# On the Absorption Spectra of Hexamminecobalt (III) and Related Complexes. II. Theoretical Study on Shifting and Splitting of the First and the Second Band Due to Substitution of Ligands*

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In a previous paper[1] we have attempted to interpret the first and the second absorption band of cobalt (III) complexes on the basis of the LCAO MO theory. The conclusion on the origin of these bands was similar to Kuroda and Ito's[2] obtained likewise from the LCAO MO treatment, and at the same time it was consistent with Tanabe and Sugano's[3] deduced from the crystal-field consideration.

In this paper we shall discuss the relation between the above-mentioned molecular-orbital approach and the crystal-field method, and then apply the two methods to the problem of splitting and shifting of the first and the second band.

## I. General Discussion on the Application of the LCAO MO and the Crystal-field Theory.

**Ia. Electronic Energy of a Complex of the MA$_6$-type.**—As was pointed out by Van Vleck[4], there are three methods of description of electronic states of metal complexes: (i) the method of electron pair bond, (ii) the molecular-orbital method, and (iii) the crystal-field method. The first is not suitable for description of excited states, and the latter two have been used by several authors to interpret spectra of transition-metal complexes[1-3,5-7]. In most cases the two ways of approach have led to similar conclusions, and have been considered by some authors as alternatives with a slight difference.

To the present author, however, they seem to be so distinctly different as to be regarded as mutually complementary. This will be made clear in the following consideration of the the two methods on the common theoretical basis, and then in their application to the interpretation of experimental data.

In general, energy of a polyatomic molecule (or ion) may approximately be written as

$$E=E^{cores}+\sum_i \varepsilon_i+\sum_{i<j} g_{ij}+CI \qquad (1)$$

where the first term on the right-hand side represents the energy concerning the atomic cores, the second the energy of the outer-shell electrons in the field of all the atomic cores, the third the interaction energy of these electrons, and $CI$ the energy of configuration interaction. (In this paper, "energy of an electron" or "energy of an orbital" will refer to $\varepsilon_i$ only, excluding $g_{ij}$.)

In applying Eq. (1) to the case of a complex of the type MA$_6$ (where M represents an ion or an atom of a transition metal of the first series, and A a ligand molecule or ion), we shall, to a first approximation, assume only the $3d$ electrons of the central metal ion to be

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[1] H. Yamatera, *J. Inst. Polytech. Osaka City Univ.*, **5**, Series C, 163 (1956).

[2] Y. Kuroda and K. Ito, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 545, 762, 766 (1955). K. Ito and Y. Kuroda, ibid. **76**, 943 (1955).

[3] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753, 766 (1954).

[4] J. H. Van Vleck, *J. Chem. Phys.*, **3**, 807 (1935).

[5] H. Hartmann and F. E. Ilse, *Z. physik. Chem.*, **197**, 239 (1951); *Z. Naturforsch.*, **6a**, 751 (1951). H. Hartmann and H. L. Schläfer, *Z. physik. Chem.*, **197**, 116 (1951); *Z. Naturforsch.*, **6a**, 754, 760 (1951); *Z. Angewandte Chem.*, **66**, 768 (1954). H. Hatmann, *Z. Naturforsch.*, **6a**, 781 (1951). H. L. Schläfer, *Z. physik. Chem. Neue Folge*, **3**, 222 (1955); **4**, 116 (1955); **6**, 201 (1956); **8**, 373 (1956); *Recueil trav. chim.*, **75**, 648 (1956). H. Hartmann and H.-H. Kruse, *Z. physik. Chem. Neue Folge*, **5**, 9 (1955).

[6] L. E. Orgel, *J. Chem. Soc.*, **1952**, 4756; *J. Chem. Phys.*, **23**, 1004, 1819, 1824 (1955). J. S. Griffith and L. E. Orgel, *J. Chem. Soc.*, **1956**, 4981.

[7] Chr. K. Jørgensen, *Acta Chem. Scand.*, **9**, 116, 405, 717, 1362 (1955). C. J. Ballhausen and Chr. K. Jørgensen, ibid., **9**, 397 (1955). F. Basolo, C. J. Ballhausen and J. Bjerrum, ibid., **9**, 810 (1955). C. J. Ballhausen, ibid., **9**, 821 (1955); and a number of related works made in Copenhagen.

the outer-shell electrons, and the others to be included in the atomic cores. This assumption should be valid for our purpose, since we shall deal with the electronic transitions, in which the latter electrons will not participate.

In the complex belonging to the point group $O_h$, the 3*d* orbitals are classified into two groups: $d_{z^2}$ and $d_{x^2-y^2}$ which belong to the irreducible representation $E_g$, and $d_{xy}$, $d_{yz}$ and $d_{zx}$ which belong to the irreducible representation $T_{2g}$. We shall discuss how the energies of these electrons in the complex are different from those in the isolated ion.

In the isolated ion the five 3*d* orbitals have a degenerate energy $\varepsilon^{\circ\circ}$, but in the complex these orbitals will have energies more or less effectively altered (and consequently the degeneracy partly removed) by electrostatic and antibonding (or bonding) effects of the ligands and may be written as

$$\varepsilon_i=\varepsilon^{\circ\circ}+U_i+\varepsilon_i'',$$

where $U_i$ represents the electrostatic energy of the electron in the field of the dipolar ligand molecules or the ligand ions and $\varepsilon_i''$ represents the increase in the orbital energy resulting from the antibonding interaction with ligand orbitals*. Whereas the crystal-field theory deals with the effect of the second term $U_i$ and usually neglects the third term $\varepsilon_i''$, the simple LCAO MO theory is primarily concerned with the third term. Such a situation will be shown in detail in the following paragraph, and schematically in Fig. 1.

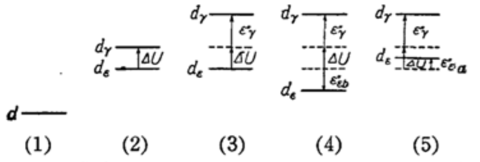

Fig. 1. Schematical representation of the energy difference between the $d_\gamma$ and $d_\varepsilon$ orbitals.

(1) No effect: for the isolated ion.

(2) $\Delta\varepsilon=\Delta U$
Electrostatic effect only.

(3) $\Delta\varepsilon=\Delta U+\varepsilon''_\gamma$
$\sigma$-antibonding effect besides electrostatic one: for the complex, in which $\pi$-interaction is negligible, e. g., $[Co(NH_3)_6]^{3+}$, if hyperconjugation is neglected.

(4) $\Delta\varepsilon=\Delta U+\varepsilon''_\gamma-\varepsilon''_{\varepsilon b}(\varepsilon''_{\varepsilon b}<0)$
$\sigma$-antibonding and $\pi$-bonding effects besides electrostatic one: for the complex, in which $\pi$ orbitals of the ligands are vacant, e. g., $[Co(CN)_6]^{3-}$, $[Co(NO_2)_6]^{3-}$.

(5) $\Delta\varepsilon=\Delta U+\varepsilon''_\gamma-\varepsilon''_{\varepsilon a}(\varepsilon''_{\varepsilon a}>0)$
$\sigma$- and $\pi$-antibonding effects besides electrostatic one: for the complex, in which $\pi$ orbitals of the ligands are occupied, e. g., $[Co(H_2O)_6]^{3+}$, $[CoF_6]^{3-}$.

**Ib. Energy Difference between Two Kinds of *d* Orbital.**—An approximate molecular orbital of the complex may be written as

$$d_i=\lambda_{iM}d_i^\circ+\lambda_{iL}\phi_i^\circ$$

where $d_i^\circ$ represents one of the atomic 3*d* orbitals of the metal ion, $\phi_i^\circ$ a group orbital* of the ligands belonging to the same representation as $d_i^\circ$, and $\lambda_{iM}$ as well as $\lambda_{iL}$ is the appropriate numerical factor. In the case of the regular-octahedral complex, donor atoms of the ligands have group $\sigma$ orbitals of $E_g$ symmetry (occupied by lone pair electrons); the molecular orbital $d_\gamma$ of this symmetry may be an antibonding orbital with $\lambda_{iL}$ of smaller absolute value than, and of opposite sign to $\lambda_{iM}$. On the other hand, the donor atoms can have no $\sigma$ but only $\pi$ orbitals of $T_{2g}$ symmetry, and hence the molecular orbital $d_\varepsilon$ of this symmetry is nearly nonbonding or slightly antibonding, except that it is bonding to some extent when the donor atoms have $\pi$ orbitals suitable for bonding with the metal.

The Hamiltonian operator for the system may be written as

$$\mathbf{H}=\mathbf{H}_{cores}^{cores}+\mathbf{H}_{electrons}^{cores}+\mathbf{V}^{electrons}$$

$$=\mathbf{H}_{cores}^{cores}+\sum_i \mathbf{H}_i^{cores}+\sum_{i<j}\mathbf{V}_{ij}$$

where the first term represents the kinetic and potential energies of the atomic cores, the second the kintic energy of the outer-shell electrons and their potential energy in the field of the cores, and the third the potential energy arising from interactions of the outer-shell electrons. Each term of this expression corresponds to each (except the last) of Eq. (1). Now, $\mathbf{H}_i^{cores}$ may approximately be written as

$$\mathbf{H}_i^{cores}=\mathbf{H}_i^{\mathrm{M}}+\mathbf{U}_i$$

where $\mathbf{H}_i^{\mathrm{M}}$ corresponds to the energy of the electron in the field of the central metal core and $\mathbf{U}_i$ to the potential energy of the electron in the field of the ligands. Then the energy of the $d_i$ orbital may be written as

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* According to the present approximation, $U_i$ corresponds to the first order perturbation energy and $\varepsilon''_i$ to the second order, but not necessarily less important, one.

* See, e. g., foot note on p. 100.

$$\left.\begin{aligned}\varepsilon_i &= \int d_i^\circ \mathbf{H}_i^{\mathrm{M}} d_i^\circ dv + \int d_i^\circ \mathbf{U}_i d_i^\circ dv \\ &\quad + \frac{\{H(d_i^\circ,\phi_i^\circ) - S(d_i^\circ,\phi_i^\circ)\varepsilon(d_i^\circ)\}^2}{\varepsilon(d_i^\circ) - \varepsilon(\phi_i^\circ)} + \cdots \\ &= \varepsilon^{\circ\circ} + U_i + \varepsilon_i'' + \cdots\cdots \end{aligned}\right\} \quad (2)$$

where $\varepsilon(d_i^\circ) = \int d_i^\circ \mathbf{H}_i^{cores} d_i^\circ dv$, $\varepsilon(\phi_i^\circ) = \int \phi_i^\circ \mathbf{H}_i^{cores} \phi_i^\circ dv$, $H(d_i^\circ, \phi_i^\circ) = \int d_i^\circ \mathbf{H}_i^{cores} \phi_i^\circ dv$ and $S(d_i^\circ, \phi_i^\circ) = \int d_i^\circ \phi_i^\circ dv$. The energy $\varepsilon_\gamma$ of the antibonding $d_\gamma$ orbital may be given by this expression, if we replace the subscript $i$ with $\gamma$. In the case the $d_\varepsilon$ orbital with only a slight $\pi$-interaction, the third term may be neglected.

The third term of Eq. (1), i.e., the interaction energy of the outer-shell electrons, may be evaluated in terms of Slater-Condon parameters, if the deformation of the orbitals is neglected.

It is empirically known that, if we replace some of the ammonia molecules of hexamminecobalt (III) ion with other ligands, the absorption maxima of the first and the second band will shift considerably, but the separation between the two maxima will undergo only a slight change (Kuroya's formula[8]: $\nu_2 = \nu_1 + 25$, where $\nu_1$ and $\nu_2$ represent the frequencies at the absorption maxima in $10^{13}$ sec.$^{-1}$). This allows us to make the following approximation in reference to Eqs. (4b) and (4c) below, which show that the upper levels related to the two absorption bands have the same $\sum_i \varepsilon_i$ value. Thus we assume that the third and the fourth term of Eq. (1) are nearly constant* for corresponding electronic states of the complexes, irrespective of the kinds of the ligand attached to the metal. Upon this approximation, we have only to estimate the change in the second term of Eq. (1), in order to account for splitting and shifting of the absorption bands caused by replacement of some of the ligands. Before we proceed to this problem, we shall correlate the energy difference between the two kinds of $d$ orbital in hexamminecobalt (III) ion $[\mathrm{Co(NH_3)_6}]^{3+}$, $\Delta\varepsilon (= \varepsilon_\gamma - \varepsilon_\varepsilon)$**, with the observed wavenumbers of the absorption maxima of the complex.

**Ic. Correlation between $\Delta\varepsilon$ and the Absorption Wavenumbers.**—In the case of the hexamminecobalt(III) ion, the first and the second adsorption band should correspond to the forbidden electronic transitions from the ground state $^1A_{1g}$ to the excited states $^1T_{1g}$ and $^1T_{2g}$, respectively[1-3,6]. The electron configurations of these states and of the state $^5T_{2g}$ (the ground state of a paramagnetic cobalt(III) complex) are:

$$(d_{xy})^2(d_{yz})^2(d_{zx})^2, \qquad {}^1A_{1g}, \qquad (3a)$$

$$\left.\begin{aligned}&(d_{xy})\ (d_{yz})^2(d_{zx})^2(d_{x^2-y^2})\\&(d_{xy})^2(d_{yz})\ (d_{zx})^2(d_{y^2-z^2})\\&(d_{xy})^2(d_{yz})^2(d_{zx})\ (d_{z^2-x^2})\end{aligned}\right\}\ {}^1T_{1g}, \qquad (3b)$$

$$\left.\begin{aligned}&(d_{xy})\ (d_{yz})^2(d_{zx})^2(d_{z^2})\\&(d_{xy})^2(d_{yz})\ (d_{zx})^2(d_{x^2})\\&(d_{xy})^2(d_{yz})^2(d_{zx})\ (d_{y^2})\end{aligned}\right\}\ {}^1T_{2g}, \qquad (3c)$$

$$(d_{xy})^2(d_{yz})(d_{zx})(d_{z^2})(d_{x^2-y^2}), \text{ etc., } {}^5T_{2g}. \qquad (3d)$$

According to Eq. (1), the energies of these states may be written as:

$$E(^1A_{1g}) = E^{cores} + 6\varepsilon_\varepsilon + 15F_0 - 30F_2 - 60F_4 - (CI)_1 \qquad (4a)$$

$$E(^1T_{1g}) = E^{cores} + 5\varepsilon_\varepsilon + \varepsilon_\gamma + 15F_0 - 30F_2 - 95F_4 - (CI)_2 \qquad (4b)$$

$$E(^1T_{2g}) = E^{cores} + 5\varepsilon_\varepsilon + \varepsilon_\gamma + 15F_0 - 14F_2 - 175F_4 - (CI)_3 \qquad (4c)$$

$$E(^5T_{2g}) = E^{cores} + 4\varepsilon_\varepsilon + 2\varepsilon_\gamma + 15F_0 - 35F_2 - 315F_4 \qquad (4d)$$

where $F_0$, $F_2$ and $F_4$ are the Slater-Condon parameters and $(CI)_1$, $(CI)_2$ and $(CI)_3$ represent the stabilization energies arising from configuration interactions.

Then the energy difference, $\Delta\varepsilon$, may be obtained from the observed wavenumbers of the absorption bands, provided that the values of Slater-Condon parameters and the configuration-interaction terms are estimated.

The values of Slater-Condon parameters have been presented by Orgel[9] and also can easily be calculated from the values of Racah's parameters given by Tanabe and Sugano[3]. The Orgel's values and those obtained according to Tanabe and Sugano differ only slightly from each other, and we shall use the former, 1800 cm$^{-1}$ for $F_2$ and 150 cm$^{-1}$ for $F_4$. The values of $(CI)_1$, $(CI)_2$ and $(CI)_3$ were estimated to be about 3500 cm$^{-1}$, 1500 cm$^{-1}$ and 6000 cm$^{-1}$, respectively. The values of $\Delta\varepsilon$ was thus found to be 24300 cm$^{-1}$ or 20450 cm$^{-1}$ corresponding to the observed absorption maximum of the first band at 21050 cm$^{-1}$ or of the

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[8] H. Kuroya, *J. Inst. Polytech. Osaka City Univ.*, 1, Series C, 29 (1950).

* If deformation of the orbitals is slight (or similar, even if not slight, among the complexes), the energy arising from interactions of electrons may approximately be constant. If the electrostatic or the bonding (or antibonding) effect is strong enough, the configuration interaction may be negligible.

** The term $\Delta\varepsilon$ is numerically equivalent to 10 Dq in the crystal-field theory.

[9] The third paper of ref. (6).

second band at 29500 cm$^{-1}$, respectively. Agreement between the two values is not satisfactory. Further difficulty may arise, if we place a limit on the value of $\Delta\varepsilon$ required to produce a diamagnetic complex by equating $E(^1A_{1g})$ to $E(^5T_{2g})$. The critical value thus obtained is about 21900 cm$^{-1}$, which cannot be consistent with the lower value of $\Delta\varepsilon$ shown above. Moreover, in the case of hexaquocobalt (III) ion $[Co(H_2O)_6]^{3+}$ even the higher of the estimated $\Delta\varepsilon$ values (about 19600 cm$^{-1}$) cannot exceed the critical value.

These inconsistencies might be partly due to some errors in the estimation of configuration-interaction energies, but they seem to have more probably resulted from that the orbitals of the metal in the complex were assumed to be the same as those in the isolated ion. As a trial, we have made an estimation of $\Delta\varepsilon$ for hexamminecobalt (III) ion $[Co(NH_3)_6]^{3+}$ and its limit for diamagnetic cobalt (III) complexes using smaller values of $F_2$, $F_4$, $(CI)_1$, $(CI)_2$ and $(CI)_3$. By the use of their values 20% reduced, we have obtained 23650 cm$^{-1}$ or 22340 cm$^{-1}$ as the $\Delta\varepsilon$ value for this complex and 17500 cm$^{-1}$ as its limit. Such a decrease in the values of the parameters seems probable, since the amount of positive charge on the cobalt in a complex should be considerably less than three. In addition, this limit of $\Delta\varepsilon$ will disclose why many cobalt complexes, even those such as trifluorotriamminecobalt (III) $[Co(NH_3)_3F_3]$, are diamagnetic and hexafluorocobalt (III) ion $[CoF_6]^{3-}$ is paramagnetic, since, from the spectral data10) of *trans*-difluorotetramminecobalt (III) ion $[Co(NH_3)_4F_2]^+$, the $\Delta\varepsilon$ value may be smaller by 8000–9000 cm$^{-1}$ in hexafluorocobalt (III) ion $[CoF_6]^{3-}$ than in hexamminecobalt (III) ion $[Co(NH_3)_6]^{3+}$. So we tentatively suggest the following values: $\Delta\varepsilon = 23500$ cm$^{-1}$ for hexammine cobalt (III) ion $[Co(NH_3)_6]^{3+}$, and $\Delta\varepsilon > 17500$ cm$^{-1}$ for diamagnetic cobalt complexes[*].

## II. Molecular-orbital Prediction of Shifiting and Splitting of the Bands

In the preceding chapter we have discussed the problem of applying the crystal-field and the LCAO MO method to the metal complexes, and correlated the absorption spectra of cobalt(III) complexes with the energy difference between the orbitals $d_\gamma$ and $d_\varepsilon$.

In this and the following chapters, we shall discuss the interrelation of the absorption spectra of the six types of complex, $CoA_6$, $CoA_5B$, *cis*- and *trans*-$CoA_4B_2$, *cis*- and *trans*-$CoA_3B_3$ (the sign of the charge is omitted), where the B ligand occupies the positions indicated in Table II below. As was mentioned above, each of the excited states of $CoA_6$ related to the first and the second band is triply degenerate. By replacement of some of the ligands the degeneracy may be partly or completely removed, and splitting of the bands will occur. The result of the qualitative consideration on the basis of the group theory is included in Table II below.

**IIa. CoA$_6$-like Description of the Complex of the Lower Symmetry.**—We shall first consider the $CoA_5B$-type of complex, which has the symmetry $C_{4v}$. In this symmetry, the orbitals[*] $d_{z^2}$, $d_{x^2-y^2}$ and $d_{xy}$ belong to the representations $A_1$, $B_1$ and $B_2$, respectively, and both $d_{yz}$ and $d_{zx}$ belong to $E$. Then the ground state of this complex is $(d_{xy})^2(d_{yz})^2(d_{zx})^2$, $^1A_1$, and the excited states might be written as follows:

$$\begin{array}{ll}
(d_{xy})\,(d_{yz})^2(d_{zx})^2(d_{x^2-y^2}), & {}^1A_2, \\
\left.\begin{array}{l}(d_{xy})^2(d_{yz})\,(d_{zx})^2(d_{x^2-y^2}) \\ (d_{xy})^2(d_{yz})^2(d_{zx})\,(d_{x^2-y^2})\end{array}\right\} & {}^1E, \\
(d_{xy})\,(d_{yz})^2(d_{zx})^2(d_{z^2}), & {}^1B_2, \\
\left.\begin{array}{l}(d_{xy})^2(d_{yz})\,(d_{zx})^2(d_{z^2}) \\ (d_{xy})^2(d_{yz})^2(d_{zx})\,(d_{z^2})\end{array}\right\} & {}^1E.
\end{array}$$

However, we must take into account the configuration interaction which may mix the two states of the same $E$ symmetry. In doing this we note the fact that the geometrical structure and the spectrum of $CoA_5B$ are only slightly different from those of $CoA_6$. This fact allows us to make a reasonable assumption that as a result of configuration interaction we should have each state of $CoA_5B$ corresponding to each of $CoA_6$. The two pairs of $E$ states thus obtained are:

$$\left.\begin{array}{l}(d_{xy})^2(d_{yz})\,(d_{zx})^2\left(-\frac{1}{2}d_{x^2-y^2}-\frac{1}{2}\sqrt{3}\,d_{z^2}\right) \\ (d_{xy})^2(d_{yz})^2(d_{zx})\left(-\frac{1}{2}d_{x^2-y^2}+\frac{1}{2}\sqrt{3}\,d_{z^2}\right)\end{array}\right\}{}^1E,$$

$$\left.\begin{array}{l}(d_{xy})^2(d_{yz})\,(d_{zx})^2\left(\frac{1}{2}\sqrt{3}\,d_{x^2-y^2}-\frac{1}{2}d_{z^2}\right) \\ (d_{xy})^2(d_{yz})^2(d_{zx})\left(-\frac{1}{2}\sqrt{3}\,d_{x^2-y^2}-\frac{1}{2}d_{z^2}\right)\end{array}\right\}{}^1E,$$

where the four orbitals described in linear combinations of $d_{x^2-y^2}$ and $d_{z^2}$ correspond to $d_{y^2-z^2}$, $d_{z^2-x^2}$, $d_{x^2}$ and $d_{y^2}$ of $CoA_6$, respectively. Therefore, in spite of the fact that $CoA_5B$ have none of the orbitals,

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10) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **101**, 271 (1952).

[*] These values are slightly different from those given by Tanabe and Sugano (ref. 3) and by Orgel (the third paper of ref. 6).

[*] In this paper, $d_{z^2}$, $d_{x^2-y^2}$, etc. represent the molecular orbitals of the complex, i.e., the deformed atomic $d$ orbitals.

$d_{y^2-z^2}$, $d_{z^2-x^2}$, $d_{x^2}$ and $d_{y^2}$, we shall use these notations in the sense given here.

The situation is similar in the cases of *trans*-$\mathrm{CoA_4B_2}$ and *trans*-$\mathrm{CoA_3B_3}$, where we can use the same approximate notations as above. On the other hand, the situation is different in the cases of *cis*-$\mathrm{CoA_4B_2}$ and *cis*-$\mathrm{CoA_3B_3}$, where these approximations cannot be justified. However, it will be shown in the following paragraph that consideration on these (suppositional) orbitals is still of great convenience for the disussion of the electronic transitions corresponding to the absorption bands.

In *cis*-$\mathrm{CoA_4B_2}$, the electron configuration of the ground state may be written as:

$$(d_{xy})^2(d_{yz+zx})^2(d_{yz-zx})^2,\ {}^1A_1,$$

where $d_{yz+zx}=(1/\sqrt{2})(d_{yz}+d_{zx})$ and $d_{yz-zx}=(1/\sqrt{2})(d_{yz}-d_{zx})$. In this case, instead of $d_{yz}$ and $d_{zx}$ themselves, their linear combinations should be the molecular orbitals of the complex, since the $z'$- and the $x'$-axis required by the symmetry of the complex should bisect respectively the $\pm x$- and the $y$-axis, and $y'$-axis should fall on the $z$-axis (as is shown in Fig. 2)*. The electron configuration of the excited states in a simple molecular-orbital method may be written as follows:

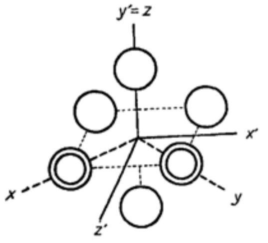

Fig. 2. Axes of *cis*-$\mathrm{CoA_4B_2}$.

$$\begin{array}{ll}
(d_{xy})\ (d_{yz+zx})^2(d_{yz-zx})^2(d_{x^2-y^2}), & {}^1B_1,\\
(d_{xy})^2(d_{yz+zx})\ (d_{yz-zx})^2(d_{x^2-y^2}), & a^1A_2,\\
(d_{xy})^2(d_{yz+zx})^2(d_{yz-zx})\ (d_{x^2-y^2}), & a^1B_2,\\
(d_{xy})\ (d_{yz+zx})^2(d_{yz-zx})^2(d_{z^2}), & {}^1A_1,\\
(d_{xy})^2(d_{yz+zx})\ (d_{yz-zx})^2(d_{z^2}), & b^1B_2,\\
(d_{xy})^2(d_{yz+zx})^2(d_{yz-zx})\ (d_{z^2}), & b^1A_2,
\end{array}$$

where $a$ and $b$ are used to distinguish the two states belonging to the same representation. As a result of configuration interaction, we shall take the following linear combinations instead of the simple $a^1A_2$, $a^1B_2$, $b^1B_2$ and $b^1A_2$.

$$\begin{aligned}
(a'^1A_2)&=\frac{1}{2}(a^1A_2)+\frac{1}{2}\sqrt{3}(b^1A_2),\\
(a'^1B_2)&=\frac{1}{2}(a^1B_2)+\frac{1}{2}\sqrt{3}(b^1B_2),\\
(b'^1B_2)&=-\frac{1}{2}\sqrt{3}(a^1B_2)+\frac{1}{2}(b^1B_2),\\
(b'^1A_2)&=-\frac{1}{2}\sqrt{3}(a^1A_2)+\frac{1}{2}(b^1A_2).
\end{aligned}$$

These states of *cis*-$\mathrm{CoA_4B_2}$ correlate with each electron configuration of the excited states of $\mathrm{CoA_6}$ (the expressions (3b) and (3c) in the preceding chapter) as follows:

$$\begin{aligned}
{}^1T_{1g}:\ &{}^1B_1,\ (1/\sqrt{2})\{(a'^1A_2)+(a'^1B_2)\},\\
&(1/\sqrt{2})\{-(a'^1A_2)+(a'^1B_2)\},\\
{}^1T_{2g}:\ &{}^1A_1,\ (1/\sqrt{2})\{(b'^1A_2)+(b'^1B_2)\},\\
&(1/\sqrt{2})\{b'^1A_2)-(b'^1B_2)\}.
\end{aligned}$$

To the approximation we are adopting, the pair of states $(a'^1A_2)$ and $(a'^1B_2)$ will have the same energy, and accordingly their linear combination will also have the same energy as the component states. This is also the case with the other pair. For this reason, an approximation, with which *cis*-$\mathrm{CoA_4B_2}$ is assumed to have the same types of orbital as $\mathrm{CoA_6}$, will be applied in the following paragraphs.

A similar discussion should also be relevant to *cis*-$\mathrm{CoA_3B_3}$; its details, however, are too complicated to be mentioned here.

**IIb. Effect of Replacement of Ligands on the Antibonding Interaction Energy of *d* Orbitals.**—Now we shall discuss how the replacement of ligands changes the antibonding (or bonding) interaction energy of the $d$ orbital ($\varepsilon''_i$ in Eq. (2)); the change in the electrostatic energy ($U_i$ in the equation) will be discussed in the following chapter. As was already shown in Eq. (2), the antibonding (or bonding) interaction energy may be written as follows:

$$\varepsilon''_i=\frac{\{H(d^\circ_i,\phi^\circ_i)-S(d^\circ_i,\phi^\circ_i)\varepsilon(d^\circ_i)\}^2}{\varepsilon(d^\circ_i)-\varepsilon(\phi^\circ_i)} \tag{5}$$

With the usual approximation that $H(d^\circ_i,\phi^\circ_i)$ is proportional to the overlap integral $S(d^\circ_i,\phi^\circ_i)$, $\varepsilon''_i$ will be proportional to the square of the overlap integral.

We shall, for the present, assume that the orbitals $d_{xy}$, $d_{yz}$ and $d_{zx}$ are nonbonding, and discuss only the change in $S(d^\circ_{x^2-y^2},\phi^\circ_{x^2-y^2})$ and $S(d^\circ_{z^2},\phi^\circ_{z^2})$ due to the replacement of ligands. From the explicit representation of the group $\phi^\circ_i$ orbitals*, the following relations can easily be seen:

---

* It is also possible to take the new axes in an alternative manner; the $x'$- and the $y'$-axis may be interchanged.

$$\left.\begin{aligned}
S(d^{\circ}_{x^2-y^2},\phi^{\circ}_{x^2-y^2}) &= (1/\sqrt{4})\{S(d^{\circ}_{x^2-y^2},\sigma^{\circ}_{+x}) \\
&\quad +S(d^{\circ}_{x^2-y^2},\sigma^{\circ}_{-x})-S(d^{\circ}_{x^2-y^2},\sigma^{\circ}_{+y}) \\
&\quad -S(d^{\circ}_{x^2-y^2},\sigma^{\circ}_{-y})\}, \\
S(d^{\circ}_{z^2},\phi^{\circ}_{z^2}) &= (1/\sqrt{12})\{2S(d^{\circ}_{z^2},\sigma^{\circ}_{+z}) \\
&\quad +2S(d^{\circ}_{z^2},\sigma^{\circ}_{-z})-S(d^{\circ}_{z^2},\sigma^{\circ}_{+x}) \\
&\quad -S(d^{\circ}_{z^2},\sigma^{\circ}_{-x})-S(d^{\circ}_{z^2},\sigma^{\circ}_{+y}) \\
&\quad -S(d^{\circ}_{z^2},\sigma^{\circ}_{-y})\}.
\end{aligned}\right\} \quad (6)$$

where $S(d^{\circ}_{x^2-y^2},\sigma^{\circ}_{+x})$, for example, represents the overlap integral of $d^{\circ}_{x^2-y^2}$ and $\sigma^{\circ}_{+x}$ (the $\sigma$ orbital of the ligand on the $+x$ axis). From the angular dependence of the *d* functions, the following relations will easily be obtained for the $CoA_6$-type of complex.

$$\left.\begin{aligned}
&S_A(d^{\circ}_{x^2-y^2},\phi^{\circ}_{x^2-y^2}) = S_A(d^{\circ}_{z^2},\phi^{\circ}_{z^2}) = S_A, \\
&S_A(d^{\circ}_{x^2-y^2},\sigma^{\circ}_{+}) = S_A(d^{\circ}_{x^2-y^2},\sigma^{\circ}_{-x}) \\
&\qquad = -S_A(d^{\circ}_{x^2-y^2},\sigma^{\circ}_{+y}) \\
&\qquad = -S_A(d^{\circ}_{x^2-y^2},\sigma^{\circ}_{-y}) = (1/2)S_A, \\
&S_A(d^{\circ}_{z^2},\sigma^{\circ}_{+z}) = S_A(d^{\circ}_{z^2},\sigma^{\circ}_{-z}) = (1/\sqrt{3})S_A, \\
&S_A(d^{\circ}_{z^2},\sigma^{\circ}_{+x}) = S_A(d^{\circ}_{z^2},\sigma^{\circ}_{-x}) \\
&\qquad S_A(d^{\circ}_{z^2},\sigma^{\circ}_{+y}) = S_A(d^{\circ}_{z^2},\sigma^{\circ}_{-y}) \\
&\qquad = -(1/\sqrt{12})S_A,
\end{aligned}\right\} \quad (7)$$

where the subscript A refers to $CoA_6$. When one of the ligands A was replaced by another ligand B, the change in $S(d^{\circ}_{x^2-y^2},\phi^{\circ}_{x^2-y^2})$ and $S(d^{\circ}_{z^2},\phi^{\circ}_{z^2})$ will depend on the position of the replacement as well as on the nature of the ligands A and B. In order to separate these two factors, we shall use a notation $S_r$ of the following definition:

$S_r=S_A$ or $S_B$, according to whether the *r* position is occupied by A or B, (8)

where *r* stands for $+x$, $-x$, $+y$, $-y$, $+z$ or $-z$. Then, making use of the relations (7) and (8) in Eq. (6), we can obtain the following expressions for any complex of the $CoA_{6-n}B_n$-type:

$$\left.\begin{aligned}
S(d^{\circ}_{x^2-y^2},\phi^{\circ}_{x^2-y^2}) &= (1/4)(S_{+x}+S_{-x} \\
&\quad +S_{+y}+S_{-y}), \\
S(d^{\circ}_{z^2},\phi^{\circ}_{z^2}) &= (1/12)(4S_{+z}+4S_{-z} \\
&\quad +S_{+x}+S_{-x}+S_{+y}+S_{-x}).
\end{aligned}\right\} \quad (9)$$

Thus we can expect that a replacement in the $\pm z$ position will have no effect on $S(d^{\circ}_{x^2-y^2},\phi^{\circ}_{x^2-y^2})$, whereas on $S(d^{\circ}_{z^2},\phi^{\circ}_{z^2})$ it will have four times as large an effect as that in the $\pm x$ or $\pm y$ position.

If the change in *S*, $\varDelta S$, is small, the change in $S^2$ may be nearly equal to $2S\varDelta S$. The numerator of Eq. (5) is thus expected to change in proportion to $\varDelta S$.

The value of $\varepsilon''_i$ will also depend on $\varepsilon(d^{\circ}_i)$ and $\varepsilon(\phi^{\circ}_i)$, which appear in the denominator of Eq. (5). The change in $\varepsilon(d^{\circ}_i)$ due to the replacement is likely to be much smaller than that in $\varepsilon(\phi^{\circ}_i)$. Therefore we shall consider the latter only. The explicit forms of the $\phi^{\circ}_{x^2-y^2}$ and $\phi^{\circ}_{z^2}$ orbitals* will lead to the following expressions for any octahedral complex of the $CoA_{6-n}B_n$-type:

$$\begin{aligned}
\varepsilon(\phi^{\circ}_{x^2-y^2}) &= (1/4)\{\varepsilon(\sigma^{\circ}_{+x})+\varepsilon(\sigma^{\circ}_{-x}) \\
&\qquad +\varepsilon(\sigma^{\circ}_{+y})+\varepsilon(\sigma^{\circ}_{-y})\}, \\
\varepsilon(\phi^{\circ}_{z^2}) &= (1/12)\{4\varepsilon(\sigma^{\circ}_{+z})+4\varepsilon(\sigma^{\circ}_{-z})+\varepsilon(\sigma^{\circ}_{+x}) \\
&\qquad +\varepsilon(\sigma^{\circ}_{-x})+\varepsilon(\sigma^{\circ}_{+y})+\varepsilon(\sigma^{\circ}_{-y})\},
\end{aligned}$$

where $\varepsilon(\sigma^{\circ}_{+x})$, for example, represents the energy of the $\sigma$ orbital of the ligand on the $+x$ axis. These expressions have quite similar forms to the expressions (9), and accordingly we can expect that the different ways of replacement of the ligands will have relative effects on $\varepsilon(\phi^{\circ}_{x^2-y^2})$ and $\varepsilon(\phi^{\circ}_{z^2})$ similar to those on $S(d^{\circ}_{x^2-y^2},\phi^{\circ}_{x^2-y^2})$ and $S(d^{\circ}_{z^2},\phi^{\circ}_{z^2})$.

A combination of the results obtained above will lead to the conclusion shown in Table I. The same conclusion may also be obtained with the rough approximation that the relative effect of the replacement is proportional to the electron density of the *d* orbital in the direction concerned.

TABLE I

CHANGE IN $\varepsilon''_{x^2-y^2}$ AND $\varepsilon''_{z^2}$ DUE TO THE REPLACEMENT OF THE LIGAND A WITH B IN EACH POSITION OF THE COMPLEX

| Position of replacement | $\pm z$ | $\pm x$ | $\pm y$ |
|---|---|---|---|
| Change in $\varepsilon''_{x^2-y^2}$ | 0 | $\frac{1}{4}\delta_\sigma$ | $\frac{1}{4}\delta_\sigma$ |
| Change in $\varepsilon''_{z^2}$ | $\frac{1}{3}\delta_\sigma$ | $\frac{1}{12}\delta_\sigma$ | $\frac{1}{12}\delta_\sigma$ |

The parameter $\delta_\sigma$ denotes the difference between $CoA_6$ and $CoB_6$ in $\varepsilon''_\gamma$.

### IIc. Prediction of the Shifts of the First and the Second Band Due to the Replacement of the Ligands.

— The prediction is made in Table II. As regards the effect of the change in $\sigma$-interaction, represented in terms of $\delta_\sigma$, consideration has been made above, and the result shown in Table I was utilized for the preparation of Table II. The effect of the change in

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* $\phi^{\circ}_{x^2-y^2}=(1/\sqrt{4})(\sigma^{\circ}_{+x}+\sigma^{\circ}_{-x}-\sigma^{\circ}_{+y}-\sigma^{\circ}_{-y})$,
$\phi^{\circ}_{z^2}=(1/\sqrt{12})(2\sigma^{\circ}_{+z}+2\sigma^{\circ}_{-z}$
$-\sigma^{\circ}_{+x}-\sigma^{\circ}_{-x}-\sigma^{\circ}_{+y}-\sigma^{\circ}_{-y})$,
where the overlap of $\sigma^{\circ}$ orbitals was neglected.

TABLE II

PREDICTED SHIFTS OF THE FIRST AND THE SECOND BAND DUE TO THE REPLACEMENT OF THE LIGANDS (RESULTS OF THE MOLECULAR-ORBITAL TREATMENT)

| | Electronic transition | $CoA_5B$ $(+z)$ | *trans*-$CoA_4B_2$ $(+z, -z)$ | *cis*-$CoA_4B_2$ $(+x, +y)$ | *trans*-$CoA_3B_3$ $(+x, -x, +z)$ | *cis*-$CoA_3B_3$ $(+x, +y, +z)$ |
|---|---|---|---|---|---|---|
| The first band | $d_{xy}\to d_{x^2-y^2}$ | $0$ $(A_2)$ | $0$ $(A_{2g})$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi$ $(B_1)$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi(A_2)$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi$ |
| | $d_{yz}\to d_{y^2-z^2}$ | $\frac{1}{4}\delta_\sigma+\frac{1}{4}\delta_\pi$ $(E)$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi$ $(E_g)$ | $\frac{1}{4}\delta_\sigma+\frac{1}{4}\delta_\pi$ $(A_2, B_2)$ | $\frac{1}{4}\delta_\sigma+\frac{1}{4}\delta_\pi(B_2)$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi(A_2, E)$ |
| | $d_{zx}\to d_{z^2-x^2}$ | $\frac{1}{4}\delta_\sigma+\frac{1}{4}\delta_\pi$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi$ | $\frac{1}{4}\delta_\sigma+\frac{1}{4}\delta_\pi$ | $\frac{3}{4}\delta_\sigma+\frac{3}{4}\delta_\pi(B_1)$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi$ |
| The second band | $d_{xy}\to d_{z^2}$ | $\frac{1}{3}\delta_\sigma$ $(B_2)$ | $\frac{2}{3}\delta_\sigma$ $(B_{2g})$ | $\frac{1}{6}\delta_\sigma+\frac{1}{2}\delta_\pi$ $(A_1)$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi(A_2)$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi$ |
| | $d_{yz}\to d_{x^2}$ | $\frac{1}{12}\delta_\sigma+\frac{1}{4}\delta_\pi$ $(E)$ | $\frac{1}{6}\delta_\sigma+\frac{1}{2}\delta_\pi$ $(E_g)$ | $\frac{5}{12}\delta_\sigma+\frac{1}{4}\delta_\pi$ $(A_2, B_2)$ | $\frac{3}{4}\delta_\sigma+\frac{1}{4}\delta_\pi(B_2)$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi(A_1, E)$ |
| | $d_{zx}\to d_{y^2}$ | $\frac{1}{12}\delta_\sigma+\frac{1}{4}\delta_\pi$ | $\frac{1}{6}\delta_\sigma+\frac{1}{2}\delta_\pi$ | $\frac{5}{12}\delta_\sigma+\frac{1}{4}\delta_\pi$ | $\frac{1}{4}\delta_\sigma+\frac{3}{4}\delta_\pi(B_1)$ | $\frac{1}{2}\delta_\sigma+\frac{1}{2}\delta_\pi$ |

$(+z)$, $(+z, -z)$, etc. show the position of the replacement, and $(A_2)$, $(E)$, etc. are the symmetries of the excited states.

$\pi$-interaction, represented in terms of $\delta_\pi$, was easily estimated on the assumption that the $\pi$-interaction is a small perturbation.

## III. Crystal-field Prediction of Shifting and Splitting of the Bands

In the preceding chapter we have considered the problem of shifting and splitting of the first and the second band on the basis of the molecular-orbital theory. In this chapter we shall treat of the same problem on the basis of the crystal-field theory.

**IIIa. Energy of Electrostatic Interaction of the Orbital Electron with a Point Charge or Dipole.**—The applied method of calculation is very similar to that given by Ilse and Hartmann[11], although a slight refinement has been made. Electrostatic interaction between an orbital electron and a point charge $(-Z)$ may be written as follows:

$$u^e(n,l,m)=Z\int|\psi_{n,l,m}|^2\frac{1}{r_>}\sum_k\left(\frac{r_<}{r_>}\right)^k \times\mathbf{P}_k(\cos\theta)r^2\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$
$$=Z\sum_k I_k(n,l)J_k(l,m),$$

where $\psi_{n,l,m}$ is the wave function of the electron with quantum numbers $n$, $l$ and $m$, $r_>=R$ and $r_<=r$ if $R>r$, $r_>=r$ and $r_<=R$ if $r>R$, $\mathbf{P}_k(\cos\theta)$ is Legendre function of the $k$th order, $r, \theta, \phi$ are the coordinates of the electron, and $R$ is the coordinate of the point charge on the coordinate axis. The radial part of the integral (including the normalization factor of that part) is represented by $I_k(n,l)$ and the angular part by $J_k(l,m)$.

For a point dipole with a dipole moment $\mu$, the electrostatic interaction energy will be

$$u^\mu(n,l,m)=\sum_k I_k{}^\mu(n,l)J_k(l,m),$$

where $I_k{}^\mu=-(dI_k/dR)$.

When a ligand has a charge as well as a dipole moment, the total energy of electrostatic interaction between the ligand and an orbital electron will be

$$u=u^e+u^\mu.$$

As for the $3d$ electrons, $I_kJ_k$ and $I_k{}^\mu J_k$ are different from zero, only when $k=0$, 2 and 4. The results of calculation are as follows:

$$\begin{aligned}I_0(3d)&=R^{-1}-R^{-1}e^{-2\rho}\{(2/45)\rho^5+(2/9)\rho^4\\&\quad+(2/3)\rho^3+(4/3)\rho^2+(5/3)\rho+1\}\\&\approx R^{-1},\\I_2(3d)&=14R^{-1}\rho^{-2}-R^{-1}e^{-2\rho}\{(2/9)\rho^5\\&\quad+(10/9)\rho^4+(11/3)\rho^3+(28/3)\rho^2\\&\quad+(56/3)\rho+28+28\rho^{-1}+14\rho^{-2}\}\\&\approx 14R^{-1}\rho^{-2},\\I_4(3d)&=315R^{-1}\rho^{-4}-R^{-1}e^{-2\rho}\{(2/5)\rho^5+2\rho^4\\&\quad+8\rho^3+28\rho^2+84\rho+210+420\rho^{-1}\\&\quad+630\rho^{-2}+630\rho^{-3}+315\rho^{-4}\}\\&\approx 315R^{-1}\rho^{-4},\end{aligned}$$

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[11] F. E. Ilse and H. Hartmann, *Z. physik. Chem.*, **197**, 239 (1951).

$$I_0^{\mu}(3d) \approx R^{-2}, \quad I_2^{\mu}(3d) \approx 42R^{-2}\rho^{-2}, \quad I_4^{\mu}(3d) \approx 1575R^{-2}\rho^{-4},$$

$$J_0(l,m)=1 \text{ (for every value of } l \text{ and } m),$$

$$J_2(d,0)=2/7, \quad J_2(d,\pm1)=1/7, \quad J_2(d,\pm2)=-(2/7),$$

$$J_4(d,0)=6/21, \quad J_4(d,\pm1)=-(4/21), \quad J_4(d,\pm2)=1/21,$$

where the Slater atomic orbital was used in the calculation of $I_k(3d)$ ($\rho=\zeta R$, $\zeta=Z_{eff}/n_{eff}$).

Thus we obtain:

$$\left.\begin{aligned} u(3d,0) &\approx R^{-1}(1+4\rho^{-2}+90\rho^{-4}) \\ u(3d,\pm1) &\approx R^{-1}(1+2\rho^{-2}-60\rho^{-4}) \\ u(3d,\pm2) &\approx R^{-1}(1-4\rho^{-2}+15\rho^{-4}) \end{aligned}\right\} \quad (10a)$$

$$\left.\begin{aligned} u^{\mu}(3d,0) &\approx \mu R^{-2}(1+12\rho^{-2}+450\rho^{-4}) \\ u^{\mu}(3d,\pm1) &\approx \mu R^{-2}(1+6\rho^{-2}-300\rho^{-4}) \\ u^{\mu}(3d,\pm2) &\approx \mu R^{-2}(1-12\rho^{-2}+75\rho^{-4}) \end{aligned}\right\} \quad (10b)$$

It is convenient for our purposes to take the $d$ orbitals such as $d_{z^2}$, $d_{x^2-y^2}$, $d_{xy}$, etc. rather than the $d$ orbitals classified by the magnetic quantum number. If the axis of the spherical coordinate, on which the point charge (and dipole) lies, is taken as the $z$-axis, the following relations will easily be found:

$$\left.\begin{aligned} & u(z^2)=u(0), \quad u(x^2-y^2)=u(xy)=u(2), \\ & \qquad u(yz)=u(zx)=u(1), \\ & u(x^2)=u(y^2)=\frac{1}{4}u(0)+\frac{3}{4}u(2), \\ & u(y^2-z^2)=u(z^2-x^2)=\frac{3}{4}u(0)+\frac{1}{4}u(2). \end{aligned}\right\} \quad (11)$$

where $z^2$, $x^2-y^2$, etc. stand for $d_{z^2}$, $d_{x^2-y^2}$, etc., and 0, 1 and 2 represent $d$ orbitals with magnetic quantum numbers 0, ±1 and ±2, respectively.

**IIIb. Electrostatic Energy of the 3*d* Electron Arising from the Interaction with the Six Ligands Regarded as Point Charges (and Dipoles). Effect of Replacement of the Ligands.**—In a complex $MA_6$ of the $O_h$ symmetry, the total electrostatic energy of the $3d$ electron of the metal, arising from interaction with the six A ligands, can easily be calculated by the use of Eq. (11) and similar equations for a charge (and dipole) on the $x$- and the $y$-axis:

$$U_0(z^2)=U_0(x^2-y^2)=3u_A(0)+3u_A(2),$$

$$U_0(xy)=U_0(yz)=U_0(zx)=4u_A(1)+2u_A(2),$$

where the subscript A refers to the ligand A. The difference in electrostatic energy between the two kinds of $d$ orbital are then:

$$\Delta U_0=3u_A(0)+u_A(2)-4u_A(1). \quad (12)$$

For a complex $MA_5B$ (with B on the $z$-axis), the following relations can be found:

$$U_1(z^2)=U_0(z^2)+\Delta u(0)$$

$$U_1(x^2)=U_0(z^2)+\frac{1}{4}\Delta u(0)+\frac{3}{4}\Delta u(2)$$

$$U_1(x^2-y^2)=U_0(x^2-y^2)+\Delta u(2)$$

$$U_1(y^2-z^2)=U_0(x^2-y^2)+\frac{3}{4}\Delta u(0)+\frac{1}{4}\Delta u(2)$$

$$U_1(xy)=U_0(xy)+\Delta u(2)$$

$$U_1(yz)=U_0(xy)+\Delta u(1)$$

where $U_1$ and $U_0$ refer to $MA_5B$ and $MA_6$, respectively, and $\Delta u(m)$ is the increase in electrostatic energy of the orbital electron (with the magnetic quantum number $m$) due to the replacement of the ligand A on the $z$-axis with B. In the case of the cobalt (III) complex, shifting of the sub-bands of the first and the second band will thus caused as follows:

$$\begin{aligned} Ib:\ & U_1(x^2-y^2)-U_1(xy) \\ & =U_0(x^2-y^2)-U_0(xy)\equiv\Delta U_0, \end{aligned} \quad (13a)$$

$$\begin{aligned} Ia:\ & U_1(y^2-z^2)-U_1(yz) \\ & =\Delta U_0+\frac{3}{4}\Delta u(0)+\frac{1}{4}\Delta u(2)-\Delta u(1) \\ & =\Delta U_0+\delta_1, \end{aligned} \quad (13b)$$

$$\begin{aligned} IIb:\ & U_1(z^2)-U_1(xy)=\Delta U_0+\Delta u(0)-\Delta u(2) \\ & =\Delta U_0+\delta_2, \end{aligned} \quad (13c)$$

$$\begin{aligned} IIa:\ & U_1(x^2)-U_1(yz) \\ & =\Delta U_0+\frac{1}{4}\Delta u(0)+\frac{3}{4}\Delta u(2)-\Delta u(1) \\ & =\Delta U_0+\delta_3. \end{aligned} \quad (13d)$$

These equations show that the sub-band *Ib* will not be shifted, while *Ia*, *IIb* and *IIa* will be shifted by the magnitudes $\delta_1$, $\delta_2$ and $\delta_3$, respectively. (The *Ib* and the *IIb* sub-band correspond to the absorptions which are only slightly induced by the light polarized in the $z$-direction.)

The result of similar calculation for each substituted complex is shown in Table III.

**IIIc. Polarization of the Ligand in the Electric Field of the Central Metal Ion.**—If we assume an ionic model for a metal complex, the ligand molecule or ion should be affected by the strong electric field of the central ion, and thus be polarized very strongly. The polarizability of a molecule or an ion in such a strong field should be dependent on the field strength $F$, and will be represented by

TABLE III

PREDICTED SHIFTS OF THE FIRST AND THE SECOND BAND DUE TO THE REPLACEMENT OF THE LIGANDS (RESULTS OF THE CRYSTAL-FIELD TREATMENT)

| | Electronic transition | $MA_5B$ | | *trans*-$MA_4B_2$ | | *cis*-$MA_4B_2$ | | *trans*-$MA_3B_3$ | | *cis*-$MA_3B_3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $(+z)$ | | $(+z, -z)$ | | $(+x, +y)$ | | $(+x, -x, +z)$ | | $(+x, +y, +z)$ | |
| The first band | $d_{xy}\rightarrow d_{x^2-y^2}$ | 0 | $(A_2)$ | 0 | $(A_{2g})$ | $2\delta_1$ | $(B_1)$ | $2\delta_1$ | $(A_2)$ | $2\delta_1$ | $(A_2, E)$ |
| | $d_{yz}\rightarrow d_{y^2-z^2}$ | $\delta_1$ | $(E)$ | $2\delta_1$ | $(E_g)$ | $\delta_1$ | $(A_2, B_2)$ | $\delta_1$ | $(B_2)$ | $2\delta_1$ | |
| | $d_{zx}\rightarrow d_{z^2-x^2}$ | $\delta_1$ | | $2\delta_1$ | | $\delta_1$ | | $3\delta_1$ | $(B_1)$ | $2\delta_1$ | |
| The second band | $d_{xy}\rightarrow d_{z^2}$ | $\delta_2$ | $(B_2)$ | $2\delta_2$ | $(B_{2g})$ | $2\delta_3$ | $(A_1)$ | $\delta_2+2\delta_3$ | $(A_2)$ | $\delta_2+2\delta_3$ | $(A_1, E)$ |
| | $d_{yz}\rightarrow d_{x^2}$ | $\delta_3$ | $(E)$ | $2\delta_3$ | $(E_g)$ | $\delta_2+\delta_3$ | $(A_2, B_2)$ | $2\delta_2+\delta_3$ | $(B_2)$ | $\delta_2+2\delta_3$ | |
| | $d_{zx}\rightarrow d_{y^2}$ | $\delta_3$ | | $2\delta_3$ | | $\delta_2+\delta_3$ | | $3\delta_3$ | $(B_1)$ | $\delta_2+2\delta_3$ | |

$(+z)$, $(+z, -z)$, etc., show the position of the replacement, and $(A_2)$, $(E)$, etc. are the symmetries of the excited states.

$\alpha_0+\beta F^2$. An approximate expression for the induced dipole moment of a molecule in a strong field has been given by Coulson et al.[12] as follows:

$$\mu=\frac{2}{3}\frac{M^2}{E_2-E_1}F+\left\{\frac{E_2-E_1}{45kT}-\frac{1}{10}\right\}\frac{8M^4}{(E_2-E_1)^3}F^3+\cdots\cdots$$

where $M$ is the moment of the first allowed transition and $E_2-E_1$ its energy. We have made use of this expression and estimated the dipole moment of an ammonia molecule and of a chloride ion in a cobalt complex:

$$\begin{aligned}\mu_{NH_3}&=1.47\times10^{-18}+2.26\times10^{-24}F+5\times10^{-35}F^3 \text{ e. s. u.}\\&=0.578+1.08Z+35Z^3 \text{ atomic units,}\end{aligned}\tag{14a}$$

$$\begin{aligned}\mu_{Cl^-}&=3.05\times10^{-24}F+9\times10^{-35}F^3 \text{ e. s. u.}\\&=1.06Z+25Z^3 \text{ atomic units,}\end{aligned}\tag{14b}$$

where $Z$ is the charge on the central ion*, and the distances between the central ion and the ligands were taken as 3.76 and 4.40 atomic units, respectively, in the replacement of $F$ with $Z$. (These expressions will be good approximations only for small values of $Z$, i. e., for $Z\leq0.2$.)

**IIId Calculation of the Position of the Bands on the Assumption of the Ionic Model.**—As was mentioned in a previous chapter, the positions of the first and the second band of $[Co(NH_3)_6]^{3+}$ are closely connected with $\Delta\varepsilon$, the energy difference between the two kinds of 3*d* orbital. If we assume the ionic model, $\Delta\varepsilon$ will correspond to $\Delta U_0$ in Eq. (12), which may be calculated by means of Eq. (10b) as follows:

$$\Delta\varepsilon=\Delta U_0=2625\,\mu_A R_A^{-2}\rho_A^{-4}.$$

The result of calculation with $\mu_A=\mu_{NH_3}$ (Eq. (14a)), $R_A=3.76$ and $\rho_A=2.3\times3.76$ is shown against $Z$ in Fig. 3.

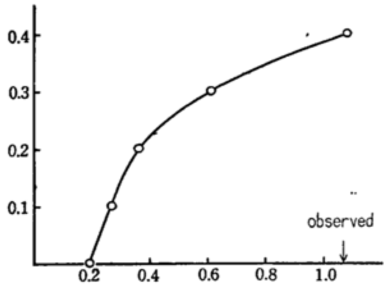

Fig. 3. Relationship between the charge on the cobalt ($Z$) and the crystal-field splitting of $d$-level ($\Delta U_0$) in $[Co(NH_3)_6]^{3+}$.

The magnitudes of shifts of the subbands due to the replacement of the ligand A ($NH_3$) with B ($Cl^-$), given in Eqs. (13a)—(13d), may be obtained in the following expressions by the use of Eqs. (10a) and (10b):

$$\left.\begin{aligned}\delta_1&=(525/4)D_4,\\\delta_2&=8D_2+75D_4,\\\delta_3&=-4D_2+(375/4)D_4,\end{aligned}\right\}\tag{15}$$

where
$$\begin{aligned}D_2&=Z_B R_B^{-1}\rho_B^{-2}-Z_A R_A^{-1}\rho_A^{-2}+3\mu_B R_B^{-2}\rho_B^{-2}-3\mu_A R_A^{-2}\rho_A^{-2},\\D_4&=Z_B R_B^{-1}\rho_B^{-4}-Z_A R_A^{-1}\rho_A^{-4}+3\mu_B R_B^{-2}\rho_B^{-4}-3\mu_A R_A^{-2}\rho_A^{-4}.\end{aligned}$$

The results of the numerical calculation by the use of Eqs. (14a) and (14b) are shown in Fig. 4 for $Z=0\sim0.4$.

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[12] C. Coulson, A. Maccoll and L. E. Sutton, *Trans. Faraday Soc.*, **48**, 111 (1952).

* If the electrostatic effect of the ligands is taken into account, $Z$ should be considered as the effective charge at the position of the central ion,—the effective charge required to produce the electric field at the position of the sixth ligand, which is equivalent to the field produced by the central ion and the other five ligands.

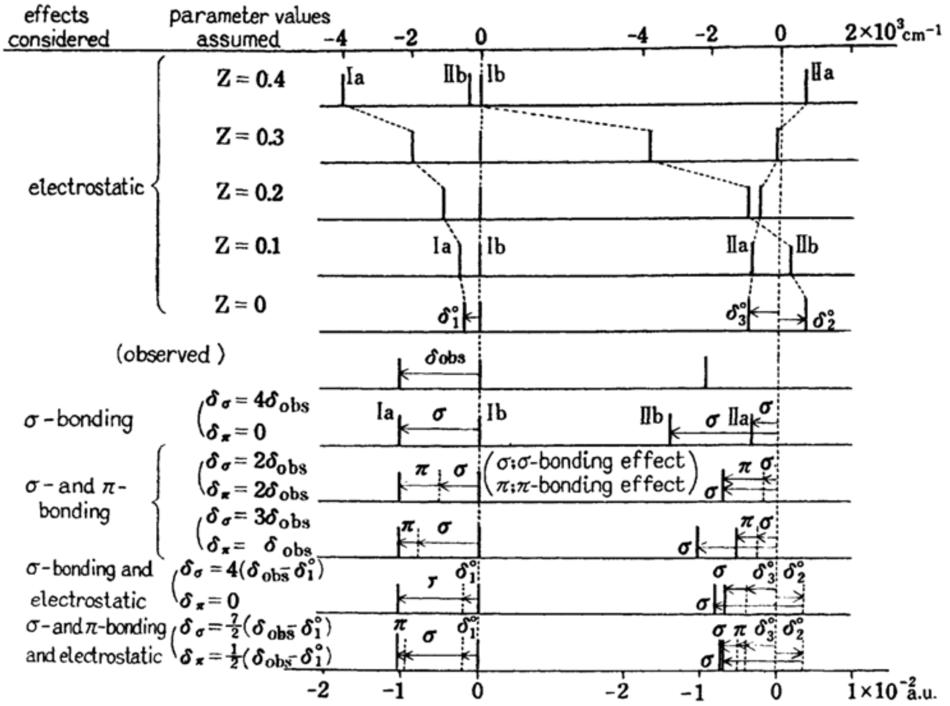

Fig. 4. The predicted and the observed positions of the bands of $[Co(NH_3)_5Cl]^{2+}$.

## IV. Comparison of the Theoretical Prediction with Observation

We shall compare observed features of shifting and splitting of the bands primarily with the molecular-orbital prediction (Table II). It must be mentioned here that the success of the molecular-orbital prediction in interpreting the observed data will not necessarily exclude the electrostatic consideration; in this connection further mention will be made below.

**IVa Existence of the Unshifted Sub-band in Mono- and *trans*-Di-substituted Cobalt(III) Ammines.**—Absorption spectra of mono- and *trans*-di-substituted cobalt (III) ammines have been studied extensively by Linhard et al.[13], who found that, in acido- and halogeno-pentamminecobalt (III) ion, the first band was split into two sub-bands, *Ia* and *Ib*, and, while the stronger *Ia* shifted to longer wavelengths, the weaker *Ib* did not change its position of the first band of hexamminecobalt(III) ion. They also found that this feature of splitting was observed more distinctly in the case of *trans*-disubstituted complexes, but the feature was different for the *cis*-isomers.

A quantitative study on the dichroism of crystals of *trans*-dihalogeno-bis(ethylenediammine)cobalt(III) salts was made by Yamada et al.[14], and one of their results is reproduced in Fig. 5. It shows that, at the *Ia* band, both polarized lights are more or less strongly absorbed, whereas at the *Ib* band the light polarized in the direction of the *a*-axis, which is nearly parallel to the Cl-Co-Cl direction, is only slightly absorbed.

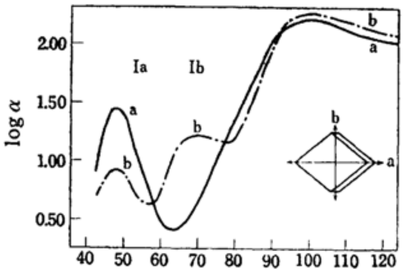

Fig. 5. Absorption spectra of $[Co(en)_2Cl_2]ClO_4$[14].

All these observed facts are predicted in Table II. By a glance at it, one can expect that a sub-band without shift will appear only in the first bands of $CoA_5B$

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[13] M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **264**, 321 (1951); **266**, 49 (1951); **271**, 101 (1952), etc.

[14] S. Yamada, A. Nakahara, Y. Shimura and R. Tsuchida, This Bulletin, **28**, 222 (1955).

and *trans*-$CoA_4B_2$. As for the polarization of the transition, a more detailed explanation seems to be necessary.

All the transitions listed in Table II are more or less completely forbidden transitions, which will become allowed by coupling with suitable vibrational transitions. The required symmetries of the vibrational transitions to make each electronic transition allowed through coupling, and the direction of the transition moment in each case are shown in Table IV. Since no vibration of the symmetry given in parentheses is present in *trans*-$CoA_4B_2$, we should expect that the transition $d_{xy}\rightarrow d_{x^2-y^2}$, which corresponds to the *Ib* band, will not absorb the light polarized in the $z$-direction (the Cl-Co-Cl direction), while the transitions $d_{yz}\rightarrow d_{y^2-z^2}$ and $d_{zx}\rightarrow d_{z^2-x^2}$ will absorb both lights polarized in the directions parallel and perpendicular to the $z$-axis. This is in quite agreement with the observation.

TABLE IV

COUPLING OF THE ELECTRONIC AND THE VIBRATIONAL TRANSITION AND THE DIRECTION OF THE TRANSITION MOMENT (FOR *trans*-$CoA_4B_2$)

| Electronic transition | Symmetry of the excited state | Required symmetries of vibrational transitions | Direction of transition moment |
|---|---|---|---|
| $d_{xy}\rightarrow d_{x^2-y^2}$ | $^1A_{2g}$ | $(A_{1u})$<br>$E_u$ | $(z)$<br>$x,\ y$ |
| $d_{yz}\rightarrow d_{y^2-z^2}$<br>$d_{zx}\rightarrow d_{z^2-x^2}$ | $^1E_g$ | $(A_{1u}),\ A_{2u},\ (B_{1u}),\ B_{2u}$<br>$E_u$ | $x,\ y$<br>$z$ |
| $d_{xy}\rightarrow d_{z^2}$ | $^1B_{2g}$ | $(B_{1u})$<br>$E_u$ | $(z)$<br>$x,\ y$ |
| $d_{yz}\rightarrow d_{x^2}$<br>$d_{zx}\rightarrow d_{y^2}$ | $^1E_g$ | $(A_{1u}),\ A_{2u},\ (B_{1u}),\ B_{2u}$<br>$E_u$ | $x,\ y$<br>$z$ |

**IVb Relative Magnitude of the Shift of the First Band in Connection with the Number and the Position of Substitution.**—The shift of the *Ia* band was found by Linhard et al.[13] to be about twice as great for a *trans*-disubstituted complex as for the corresponding monosubstituted one. For the *cis*-disubstituted complex which shows no marked splitting, the shift of the first band was intermediate between those of the *Ia* bands of the mono- and the *trans*-di-substituted complex. Later they found, however, the splitting in the case of the *cis*-form, too. Although no explicit statement was made by them, it seems to be shown in their figures of the absorption curves that the positions of the less and the more greatly shifted sub-band are in the neighborhood of the *Ia* band of the corresponding mono- and the *trans*-di-substituted complex, respectively. All these are predicted in Table II.

**IVc Dissimilarity between the First and the Second Band in Dichroism.**—Crystals of many kinds of cobalt (III) complex salt were quantitatvely examined in dichroism by Kobayashi[15], who found the first and the second band to behave dissimilarly, as is shown in Table V (partial reproduction of the result given by Kobayashi). In every case, the first and the second band were shifted to mutually opposite directions with alteration of the direction of polarization of the light.

TABLE V

POSITION OF THE ABSORPTION MAXIMA OF THE CRYSTALS OF COBALT (III) COMPLEX SALTS MEASURED WITH POLARIZED LIGHT[15]

| Complex salt | | With the light polarized in the direction of | | |
|---|---|---|---|---|
| | | $a$-axis | | $b$-axis |
| $[Co(NH_3)_5Cl]SO_4\cdot 2H_2O$ | $\nu_1$ | 62.4 | $>$ | 58.0 |
| | $\nu_2$ | 79.4 | $<$ | 82.0 |
| $[Co(NH_3)_5CO_3]NO_3\cdot H_2O$ | $\nu_1$ | 60.2 | $<$ | 61.8 |
| | $\nu_2$ | 86.2 | $>$ | 79.0 |
| $[Co(NH_3)_5C_2O_4]Br\cdot 1\frac{1}{2}H_2O$ | $\nu_1$ | 60.4 | $<$ | 61.0 |
| | $\nu_2$ | 85.0 | $>$ | 82.4 |
| $[Co(NH_3)_4CO_3]Br$ | $\nu_1$ | 56.0 | $<$ | 57.0 |
| | $\nu_2$ | 83.0 | $>$ | 79.4 |
| $[Co(NH_3)_4(H_2O)Cl]Cl$ | $\nu_1$ | 57.6 | $>$ | 55.4 |
| | $\nu_2$ | 79.4 | $<$ | 83.8 |
| $[Co(NH_3)_4(H_2O)Cl]SO_4$ | $\nu_1$ | 57.6 | $>$ | 55.6 |
| | $\nu_2$ | 79.8 | $<$ | 83.4 |

The notations $\nu_1$ and $\nu_2$ mean the frequencies of light at the first and the second absorption maximum (in $10^{13}$ sec$^{-1}$).

This feature of shifting of the bands may also be predicted in Table II. It was mentioned in the preceding paragraphs under **IVa** that in *trans*-$CoA_4B_2$ the transition $d_{xy}\rightarrow d_{x^2-y^2}$ will not be caused by absorption of the $z$-polarized light. The same statement is also valid for $d_{xy}\rightarrow d_{z^2}$ in place of $d_{xy}\rightarrow d_{x^2-y^2}$, as is seen from Table IV. This selection rule will not so strictly hold in the cases of $CoA_5B$ and *cis*-$CoA_4B_2$ on account of their lower symmetries, but it is very likely that the transitions $d_{xy}\rightarrow d_{x^2-y^2}$ and $d_{xy}\rightarrow d_{z^2}$ will be caused much less strongly by absorption of the $z$-polarized light than by absorption of the $x$- or the $y$-polarized light. Then it can

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15) R. Tsuchida and M. Kobayashi, "The Colors and Structures of Metallic Compounds" (in Japanese), Zoshindo, Osaka, 1944, p. 184.

be seen in Table II that if we change the direction of polarization of the light from *z* to *x* or *y*, the first band will be shifted to the blue and the second to the red in the cases of $CoA_5B$ and *trans*-$CoA_4B_2$, and to the reversed directions in the case of *cis*-$CoA_4B_2$ ($\delta_\sigma$ is assumed to be a negative quantity in cm.$^{-1}$ or sec.$^{-1}$ and $\delta_\pi$ to be much smaller than $\delta_\sigma$ in the absolute value, as is the case with most of the substituted ammines). Thus by assuming favorably either of the *a*- or the *b*-axis in Table V to be nearly parallel to the *z*-axis, we can interpret satisfactorily the qualitative feature shown in the table.

**IVd Difference between the Two Isomers of the $CoA_3B_3$-type of Complex in the Absorption Curve.**—Absorption spectra of the $\alpha$- and the $\beta$-isomer of tris-(glicinato)cobalt(III) were measured by Shimura and Tsuchida[16]. The first band of the $\beta$-form was found to be normal, while that of the $\alpha$-form was found to show distinct indication of splitting. It was empirically concluded by them that the $\alpha$-form should correspond to *trans*-form (more correctly *cis-trans*-form as named by them) and the $\beta$-form to *cis*-form (*cis-cis*-form). Theoretical prediction in Table II is in agreement with this empirical conclusion.

**IVe The Less Distinct Splitting of the Second Band.**—If the change in $\sigma$-interaction were the only important reason for the splitting of the bands, the extent of splitting should be the same for the first and the second band. But many experimental results show that the splitting of the second band is less distinct than that of the first. This may be explained by considering (a) the $\pi$-interaction, (b) the electrostatic interaction with the ligands (the "crystal field"), and (c) the configuration interaction.

The effect of (a) has already been given in Table II. As regards the first band, this effect of $\pi$-interaction on the shift of sub-bands is proportional to that of $\sigma$-interaction, whereas concerning the second band the $\pi$-effect is smaller for the sub-band of larger $\sigma$-effect and it will make the splitting narrower. (Here $\delta_\pi$ is assumed to be of the same sign as $\delta_\sigma$, as is the case with the replacement of the ammonia molecule with a halide ion.)

As will be mentioned below, the electrostatic effect (b), given in Table III, may be partly responsible for the less distinct splitting of the second band.

The effect of (c) appears to be important in some cases. The configuration interaction is small for the first excited state, but it is considerably great for the second and will be changed to an appreciable extent by the replacement of the ligands. Thus the observed magnitude of the shift of the second band may deviate from that predicted. The deviation is likely to be considerable with some of the multiple substitutions, such as substitutions of ammonia molecules with oxalate ions to form bis(oxalato)diammine- and tris(oxalato)-cobaltate(III) ions. (Shimura and Tsuchida[17] found that, in the series of complex, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(C_2O_4)]^+$, $[Co(NH_3)_2(C_2O_4)_2]^-$ and $[Co(C_2O_4)_3]^{3-}$, the first band is shifted linearly, but the second not linearly.)

Although these effects make the situation complicated with the second band, they can at least qualitatively account for the observed data.

**IVf Remarks on the Electrostatic Effect and Conclusion.**—In the preceding paragraphs, we have shown that the molecular-orbital consideration (Table II) is satisfactory in interpreting the shifts of the bands, if values of the parameters are suitably chosen and effects of the electrostatic and the configuration interaction are subsidiarily taken into account. However, the following must be noted: if we could choose values of the parameters quite freely, the electrostatic prediction (Table III) would be equally satisfactory; i. e., Tables II and III would become the same for $\delta_1=\frac{1}{4}\delta_\sigma+\frac{1}{4}\delta_\pi$, $\delta_2=\frac{1}{3}\delta_\sigma$ and $\delta_3=\frac{1}{12}\delta_\sigma+\frac{1}{4}\delta_\pi$. (Among the three parameters in the electrostatic case, only two are independent, as is seen from Eq. (15).) Therefore we need to evaluate the parameters, before we come to a conclusion on the relative importance of the two effects, the bonding (antibonding) and the electrostatic. The latter effect was theoretically estimated in the preceding chapter; but the former not, owing to the difficulty in the quantitative theoretical treatment.

As is shown in Figs. 3 and 4, an assumption of $Z=0.3\sim0.4$ would account for the $\Delta\varepsilon$ value and the shift of the first band, whereas any assumption of the $Z$ value would not simultaneously

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[16] Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

[17] Y. Shimura and R. Tsuchida, ibid., **28**, 572 (1955).

interpret the shifts of all the sub-bands. These results appear to suggest that the purely ionic model, where $Z=3$, would be a bad approximation, although there are some restrictions in discussing the results, e. g., that the $Z$ value given above should not be taken too literally on account of the poor approximation of Eqs. (14a) and (14b) for such a high value of $Z$, and that the results would be somewhat different with possible modifications of the assumption in the calculation*. A compromising ionic model, in which electrons of the ligands have been partially transferred to the 4*s* and the 4*p* orbitals of the metal but not to the 3*d* orbitals, would be possible, but it does not seem to be a good approximation.

In the lower part of Fig. 4 are given the positions of the bands observed and those predicted in Table II (with various sets of parameter values, which are consistent with the observed shift of Ia) together with those predicted in consideration of both effects of the electrostatic and the bonding (antibonding) interaction. It may be seen from these that by considering the electrostatic effect we can interpret the observed data without assuming the $\pi$-effect to be unreasonably strong.

It is very likely that the model of bonding (antibonding) interaction is a better approximation for cobalt (III) complexes and is further improved by the consideration of the electrostatic effect (and also of the effect of configuration interaction), although the arbitrariness in choice of the parameter values prevents us from drawing a decisive conclusion.

Contrary to this less ionic complex, however, a more ionic one would be more satisfactorily approximated by the ionic model.

## Summary

A general theory has been presented to discuss spectra of transition metal complexes and to apply them to the problem of shifting and splitting of the absorption bands of the cobalt (III) complex due to replacement of some of the ligands. The problem was discussed from the molecular-orbital and the electrostatic point of view.

The relative magnitude of the shift of each sub-band was predicted in connection with the number and the position of the replacement. In the case where the molecular-orbital treatment is a good approximation, the shift was given in terms of two parameters, $\delta_\sigma$ and $\delta_\pi$, which are associated with the change in the $\sigma$- and the $\pi$-antibonding (or bonding) energy, respectively. With an ionic model of the complex, the shift was given in terms of the parameters, $\delta_1$, $\delta_2$ and $\delta_3$ (only two among the three being independent), which are associated with the change in the electrostatic effect of the ligands. In this case, results of numerical calculation for the chloropentamminecobalt (III) ion $[Co(NH_3)_5Cl]^{2+}$ were also given on some assumptions.

The agreement between the prediction

TABLE VI
EXPRESSIONS FOR THE ENERGY OF INTERACTION BETWEEN *d* ELECTRONS

$(aa|g|aa)=F_0+4F_2+36F_4$, for every $d$ orbitals.
$(aa|g|ab)=0$ , for $a\neq b$.
$(ab|g|ab)\equiv J(a,b)$ and
$(aa|g|bb)=(ab|g|ba)\equiv K(a,b)$:

| $a$ | $b$ | $J(a,b)$ | $K(a,b)$ |
|---|---|---|---|
| $d_{z^2}$ | $d_{x^2-y^2}$, $d_{xy}$ | $F_0-4F_2+6F_4$ | $4F_2+15F_4$ |
| $d_{z^2}$ | $d_{yz}$ , $d_{zx}$ | $F_0+2F_2-24F_4$ | $F_2+30F_4$ |
| $d_{x^2-y^2}$ | $d_{xy}$ | $F_0+4F_2-34F_4$ | $35F_4$ |
| $d_{x^2-y^2}$ | $d_{yz}$ , $d_{zx}$ | $F_0-2F_2-4F_4$ | $3F_2+20F_4$ |
| $d_{xy}$ | $d_{yz}$ , $d_{zx}$ | | |
| $d_{yz}$ | $d_{zx}$ | | |

$(ab|g|ac)=0$, with the following exceptions:

| $a$ | $b$ | $c$ | $(ab|g|ac)$ cf. Eq. (16) |
|---|---|---|---|
| $d_{zx}$ | $d_{z^2}$ | $d_{x^2-y^2}$ | $-2\sqrt{3}\,F_2+10\sqrt{3}\,F_4$ |
| $d_{yz}$ | $d_{z^2}$ | $d_{x^2-y^2}$ | $2\sqrt{3}\,F_2-10\sqrt{3}\,F_4$ |

$(aa|g|bc)=(ac|g|ba)=0$,
with the following exceptions:

| $a$ | $b$ | $c$ | $(aa|g|bc)$ cf. Eq. (16) |
|---|---|---|---|
| $d_{zx}$ | $d_{z^2}$ | $d_{x^2-y^2}$ | $\sqrt{3}\,F_2-5\sqrt{3}\,F_4$ |
| $d_{yz}$ | $d_{z^2}$ | $d_{x^2-y^2}$ | $-\sqrt{3}\,F_2+5\sqrt{3}\,F_4$ |

$(ab|g|cd)=0$, with the following exceptions:

| $a$ | $b$ | $c$ | $d$ | $(ab|g|cd)$ cf. Eq. (16) |
|---|---|---|---|---|
| $d_{z^2}$ | $d_{xy}$ | $d_{zx}$ | $d_{yz}$ | $\sqrt{3}\,F_2-5\sqrt{3}\,F_4$ |
| $d_{z^2}$ | $d_{xy}$ | $d_{yz}$ | $d_{zx}$ | |
| $d_{z^2}$ | $d_{zx}$ | $d_{xy}$ | $d_{yz}$ | $-2\sqrt{3}\,F_2+10\sqrt{3}\,F_4$ |
| $d_{x^2-y^2}$ | $d_{xy}$ | $d_{zx}$ | $d_{yz}$ | $3F_2-15F_4$ |
| $d_{x^2-y^2}$ | $d_{xy}$ | $d_{yz}$ | $d_{zx}$ | $-3F_2+15F_4$ |

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* For example, an assumption of the polarizability independent of the field strength will lead to the result, which indicates a linear relationship between the $Z$ value and the magnitude of shift of each sub-band and approximates the above-mentioned result for small $Z$ values.

and the observation was generally satisfactory in the molecular-orbital case, and is expected to be quite satisfactory if effects of the electrostatic and the configuration interaction are also taken into account.

We are greatly indebted to Professor R. Tsuchida of Osaka University and his co-workers, without whose extensive study on dichroism of the complex salts this investigation would have been confronted with many difficulties. We are also indebted to Professor M. Linhard and his coworkers for their invaluable works, by which this investigation was stimulated and supported. We wish to express our sincere thanks to Former Professor Y. Nakatsuka of Osaka City University and Professor Emeritus K. Kimura of the University of Tokyo for their kind encouragement throughout the work, to Professor R. Fujishiro of Osaka City University for his helpful suggestions, and to Mr. M. Mori of our Laboratory for discussions.

We are also grateful to the Ministry of Education for financial assistance.

## Appendix

In the course of this work a set of expressions in terms of Slater-Condon parameters was prepared for the energy of interaction between *d* electrons of real eigenfunctions. Although some of the expressions have already been given by Orgel⁽⁹⁾, their full table will be given below (Table VI on p. 107).

For the case of the real functions, the following general relations can easily be seen:

$$\begin{aligned}&(ab|g|cd)=(ad|g|cb)=(cd|g|ab)\\&=(cb|g|ad)=(ba|g|dc)=(da|g|bc)\\&=(dc|g|ba)=(bc|g|da),\end{aligned} \qquad (16)$$

where

$$(ab|g|cd)=\iint a(1)b(2)\frac{1}{r_{12}}c(1)d(2)dv_1dv_2.$$

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