Ground States of the Square Planar Low-Spin Cobalt(II) Complexes[1]

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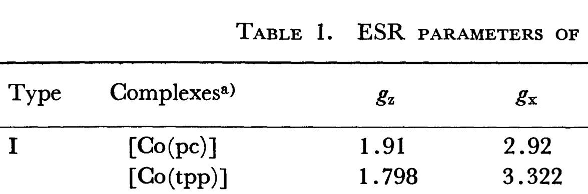
In order to investigate the ground state configuration of some square planar cobalt(II) complexes such as Schiff base complexes of the *cis*-$[CoN_2O_2]$ type, whose ESR spectra are quite different from those of cobalt(II) phthalocyanine and porphyrins, the spin-orbit matrix based on the four zero-order wave functions, $(yz)^1$, $(xz)^1$, $(z^2)^1$, and $(xy)^1$[2] were diagonalized on assuming reasonable values for necessary parameters. The result has clearly shown that an unpaired electron is localized in d_{yz} orbital in the ground state for these complexes. ESR spectra of a series of cobalt(II) complexes with N_4-macrocyclic ligands were measured and interpreted in terms of the conclusion obtained here.

In recent years the electronic states of low-spin cobalt(II) complexes have attracted attention because of their close relation to Vitamin B_{12} and biological oxygen carriers. As the consequence of studies on ESR and magnetism, it was established that the electronic configuration of the ground state is $(d_{xy})^2(d_{xz})^2(d_{yz})^2(d_{z^2})^1$, (denoted by $(z^2)^1$[2]) for cobalt(II) phthalocyanine[3,4] and porphyrins,[5] where x, y, and z axes were adopted as shown in Fig. 1-a. This is referred to as Type I. On the other hand, there is another type(Type II) of low-spin cobalt(II) complexes whose ESR spectra show a quite different pattern from that of the former group, as shown in Table 1. They include Schiff base complexes such as [Co(salen)] and [Co(acen)], where H_2 salen and H_2acen denote *N,N'*-disalicylideneethylenediamine and *N,N'*-bis(1-acetonylethylidene)ethylenediamine, respectively. Their ESR spectra differ a great deal from those of the Type I group in (1) the large separation between g_x and g_y (whereas the porphyrin group shows axial symmetry of g-tensors) and (2) the very small $|A_z|$ and $|A_y|$ values as compared with those of the Type I group. For the ground state configuration of the Type II compounds, three possibilities which have given rise to much argument can be considered.[6–13] Recently the correct values of g- and A-tensors for [Co(acen)][11] and [Co(amben)][13] were determined in the single crystals of the corresponding nickel(II) complexes, where H_2amben denotes *N,N'*-bis(*o*-aminobenzylidene)ethylenediamine. In their attempt to interpret the result by use of perturbation calculation, Cariati *et al.*[11] could not give an unambiguous assignment of the ground state configuration. They suggested the mixing of the two configurations for the ground state. However, their conclusion is unsatisfactory, since 1) they employed a positive value (0.28) for the Fermi hyperfine coulpling constant to fit A_i[14] values with the experimental ones in the case of the $(z^2)^1$ configuration, which is not compatible with the generally accepted view that the Fermi hyperfine coulpling constant assumes a negative value in the case of the $(z^2)^1$ configuration as the consequence of the coupling with the $(4s)^1$[2] configuration, and 2) in order to fit g_i[14] values with the experimental ones, the energy separation between d_{xz} and d_{yz} orbitals was assumed to be $6—7\times10^3\ cm^{-1}$ in the case of both $(z^2)^1$ and $(yz)^1$ electronic configuration. Similar results have also been reported.[13,15,16] However, there appears no reasonable evidence to assume such a large separation between d_{xz} and d_{yz} orbitals for the complexes of the planar *cis*-$[CoN_2O_2]$ and $[CoN_4]$ types.



1a 1b

Fig. 1. x, y, and z axis in the square planer complexes.

This unsatisfactory result seems to be due to the inadequate application of the perturbation theory to the present system. Calculation of g- and A-values for these systems have so far been carried out by use of the well-known formula of the first order perturbation theory for a nondegenerate ground state.[17]

$$|\psi_g> = N\left[|\psi_g^0> - \Sigma\frac{\langle\psi_e^0|\lambda\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{S}}|\psi_g^0\rangle}{\Delta_e}|\psi_e^0\rangle\right] \qquad (1)$$

However, application of equation (1) is valid only when $\Delta_e \gg \lambda$. In our system there is a sufficient probability for some of d_{xy}, d_{xz}, d_{yz}, and d_{z^2} orbitals to be

Table 1. ESR parameters of square planar cobalt(II) complexes

Type	Complexes[a]	g_z	g_x	g_y	$\|A_z\|$	$\|A_x\|$ (10^{-4} cm^{-1})	$\|A_y\|$	Ref.
I	[Co(pc)]	1.91	2.92	2.89	160	270	260	3
	[Co(tpp)]	1.798	3.322	3.322	197	315	315	5
II	[Co(acen)]	2.00	3.26	1.88	34	116	38	11
	[Co(salen)]	1.74	3.805	1.66	30	291	50	8
	$[Co(sac)_2]$	1.899	3.280	1.904	35	105	35	27

a) H_2pc: phthalocyanine, H_2tpp: $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin, H_2acen: *N,N'*-bis(1-acetonylethylidene)ethylenediamine, H_2salen: *N,N'*-bis(salicylidene)ethylenediamine, Hsac: dithioacetylacetone.

energetically close to each other. Thus, in diagonalizing the 4×4 spin-orbit matrix based on the $(xy)^1$,$(xz)^1$, $(yz)^1$ and $(z^2)^1$ states,[18] we have calculated g_i- and A_i-values as the function of various parameters and compared the results with the experimental values in order to elucidate the ground state of the Type II complexes. In order to examine the conclusion thus reached, we have measured the ESR spectra of a series of cobalt(II) complexes with N_4-macrocyclic ligands.

Calculation

In performing the perturbation calculation for the spin-orbit interaction, we have adopted the eight zero-order wave functions, $(\chi)^{+\mathrm{or}-}$, where $(\chi)^+$ denotes an antisymmetrized determinatal function, $|\overset{+}{(d_{x^2-y^2})}\overset{-}{(d_{x^2-y^2})}\overset{+}{(\chi)}|$ $(\chi=d_{xz}, d_{yz}, d_{xy}$, and $d_{z^2})$ based on the three electron hole formalism. Hence the wave functions for the system were formulated according to the Kramers theorem[19] as follows.

$$\Psi^+ = c_1\overset{+}{(yz)}{}^1 + ic_2\overset{+}{(xz)}{}^1 - ic_3\overset{-}{(z^2)}{}^1 + c_4\overset{-}{(xy)}{}^1 \tag{2}$$

$$\Psi^- = c_1\overset{-}{(yz)}{}^1 - ic_2\overset{-}{(xz)}{}^1 - ic_3\overset{+}{(z^2)}{}^1 - c_4\overset{+}{(xy)}{}^1 \tag{3}$$

The coefficients c_1, c_2, c_3, and c_4 were determined by diagonalizing the following 4×4 matrix,

$$\begin{array}{c|cccc}
 & \overset{+}{(yz)}{}^1 & \overset{+}{(xz)}{}^1 & \overset{-}{(z^2)}{}^1 & \overset{-}{(xy)}{}^1 \\
\hline
 & \Delta_4 & i\dfrac{\lambda}{2} & -i\dfrac{\sqrt{3}}{2}\lambda & -\dfrac{\lambda}{2} \\
 & -\dfrac{i}{2}\lambda & \Delta_1 & \dfrac{\sqrt{3}}{2}\lambda & \dfrac{i}{2}\lambda \\
 & i\dfrac{\sqrt{3}}{2}\lambda & \dfrac{\sqrt{3}}{2}\lambda & \Delta_2 & 0 \\
 & -\dfrac{\lambda}{2} & -i\dfrac{\lambda}{2} & 0 & \Delta_3
\end{array}$$

where λ denotes the spin-orbit coupling constant for the system, $\lambda=-k\zeta_{3d}$, ζ_{3d} being the free ion value for Co^{2+}(-515 cm^{-1}), and k is the orbital reduction factor evaluated at 1.0, 0.9, 0.8 and 0.7. The diagonal elements, Δ_1, Δ_2, Δ_3, and Δ_4 are functions of ligand field and interelectronic repulsion.

Based on Eqs. 2 and 3, g_i- and A_i-values can be expressed in terms of k, c_1, c_2, c_3, and c_4 (and κ in the case of A_i/P), where P and κ denote $2g_N\beta_e\beta_N\langle r^{-3}\rangle_{3d}$[20] and Fermi hyperfine coupling energy in units of P, respectively.

$$g_z = 2[c_1^2+c_2^2-c_3^2-c_4^2-2kc_1c_2] \tag{4}$$

$$g_x = 2[c_1^2-c_2^2+c_3^2-c_4^2-2\sqrt{3}kc_1c_3-2kc_2c_4] \tag{5}$$

$$g_y = 2[c_1^2-c_2^2-c_3^2+c_4^2+2\sqrt{3}kc_2c_3-2kc_1c_4] \tag{6}$$

$$\begin{aligned}A_z/P = 2[&-2c_1c_2-\frac{\kappa}{2}(c_1^2+c_2^2-c_3^2-c_4^2)\\ &+\frac{1}{7}(c_1^2+c_2^2-2c_3^2+2c_4^2+3c_1c_4\\ &-\sqrt{3}c_1c_3-3c_2c_4-\sqrt{3}c_2c_3)]\end{aligned} \tag{7}$$

$$\begin{aligned}A_x/P = 2[&-2\sqrt{3}c_1c_3-2c_2c_4-\frac{\kappa}{2}(c_1^2-c_2^2+c_3^2-c_4^2)\\ &+\frac{1}{7}(-2c_1^2+c_2^2-c_3^2-c_4^2-3c_1c_2-3c_1c_4\\ &-\sqrt{3}c_2c_3-2\sqrt{3}c_3c_4)]\end{aligned} \tag{8}$$

$$\begin{aligned}A_y/P = 2[&2\sqrt{3}c_2c_3-2c_1c_4-\frac{\kappa}{2}(c_1^2-c_2^2-c_3^2+c_4^2)\\ &+\frac{1}{7}(c_1^2+2c_2^2+c_3^2+c_4^2+3c_1c_2\\ &+\sqrt{3}c_1c_3-3c_2c_4-2\sqrt{3}c_3c_4)]\end{aligned} \tag{9}$$

Throughout the calculation $P=0.020$ cm^{-1} was adopted (free ion value for P is 0.025 cm^{-1},[21]).

Results and Discussion

After several preliminary calculations we have become convinced that the small $|A_z|$ and $|A_y|$ values of Type II complexes can not be accounted for on the basis of $(z^2)^1$ ground state, where a negative value is to be assigned to the Fermi hyperfine coupling constant, κ.[4,22,23] The $(xy)^1$ ground state is also improbable, because 1) the d_{xy} orbital is practically nonbonding in the Schiff base complexes, and 2) the interelectronic repulsion in the $(xy)^1$ state is higher (at least 6000 cm^{-1}) than that in both the $(z^2)^1$ and $(yz)^1$ states.[24] Recently McGarvey[12] investigated the contributions from the spin-quartet states and the mixing of d_{z^2} and d_{xy}[25] orbitals to the ESR parameters of low-spin cobalt(II) complexes. He showed that the contributions from the spin-quartet states are very important for 5- and 6-coordinated complexes, but can be neglected for 4-coordinated planar complexes. This can be explained as follows. The energy separation between d_{z^2} and $d_{x^2-y^2}$ orbitals in the square planar complexes is larger than that in 5- and 6-coordinated complexes, so that the energy gap between the ground doublet state, $|\overset{+}{(d_{x^2-y^2})}\overset{-}{(d_{x^2-y^2})}\overset{+}{(d_{z^2})}|$ and the excited quartet states such as $|\overset{+}{(d_{x^2-y^2})}\overset{+}{(d_{z^2})}\overset{+}{(d_{yz})}|$ *etc.* is larger than in the former complexes.

McGarvey also took a sizeable mixing of d_{z^2} and d_{xy}[25] into consideration in order to explain the ESR parameters of $[Co(sac)_2]$ and $[Co(mnt)_2]^{2-}$ on the basis of $(z^2)^1$ ground state, these complexes being classified as Type II complexes in this paper. However, his interpretation appears to be imcompatible with our experimental results. Accordingly, we considered here only the $(yz)^1$ configuration for the ground state of the Type II compounds throughout the calculation, assuming the contribution from the spin-quartet states to be negligibly small. This means that we have set Δ_4 to be zero in the 4×4 matrix, therefore Δ_1, Δ_2, and Δ_3 are the energy separation from the ground $(yz)^1$ state for $(xz)^1$, $(z^2)^1$, and $(xy)^1$, respectively.

It has been known that a sharp absorption band is always observed around 8000 cm^{-1} in the complexes with quadridentate Schiff bases of the *cis*-$[CoN_2O_2]$ type.[26] Judging from its intensity ($\log\varepsilon\approx1.5$), this is undoubtedly a spin-allowed d-d transition. This band is most probably assigned to the $(yz)^1\rightarrow(xy)^1$ transition, since the interelectronic repulsion energy in $(xy)^1$ state is much larger than that in $(yz)^1$ and $(z^2)^1$ states, and there seems to be no particular reason to separate the $(xz)^1$ and $(z^2)^1$ states from the $(yz)^1$ state in such a high energy as 8000 cm^{-1}. Furthermore, it has been revealed in the course of calculation that the large g_x values, 3.2—3.9 (Table 1), can be accounted for in terms of the orbital contribution from the $(xy)^1$ and $(z^2)^1$ states, only when these states are separated from the ground state by less than 3000 cm^{-1}. Thus, Δ_3 was fixed at 8000 cm^{-1} throughout the calculation.

In Figs. 2—9, g_i and A_i values are plotted as functions of Δ_1 and Δ_2. The g_z, g_x, and g_y values vary sensitively with Δ_1 and Δ_2, as seen in Figs. 4, 5 and 6. respectively. It should be noted that g_z(Fig. 4) can be fitted to the experimental value (*e.g.*, 2.00 for [Co(acen)]) by assuming a reasonable d_{xz}-d_{yz} separation, *i.e.*, 0—3000 cm^{-1}, whereas in the case of the calculation based on Eq. 1, an unreasonably large separation ($\geq$5000 cm^{-1}) has to be assumed in order to fit the calculated g_z value to the experimental one.[13,15,16]

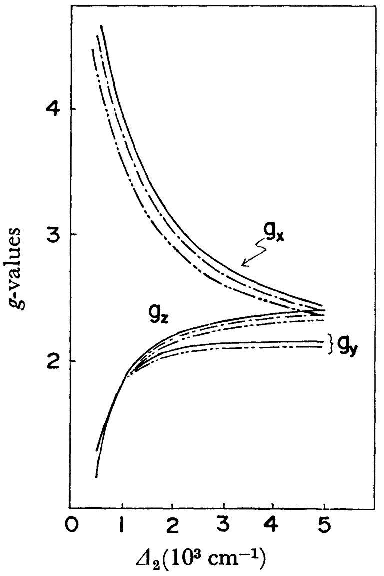


Fig. 2. The variation of g_i-values(i=x, y, z,) *versus* Δ_2, with $k=1.0$(——), $k=0.9$(—·—) and $k=0.8$(—··—). Other parameters, Δ_1 and λ are fixed to be 2000 and -450 cm^{-1}, respectively.

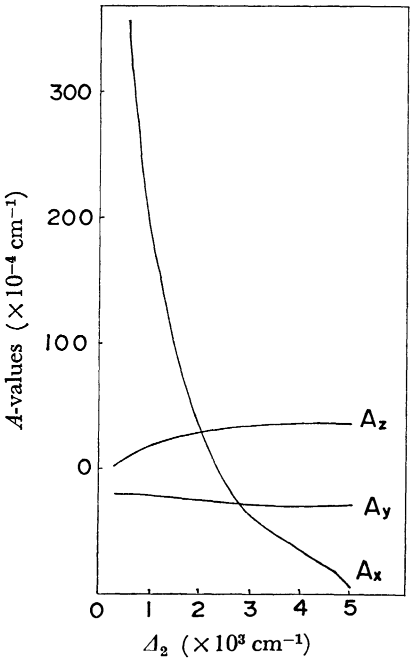


Fig. 3. The variation of A_i-values(i=x, y, z) *versus* Δ_2 with $\Delta_1=2000$ cm^{-1}, $\lambda=-450$ cm^{-1} and $\kappa=0.5$.

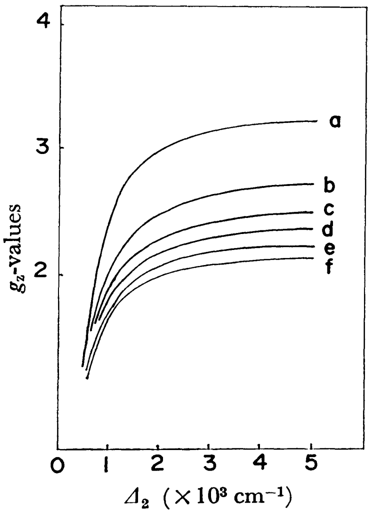


Fig. 4. The variation of g_z as a function of Δ_2. Δ_1 are (a) 500 cm^{-1}, (b) 1000 cm^{-1}, (c) 1500 cm^{-1}, (d) 2000 cm^{-1}, (e) 3000 cm^{-1} and (f) 5000 cm^{-1}. In all cases, k and λ are fixed to be 1.0 and -450 cm^{-1}, respectively.

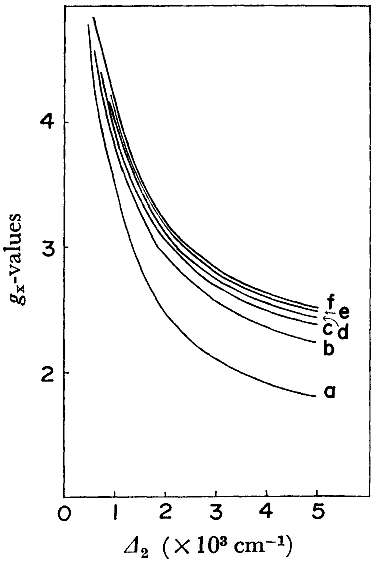


Fig. 5. The variation of g_x as a function of Δ_2. Δ_1 are (a) 500 cm^{-1}, (b) 1000 cm^{-1}, (c) 1500 cm^{-1}, (d) 2000 cm^{-1} (e) 3000 cm^{-1}, and (f) 5000 cm^{-1}. Other parameters, k and λ are fixed to be 1.0 and -450 cm^{-1}, respectively.

The g_x value(Fig. 5) sharply increases with the decrease of Δ_2, the effect of Δ_1 being minor compared with that of Δ_2. Accordingly, Δ_2 can be estimated as 900—1500 cm^{-1} for [Co(acen)] from Fig. 5 and experimental g_x value (3.26).[11] The A_x value (Fig. 8) highly dependent on Δ_2, and suffers little effect from the variation of Δ_1, thereby enabling us to estimate the Δ_2 value for [Co(acen)] at 1300—1600 cm^{-1} from the

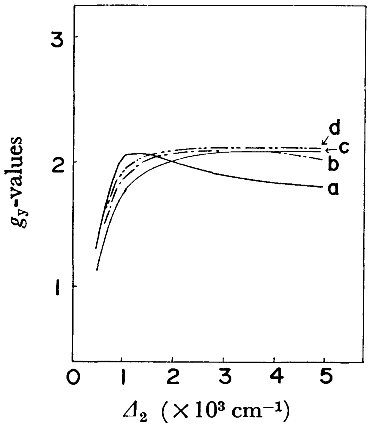


Fig. 6. The variation of g_y as a function of Δ_2. Δ_1 are (a) 500 cm^{-1}, (b) 1000 cm^{-1}, (c) 1500 cm^{-1}, and (d) 5000 cm^{-1}. In all cases, k and λ are fixed to be 1.0 and -450 cm^{-1}, respectively.

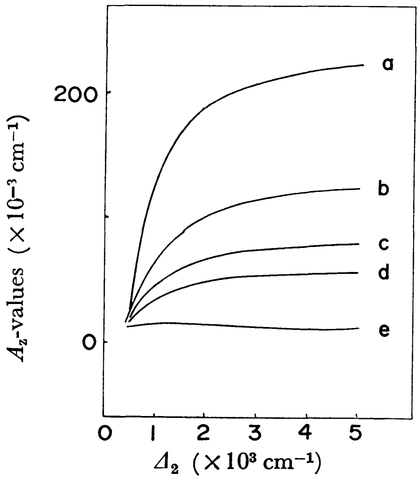


Fig. 7. The variation of A_z as a function of Δ_2. Δ_1 are (a) 500 cm^{-1}, (b) 1000 cm^{-1}, (c) 1500 cm^{-1}, (d) 2000 cm^{-1}, (e) 5000 cm^{-1}. Other parameters, κ and λ are fixed to be 0.4 and -450 cm^{-1}, respedtively.

experimental value of $|A_x|$ (115.8×10^{-4} cm^{-1}).[11] This is compatible with the value, 900—1500 cm^{-1}, estimated from g_x according to the diagram in Fig. 5.

On the basis of the above discussion, assuming reasonable values for the necessary parameters, we obtained satisfactory agreement between calculated and experimental g_i and A_i values in the case of the two examples of Type II complexes, as shown in Table 2, where both ESR spectra were measured on single crystals. From the c_1, c_2, c_3 and c_4 values listed in Table 2, it can be concluded that an unpaired electron is localized in the d_{yz} orbital, *i.e.*, mixing of the $(z^2)^1$ is very small.

It is well known that the ESR spectrum of [Co(mnt)$_2$]$^{2-}$, (where H$_2$mnt denotes 2,3-dimercaptomaleonitrile) shows[20] a pattern similar to that of both [Co(acen)] and [Co(salen)], undoubtedly belonging to Type II. However, analysis of the ESR spectra on single crystals revealed that the directions of principal axes of g-tensors are, as depicted in Fig. 1-b,[20] different from those of [Co(acen)]. Thus, on the basis of the

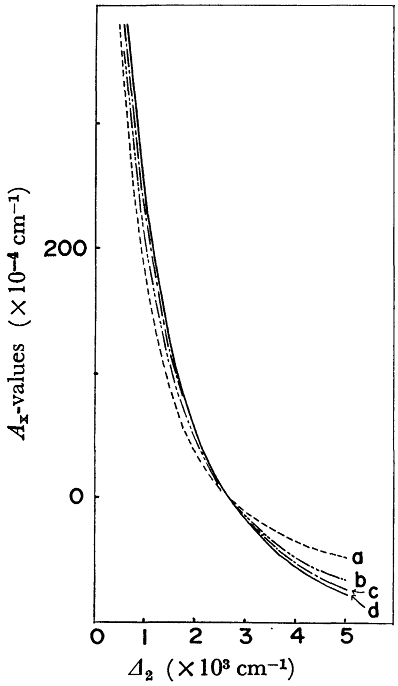


Fig. 8. The variation of A_x as a function of Δ_2. Δ_1 are (a) 500 cm^{-1}, (b) 1000 cm^{-1}, (c) 1500 cm^{-1}, and (d) 3000 cm^{-1}. Other parameters, κ and λ are fixed to be 0.4 and -450 cm^{-1}, respectively.

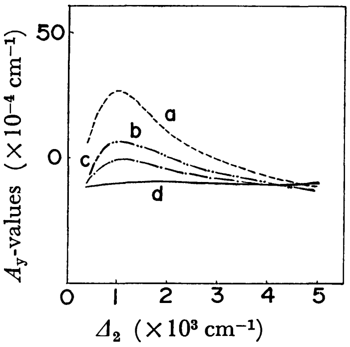


Fig. 9. The variation of A_y as a function of Δ_2. Δ_1 are (a) 500 cm^{-1}, (b) 1000 cm^{-1}, (c) 1500 cm^{-1}, and (d) 3000 cm^{-1}. Other parameters, κ and λ are fixed to be 0.4 and -450 cm^{-1}, respectively.

new x, y, and z axes we formulated equations similar to Eqs. 2—9 according to the same principle. The results was very similar to that obtained in the case of the coordinated system in Fig. 1-a. For example, a similarity of results of the calculation based on the different coordinate systems can be seen, if we compare Figs. 10, 11 and Table 3 (based on the coordinate system in Fig. 1-b) with Figs. 2,3 and Table 2 (based on the coordinate system in Fig. 1-a), respectively. It was confirmed by repeated examination that the choice of the x and y axes does not bring about any significant effect on the calculated values.

From the above discussion, we can conclude that in Type II complexes an unpaired electron is localized in the d_{yz} orbital in the ground state. It should be emphasized that in this approach we could interpret the ESR parameters of the compounds on the assump-

Table 2. Calculated values of g_i, A_i(i=x, y, z) and $c_j(j=1, 2, 3, 4)$ for the coordinate system of Fig. 1-a Experimentally obtained values are given in parentheses.

	[Co(acen)]$^{a)}$	[Co(salen)]$^{b)}$
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)
$\|A_z\|$ ($\times 10^{-4}$ cm^{-1})	23(34)	14(30)
$\|A_x\|$ ($\times 10^{-4}$ cm^{-1})	114(116)	250(291)
$\|A_y\|$ ($\times 10^{-4}$ cm^{-1})	22(38)	22(50)
c_1	0.9699	0.9322
c_2	−0.0632	−0.0344
c_3	−0.2332	−0.3617
c_4	−0.0292	−0.0269

a) Assumed values: $\Delta_1=2000$ cm^{-1}, $\Delta_2=1400$ cm^{-1}, $\Delta_3=8000$ cm^{-1}, $\lambda=-450$ cm^{-1}, $k=0.9$ and $\kappa=0.5$. b) Assumed values: $\Delta_1=2000$ cm^{-1}, $\Delta_2=800$ cm^{-1}, $\Delta_3=8000$ cm^{-1}, $\lambda=-450$ cm^{-1}, $k=0.8$, and $\kappa=0.5$.

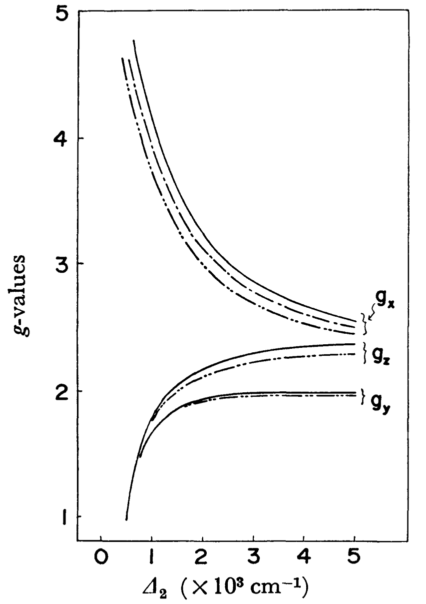


Fig. 10. The variation of g_i-values (i=x, y, z) *versus* Δ_2 in the case of the coordinate system of Fig. 1-b, with $k=1.0$ (——), $k=0.9$ (—·—), and $k=0.8$ (—··—). Other parameters Δ_1, λ, and Δ_3 (in this case, this means the energy separation between (yz)^1 and (x^2−y^2)^1) are fixed to be 2000, −450, and 8000 cm^{-1}, respectively.

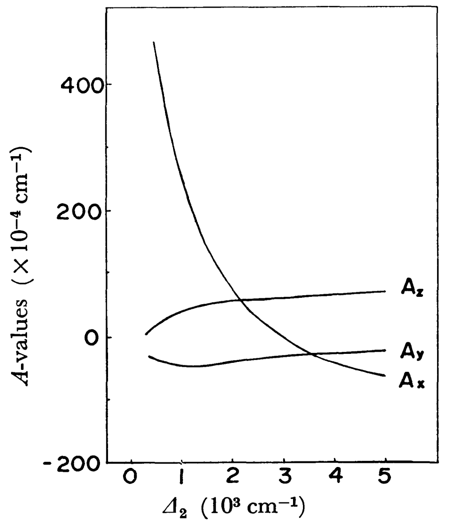


Fig. 11. The variation of A_i-values (i=x, y, z) *versus* Δ_2 in the case of the coordinate system of Fig. 1-b. Other parameters, Δ_1, λ, Δ_3, and κ are fixed to be 2000, −450, 8000 cm^{-1} and 0.4, respectively.

Table 3. Calculated values of g_i, A_i (i=x, y, z), and $c_j(j=1, 2, 3, 4)$ for the coordinate system of Fig. 1-b Experimentally obtained values are given in parentheses.

	[Co(acen)]$^{a)}$	[Co(salen)]$^{b)}$
g_z	2.02(2.00)	1.78(1.74)
g_x	3.40(3.26)	3.90(3.805)
g_y	1.86(1.88)	1.68(1.66)
$\|A_z\|$ ($\times 10^{-4}$ cm^{-1})	42(34)	40(30)
$\|A_x\|$ ($\times 10^{-4}$ cm^{-1})	130(116)	254(291)
$\|A_y\|$ ($\times 10^{-4}$ cm^{-1})	53(38)	42(50)
c_1	0.9729	0.9499
c_2	−0.0663	−0.0466
c_3	−0.2195	−0.3077
c_4	−0.0294	−0.0279

a) Assumed values: $\Delta_1=2000$ cm^{-1}, $\Delta_2=1500$ cm^{-1}, $\Delta_3=8000$ cm^{-1}, $\lambda=-450$ cm^{-1}, $k=0.9$, and $\kappa=0.45$. b) Assumed values: $\Delta_1=2000$ cm^{-1}, $\Delta_2=1000$ cm^{-1}, $\Delta_3=8000$ cm^{-1}, $\lambda=-450$ cm^{-1}, $k=0.9$, and $\kappa=0.5$.

tion of reasonably small energy separation for the d$_{xz}$ and d$_{yz}$ orbitals, for which in the previous calculations[13,15,16] a large separation had to be assumed in order to fit the calculated values to the experimental ones. The present result has enabled us to analyze the ground state configuration of low-spin square planar cobalt(II) complexes from their ESR spectra (even spectra of powder samples), where the magnitude of hyperfine coupling energy of the peaks around the $g=2.0$ is most characteristic (*cf.* Table 1).

The presently obtained experimental results support the above conclusion. The powder ESR spectra of diluted cobalt(II) complexes with the N$_4$-macrocyclic ligands, **L-a**, **L-b**, and **L-c** (Fig. 13) are shown in Fig. 12. It is evident that the ESR pattern of [Co(**L-a**)]$^{2+}$ entirely differs from that of both [Co(**L-b**)] and [Co(**L-c**)]. According to our criterion, [Co(**L-a**)]$^{2+}$ belongs to Type I complexes because of the hyperfine splitting ($|A_3|=138\times 10^{-4}$ cm^{-1}) of the highest field absorption ($g_3=2.00$). On the other hand, two absotptions (g_2, g_3) were observed around $g=2.0$ for [Co(**L-b**)] and [Co(**L-c**)], their hyperfine splittings being very small ($|A_2|$, $|A_3|<50\times 10^{-4}$ cm^{-1}). The features of [Co(**L-b**)] and [Co(**L-c**)] are very similar to those of [Co(amben)] and [Co(acen)], respectively. It should be noted that the hyperfine splitting at the lowest fields aborption of [Co(**L-c**)], ($g_1=3.153$, $|A_1|=126\times 10^{-4}$ cm^{-1}), is much larger than that of [Co(**L-b**)], ($g_1=2.636$, $|A_1|\cong 0$). This can be readily elucidated in terms of our calculated results based on the (yz)^1 ground state configuration. One absorption band is observed in the range 10000—12000 cm^{-1} for [Co(amben)][29] and [Co(**L-b**)]. For these cases, we have calculated g_i and A_i

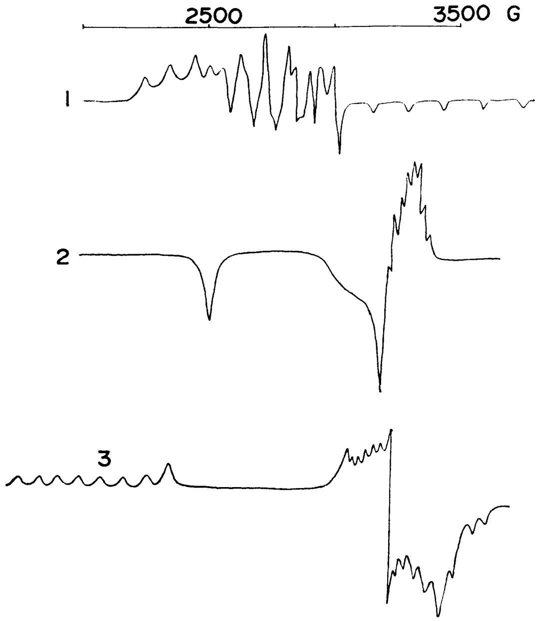


Fig. 12. ESR spectra of some square planar cobalt(II) complexes (obtained at 77 K, and $G=10^{-4}$ T). 1; $[Co(\mathbf{L\text{-}a})]^{2+}$ 2; $[Co(\mathbf{L\text{-}b})]$ 3; $[Co(\mathbf{L\text{-}c})]$.

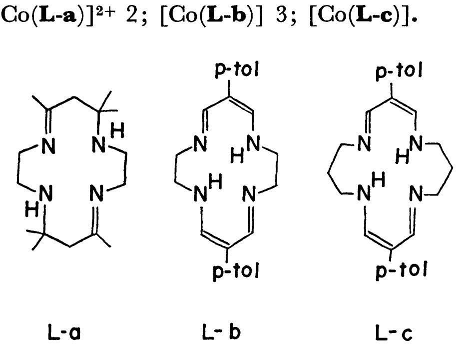


Fig. 13. Some N_4-macrocyclic ligands used in this paper, where *p*-tol represents *p*-tolyl.

values, assuming Δ_3 to be 10000—12000 cm^{-1}. As a result, it was found that the variation of Δ_3 in the range 8000—12000 cm^{-1} brings about no significant effect on the calculated values, shown in Figs. 2—9. As shown in Figs. 8 and 3, A_x is very sensitive to the energy separation between $(yz)^1$ and $(z^2)^1$. As this energy separation increases from 1400 to 2500 cm^{-1}, g_x varies from 3.2, to 2.7, and A_x, from 140×10^{-4} cm^{-1} to zero. Thus, we can elucidate the ESR parameters of [Co(amben)], $[Co(\mathbf{L\text{-}b})]$ and $[Co(\mathbf{L\text{-}c})]$ in tersm of our calculated results based on the $(yz)^1$ ground state configuration.

McGarvey took a sizeable mixing of d_{z^2} and d_{xy} orbitals into consideration in order to explain the ESR parameters of $[Co(sac)_2]$ and $[Co(mnt)_2]^{2-}$. According to his discussion, there should be a large difference in the mixing of d_{z^2} and d_{xy} orbitals in $[Co(\mathbf{L\text{-}a})]^{2+}$, $[Co(\mathbf{L\text{-}b})]$ and $[Co(\mathbf{L\text{-}c})]$. However, this is naturally unrealistic since all these complexes have effective D_{2h} symmetry and such a large difference can not be expected.

Experimental

Preparation. The perchlorate of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacycotetradeca-1,7-diene, **L-a**, and the tetraphenylborate of $[Ni(\mathbf{L\text{-}a})]^{2+}$ were prepared according to the methods of Curtis.$^{30)}$ The ligands, **L-b** and **L-c**, 6,13-di-*p*-tolyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene, and 3,11-di-*p*-tolyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraene, were obtained from the reaction mixtures of 4-*p*-tolyl-1,2-dithiolium hydrogensulfate and ethylenediamine or 1,3-propanediamine, according to methods similar to those described by Tang *et al.*$^{31)}$ Low-spin square planar nickel(II) and cobalt(II) complexes with **L-b** and **L-c** were also prepared according to the methods of Tang *et al.*$^{31)}$

Measurements. 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 JES-3X-ME using an X-band. DPPH was used as a standard marker.

The calculations were performed on the Facom 230–75 computer at the Computer Center of Kyushu University. Secular determinants were solved by program HERMTS.

References

1) Part V of the series, "Investigation on Low-spin Cobalt(II) Complexes."

2) The electronic configurations of low-spin cobalt(II) complexes such as $(d_{xy})^2(d_{xz})^2(d_{yz})^2(d_{z^2})^1$, $(d_{xy})^2(d_{xz})^2(d_{z^2})^2(d_{yz})^1$, $(d_{xz})^2(d_{yz})^2(d_{z^2})^2(d_{xy})^1$, and $(d_{xz})^2(d_{yz})^2(d_{xy})^2(4s)^1$ are denoted by $(z^2)^1$, $(yz)^1$, $(xy)^1$, and $(4s)^1$, respectively, in this paper.

3) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discuss. Faraday Soc.*, **26**, 72 (1958).

4) J. S. Griffith, *Discuss. Faraday Soc.*, **26**, 81 (1958).

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

6) L. M. Engelhardt, J. D. Duncan, and M. Green, *Inorg. Nucl. Chem. Lett.*, **8**, 725 (1972).

7) Y. Nishida and S. Kida, *Chem. Lett.*, **1973**, 57.

8) A. Zelewsky and H. Fierz, *Helv. Chim. Acta*, **56**, 977 (1973).

9) C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, and R. Ugo, *J. Chem. Soc. Dalton Trans.*, **1973**, 754.

10) K. Migita, M. Iwaizumi, and T. Isobe, *J. Am. Chem. Soc.*, **97**, 4228 (1975).

11) F. Cariati, F. Morazzoni, C. Busetto, E. D. Piero, and A. Zaetta, *J. Chem. Soc. Dalton Trans.*, **1976**, 342.

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

13) V. Malatesta and B. R. McGarvey, *Can. J. Chem.*, **53**, 3791 (1975).

14) The subscript i in g_i and A_i denotes three principal axes of each tensor, *i.e.*, i=x, y, or z.

15) C. Busetto, F. Cariati, P. C. Funtucci, D. Galizzioli, and F. Morazzoni, *Inorg. Nucl. Chem. Lett.*, **9**, 313 (1973) and Ref. 6.

16) For the $(yz)^1$ ground state, *cf.* our unpublished work and T. Kawakita, K. Migita, M. Chikira, M. Iwaizumi, and T. Isobe, presented at the 24th symposium on the coordination chemistry, Kanazawa, 1974.

17) For example, R. B. Bentley, F. E. Mabbs, W. R. Smail, M. Gerloch, and J. Lewis, *J. Chem. Soc.*, *A*, **1970**, 3003.

18) For the sake of simplicity, we made allowance only for the contribution from the states where $d_{x^2-y^2}$ is vacant, since in the present system we can assume that energy separation between $d_{x^2-y^2}$ orbital and any of the other d-orbitals is sufficiently large. In this system, the quartet terms were also neglected, since according to McGarvey$^{12)}$ they are neglible for the square planar cobalt(II) complexes.

19) J. S. Griffith, "The Theory of Transition Metal Ions,"

Cambridge University Press, London (1961), pp. 205—209.

20) A. H. Maki, N. Edelstein, A. Davidson, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

21) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

22) P. A. Narayana and K. V. L. N. Sastry, *J. Chem. Phys.*, **57**, 3266 (1972), and *ibid.*, **58**, 4381 (1973).

23) H. Kon and N. Kataoka, "Electron Spin Resonance of Metal Complexes," ed by T. F. Yen, Plenum Press, New York (1969), pp. 59—69.

24) Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn.*, **45**, 461 (1972).

25) Our choice of x, y axis differs from that of McGarvey,[12] so that the d_{xy} in this paper corresponds to the $d_{x^2-y^2}$ in McGarvey's paper.

26) H. Nishikawa and S Yamada, *Bull. Chem. Soc. Jpn.*, **37**, 8 (1964).

27) A. K. Gregson, R. L. Martin, and S. Mitra, *Chem. Phys. Lett.*, **5**, 310 (1970).

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

29) M. Green and P. A. Tasker, *Inorg. Chim. Acta*, **5**, 65 (1971).

30) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

31) S. C. Tang, S. Koch, G. N. Weinstein, R. W. Lane, and R. H. Holm, *Inorg. Chem.*, **12**, 2589 (1973).