of d-electrons, and hence the different electronic configurations.

(i) ESR studies on low-spin cobalt(II) complexes

For the elucidation of the d-orbital splitting of low-spin cobalt(II) complexes, study by ESR is the most effective among various approaches.

As already mentioned, the highest-energy d-orbital is undoubtedly the $d_{x^2-y^2}$ orbital in square planar complexes; hence in low-spin cobalt(II) seven electrons are accomodated in the remaining four d-orbitals, yielding one unpaired electron. The problem of determining in which orbital the unpaired electron is localized has been a subject of arguments for the last two decades. These arguments were mainly based on ESR data. Griffith was the first to interpret ESR data of low-spin cobalt(II) complexes [41], and concluded that the unpaired electron is in the d_{z^2}-orbital in cobalt(II) phthalocyanine on the basis of analysis of the ESR parameters. He explained the large $|A_z|$ value in terms of the negative Fermi hyperfine coupling constant (K) due to coupling between the $4s$ and $3d_{z^2}$ orbitals [42], whereas for ordinary copper(II) complexes positive K is usually assumed [43,44]. ESR spectra similar to cobalt(II) phthalocyanine were observed for various cobalt(II) porphyrins [45—49], and hence they were assumed to adopt the same electronic configuration as that of the phthalocyanine. Recently, several workers have studied the electronic states of cobalt(II) phthalocyanines and porphyrins in more detail [45—51]. All these studies support the $(d_{z^2})^1$ ground state configuration.

On the other hand, Maki et al. [52] reported that $[Co(mnt)_2]^{2-}$ shows an ESR spectrum quite different from those of the above compounds [45—51], (cf. Table 4). Based on the ESR parameters they assigned the $(d_{yz})^1$ configuration to the ground state, where they adopted the coordinate system in which x and y axes bisect the bond angles. (Throughout the present paper $(d_{xz})^1$, $(d_{z^2})^1$ and $(d_{xy})^1$ represent $(d_{x^2-y^2})^2\,(d_{xz})^1$, $(d_{x^2-y^2})^2\,(d_{z^2})^1$ and $(d_{x^2-y^2})^2$-$(d_{xy})^1$, respectively, based on the electron-hole formalism.) However, in the calculation, Maki et al. [62] did not take account of the contribution from the d_{xz} orbital to the orbital angular momentum.

In 1972—1973, ESR spectra of the $[CoN_2O_2]$ type Schiff base complexes were measured in powder and frozen solution. Based on these data Engelhardt et al. [53] and Busetto and co-workers [54,55] assumed the $(d_{z^2})^1$ configura-

TABLE 3

Abbreviations of the ligands

Ligand	Abbreviation
phthalocyanine	H_2pc
$\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin	H_2tpp
N,N'-bis(1-acetonylethylidene)ethylenediamine	H_2acen
N,N'-bis(salicylidene)ethylenediamine	H_2salen
N,N'-bis(*o*-aminobenzylidene)ethylenediamine	H_2amben
dithioacetylacetone	Hsac
2,3-dimercaptomaleonitrile	H_2mnt
ethylenebis(diphenylphosphine)	dpe
N,N'-bis(1-phenyl-2-thiobenzoylvinyl)ethylenediamine	H_2nsen
N,N-bis(1-phenyl-2-thiobenzoylvinyl)ethylenediamine	H_2nstn
N,N'-ethylenebis(benzoylacetoimine)	$H_2benacen$
N,N'-bis(salicylidene)-1,2-R-propylenediamine	$H_2sal(-)pn$
N,N'-bis(1-acetonylethylidene)-1,2-R-propylenediamine	$H_2ac(-)pn$
N,N'-propylenebis(salicylamide)	$H_4sad(-)pn$
1,10-dihydroxy-1,10-diethoxy-3,5,8-trimethyl-4,7-diaza-deca-1,3,7,9-tetraene(cf. Fig. 16)	$H_2ae(-)pn$

tion for the ground state. On the other hand Nishida and Kida [56] proposed the $(d_{yz})^1$ configuration. Afterwards, however, it was revealed by single-crystal measurements that the discussion of Nishida and Kida was based on the erroneous assignment of g_x, g_y and g_z. Based on the single-crystal data of [Co(salen)] diluted in [Ni(salen)], Zelewsky and Fierz [57] concluded that the ground state is $(d_{yz})^1$ (for abbreviations see Table 3). By contrast, Cariati et al. [59] did not assign a discrete electronic configuration to the ground state, but suggested a mixing of the $(d_{z^2})^1$ and the $(d_{yz})^1$ configurations for [Co(acen)] diluted in a single crystal of [Ni(acen)]. Fantucci and Velenti [60] made a detailed MO calculation for [Co(acen)], and proposed the $(d_{yz})^1$ ground state configuration. McGarvey [61] developed the theory for the spin Hamiltonian parameters of low-spin cobalt(II) complexes to the third order degree in perturbation theory for all reasonable ground states allowing for the contribution from the quartet states, and from the configuration interaction due to the lowering of symmetry. On this theoretical basis Malatesta and McGarvey [58] examined the single-crystal ESR spectra of [Co(amben)] and [Co(benacen)] and concluded that the experimentally obtained ESR parameters can be explained on the basis of assumption of either the $(d_{z^2})^1$ or $(d_{yz})^1$ ground state, but the values of parameters used for the calculation of the $(d_{z^2})^1$ ground state were not as satisfactory as in the case of the $(d_{yz})^1$ ground state. However, in either case they had to assume an extremely large energy for the splitting between $(d_{xz})^1$ and $(d_{yz})^1$ in order to obtain good accordance between the theoretical and experimental values, e.g., $\geqslant 8000$ cm^{-1} for [Co(benacen)] and $\geqslant 11000$ cm^{-1} for [Co(amben)] in the case of the $(d_{yz})^1$ ground state. Such assumptions do not seem to be reasonable for the compounds such as *cis*-

$[CoN_2O_2]$ and $[CoN_4]$ types. In fact, they stated in the same paper that d_{xz} and d_{yz} orbitals are nearly degenerate in the copper(II) complexes of the same ligands, and hence could not give a reasonable explanation for such large energies for the splitting between the $(d_{xz})^1$ and the $(d_{yz})^1$ states in the cobalt(II) complexes.

Nishida and co-workers [62,63,66] have pointed out that square planar low-spin cobalt(II) complexes are classified into two types on the basis of ESR spectra. The criteria are that: (1) the difference between g_x and g_y is small in Type-I complexes, but very large in Type-II complexes; (2) although g_z is nearly 2.0 in both types, $|A_z|$ values of Type-I are much larger than those of Type-II. Diagnosis on this basis can be carried out not only for single-crystal spectra but also for powder (diluted in diamagnetic host compound) or frozen solution spectra. Typical spectra of both types are shown in Fig. 6. The ESR parameters obtained from single-crystal spectra are listed in Table 4. As seen in Table 4, phthalocyanine and porphyrins are classified as Type-I, and $[Co(mnt)_2]^{2-}$, $[Co(sac)_2]$ and the Schiff base complexes of the $[Co(N_2O_2)]$ type belong to Type-II. We have attributed the difference between the two types to the different ground state configurations. As mentioned above, conclusions of many studies converged to the $(d_{z^2})^1$ ground state for the Type-I complexes, and there is little ambiguity for this assignment. However, there have been controversies over the ground state of the Type-II complexes. Very recently Hitchman [64] and the present authors [62] have carried out detailed analy-

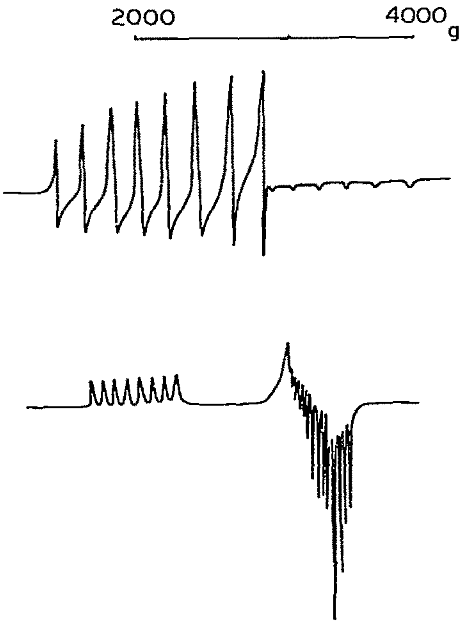


Fig. 6. Powder ESR spectra of cobalt(II) complexes. Upper, [Co(pc)] (Type-I complex) [46]; Lower, [Co(acen)] (Type-II complex) [56].

TABLE 4

ESR parameters of square planar cobalt(II) complexes obtained from single-crystal spectra

Type	Complex	g_z	g_x	g_y	$\lvert A_z\rvert$	$\lvert A_x\rvert$ (10^{-4} cm^{-1})	$\lvert A_y\rvert$	Ref.
I	[Co(pc)]^{a}	1.91	2.92	2.89	160	270	260	41, 42, 46
	[Co(mes)$_2$-(PEt$_2$Ph)$_2$]^{c}	1.74	3.72	1.96	140	390	50	74
II	[Co(acen)]	2.00	3.26	1.88	34	116	38	59
	[Co(salen)]^{a}	1.74	3.805	1.66	30	291	50	57
	[Co(amben)]^{b}	2.00	2.66	1.98	24	4	30	58
	[Co(benaca)]^{b}	1.954	3.372	1.882	47	166	37	58
	[Co(sac)$_2$]^{b}	1.899	3.280	1.904	35	105	35	68
	[Co(mnt)$_2$]$^{2-\,b}$	1.977	2.798	2.025	23	50	28	52

[a] The x and y axes are not clearly defined. [b] The coordinate system was adopted so that x and y axes bisect the bond angles. [c] mes represents mesityl.

sis on ESR parameters of cobalt(II) Schiff base complexes (belonging to Type-II), and independently reached the same conclusion that the ground state is the $(d_{yz})^1$ configuration, but there are some differences in the estimation of the orbital and electron repulsion energies.

Hitchman [64] estimated the energies of excited levels of [Co(salen)] using the ligand bonding parameters derived from analogous copper(II) complexes by the angular overlap MO model. In this approach the energy order of the d-orbitals was estimated as $d_{x^2-y^2} >> d_{xy} > d_{yz} > d_{z^2} \sim d_{xz}$, but he suggested the $(d_{yz})^1$ ground state, taking the electron repulsion energies into consideration (where $B = 750$ cm^{-1} and $C = 3150$ cm^{-1} were estimated). Based on this model, he calculated the ESR parameters and was successful in obtaining good agreement with experiment.

(ii) Studies of the present authors; outline of the theoretical approach

The present authors considered that the unsatisfactory results so far obtained on the basis of the calculation of ESR parameters mainly resulted from inadequate application of the equation of first-order perturbation to the spin—orbit coupling [62].

$$|\psi_g> = N\left[|\psi_g^0> - \Sigma \frac{\langle\psi_e^0|\lambda\hat{l}\cdot\hat{S}|\psi_g^0\rangle}{\Delta e}|\psi_e^0>\right]$$

As is well known, this approximation is valid only when the energy separations of the ground state and excited states to be coupled by the perturbation is large compared to the spin—orbit coupling constant, λ($\lambda = -515$ cm^{-1} for Co^{2+} ion), and there is a sufficient probability for the d_{xy}, d_{xz}, d_{yz} and d_{z^2} orbitals to lie close together in less than 1000 cm^{-1}. Therefore, diagonalizing the 4 × 4 spin—orbit matrix based on the $(xy)^1$, $(xz)^1$, $(yz)^1$ and $(z^2)^1$ states, we have calculated ESR parameters (g_x, g_y, g_z, A_x, A_y, A_z) as functions of various parameters such as Δ_{xz}, Δ_{z^2}, Δ_{xy} and λ (where Δ_m represents the energy separation between $(m)^1$ and $(yz)^1$ states ($m = xz$, z^2 and xy) and λ, the spin—orbit coupling constant). On the basis of the $(yz)^1$ ground state we were successful in obtaining satisfactory agreement between the experimental and calculated values for [Co(salen)] and [Co(acen)] by using reasonable values of the necessary parameters. The best-fit values are shown in Table 5. It should be noted that good agreement was obtained assuming $\Delta_{xz} = 2000$ cm^{-1} whereas other authors had to use rather unreasonably large values in order to attain good agreement between calculated and experimental values. Some of the important results are depicted in Figs. 7 and 8 as diagrams of g_i and $A_i (i = x, y, z)$ versus Δ_{z^2}, the other parameters being fixed at appropriate values, e.g., $\Delta_{xz} = 2000$ cm^{-1}, $\Delta_{xy} = 8000$ cm^{-1}, $\lambda = -450$ cm^{-1}, $P = 0.020$ cm^{-1} and K = 0.5, (where Δ_{xy} was estimated based on the assignment of the absorption band at about 8000 cm^{-1} to the $d_{xy} \rightarrow d_{yz}$ transition). According to the diagrams, one can account well for the characteristic features of the Type-II complexes, such as (1) g_y and $g_z \approx 2.0$ whereas $g_x = 3$—4 and (2) $|A_z|$ and $|A_y| < 60 \times 10^{-4}$ cm^{-1}, whereas $|A_x|$ varies from 50 to 400 × 10^{-4} cm^{-1}, if $\Delta_{z^2} = 1000$ cm^{-1} is assumed. Thus, it was concluded that the order of the energy levels is $(d_{yz})^1 < (d_{z^2})^1 \simeq (d_{xz})^1 < (d_{xy})^1$ in Type-II complexes.

In order to examine the validity of the above result, we have measured ESR and electronic spectra of many square planar complexes of cobalt(II), nickel(II) and copper(II) and tried to interpret the experimental data in terms of our calculated results. So far, this has been successful and will be described in the following sections.

(iii) Studies on [CoN$_4$]-type complexes

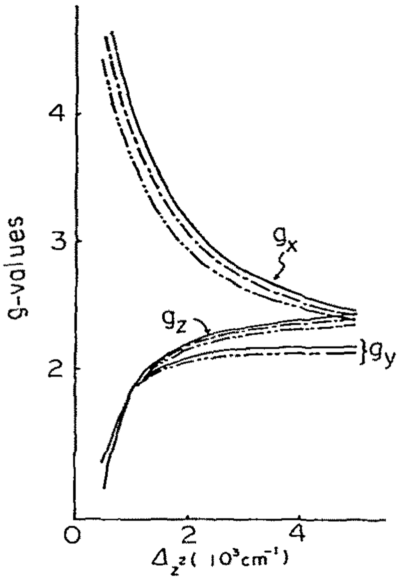
Powder ESR spectra were measured for the [CoN$_4$] type complexes (Fig. 9) (diluted in the nickel(II) homologues) [65] and are shown in Fig. 10; the ESR parameters are listed in Table 6. It is obvious from the magnitude of the

TABLE 5

The best-fit values for the ESR parameters of [Co(acen)] and [Co(salen)] complexes [62][a]

Parameter	[Co(acen)]	[Co(salen)]
g_z	2.00(2.00)	1.79(1.74)
g_x	3.36(3.26)	3.84(3.805)
g_y	1.94(1.88)	1.80(1.66)
$\lvert A_z \rvert$ (10^{-4} cm^{-1})	23(34)	14(30)
$\lvert A_x \rvert$ (10^{-4} cm^{-1})	114(116)	250(291)
$\lvert A_y \rvert$ (10^{-4} cm^{-1})	22(38)	22(50)

[a] Experimentally obtained values are given in parentheses.



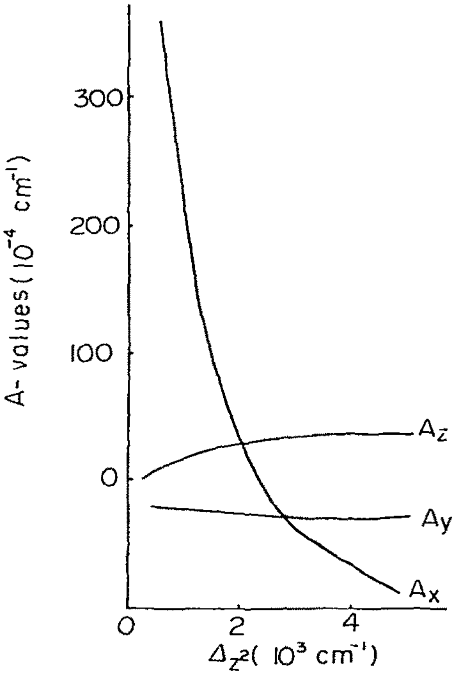


Fig. 7. The variations of $g_i (i = x, y, z)$ versus Δ_{z^2}, with k(orbital reduction factor) = 1.0 (————), k = 0.9 (· — · — ·) and k = 0.8 (·· — ·· — ··). Other parameters are fixed [62].

Fig. 8. The variations of $A_i (i = x, y, z)$ versus Δ_{z^2}. Other parameters are fixed [62].

$|A_3|$ values in the table that [Co(D-14)]$^{2+}$ and [Co(E-14)]$^+$ belong to Type-I, whereas other complexes with H_2(A-14) and H_2(A-16), etc. are of Type-II (see Fig. 9 for abbreviations).

As seen in Fig. 10 and Table 6, the $|A_1|(A_x)$ value for [Co(A-14)] is smaller than that for [Co(A-16)], and the same trend is also observed for the $g_1(g_x)$ values. Both facts are consistent in suggesting that the Δ_{z^2} of the former is larger than that of the latter, where Δ_{z^2} represents the energy separation between $(d_{z^2})^1$ and $(d_{yz})^1$ states. Similar relations are also seen in the case of the [CoN_2O_2] type complexes. Fig. 7 predicts that g_y and g_z decrease with increasing g_x (decreasing Δ_{z^2}). In fact, such a trend is readily found in Table 6.

(iv) [CoS_4]-, [CoN_2S_2]- and [CoP_4]-type complexes

The ESR spectra of [Co(nsen)] and [Co(nstn)] [66] are similar to that of [Co(acen)] [56] in general pattern as seen in Fig. 6. Hence they obviously belong to Type-II.

As an example of [CoP_4] type complexes, the ESR spectrum of [Co-(dpe)$_2$]$^{2+}$ [67], is depicted in Fig. 11. Judged from the $|A_3|$ values this com-

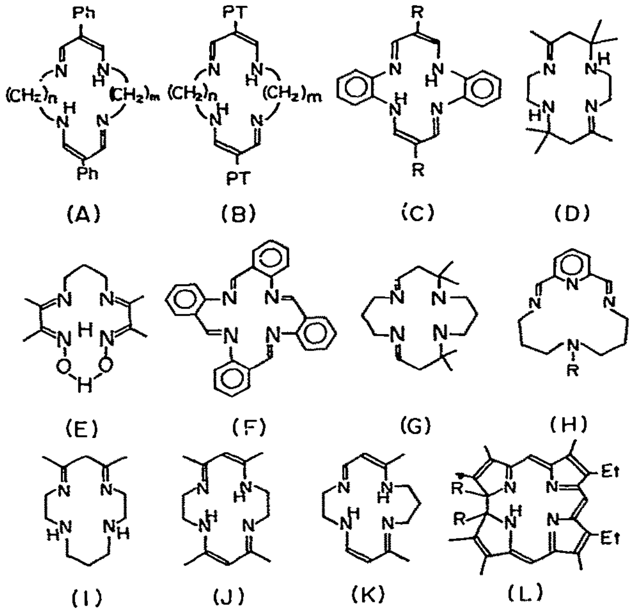


Fig. 9. Structural formulas of the 4N-donating macrocyclic ligands cited in this paper. Abbreviations are, (A), $n = m = 2$, H_2(A-14); $n = 2$, $m = 3$, H_2(A-15); $n = m = 3$, H_2(A-16) [92]: (B), $n = m = 2$, H_2(B-14); $n = m = 3$, H_2(B-16) [62]: (C), R = phenyl, H_2(C-14); R = *p*-tolyl, H_2(C-14′) [63]: (D), (D-14) [81]: (E), H(E-14) [91]: (F), (F-16) [82]: (G), (G-16) [83]: (H), (H-14) [84]: (I), (I-14) [85]: (J), H_2(J-14) [88]: (K), H_2(K-15) [89]: (L), H(L-15) [76].

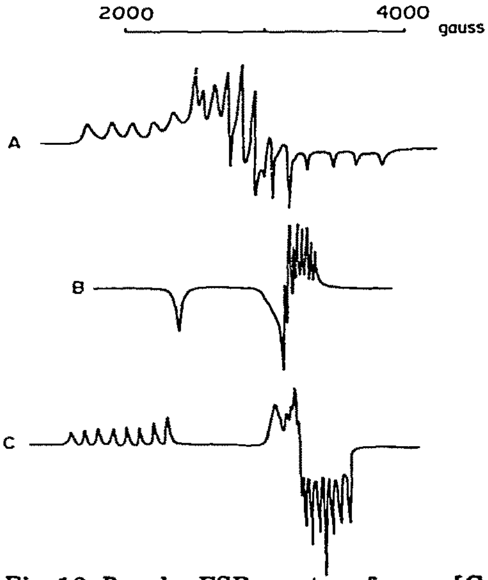


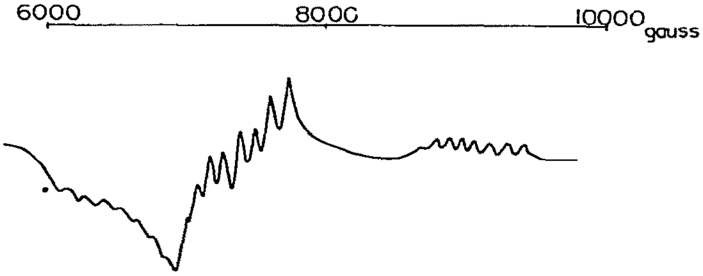
Fig. 10. Powder ESR spectra of some [CoN_4] type complexes [65] A, [Co(F-14)]$^+$; B, [Co(A-14)]; C, [Co(A-16)].

TABLE 6

ESR parameters of some [CoN_4], [CoN_2S_2], [CoS_4] and [CoP_4] complexes

Type	Complex	g_1	$_2$	g_3	$\lvert A_1\rvert$ (${10^{-4}}$ cm^{-1})	$\lvert A_2\rvert$	$\lvert A_3\rvert$	Ref.
I	[$Co(en)_2$](AgI_2)$_2$	$g_\perp = 2.50$	$g_\parallel = 2.00$		a			75
	[Co(D-14)]$^{2+}$	2.57	2.37	2.02	102	83	138	62
	[Co(E-14)]$^+$	2.88	2.28	2.04	199	97	173	65
	[Co(L-15)]$^+$	$g_\perp = 2.374$	$g_\parallel = 1.993$		$\lvert A_\perp\rvert = 80$	$\lvert A_\parallel\rvert = 146$		76
	[$Co(dpe)_2$](ClO_4)$_2$	2.80	2.44	1.97	161	132	134	67
	[Co(F-16)]$^{2+}$	2.62		2.018	106		130	77
	[Co(tpp)]	$g_\parallel = 1.798$	$g_\perp = 3.322$		$\lvert A_\parallel\rvert = 197$	$\lvert A_\perp\rvert = 315$		45
II	[Co(A-14)]	2.676		1.97	0		32	65
	[Co(A-15)]	2.874	2.04	1.94	47		35	65
	[Co(A-16)]	3.252	1.97	1.87	147		35	65
	[Co(C-14)]	4.256	1.71	1.53	397	30	55	63
	[Co(C-14′)]	4.057	1.70	1.55	352			63
	[$Co(Me\text{-}dtbiu)_2$] [b]	4.155			381			69
	[$Co(sadad)_2$] [c]	3.504		1.86	203		30	79
	[Co(nsen)] [d]	3.192		1.94	126			66
	[Co(nstn)] [d]	3.290		1.96	163			66

[a] Not resolved. [b] H(Me-dtbiu) represents N,N-methyl-phenyl-dithiobiuret. [c] H(sadad) represents salicylaldoxime. [d] See Table 3.



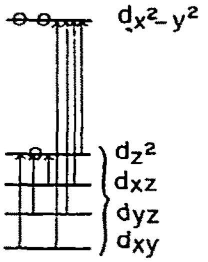


Fig. 11. Powder ESR spectrum of $[Co(dpe)_2](ClO_4)_2$ [67].

Fig. 12. Electronic transitions between *d*-orbitals in low-spin square planar cobalt(II) complexes.

plex belongs to Type-I. As for the $[CoS_4]$ type complexes, ESR spectra were studied for $[Co(mnt)_2]^{2-}$ [52], [Co(sac)] [68] and $[Co(R\text{-}dtb)_2]$ [69].

(v) Electronic spectra of square planar cobalt(II) complexes

In low-spin cobalt(II) complexes, seven spin-allowed *d—d* transitions are possible, as seen in Fig. 12. This makes the spectra complicated compared to those of square planar nickel(II) and copper(II) complexes, where only the transitions to the $d_{x^2-y^2}$ orbital are possible. Therefore, in the spectral study of square planar cobalt(II) complexes it is important to compare the spectra with those of the analogous nickel(II) and copper(II) complexes. As is well known, square planar nickel(II) and copper(II) complexes generally show *d—d* bands in the visible region (for exceptions, see the latter part of this paper), and square planar cobalt(II) complexes have a band in the near infrared region 8—12 × 10^3 cm^{-1}, which is characteristic [70]. Although there has been controversy over the origin of this band, very recently the present authors [62, 65,66] and Hitchman [64] concluded that it is due to the spin allowed $d_{xy} \rightarrow d_{yz}$ transition in the Type-II complexes. It is to be noted that the major part of this transition energy is due to the electron repulsion, 15B, as seen in Table 7.

In general, the bands corresponding to nickel(II) and copper(II) complexes are rarely observed for cobalt(II) complexes because of the overlapping of charge-transfer bands, though in fortunate cases such *d—d* bands may be observed, e.g., [Co(A-16)] [65]. The reason for the presence of the charge transfer bands in a relatively low energy region in cobalt(II) complexes is that low-spin cobalt(II) has the half-occupied d_{yz} (in the case of Type-II) or d_{z^2} (in the case of Type-I) to which the ligand electron can transfer. In Type-I complexes *d—d* bands have rarely been reported, because very intense absorptions due to the ligand always cover the *d—d* band region in metal porphyrins and phthalocyanine. The spectra of some $[CoP_4]$ type complexes [67] do contain exam-

TABLE 7

Electron repulsion energies of low-lying spin-doublet states of cobalt(II) (relative to $^2A_{1g}$) and spin-singlet states of nickel(II) (relative to $^1A_{1g}$) complexes

Co(II)			Ni(II)		
$^2A_{1g}$	$(x^2-y^2)^2(z^2)^1$	0	$^1A_{1g}$	$(x^2-y^2)^2$	0
$^2B_{2g}$	$(x^2-y^2)^2(xy)^1$	20B	^1E_g	$(x^2-y^2)^1(xz)^1$	—3B—C
^2E_g	$(x^2-y^2)^2(yz)^1$	5B	$^1B_{1g}$	$(x^2-y^2)^1(z^2)^1$	—4B—C
$^2B_{1g}$	$(x^2-y^2)^1(z^2)^2$	0	$^1A_{2g}$	$(x^2-y^2)^1(xy)^1$	—C

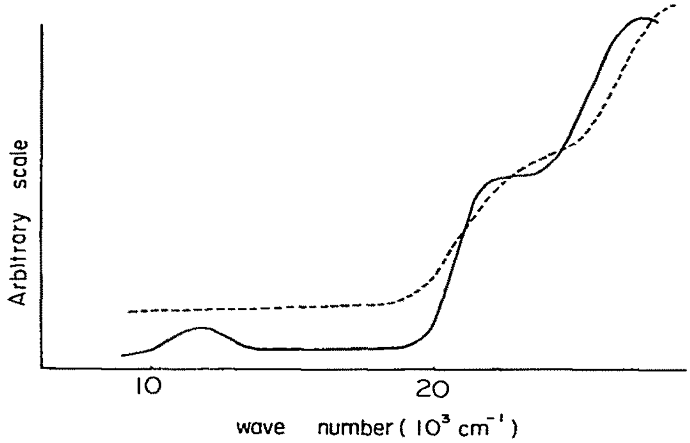


Fig. 13. Electronic reflectance spectra of [Co(dpe)$_2$](ClO$_4$)$_2$ (———) and [Ni(dpe)$_2$](ClO$_4$)$_2$ (- - - -) [67].

ples of *d*—*d* bands in Type-I complexes. For example, the spectrum of [Co(dpe)$_2$](ClO$_4$)$_2$ [67] is shown in Fig. 13.

Here again, we should pay attention to the fact that the $(d_{xy})^1$ state assumes a much higher electron repulsion energy relative to the $(d_{xz})^1$, $(d_{yz})^1$ and $(d_{z^2})^1$ states (cf. Table 7). Thus, the band at 11.7 × 10^3 cm^{-1} should be attributed to the $d_{xy} \rightarrow d_{z^2}$ transition, since the ESR indicated the $(d_{z^2})^1$ ground state. Absorption at 22—27 × 10^3 cm^{-1} are certainly attributed to transitions from low-lying *d*-orbitals to the $d_{x^2-y^2}$ orbital [67]. At any rate, the result obtained here implies that it is difficult to determine the ground state configuration of square planar cobalt(II) complexes from their electronic spectra only.

E. SPLITTING OF *d*-ORBITALS OF SQUARE PLANAR COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES

In considering the splitting of *d*-orbitals of square planar complexes, we start from the following basis: (1) there is little difference in the splitting scheme of *d*-orbitals among cobalt(II), nickel(II) and copper(II) complexes with the same ligand; (2) the magnitude of the *d*-orbital splitting for the nickel(II) and cobalt(II) complexes with the same ligand are nearly the same as each other; but (3) they are considerably larger than that for copper(II) complexes.

The first basis, (1), is evident since we assume no interelectronic interaction when we mention "orbital scheme". The second basis, (2), can be deduced from the comparison of the positions of visible bands of cobalt(II) and nickel(II) complexes with the same ligand; for example, compare the spectra of $[Ni(dpe)_2]^{2+}$ and $[Co(dpe)_2]^{2+}$ [67]. The last basis, (3), is expected from the fact that there is one electron in the $d_{x^2-y^2}$ orbital in the case of copper(II) complexes, but none in the $d_{x^2-y^2}$ orbital in the case of nickel(II) and cobalt(II).

In addition to this, more direct evidence was provided by the following facts. It is known that the spectra of square planar nickel(II) and copper(II) complexes resemble each other in the ligand field region. This was most clearly shown in the comparison of the CD spectra of the complexes of both metals [34]. However, *d—d* bands of nickel complexes are generally located to higher energy ($1—2 \times 10^3$ cm^{-1}) than the corresponding bands of copper complexes. Taking interelectronic interaction into consideration, we can estimate the *d*-orbital splittings of nickel complexes to be larger than those of copper complexes by at least 20%, even assuming a very low value for the Racah parameter B such as 500 cm^{-1}.

As already described, square planar cobalt(II) complexes are classified into Type-I and Type-II on the basis of ESR spectra, and the $(d_{z^2})^1$ and $(d_{yz})^1$ ground state configurations were assigned to these types, respectively, (see Table 4). Inspecting the ligands of Type-I and Type-II complexes (hereafter abbreviated as Type-I ligand and Type-II ligand), in detail, one can find characteristics of both types, i.e., Type-I ligands are N- or P-coordinating noncharged ligands, such as (14-D) and (dpe), or 4N-coordinating divalent negatively charged macrocyclic ligands with a well developed conjugated π-system such as porphyrins and phthalocyanine. Type-II ligands are generally divalent anions with 4N- or 2N2O-donor atoms, having no or a less developed conjugated π-system. Many synthetic 4N-coordinating macrocycles (such as A—C in Table 6) and 2N2O coordinating quadridentate Schiff bases belong to this type. These facts can be interpreted as follows. Type-I ligands are generally π-acids or have π-orbitals in donor atoms so that the energies of d_{xz} and d_{yz} orbitals of the metal ion are relatively low compared with that of the d_{z^2} orbital, giving rise to the $(d_{z^2})^1$ ground state in cobalt(II) complexes. On the other hand, Type-II ligands are generally π-bases. Therefore, the energies of the metal d_{yz} and d_{xz} orbitals are lifted by the effect of π-donation. As the result, the ground states of the cobalt(II) complexes are of the $(d_{yz})^1$ configuration.

Considering that: (1) the d_{xy} orbital is essentially non-bonding in the complexes of square planar 4N-donating ligands; (2) the energy of the d_{z^2} orbital is lower than that expected from the angular overlap model because of coupling with the 4*s* orbital [71]; and (3) the strength of σ-coordination is not an essential factor for distinguishing Type-I and Type-II ligands, we can draw the orbital energy diagrams of Fig. 14. These show the characteristic features of complexes with Type-I and Type-II ligands, where the magnitude of the π-interaction is being varied consecutively. From the diagrams, one may predict that in nickel(II) and copper(II) complexes the lowest-energy bands for Type-I complexes are generally higher in wavenumber than those for Type-II complexes [78]. In fact, this is quite in harmony with the experimental facts as shown in Table 8. It is remarkable that in the complexes [Cu(A-16)] and [Cu-(A-15)] *d*—*d* bands were observed at an unusually low frequency (9.9 and 13.0×10^3 cm^{-1}) for 4N-coordinating square planar copper(II) complexes. However, it is not necessary to consider axial coordination for these complexes, since it was confirmed that the band positions of the solution spectra are practically the same as those of the solid reflectance spectra. Accordingly, the low frequency of the bands should be attributed to the π-antibonding effect of the ligands.

It is known that nickel perchlorate forms yellow diamagnetic 1 : 2 complexes with ethylenediamine and some of its N-substituted derivatives in the solid state or in some non-aqueous solvents [72]. These complexes show one relatively sharp *d*—*d* band at 23×10^3 cm^{-1}. Since there are no bands other than this in the visible and near-ultraviolet regions, the observed band must be a superposition of the four spin-allowed *d*—*d* transitions. Accordingly, this is well explained as a case corresponding to the diagram I—2 in Fig. 14, since the complexes have no π-bonding.

In nickel(II) complexes with 2N2O-donating quadridentate Schiff bases, (cf. Fig. 16), generally one absorption peak (ϵ = 100~200) is observed at about 18×10^3 cm^{-1}. In CD spectra of [Ni(sal(—)pn)] and [Ni(ac(—)pn)], two

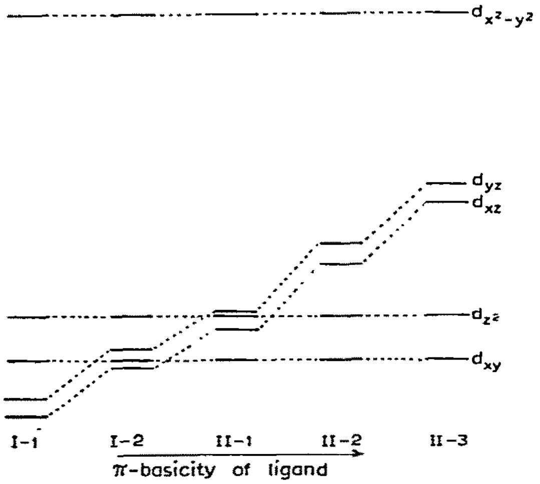


Fig. 14. The *d*-orbital energies of square planar complexes with ligands of various π-donating abilities.

TABLE 8

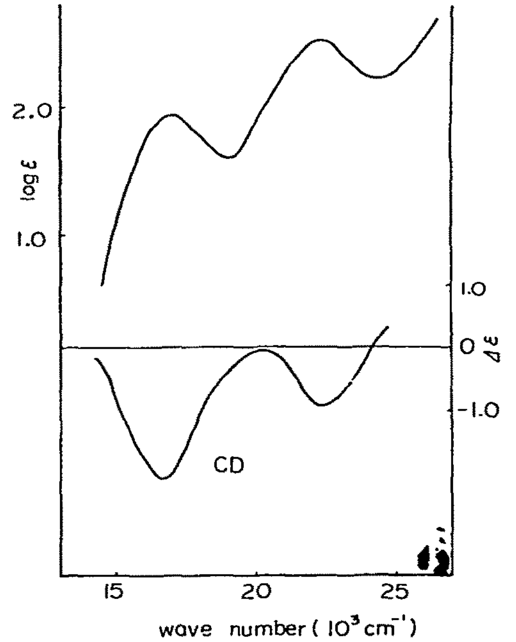
The lowest energy bands of square planar nickel(II) and copper(II) complexes (× 10^3 cm^{-1})

Type	Ligand	Ni(II)	Cu(II)	Ref.
I	ethylenediamine	22.5	19.0	80, 34
	(D-14)	22.7	19.0	81, 94
	(E-14)	[a]	21.9	91, 65
	dpe	23.0		67
	(F-16)	18.7		82
	(G-16)[b]	22.7		83
	(H-14)[b]	25.2		84
	(I-14)[b]		20.0	85
II	H_2(A-14)	16.5sh	16.0sh	65
	H_2(A-15)	14.5sh	13.0	65
	H_2(A-16)	13.0sh	9.9	65
	H_2mnt	11.7	8.33	52, 87
	H_2(acen)	17.7	15.6	90
	H_2(salen)	18.6	17.8	90
	H_2(J-14)[b]	17.9	16.2	88
	H_2(K-15)[b]	17.2		89

[a] Not observed. [b] No ESR spectra of cobalt(II) complexes with these ligands were reported, but the classification into Type I or Type II was determined by comparing the chemical structures with those whose classification had been established.

CD bands were observed at 17~18 and 21~23 × 10^3 cm^{-1} [34]. The lower-frequency band is certainly due to the same origin as that of the observed absorption band at a similar region. As for the higher-frequency band, it has been controversial whether it is due to a *d*—*d* transition or not. Very recently, however, the present authors found that [Ni(ae(—)pn)] shows two distinct bands not only in CD but also in the absorption spectrum as seen in Fig. 15. Judging from the intensity ($\epsilon = 250$), the higher-wavenumber band should be due to a *d*—*d* transition. Such a remarkable separation of *d*—*d* bands as in the above complexes can be interpreted in terms of the diagram II-3 in Fig. 14. The higher-wavenumber band can be assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition, and the lower wavenumber band to the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition. If inter-electronic repulsion is taken into consideration, the separation of the bands would be larger (by $4B$) than that estimated from the orbital energy diagram only. As for the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition, it cannot be clearly detected probably due to the weak intensity. In copper(II) complexes with the same ligands, similar spectra were observed, but a weak CD band was detected in between the separated *d*—*d* bands, which may be due to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition.

It should be noted that in general the nickel(II) and copper(II) complexes with Type-II ligands show separate *d*—*d* bands as expected from the diagrams II-2 and II-3 in Fig. 14.



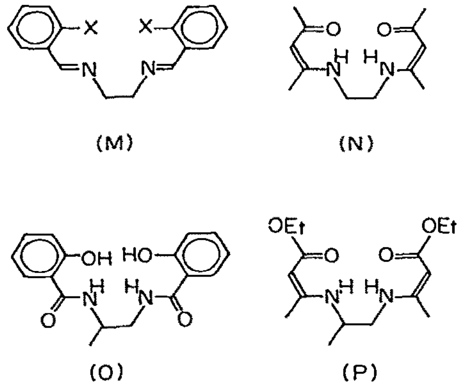


Fig. 15. Absorption and circular dichroism spectra of [Ni(ae(—)pn)] complex.

Fig. 16. Some quadridentate Schiff bases cited in this paper. Abbreviations are, (M): X = OH, H_2(salen); X = NH_2, H_2(amben); (N): H_2(acen); (O): H_2(sad(—)pn); (P): H_2(ae(—)pn).

F. CONCLUSION

(1) According to the ESR studies, square planar low-spin cobalt(II) complexes are classified into two groups; Type-I, complexes with the $(d_{z^2})^1$ ground state and Type-II, those with the $(d_{yz})^1$ ground state. The former complexes are formed with π-acidic, π-neutral or very weak π-basic ligands (Type-I ligands). On the other hand, the latter complexes are formed with fairly strong π-bases, (Type-II ligands).

(2) With this view, we can reasonably explain the fact that in square planar nickel(II) and copper(II) complexes the lowest-energy bands of those with Type-I ligands are generally observed in a higher-wavenumber region than those with Type-II ligands.

(3) Some square planar nickel(II) complexes show one *d*—*d* band, whereas others show distinctly separated bands. This is also interpreted comprehensively in terms of the π-acid—base property of ligands.

(4) As summarized above the electronic states of square planar complexes are very dependent upon the π-acid—base property of the ligands. Such a ligand property must be clearly related to the redox property of the complexes, which, therefore, will be the subject of forthcoming investigations.

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