The Electronic Structures of Cu(II) Complexes as Determined by Means of the Configurational Interaction Method

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(Received September 14, 1973)

The electronic structures of Cu(II) complexes with D_{4h} effective molecular symmetry have been investigated by means of the configurational interaction method. The locally-excited configurations of the central metal ion and the charge-transfer configurations corresponding to an electron transfer from the ligand system to the central metal ion have been taken into account. A correspondence with the crystal-field treatment has been obtained using the partitioning technique of solving the secular equation. The energies of the charge-transfer configurations, the resonance integrals, and the electrostatic contribution, D_S^{ion}, were determined so as to fit the observed d-d spectra.

There have been a number of theoretical and experimental investigations of the electronic states of transition-metal complexes. The crystal-field (CF) theory has generally been successful in the spectral assignment of the low-lying d-d spectra.[1] This method is based on an electrostatic model. On the other hand, there is much experimental evidence showing the presence of covalency between the central metal ion and the ligands.[1,2] The effect of covalency on the d-d spectra has been discussed with success in terms of a semi-empirical molecular orbital treatment based on the angular overlap model.[3,4] However, few investigations by means of the configurational interaction (CI) method have been carried out.[5] The CI method is expected to give some valuable and complemental information in this respect.

In this study the electronic structures of Cu(II) complexes with D_{4h} local symmetry were treated by means of the CI method. The physical content of the CF parameters and the nature of the bonding in these Cu(II) complexes were investigated.

Method

In the treatment of the CI method, a Cu(II) complex, CuX_4Y_2, is considered to be a composite of two component groups: a copper ion and a ligand system composed of the equatorially-coordinated ligand, X_4, and the axial ligands, Y_2. The total electronic state is described as a super-position of the various configurational wave functions:[6] the ionic configurations and the charge-transfer (CT) configurations. The ionic configurations are defined as those configurations in which the copper ion has nine valence electrons, *i.e.*, Cu^{2+}. Of the various ionic configurations, we take into account only the locally-excited configurations of the Cu^{2+} ion, which arise from the rearrangement of d-electrons, because we are primarily interested in the d-d transitions.

The wave function of an ionic configuration, which belongs to an irreducible representation, Γ, of the symmetry group D_{4h}, is given as:

$$\Phi^{ion}(\Gamma) = A\Phi_L^{ion}\Phi_M^{ion}(\Gamma) \quad (1)$$

where Φ_L^{ion} and $\Phi_M^{ion}(\Gamma)$ are the determinantal wave functions of the ligand system and the Cu(II) ion. The Φ_L^{ion} is given as:

$$\Phi_L^{ion} = |(x_1\bar{x}_1\cdots x_6\bar{x}_6)(y_1\bar{y}_1\cdots y_6\bar{y}_6)(z_1\bar{z}_1\cdots z_6\bar{z}_6)| \quad (2)$$

where x_i, y_i, and z_i are the np_x, np_y, and np_z a.o.'s of the i-th coordinated atom. The numbering of atoms and the coordinated system are shown in Fig. 1. The ns a.o. of the coordinated atom was omitted for the sake of simplicity.[7] A is the antisymmetrizer for the exchange of electrons between the ligand system and the Cu(II) ion. The energies of the ionic configurations are given, measured from the center of gravity of the $^2D(d^9)$ state of the Cu(II) ion,[8] by:

$$\begin{aligned}
&\Phi^{ion}(B_{1g}):\ E^{ion}(B_{1g}) = -2D_s^{ion} - 6D_q^{ion} + D_t^{ion}\\
&\Phi^{ion}(A_{1g}):\ E^{ion}(A_{1g}) = 2D_s^{ion} - 6D_q^{ion} + 6D_t^{ion}\\
&\Phi^{ion}(B_{2g}):\ E^{ion}(B_{2g}) = -2D_s^{ion} + 4D_q^{ion} + D_t^{ion}\\
&\Phi^{ion}(E_g):\ E^{ion}(E_g) = D_s^{ion} + 4D_q^{ion} - 4D_t^{ion}
\end{aligned} \quad (3)$$

In the CF treatment, the CF parameters, D_S^{ion}, D_q^{ion}, and D_t^{ion}, are usually determined so as to fit the observed d-d spectra, independent of their physical content. Here, they are considered to be the quantities which arise only from the effect of the ionic configurations. They are given, in the point-charge model, as:[8]

$$\begin{aligned}
D_s^{ion} &= (2/7)\langle r^2\rangle(q_e/R_e^3 - q_a/R_a^3)\\
D_q^{ion} &= (1/6)\langle r^4\rangle q_e/R_e^5\\
D_t^{ion} &= (2/21)\langle r^4\rangle(q_e/R_e^5 - q_a/R_a^5)
\end{aligned} \quad (4)$$

where q_e and q_a are the charges on the equatorially and axially coordinated atoms. R_e and R_a is the

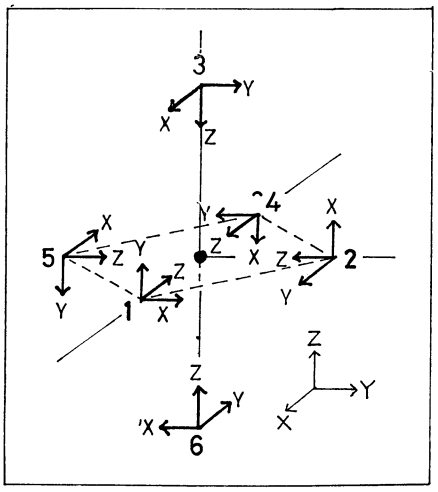

Fig. 1. Numbering and coordinate of Cu(II) complexes

distance of these atoms from the Cu(II) ion.

As to the CT configurations, we considered first those configurations which are formed by an electron transfer from the ligand system to the 3d a.o. of the Cu(II) ion (3d-CT). In these 3d-CT configurations, the copper ion has a completely filled 3d-shell. The wave function and the energy of a 3d-CT configuration, which belong to the irreducible representation of the D_{4h} symmetry group, is represented as:

$$\Phi^{CT}_{\alpha,\delta}(\Gamma) = A\Phi^{CT}_{L,\alpha\delta}(\Gamma)\Phi^{CT}_{M};\ E^{CT}_{\alpha\delta}(\Gamma) \tag{5}$$

Φ^{CT}_{M} is the determinantal wave function of the copper ion of the $3d^{10}$ configuration. $\Phi^{CT}_{L,\alpha\delta}(\Gamma)$ is the symmetry-adapted wave function of the ligand system in the 3d-CT configuration. The α and δ denote the α type of ligand and the δ type of a.o. from which an electron is transferred to the central metal ion. (α= e,a for the equatorially and axially coordinated ligand. $\delta=\sigma,\pi$ for np_z, and for np_x, np_y a.o.'s respectively) The relevant $\Phi^{CT}_{L,\alpha\delta}(\Gamma)$'s are represented as follows:

$$\begin{aligned}
\Phi^{CT}_{L,e\sigma}(B_{1g}) &= (1/2)(z_1-z_2+z_4-z_5)\\
\Phi^{CT}_{L,a\sigma}(A_{1g}) &= (1/\sqrt{2})(z_3+z_6)\\
\Phi^{CT}_{L,e\sigma}(A_{1g}) &= (1/2)(z_1+z_2+z_4+z_5)\\
\Phi^{CT}_{L,a\pi}(E_g) &= (1/\sqrt{2})(y_3+x_6)\\
\Phi^{CT}_{L,e\pi}(E_g) &= (1/\sqrt{2})(x_2+y_5)
\end{aligned} \tag{6}$$

where z_i indicates the determinantal wave function, in which the z_i a.o. is deleted from the expression of the Φ^{ion}_{L} of Eq. (2).

The off-diagonal matrix elements between the $\Phi^{ion}_{M}(\Gamma)$ and $\Phi^{CT}_{a\delta}(\Gamma)$ are calculated by the method of Longuett-Higgins and Murrell.[6] They are expressed in terms of the diatomic resonance integrals, $\beta_{a\delta}$, between the ligand a.o. located at α position and the δ-type d-a.o. of the copper ion. They are tabulated in Table 1.

TABLE 1. OFF-DIAGONAL MATRIX ELEMENTS BETWEEN Φ^{ion} AND Φ^{CT}

$\Phi^{ion}(\Gamma)$	$\Phi^{CT}_{a\delta}(\Gamma)$	$\langle\Phi^{ion}(\Gamma)\|\mathcal{H}\|\Phi^{CT}_{a\delta}(\Gamma)\rangle$
$\Phi^{ion}(A_{1g})$	$\Phi^{CT}_{a\sigma}(A_{1g})$	$\sqrt{2}\beta_{a\sigma}$
	$\Phi^{CT}_{e\sigma}(A_{1g})$	$-\beta_{e\sigma}$
$\Phi^{ion}(B_{1g})$	$\Phi^{CT}_{e\sigma}(B_{1g})$	$\sqrt{3}\beta_{e\sigma}$
$\Phi^{ion}(B_{2g})$	$\Phi^{CT}_{e\pi}(B_{2g})$	$2\beta^{in}_{e\pi}$
$\Phi^{ion}(E_g)$	$\Phi^{CT}_{a\pi}(E_g)$	$\sqrt{2}\beta_{a\pi}$
	$\Phi^{CT}_{e\pi}(E_g)$	$\sqrt{2}\beta^{out}_{e\pi}$

The CT configurations formed by an electron transfer to 4s or 4p a.o. of the Cu(II) ion (4s-CT or 4p-CT) have the resonance interaction with all the ionic configurations of Eq. (3). It can easily be shown that these resonance interactions result in a uniform energy stabilization of the low-lying ionic configurations. Hence, these 4s-CT and 4p-CT configurations do not affect the d-a.o. splittings in a higher approximation.[5a] Therefore, we did not take the 4s-CT and 4p-CT configurations into account explicitly, for we were mainly interested in the splittings of the 3d-levels. In order to see the relationship between the CI treatment described above and the CF treatment, it is necessary first to transform the basis of the CI method (ionic and CT configurations) to the ionic configurations which appear in the CF treatment. By means of the partitioning technique,[9] the secular equation in the CI treatment is transformed to:

$$\left\{\langle\Phi^{ion}|\mathcal{H}|\Phi^{ion}\rangle - \sum_{a\delta}\frac{\langle\Phi^{ion}|\mathcal{H}|\Phi^{CT}_{a\delta}\rangle\langle\Phi^{CT}_{a\delta}|\mathcal{H}|\Phi^{ion}\rangle}{\langle\Phi^{CT}_{a\delta}|\mathcal{H}|\Phi^{CT}_{a\delta}\rangle - E(\Gamma)}\right\}c^{ion} = E(\Gamma)c^{ion} \tag{7}$$

where c^{ion} is the mixing coefficient for $\Phi^{ion}(\Gamma)$. The secular equation obtained above is different from the ordinary one in the presence of the eigenvalue, E, in the denominator. It is usually solved by an iterational procedure. When the low-lying eigenvalues, $E(\Gamma)$'s, are located in a much smaller range of energy compared with $\langle\Phi^{CT}_{a\delta}|\mathcal{H}|\Phi^{CT}_{a\delta}\rangle$, *i.e.*, when the breadth of the d-d transition energies are much smaller than the energy of the CT configurations, it can be shown that the replacement of E in the denominator of Eq. (7) by an appropriate constant, $\bar{E}$, reproduces the low-lying eigenvalues of Eq. (7) with a good accuracy. The $\bar{E}$ constant has the meaning of an averaged stabilization energy and is approximately equal to the ground-state stabilization energy. The approximation is better for larger $\bar{E}$ values, *i.e.*, for a larger covalency, if the other circumstances are same. As will be shown in the next section, the quite large value of $E^{CT}_{a\delta}-\bar{E}$ estimated by the CI treatment confirms that these conditions are fullfilled. Furthermore, the success of the CF treatment itself implies that this replacement is a good approximation.

With this replacement, the expressions of the eigenvalues are obtained as;

$$\begin{aligned}
E(B_{1g}) &= -3\gamma_{e\sigma} - 2D^{ion}_{s} - 6D^{ion}_{q} + D^{ion}_{t}\\
E(A_{1g}) &= -\gamma_{e\sigma} - 2\gamma_{a\sigma} + 2D^{ion}_{s} - 6D^{ion}_{q} + 6D^{ion}_{t}\\
E(B_{2g}) &= -4\gamma^{in}_{e\pi} - 2D^{ion}_{s} + 4D^{ion}_{q} + D^{ion}_{t}\\
E(E_g) &= -2\gamma^{out}_{e\pi} - 2\gamma_{a\pi} + D^{ion}_{s} + 4D^{ion}_{q} - 4D^{ion}_{t}
\end{aligned} \tag{8}$$

where:

$$\gamma_{a\delta} = \beta^2_{a\delta}/(E^{CT}_{a\delta}-\bar{E}) \tag{9}$$

The $\gamma^{in}_{e\pi}$ and $\gamma^{out}_{e\pi}$ are related to in-plane and out-of-plane π-bondings respectively.

When we estimate the energy splittings, a constant,

$$(4/5)\gamma_{e\sigma} + (2/5)\gamma_{a\sigma} + (4/5)\gamma^{in}_{e\pi} + (4/5)\gamma^{out}_{e\pi} + (4/5)\gamma_{a\pi} \tag{10}$$

may be added to the energy expressions of Eq. (8) so as to satisfy the center-of-gravity rule.[1b] Then, we obtain exactly the same form of energy expressions as those obtained in the CF treatment (Eq. (3)) by using the following definitions:

$$\begin{aligned}
D_s &= D^{cov}_{s} + D^{ion}_{s} = (2/7)(\gamma_{e\sigma}-\gamma_{a\sigma})\\
&\quad + (2/7)(2\gamma^{in}_{e\pi}-\gamma^{out}_{e\pi}-\gamma_{a\pi}) + D^{ion}_{s}\\
D_q &= D^{cov}_{q} + D^{ion}_{q} = (3/10)\gamma_{e\sigma} - (2/5)\gamma^{in}_{e\pi} + D^{ion}_{q}\\
D_t &= D^{cov}_{t} + D^{ion}_{t} = (6/35)(\gamma_{e\sigma}-\gamma_{a\sigma})\\
&\quad - (8/35)(2\gamma^{in}_{e\pi}-\gamma^{out}_{e\pi}-\gamma_{a\pi}) + D^{ion}_{t}
\end{aligned} \tag{11}$$

The only differences are the replacement of the D^{ion}_{s}, D^{ion}_{q}, and D^{ion}_{t} of the CF treatment by the D_q, D_s, and D_t obtained above. These differences lose all their meanings when the CF quantities are considered as parameters to be determined from the observed d-d spectra. This implies that the CF parameter treatment

gives results approximately equivalent with the CI treatment with respect to the d-d transition energies. Hence, the CF treatment is valid even in the presence of a considerable covalency.

Discussion

In the square-planar Cu(II) complexes with an *N*-coordinated ligand, such as ethylenediamine and ammonia, the effect of the axial ligand and the π-bonding of the equatorial ligand can be neglected, $\gamma_{a\sigma}=\gamma_{a\pi}=\gamma_{e\pi}^{in}=\gamma_{e\pi}^{out}=0$ in Eqs. (8) and (11). Therefore, it is apparent from Eq. (8) that $E(B_{1g})$ is the lowest energy level and $E(E_g)$ is the highest. Thus, we have obtained the same expressions of the d-d transition energies as those of Smith,[7] if $(1/5)\gamma_{e\sigma}$ in the CI treatment is replaced by the covalence parameter, σ^*, of the angular overlap model. We have studied the electronic structures of these complexes in a somewhat different manner from that of Smith.

In the case of the square-planar complexes, the $D_t^{ion}/D_q^{ion}=4/7$ and $D_t^{cov}/D_q^{cov}=4/7$ relationship hold, as may be seen from Eqs. (4) and (8) respectively. Hence, the following relationship must hold:

$$D_t/D_q = 4/7 \tag{12}$$

or, equivalently:

$$4\omega_3 = 2\omega_2 + 3\omega_1 \tag{13}$$

where ω_1, ω_2, and ω_3 are the transition frequencies from the B_{1g} ground state to the A_{1g}, B_{2g}, and E_g excited states respectively. Conversely, this relationship may be used as a criterion in the spectral assignment of the square-planar Cu(II) complexes.

In Table 2, the d-d spectra of the $Cu(NH_3)_4X_2$ and $Cu(en)_2X_2$ complexes are listed,[11] along with the D_t/D_q and D_q/D_s ratios. In these complexes the axially-ligated atom lies at a distance about 0.5—0.6 Å longer than the sum of the covalent radii of the Cu(II) ion and the ligated atom, *i.e.*, at the distance of semi-coordination.[11] However, as may be seen from Table 2, the D_t/D_q ratio for these complexes lies very near to the value, 0.57, which is expected for the square-planar complexes. This indicates that the effects of the axial covalency, $\gamma_{a\sigma}$ and $\gamma_{a\pi}$, are considerably smaller than that of the equatorial σ-bonding, $\gamma_{e\sigma}$.

To see the degree of the electrostatic and the covalent contribution to the crystal field parameters, D_s, D_q, and D_t, the D_q/D_s ratio was studied. The D_q^{ion}/D_s^{ion} ratio was estimated to be about 0.1, using in Eq. (4) the value of $\langle r^2\rangle=1.1485a_0^2$ and $\langle r^4\rangle=4.1481a_0^4$ obtained from the 3d radial function of Cu^{2+}, tabulated by Richardson *et al.*[12] The D_q^{cov}/D_s^{cov} ratio is 21/20 from Eq. (11). Hence, the D_q/D_s ratio is expected to be of the order of 0.1 or 1.05, depending on whether the electrostabic or the covalent part is the main factor in determining the values of D_q and D_s. As is shown in Table 2, the experimentally-obtained D_q/D_s ratio lies near 0.73 for *N*-coordinated complexes. This value indicates that D_s^{ion} makes a rather large contribution to D_s, because D_q^{ion} is known to be much smaller than D_q^{cov}.

CI Calculation. To make the situation clear, we investigated the $Cu(en)_2(SCN)_2$ complex as a typical example by means of the CI method. Because this complex has a rather long axial distance ($R_e=2.00$ Å and $R_a=3.27$ Å),[11] the effect of axial covalency can be neglected; *i.e.*, $\beta_{a\sigma}=\beta_{a\pi}=0$. The D_q^{ion}/D_s^{ion} and D_t^{ion}/D_q^{ion} ratios were assumed to be equal to 0.1 and 0.57 respectively, following the discussion of the preceding subsection. With these approximation, the number of the unknown CI parameters is reduced to three, $\beta_{e\sigma}$, $E_{e\sigma}^{CT}$, and D_s^{ion}. These three CI parameters were determined so as to reproduce the three observed d-d spectra. The results are shown in Table 3. As is shown in Table 3, the contribution of D_q^{ion} and D_t^{ion} to D_q and D_t is rather small. This seems reasonable because, in octahedral complexes, it is generally recognized that the CF splitting, $10D_q$, is mainly caused by the effect of the covalency.[13]

Table 3. The result of the CI calculation on $Cu(en)_2(NCS)_2$.

	Obsd	Calcd
$\omega_1(A_{1g}\leftarrow B_{1g})$	14.7 kK	14.7 kK
$\omega_2(B_{2g}\leftarrow B_{1g})$	17.2 kK	17.2 kK
$\omega_3(E_g\leftarrow B_{1g})$	20.3 kK	20.3 kK
		$\beta_{e\sigma}=-3.00$ eV
		$E_{e\sigma}^{CT}=11.17$ eV
	$D_s=2.54$ kK	$D_s^{ion}=1.12$ kK
	$D_q=1.72$	$D_q^{ion}=0.11$
	$D_t=0.91$	$D_t^{ion}=0.06$

On the other hand, the contribution of $D_s^{ion}=1.12$ kK to $D_s=2.54$ kK is large and comparable with that of $D_s^{cov}=1.42$ kK, as was expected in the preceding subsection. Smith has obtained the value of $D_s^{ion}=0.72$ for $Cu(NH_3)_4(SCN)_2$ by estimating the effective charges q_e, of Eq. (4).[7] Our method of estimation seems to be superior to that of Smith in that it does not make use of q_e.

As to the energy of the charge-transfer configuration, the value of $E_{e\sigma}^{CT}=11.17$ eV was obtained. This suggests,

Table 2. The d-d transition frequencies and the ratios D_t/D_q and D_q/D_s. (Unit of R_a and ω_i is Å and kK respectively)

		R_a	ω_1	ω_2	ω_3	D_t/D_q	D_q/D_s
1	$Cu(en)_2Hg(NCS)_2$	N-2.58	13.5	16.8	17.9	0.68	0.80
2	$Cu(en)_2(NO_3)_2$	O-2.59	14.1	17.9	19.7	0.56	0.78
3	$Cu(en)_2(NCS)_2$	S-3.27	14.7	17.2	20.3	0.53	0.68
4	$Cu(en)_2(BF_4)_2$	F-2.56	16.8	18.0	20.1	0.67	0.67
5	$Cu(NH_3)_4(NO_3)_2$	N-2.65	13.4	16.2	17.1	0.65	0.79
6	$Cu(NH_3)_4(SCN)_2$	S-3.00	14.3	15.7	17.5	0.65	0.68

TABLE 4. THE d-d TRANSITION FREQUENCIES AND THE RATIOS D_t/D_q AND D_q/D_s OF SOME *O*-COORDINATED COMPLEXES

		R_a	ω_1	ω_2	ω_3	D_t/D_q	D_q/D_s
1	$Na_2Cu(SO_4)_2 2H_2O$	O-2.41	10.3	10.3	12.7	0.59	0.57
2	$Pb_2Cu(OH)_4Cl_2$	Cl-2.75	10.9	10.9	14.6	0.47	0.52
3	$Cu(UO_2)_2(AsO_4)_2 8H_2O$	O-2.55	13.0	12.0	15.0	0.64	0.52
4	$Cu(SO_4)5H_2O$	O-2.40	10.5	10.5	13.0	0.58	0.56
5	$BaCuSi_4O_{10}$	Cu-7.56	18.8	12.9	15.8	1.00	0.41

that the CT state is the state of the strong mixing of CT and the appropriate locally-excited configurations, because the CT band can be expected at about 6—7 eV.[13]

As to the diatomic resonance integral, $\beta_{e\sigma}$, the value of −3.00 eV was obtained. In the Wolfsberg-Helmholz approximation,[18] $\beta_{e\sigma}$ is estimated to be:

$$\beta_{e\sigma} = -(1/2)F_\sigma S_{e\sigma}(I(Cu^{2+}) + I(N)) \qquad (14)$$

where $S_{e\sigma}$ is the diatomic overlap integral between $3d_{x^2-y^2}$ a.o. and $2p_z$ a.o. of the ligand atom. $I(Cu^{2+})$ and $I(N)$ are the valence-state ionization potentials of the Cu^{2+} ion and nitrogen respectively. The F_σ constant is usually assumed to be 1.67.[18] Then, Eq. (14) gives $\beta_{e\sigma}=-3.54$ eV, using $S_{e\sigma}=0.0826$,[7] $I(Cu^{2+})=36.8$ eV, and $I(N)=14.5$ eV.

Using the values tabulated in Table 3 in Eq. (9), we obtain $\bar{E}=-3.44$ eV. Hence, $E_{e\sigma}^{CT}-\bar{E}$ amounts to 14.61 eV. This large value of $E_{e\sigma}^{CT}-\bar{E}$ compared with that of the d-d transition energies guarantees the validity of the replacement, $\bar{E}$, in the energy denominator to a constant, $\bar{E}$, obtained in the preceding section (Eq. (9)).

π-Bonding. In the case of Cu(II) complexes with the ligand which has a potency of the π-bonding, the treatment is complicated by the fact that we can no longer neglect $\gamma_{e\pi}^{in}$ and $\gamma_{e\pi}^{out}$ of Eqs. (8) and (11).

When the $\gamma_{e\pi}^{in}=\gamma_{e\pi}^{out}=\gamma_{e\pi}$ and $\gamma_{a\sigma}=\gamma_{a\pi}=0$ relations hold, as in $Pt(NH_3)_4CuCl_4$, Eq. (8) give same energy expressions as those of Smith by equating the covalency factors, σ* and π*, of the angular overlap model with $(1/5)\gamma_{e\sigma}$ and $(1/5)\gamma_{e\pi}$ respectively.[14] It is shown Eqs. (12) and (13) should also hold in this case. For $Pt(NH_3)_4CuCl_4$, we obtain $D_t/D_q=0.67$ and $D_q/D_s=0.43$ or $D_t/D_q=0.60$ and $D_q/D_s=0.75$, according to whether we use the assignment of Smith ($\omega_2<\omega_1<\omega_3$) or that of Hatfield and Piper ($\omega_1<\omega_2<\omega_3$)[15] respectively. The D_t/D_q ratio lies in the range of errors of Eq. (12) for both assignments. We can estimate $\gamma_{e\sigma}=(1/4)\gamma_{e\pi}$,[14] because the Wolfsberg-Helmholz relation holds approximately, as has been seen in the preceding subsection. Therefore, the D_q/D_s ratio can be expected from Eq. (11) to lie in the 0.1—0.6 range. It seems that the assignment of Smith is more reliable.

In Table 4, the d-d transition frequencies and the D_t/D_q and D_q/D_s ratios of the *O*-coordinated complexes with known crystal structures are listed. These complexes have distance longer by over 0.4 Å for the axial ligand than for the equatorial ligands.[11,16] As may be seen from Table 4, the $D_t/D_s=0.55\pm0.08$ ratios for these complexes coincide approximately with the value, 0.57, which is expected for the square-planar case, except in the case of $BaCuSi_4O_{10}$. The D_q/D_s ratio is 0.59 ± 0.08, somewhat smaller than the value for *N*-coordinated complexes, $D_q/D_s=0.73\pm0.06$. This indicates the presence of π-bonding, according to Eq. (11).

For the silicate $BaCuSi_4O_{10}$, the $D_t/D_q=1.0$ ratio was obtained following to the assignment of Clark and Burns[17] (Table 4). This high value seems unreasonable, because this complex has a complete square-planar structure ($R_e=1.91$ Å, $R_a=7.56$ Å), and because the *g*-tensor of this complex does not exhibit any abnormality compared with other complexes.[11,16] Hence, The $D_t/D_q=0.57$ ratio of square-planar complex can be expected to be fulfilled. The assignment of Clark and Burns does not seem to be very conclusive, however, because it has been made without a complete analysis of the polarized single-crystal spectrum. Another possible set of assignments which fulfills the relation of Eq. (12) is $\omega_1=15.8$ kK (or 12.9 kK), $\omega_2=12.9$ kK (or 15.8 kK), and $\omega_3=18.8$ kK. This assignment results in $D_t/D_q=0.53$ (or 0.48) and $D_q/D_s=0.42$ (or 0.70).

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