Characterization of Dimeric (Carboxylato)copper(II) Complexes by Electron Spin Resonance Spectra. Correlation of ESR Parameters with Singlet–Triplet Energy Separations

Yoneichiro Muto,[#] Michio Nakashima, Tadashi Tokii, Ikuo Suzuki,[†] Shigeru Ohba,[††] Omar W. Steward,[†††] and Michinobu Kato[*,††††,##]

Department of Chemistry, Faculty of Science and Engineering, Saga University, Honjyo-machi 1, Saga 840-8502

†Department of Electrical and Computer Engineering, Nagoya Institute of Technology, Gokiso Showa-ku, Nagoya 466-8555

††Department of Chemistry, Keio University, Hiyoshi 4-1-1, Kohoku-ku, Yokohama 223-8521

†††Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA

††††Aichi Prefectural University, Nagakute-cho, Aichi-gun, Aichi 480-1198

(Received August 16, 2001)

Linear correlations with positive slopes have been found for the zero-field splitting parameters (D) and the anisotropic exchange parameters (D^{ex}) vs the singlet–triplet separations ($-2J$) for $[Cu_2(O_2CR)_4(L)_2]$ (R = F_3C, FCH_2, Cl_3C, $ClCH_2$, CH_3, H, and C_6H_5CO) for a wide range of $-2J$ values, ca. 240–650 cm^{-1}. The values of D and D^{ex} for benzoylformate were found to be the highest ever studied. The quality of the linear relations of $-2J$, D^{ex} and D with the square of the coefficient of $2p_x$(C) of the symmetric HOMO of the bridging carboxylate ions, coeff,^{2} were found to be in the order, $-2J$ vs coeff^2 > D^{ex} vs coeff^2 > D vs coeff^2. A roughly linear relationship with a negative slope was found for D vs $-2J$ for a system, $[Cu_2(O_2CCMe_nPh_{3-n})_4(L)_2]$, in which the $-2J$ values cover a relatively small range, ca. 320–370 cm^{-1}.

During the past few decades, extensive studies on magnetic exchange interactions in dimeric copper(II) systems have been made.[1–5] Most of the magnetic studies on copper(II) dimers have been performed on di(μ-oxo)-bridged copper(II) complexes and dimeric (carboxylato)copper(II) complexes. The magnetic interaction in the copper(II) dimers is ascribed to a superexchange of the unpaired electrons of $d_{x^2-y^2}$ orbitals on each copper ion in the ground state through bridging ligands.[6] Historically, the studies of magneto–structural correlations of the (carboxylato)copper(II) dimer systems have been controversial.[1–3,5,7–9] In 1975, Hoffmann et al. proposed a fundamental spin–spin exchange mechanism for copper(II) dimeric systems based on the MO method:[10] the spin exchange occurs through overlapping of the symmetric metal MO and the symmetric HOMO of the carboxylate ion bridges. It was known that there is a correlation between the value of $-2J$ and the pK_a of the parent carboxylic acid.[7,11] However, the unexpectedly large values of $-2J$ for the (trifluoroacetato)copper(II) quinoline adduct (310 cm^{-1}) and the (formato)copper(II) adducts (ca. 500 cm^{-1}) where the conjugate acids of the ligands have a high acidity were not reasonably explained at that time. In 1981, an ab initio direct calculation of $-2J$ for (acetato)copper(II) hydrate ($-2J$ = 286 cm^{-1}) was made by de Loth, Daudey, and coworkers.[9] However, the highly sophisticated calculation had its limitations.[3,12] The weak point was that the procedure could not be used to explain the larger $-2J$ values (ca. 500 cm^{-1}) of the (formato)copper(II) dimers compared to the acetates, since the singlet–triplet energy separation is much smaller than the total energy, and hence a high precision of the theoretical calculation is required.[13] Under these circumstances, magneto–structural studies on (silanecarboxylato)copper(II) complexes ($-2J$ = ca. 1100 cm^{-1}) were carried out.[14,15] Further, a qualitative explanation has been successfully given for the magneto–structural correlation of the dimeric (carboxylato)copper(II) systems of a wide range of $-2J$ values of 220–1200 cm^{-1} based on molecular orbital calculations of the $RCOO^-$ ion (R = CH_3, H, $SiMe_3$, etc.).[17–19] Mulliken population analyses indicate that the electron population of the bridging $RCOO^-$ correlates with the $-2J$ values of the dimeric (carboxylato)copper(II) complexes. The key factor is the $2p_x$ orbital population of the central C atom in the symmetric HOMO of the bridging $RCOO^-$ ion (x is along the C–R bond): the larger is the $2p_x$ orbital population, the larger is the $-2J$ value of the (carboxylato)copper(II) complexes.

An ESR study of copper(II) dimers was initiated by Bleaney and Bowers for (acetato)copper(II) hydrate in 1952.[19] A few decades later, ESR studies of copper(II) dimers had been extensively investigated by Gatteschi and coworkers on di(μ-oxo)-

Present address: 13-3, 2-chome, Mizugae, Saga 840-0054
Present address: 5-603, 6, 4-chome, Kamezaki, Asakita-ku, Hiroshima 739-1742

bridged copper(II) complexes to elucidate the exchange interactions between the ground and excited states in these structures.[20–24] The notable conclusions of the studies are: there is no correlation between $-2J$ and D, and D is always negative for these dimeric single-atom bridged copper(II) systems.[25] Recently, we conducted an ESR study on (trichloroacetato)copper(II) (TCAC) complexes to observe the correlation of the ESR parameters, D and D^{ex}, with the Cu···Cu distances.[26] In this study, linear relationships with positive slopes were observed for D (or D^{ex}) vs Cu···Cu distances and for these ESR parameters vs $-2J$. The metal geometry of TCAC complexes varies from square pyramidal (SP) toward distorted trigonal bipyramidal (DTBP) with elongation of the Cu···Cu distance from 2.760 to 3.261 Å, accompanied by a change of $-2J$ from 240 to 79 cm^{-1} and of D from 0.369 to 0.173 cm^{-1}.

We have now extended such an ESR study to (carboxylato)copper(II) dimers with square pyramidal metal geometry (Fig. 1). In the most extensive studies made to date, the observed relationships between $-2J$ and D are rather ambiguous: there are compounds for which $-2J$ increases with increasing values of D, and *vice versa*.[27–33] A reason for this ambiguity may perhaps be in the inaccuracy of these magnetic data for the compounds within the small range of values observed for $-2J$ and D. In 1971, Yablokov et al. reported a magnetic and ESR study of (carboxylato)copper(II) complexes with a wide range of $-2J$ and D values, including (formato)copper(II) complexes.[35] They claim that in the dimeric (carboxylato)copper(II) complexes $-2J$ and D change in the same direction. However, the compounds on which their claim was based included compounds which have anomaly small $-2J$ values, ca. 100 cm^{-1}. These compounds are considered to have molecular structures different from those of the common (carboxylato)copper(II) dimers with D_{4h} symmetry.[8,35–38] Since then, to our knowledge, no explicit correlation between D and $-2J$ has been reported for dimeric (carboxylato)copper(II) complexes of D_{4h} symmetry. Under these circumstances, the finding that (silanecarboxylato)copper(II) complexes which have very large $-2J$ values is quite important. However, the ESR spectral intensity of these compounds is too weak to obtain any reasonable ESR parameter. Quite recently, Ohba et al.[40] have found that dimeric (benzoylformato)copper(II) complexes show $-2J$ values of ca. 650 cm^{-1}. In the present paper, we report on ESR spectral data for (benzoylformato)copper(II) pyridine derivatives. Newly collected data for (formato)copper(II) and (acetato)copper(II) pyridine derivatives are also included. Further, ESR, magnetic and reflectance spectral data have been systematically collected for $[Cu_2(O_2CCMe_nPh_{3-n})_4(L)_2]$ (L = pyridine, etc.) in the hope that such systematic detailed data collection would shed new light on the nature of the magneto-ESR correlations of (carboxylato)copper(II) dimers.

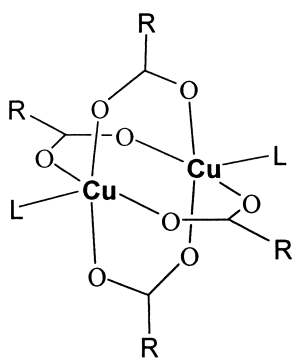

Fig. 1. Cage structure of (carboxylato)copper(II) dimers, $[Cu_2(O_2CR)_4(L)_2]$.

Experimental

Syntheses. (benzoylformato)copper(II) complexes were prepared by procedures reported by ohba et al.[39] All of the other compounds were prepared by procedures listed elsewhere.[40–42]

Physical Measurements. Polycrystalline powder ESR X-band spectra were recorded on a Jeolco JES-ME-2 spectrometer at room temperature. The resonance field values were corrected using DPPH (g = 2.0037) as an external standard. A NMR magnetic field meter EFM-2000AX (ECHO Electronics) was used as a magnetic field marker. The reflectance spectra were recorded on Hitachi 323 and Nihonbunko UV-570DS spectrophotometers. The ESR parameters for $[Cu_2(O_2CR)_4(L)_2]$ (R = CH_3, H and C_6H_5CO; L = 2-, 3-, 4-picoline and in addition pyridine for R = C_6H_5CO) are given in Table 1.[43] The ESR, magnetic and electronic reflectance spectral data for $[Cu_2(O_2CCMe_nPh_{3-n})_4(L)_2]$ (n = 0–3; L = pyridine, 2-, 3-, 4-picoline, 2, 6-lutidine and quinoline) are listed in Table 2.[43] The ESR spectra of some selected compounds in Tables 1 and 2 are given in Fig. 2. The ESR parameters ($g_{//}$, $g_\perp$ and D) were obtained from the observed values of H_{z_1}, $H_{\perp_2}$ and H_{z_2} after Chasteen.[44]

Results and Discussion

In the present study, the interpretation of the ESR spectral data of (carboxylato)copper(II) complexes was based on a pa-

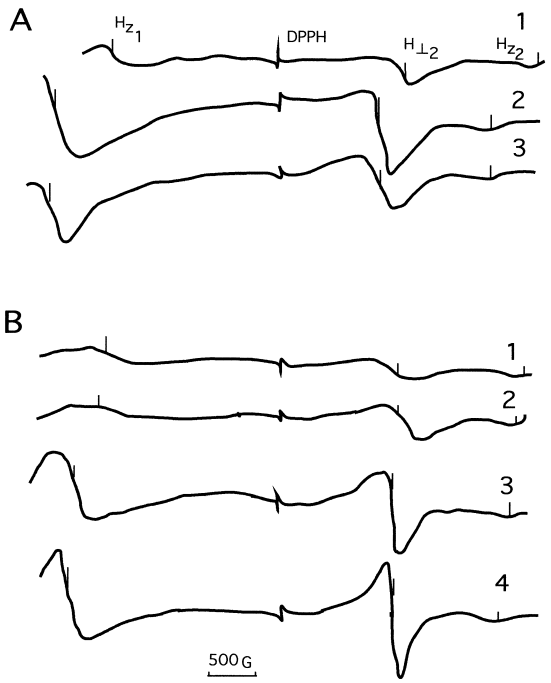

Fig. 2. ESR X-band spectra of polycrystalline samples at room temperature. A $[Cu_2(O_2CR)_4(3\text{-picoline})_2]$: curve 1, R = CH_3; curve 2, R = H; curve 3, R = C_6H_5CO.
B $[Cu_2(O_2CCMe_nPh_{3-n})_4(3\text{-picoline})_2]$: curve 1, n=0; curve 2, n = 1; curve 3, n = 2; curve 4, n = 3.

Table 1. ESR and Magnetic Data for $[Cu_2(O_2CR)_4(L)_2]$[a)]

	Compound	$g_{//}$	$g_\perp$	D^{dip} / cm^{-1}	D / cm^{-1}	D^{ex} / cm^{-1}	$-2J$ / cm^{-1}	Reference[b)]		
	R = F_3C									
1	L = quinoline	2.44	2.17	−0.300	0.425	0.725	310	46	47	
	R = FCH_2									
2	L = quinoline	2.397	2.095	−0.3402	0.395	0.735	364	48	49	50
	R = Cl_3C									
3	L = 2-F-benzothiazol	2.379	2.084	−0.3229	0.369	0.692	240	26	51	
4	4,7-Cl_2-quinoline	2.402	2.071	−0.3173	0.380	0.697	237	26	51	
	R = $ClCH_2$									
5	L = quinoline	2.375	2.087	−0.3349	0.371	0.706	331	50	52	
6	2-picoline	2.375	2.079	−0.3259	0.373	0.699	320	50	53	
	R = CH_3									
7	L = 2-picoline	2.380	2.066	−0.3540	0.356	0.710	332	*	16	
8	3-picoline	2.377	2.069	−0.3721	0.354	0.726	326	*	16	
9	4-picoline	2.389	2.072	−0.3696	0.354	0.724	333	*	16	
	R = H									
10	L = 2-picoline	2.397	2.113	−0.3377	0.420	0.758	482	*	16	
11	3-picoline	2.368	2.079	−0.3444	0.423	0.767	489	*	16	
12	4-picoline	2.296	2.135	−0.3458	0.424	0.769	489	*	16	
	R = C_6H_5CO									
13	L = 2-picoline	2.453	2.134	−0.3431	0.483	0.826	656	*	39	
14	3-picoline	2.385	2.099	−0.3381	0.469	0.807	649	*	39	
15	4-picoline	2.473	2.143	−0.3588	0.486	0.845	625	*	39	
16	pyridine	2.374	2.091	−0.3314	0.463	0.794	648	*	39	

a) For D^{dip}, D, and D^{ex}, see text and Ref. 6. b) * indicates the presnt study.

per by Solomon et al.,[6] as was also made in our previous paper on (trichloroacetato)copper(II) (TCAC) complexes.[27]

The zero-field splitting parameter (D) is given by the sum of two components,[6,46]

$$D = D^{ex} + D^{dip}, \quad (1)$$

where D^{ex} is the component from an anisotropic exchange and D^{dip} is the component from a through-space interaction between the two point magnetic moments centered on the two metal ions,

$$D^{ex} = -1/16(g_{//} - 2)^2 J_{xy,\,x^2-y^2} + 1/4(g_\perp - 2)^2 J_{xzyz,\,x^2-y^2}, \quad (2)$$

$$D^{dip} = -(g_{//}{}^2 + 0.5g_\perp{}^2)\beta^2/r^3, \quad (3)$$

where $J_{xy,\,x^2-y^2}$ and $J_{xzyz,\,x^2-y^2}$ are the exchange interactions between an unpaired electron in the $d_{x^2-y^2}$ orbital of a copper ion in the ground state and a second electron in the d_{xy} and $d_{xz,\,yz}$ orbitals, respectively, of the other copper ion in excited states. In Eq. 3, r is the Cu···Cu distance. The values of D^{dip} were calculated by Eq. 3 using the observed values of $g_{//}$ and $g_\perp$ as well as the values of r from the references given in Table 1. The values of D^{ex} were obtained by substituting the values of D and D^{dip} into Eq. 1.

In Table 1, the values of $g_{//}$, $g_\perp$, D^{dip}, D, D^{ex} and $-2J$ of $[Cu_2(O_2CR)_4(L)_2]$ are listed together with the data for some selected (carboxylato)copper(II) complexes.

It is quite important to note that there is a fundamental difference in the characteristics of the ESR parameters between (carboxylato)copper(II) complexes and di(μ-oxo)-bridged copper(II) complexes. As can be seen in Table 1, D and D^{ex} of (carboxylato)copper(II) complexes are always positive. On the other hand, D of di(μ-oxo)-bridged copper(II) complexes is always negative.[21,23] The negative D value of the latter complexes is essentially due to the orthogonality of the magnetic orbitals, d_{xy} and $d_{x^2-y^2}$, in these complexes of SP metal symmetry.

Based on a variety of magneto-optical techniques, in 1989 Solomon et al.[6] reported for (acetato)copper(II) pyrazine a number of exchange energies, $J_{n,\,x^2-y^2}$ and $J_{n,\,n}$, with n being x^2-y^2, xy, xz, yz and z^2. In this study, $J_{xzyz,\,x^2-y^2}$ and $J_{z^2,\,x^2-y^2}$ were found to be ferromagnetic in accordance with that the d orbitals are orthogonal in D_{4h} symmetry. However, $J_{xy,\,x^2-y^2}$ was found to be -25 cm^{-1}, which is weakly antiferromagnetic. In this case, the spin–orbit coupling is comparatively large and allows the ground state to mix with the d_{xy} excited state as long as $J_{xy,\,x^2-y^2}$ becomes weakly antiferromagnetic. Their results are quite remarkable in the history of ESR studies of (carboxylato)copper(II) complexes. They have afforded experimental and theoretical bases, even qualitatively, for the fact that D^{ex} and D are positive for the dimeric systems.

In 1975, Hoffmann et al.[10] proposed a fundamental MO mechanism for the superexchange interaction in (carboxylato)copper(II) complexes: the spin-exchange occurs through an overlap of the symmetric metal MO composed of $d_{x^2-y^2}$ orbitals and the symmetric highest occupied MO's (HOMO's) of the bridging carboxylate ions. The symmetric HOMO of the carboxylate ion is constructed from the $2p_x$ orbitals of the O atoms and from the $2p_x$ orbital of the central C atom as $2p_x$(O)–$2p_x$(C)–$2p_x$(O). In previous studies,[16,39] we found a linear correlation between the diagonal part of the $2p_x$(C) electron popu-

Table 2. ESR, Magnetic, and Electronic Reflectance Spectral Data for $[Cu_2(O_2CCMe_nPh_{3-n})_4(L)_2]$[a)]

Compound	$-2J$[b)]	$\nu_{max} \times 10^{-3}$[c)]			$g_{//}$	$g_\perp$	g_{av}	D[d)]	$D/(-2J)\times10^{3}$[e)]
	cm^{-1}	cm^{-1}						cm^{-1}	
L = pyridine									
n = 0[f)]	321	8.53	13.53	25.64	2.38	2.07	2.18	0.366	1.14
1	368	8.00	13.51	26.31	2.415	2.107	2.214	0.381	1.04
2	362	8.33	14.08	25.64	2.395	2.091	2.197	0.372	1.03
3	368	7.90	14.08	25.77	2.407	2.098	2.206	0.371	1.01
L = 2-picoline									
n = 0	312	9.71	13.15	25.38[sh]	2.332	2.142	2.207	0.359	1.15
1	340	7.69	13.33	25.64	2.469	2.120	2.242	0.412	1.21*
2	351	7.63	13.79	26.31	2.413	2.104	2.212	0.379	1.08
3	372	8.70	13.89	25.45	2.403	2.097	2.204	0.374	1.01
L = 3-picoline									
n = 0	337	9.09	13.15	24.45	2.388	2.162	2.240	0.430	1.28
1	346	9.17	13.51	25.19	2.431	2.117	2.226	0.420	1.21
2	358	8.85	13.61	25.91	2.397	2.099	2.203	0.376	1.05
3	363	8.83	13.69	25.77	2.384	2.094	2.195	0.369	1.02
L = 4-picoline									
n = 0[g)]	326	8.69	13.79	25.64	2.332	2.096	2.177	0.392	1.20
1	358	8.33	13.51	26.31	2.419	2.118	2.223	0.386	1.08
2	352	8.70	13.98	25.64	2.376	2.089	2.189	0.365	1.04
3	325	8.33	13.89	25.64	2.395	2.109	2.208	0.386	1.19*
L = 2,6-lutidine[h)]									
n = 2[i)]	337	8.70	13.33	27.02	2.370	2.167	2.236	0.370	1.10
3	383	9.09	13.60	25.64	2.432	2.100	2.216	0.382	1.00
L = quinoline									
n = 0	327	10.5[sh]	13.18	28.49	2.409	2.111	2.214	0.401	1.23
1[j)]	339	9.09	13.51	26.04	2.426	2.106	2.218	0.384	1.13
2[k)]	353	9.09	13.42	25.84	2.432	2.100	2.216	0.382	1.08
3	371	10.00	13.99	25.51	2.403	2.099	2.205	0.370	1.00

a) L: monodentate non-carboxylato ligand. Abbreviations: SP (square pyramidal) and TBP (trigonal bipyramidal). b) Singlet–triplet separation. c) Electronic reflectance spectral data. d) Zero-field splitting parameter.[56] e) The two values marked with an asterisk are the exceptions. f) Three dimeric compounds were obtained for L = pyridine and $n = 0$[59]: (1) a benzene solvate with $-2J = 187$ cm^{-1} which has a metal geometry distorted toward TBP; (2) a non-solvate with $-2J = 173$ cm^{-1} whose metal geometry should be similar to (1) on its small value of $-2J$; (3) a non-solvate with $-2J = 321$ cm^{-1} whose metal geometry should be SP on its common value of $-2J$. g) Were obtained two solvates (benzene and toluene) which both have metal geometries distorted toward TBP.[60] The $-2J = 326$ cm^{-1} was observed for the efflorescent sample whose metal geometry should be SP on its common value of $-2J$. h) Only a mononuclear compound, $Cu(O_2CCPh_3)_2$·(2,6-lutidine), was obtained for $n = 0$ and no product was produced for $n = 1$. i) A benzene solvate with $-2J = 310$ cm^{-1} was obtained which has a metal geometry moderately distorted toward TBP.[61] The $-2J = 337$ cm^{-1} was measured for the efflorescent sample whose metal geometry should be SP on its common value of $-2J$. j) Diquinoline adduct with SP metal geometry.[16] k) Non-adduct with SP metal geometry.[16]

lation in the symmetric HOMO of the carboxylate ion, i. e., twice the square of the coefficient of the $2p_x$(C) atomic orbital and the $-2J$ for (carboxylato)copper(II) complexes.

In the present study, linear correlations were observed between the data of the ESR and magnetic parameters in Table 1 and the square of the coefficient of the $2p_x$(C) of the symmetric HOMO of the carboxylate ion, $[\text{coeff. } 2p_x(C)_{\text{sym. HOMO}}]^2$ (coeff^2). They are shown in Fig. 3, Fig. 4, Fig. 5, Fig. 6 and Fig. 7. The results of linear-regression analyses are listed in Table 3. The observed orders of the linearities of these correlations in terms of R^2 are:

$$D^{ex} \text{ vs } -2J > D \text{ vs } -2J, \quad (4)$$

and

$$-2J \text{ vs coeff}^2 > D^{ex} \text{ vs coeff}^2 > D \text{ vs coeff}^2, \quad (5)$$

The observed order may be interpreted based on the characteristics of the ESR and magnetic parameters. The ground-state exchange energy, $-2J_{x^2-y^2,\ x^2-y^2}$, is quite straightforward, since it is related to the exchange pathway proposed by Hoffmann et al.,[10] and has no contribution from excited states. On the other hand, D^{ex} is composed of two exchange energies, $J_{xy,\ x^2-y^2}$ and $J_{xzyz,\ x^2-y^2}$. D is composed of D^{ex} and, D^{dip} which has no contribution from the excited states. Thus, D is the most complex. The simplicity of the parameters apparently correlates with the quality of the linear relations.

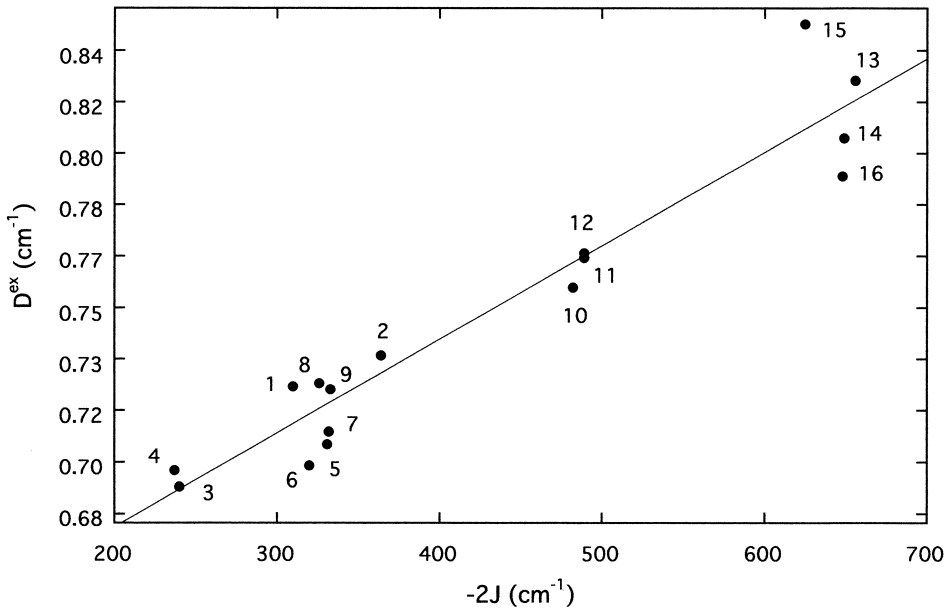

Fig. 3. D^{ex} vs $-2J$ for $[Cu_2(O_2CR)_4(L)_2]$. The numbers in the figure are those for the compounds listed in Table 1.

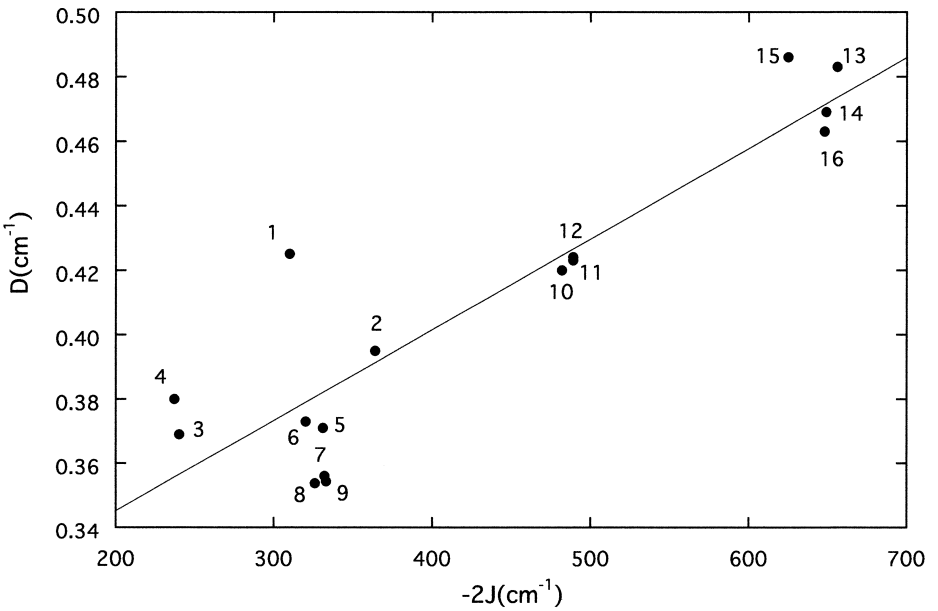

Fig. 4. D vs $-2J$ for $[Cu_2(O_2CR)_4(L)_2]$. The numbers in the figure are those for the compounds listed in Table 1.

The ground state $J_{x^2-y^2,\, x^2-y^2}$ spin-exchange pathway in (carboxylato)copper(II) dimers is depicted after Hoffmann[10] and Yamanaka[16] as

$$d_{x^2-y^2}(Cu)_{sym.\,MO} - [2p_x\,(O)\text{–}2p_x\,(C)\text{–}2p_x\,(O)]_{sym.\,HOMO} - d_{x^2-y^2}\,(Cu)_{sym.\,MO}, \quad (6)$$

In the exchange mechanism, the inclusion of an effective spin–orbit coupling would allow the ground state to mix with the excited d_{xy} state, leading an electron in the d_{xy} to exchange by pathway (6).

The observed order of the quality of the linear relations, (4) and (5), would reflect the validity of the correlation among three equations (Eqs. 1, 2, and 3) and of the ground state-excited state exchange mechanism of $J_{xy,\, x^2-y^2}$.

In order to examine the historically ambiguous relation between $-2J$ and D, systematic ESR, magnetic and electronic spectral studies were carried out on the $[Cu_2(O_2CCMe_nPh_{3-n})_4(L)_2]$ system (see Table 2).[54] Unfortunately, we were unable to obtain systematic data of D^{ex} for the system, since a structural determination could not be made for most of the compounds, which were obtained as polycrystalline materials. Some were obtained as crystalline solvates, and the most of them were found to have a DTBP metal geometry. Their $-2J$ values increased after efflorescences, suggesting that the TBP distortion was relaxed toward SP upon removing the solvent molecules.[59,60] The Compounds in Table 2 are generally assumed to have the square-pyramidal D_{4h} metal geometry found in com-

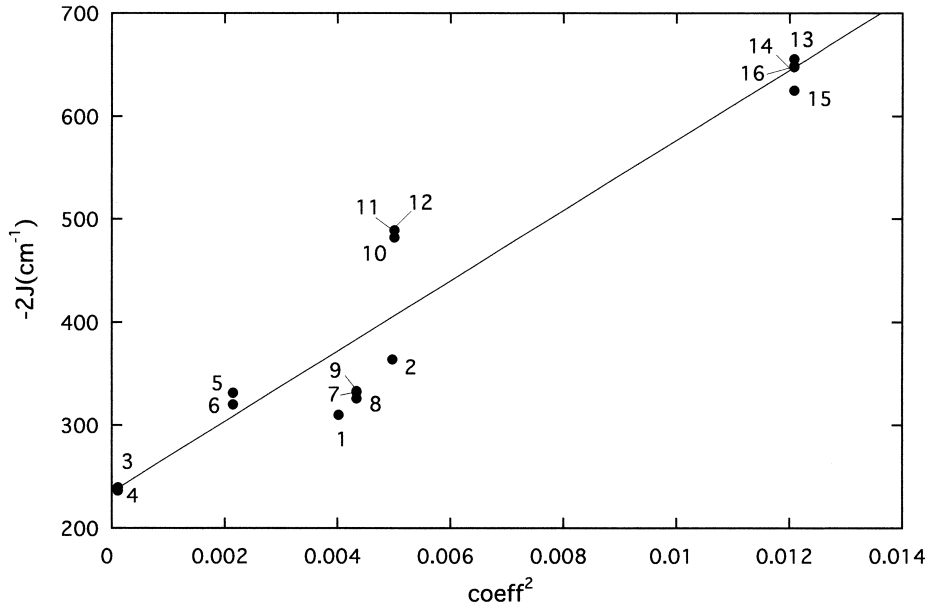

Fig. 5. $-2J$ vs coeff^2 for $[Cu_2(O_2CR)_4(L)_2]$. The numbers in the figure are those for the compounds listed in Table 1.

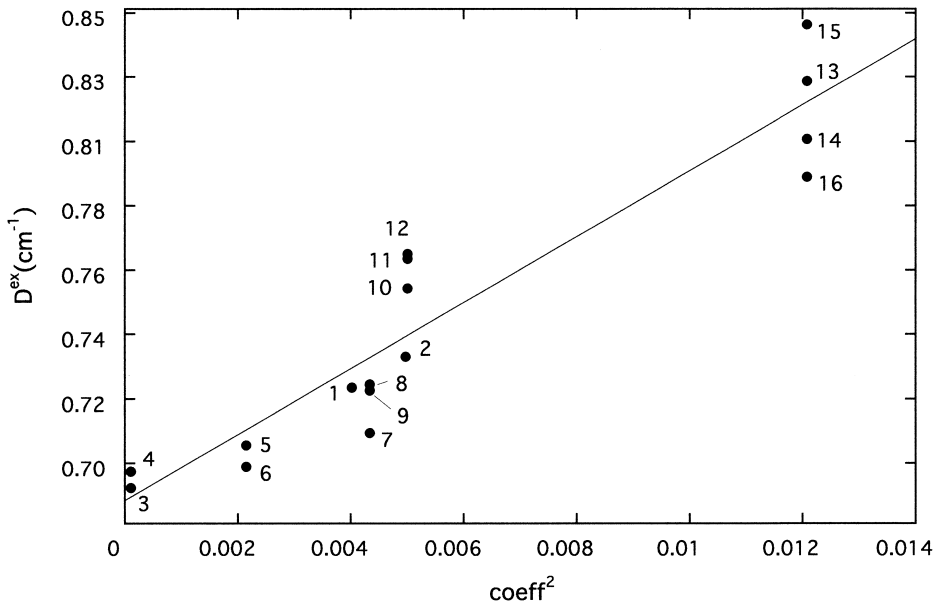

Fig. 6. D^{ex} vs coeff^2 for $[Cu_2(O_2CR)_4(L)_2]$. The numbers in the figure are those for the compounds listed in Table 1.

mon (carboxylato)copper(II) complexes based on their relatively large $-2J$ values. In this system, the electron-donating character of the CMe_nPh_{3-n} group should increase along with an increase of n as the result of the larger electron donating property of Me than the Ph group. The ν_{max} of band I, which appears at about 13000–14000 cm^{-1}, is taken as a diagnosis of the ligand field strength in the (carboxylato)copper(II) complexes, and there is a parallel relationship between the ν_{max} and $-2J$ values.[5] For most of the complexes with the same L, the values of $-2J$ and ν_{max} both increase with an increase of n, a reasonable trend of the electronic property of the CMe_nPh_{3-n} group. However, although there are a few irregularities in Table 2, D and $-2J$ apparently vary in an opposite direction to each other with a change of n. This tendency observed between D and $-2J$ is more easily observed by consulting the last column of Table 2: the value of $D/(-2J)$ decreases as n increases with some irregularities indicated by asterisks. A linear-regression analysis was carried out for the data of D and $-2J$ in Table 2; the linearity for D vs $-2J$ is quite poor in terms of R^2 (= 0.0333) with a negative slope of $a = -1.74 \times 10^{-4}$ and $b = 0.444$ for the linear equation, $y = ax + b$. Even though some irregularities are observed, it is notable that we have been able to confirm the reverse relation between D and $-2J$ for the system, $[Cu_2(O_2CCMe_nPh_{3-n})_4(L)_2]$, while referring to the ambiguity in the relation between D and $-2J$ for (carboxylato)copper(II) complexes in past studies.[27–33] A possible mechanism for the antiparallel relation between D and $-2J$ may be as follows. When n of the system increases, the

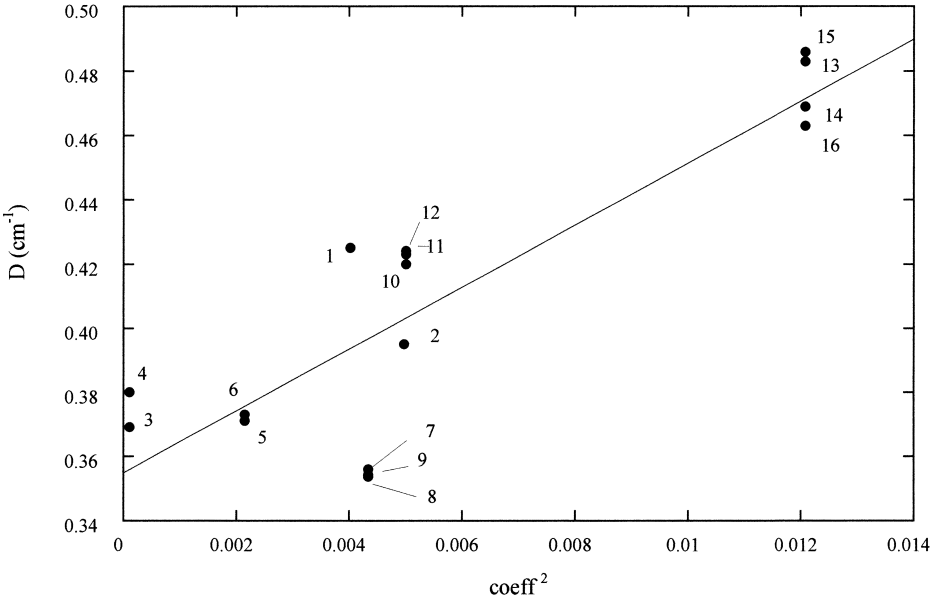

Fig. 7. D vs coeff^2 for $[Cu_2(O_2CR)_4(L)_2]$. The numbers in the figure are those for the compounds listed in Table 1.

Table 3. The Results of the Linear-Regression Analyses of the Data of D, D^{ex} and $-2J$ for $[Cu_2(O_2CR)_4(L)_2]$[a),b)]

Linear correlations	a	b	R^2
D^{ex} vs $-2J$	3.09×10^{-4}	0.617	0.919
D vs $-2J$	2.81×10^{-4}	0.289	0.812
$-2J$ vs coeff^2	3.41×10^{4}	2.35×10^{2}	0.897
D^{ex} vs coeff^2	1.088×10^{1}	0.688	0.879
D vs coeff^2	9.65	0.355	0.737

a) The equation employed for the analyses is $y = ax + b$, where y is one of D^{ex}, D, and $-2J$, and x is $-2J$ or coeff^2. The evaluation of the analyses is expressed by the coefficient of determination, R^2, which is the square of the correlation coefficient R, $R = S_{xy}/S_xS_y$, where S_{xy} is the covariance of x and y, and S_x and S_y are the standard deviations of the distributions of x and y.

b) coeff^2 is the square of the coefficient of $2p_x$(C) of the symmetric HOMO of $RCOO^-$, $[\text{coeff. } 2p_x(C)_{\text{sym. HOMO}}]^2$: the values are 4.02×10^{-3} ($R = F_3C$), 4.97×10^{-3} (FCH_2), 0.1103×10^{-3}(Cl_3C), 2.15×10^{-3}($ClCH_2$), 4.34×10^{-3} (CH_3), 5.01×10^{-3} (H), and 12.08×10^{-3} (C_6H_5CO) (see Ref. 17 and 40).

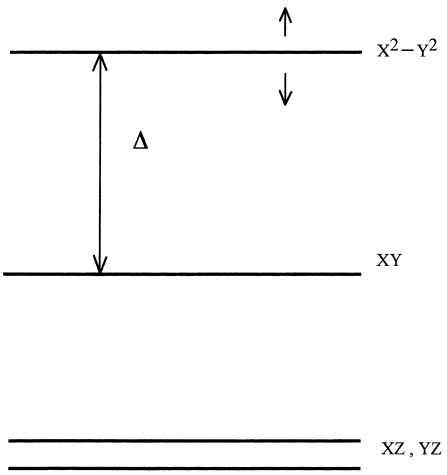

Fig. 8. Schematic energy-level splitting diagram of the 3d orbitals of the D_{4h} (acetato)copper(II) system.[6, 61]

electron-donating property of the CMe_nPh_{3-n} group increases. Then, the $d_{x^2-y^2}$ orbital will go upward to yield an increase in the energy separation between the $d_{x^2-y^2}$ and d_{xy} orbitals, Δ, which is an unfavorable condition for the $d_{x^2-y^2}$ ground state to mix with the d_{xy} excited state by spin–orbit coupling. As a result, the antiferromagnetism of the exchange interaction, J_{xy,x^2-y^2}, decreases, leading to a decrease in the value of D (see Ref. 56 and the schematic energy-level splitting diagram of the 3d orbitals in Fig. 8). Another possible mechanism for the reverse relation between $-2J$ and D is as follows. A systematic small change in the metal geometry can be produced by a systematic structural change of the CMe_nPh_{3-n} group, which is accomplished by successive changes of n. If the structural change is such as to cause the metal geometry to deviate from D_{4h} symmetry, this change should result in some direct mixing of the orthogonal magnetic orbitals, depending on the magnitude of the structural change. The observation that the larger is the number of bulky guoup (Ph), the larger is the value of D, seems to suggest that the second mechanism also is a reasonable possibility. The two mechanisms given above could be operative simultaneously. The magnitude of the ESR parameters may be assumed to be determined by two factors. One is the efficiency of the mixing of the ground state ($d_{x^2-y^2}$) and the excited state (d_{xy}) by spin–orbit coupling. Another is the $2p_x$(C) electron population in the exchange pathway of (6). In $[Cu_2(O_2CCMe_nPh_{3-n})_4(L)_2]$, the first factor may be the most effective in determining the size of D, since the $2p_x$(C) electron population does not vary much as a whole in the system, as is seen from the small size of the variation in $-2J$, ca. 50 cm^{-1} (= 370–320 cm^{-1}). On the other hand, in $[Cu_2(O_2CR)_4(L)_2]$, the $2p_x$(C) electron population is to be considered much more important in determining the size of the ESR parameters, since

the variation in $-2J$ in this system is quite large, ca. 400 cm^{-1} (= 650–240 cm^{-1}).

The data collected in Tables 1 and 2 suggest that dimeric copper(II) carboxylates can be grouped into two: one where D (or D^{ex}) is proportional to $-2J$ and the other where D is inversely proportional to $-2J$. Thus, the size and the electronic property of R in the bridging $RCOO^-$ are the key factors. The copper(II) carboxylates with R, whose electronic property makes the $2p_x$ orbital population of the central C atom in the symmetric HOMO of the bridging $RCOO^-$ ion to widely change, yield a proportional relationship between D (or D^{ex}) and $-2J$ (Table 1). In copper(II) silanecarboxylates and benzoylformates whose $-2J$ values are large, the Si atom and the C=0 group, which are directly bonded to the COO bridge, are both σ-donors and π-acceptors.[40] On the other hand, the copper(II) carboxylates with a large R and whose electronic property can only slightly influence the $2p_x$ orbital population of the central C atom in the symmetric HOMO of the bridging $RCOO^-$, give rise to the relationship of inverse proportionality between D and $-2J$ (Table 2), where the greater is the steric hindrance of R, the smaller is the value of $-2J$ and the greater does the value of D become.

It would be hoped that the data of the present study will be much help in interpreting the ESR spectra observed for the related compounds and dimeric Cu(II) containing proteins and enzymes.[63,63]

The authors wish to express their thanks to Professor Edward I. Solomon of Stanford University for his helpful discussions.

References

1 M. Melnik, *Coord. Chem. Rev.*, **36**, 1 (1981).
2 M. Melnik, *Coord. Chem. Rev.*, **42**, 259 (1982).
3 D. N. Hendrickson, "Magneto–Structural Correlations in Exchange Coupled Systems," ed by R. D. Willett, D. Gatteschi, O. Kahn, and D. Reidel, Dordrecht (1985), NATO ASI Ser. C, Vol. 140, p. 523.
4 W. E. Hatfield, "Magneto-Structural Correlations in Exchange Coupled Systems," ed by R. D. Willett, D. Gatteschi, O. Kahn, and D. Reidel, Dordrecht (1985), NATO ASI Ser. C, Vol. 140, p. 555.
5 M. Kato and Y. Muto, *Coord. Chem. Rev.*, **92**, 45 (1988).
6 P. K. Ross, M. D. Allendorf, and E. I. Solomon, *J. Am. Chem. Soc.*, **111**, 4009 (1989).
7 R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J. Chem. Soc., Dalton Trans.*, **1972**, 428.
8 R. J. Doedens, "Progress in Inorganic Chemistry," ed by S. J. Lippard, John Wiley & Sons, New York (1976), Vol. 21, p. 209.
9 P. de Loth, P. Cassoux, J. P. Daudey, and J. P. Malrieu, *J. Am. Chem. Soc.*, **103**, 4007 (1981).
10 P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975).
11 M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).
12 O. Kahn, "Molecular Magnetism," VCH Publishers, New York (1993).
13 Private communication between S. Ohba and J. P. Daudey in 1990.
14 O. W. Steward, R. C. McAfee, S-C. Chang, S. R. Piskor, W. J. Schreiber, C. F. Jury, C. E. Taylor, J. F. Pletcher, and C-S. Chen, *Inorg. Chem.*, **25**, 771 (1986).
15 H. Uekusa, S. Ohba, Y. Saito, M. Kato, O. W. Steward, T. Tokii, and Y. Muto, *Acta Crystallogr., Sect. C*, **46**, 1805 (1990).
16 M. Yamanaka, H. Uekusa, S. Ohba, Y. Saito, S. Iwata, M. Kato, T. Tokii, Y. Muto, and O. W. Steward, *Acta Crystallogr., Sect. B*, **47**, 344 (1991).
17 S. Ohba, M. Kato, T. Tokii, Y. Muto, and O. W. Steward, *Mol. Cryst. Liq. Cryst.*, **233**, 335 (1993).
18 S. Ohba, *Nippon Kessho Gakkai Shi*, **35**, 334 (1993).
19 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).
20 L. Banci, A. Bencini, and D. Gatteschi, *J. Am. Chem. Soc.*, **105**, 761 (1983).
21 A. Bencini, D. Gatteschi, and C. Zanchini, *Inorg. Chem.*, **24**, 700 (1985).
22 A. Bencini, D. Gatteschi, C. Zanchini, and W. Haase, *Inorg. Chem.*, **24**, 3485 (1985).
23 M.-F. Charlot, Y. Journaux, O. Kahn, A. Bencini, D. Gatteschi, and C. Zanchini, *Inorg. Chem.*, **25**, 1060 (1986).
24 A. Bencini, D. Gatteschi, and C. Zanchini, *Inorg. Chem.*, **25**, 2211 (1986).
25 To our knowlede, for the single-atom bridged dimeric copper(II) complexes, noteworthy experimental studies have not been reported since Gatteschi and coworkers' extensive studies. However, quite recently theoretical studies to explain the relation between $-2J$ and molecular geometry in such dimeric copper(II) complexes have appeared: see D. A. Case, L. Noodleman and J. Li, "Metal–Ligand Interactions in Chemistry, Physics and Biology," ed by N. Russo and D. R. Salahub, Kluwer Academic Publishers, Dordrecht (2000), NATO Science Ser. C, Vol. 546, p. 19, and the references therein.
26 Y. Muto, H. Horie, T. Tokii, M. Nakashima, M. Koikawa, O. W. Steward, S. Ohba, H. Uekusa, S. Husebye, I. Suzuki, and M. Kato, *Bull. Chem. Soc. Jpn.*, **70**, 1573 (1997).
27 J. Lewis, F. E. Mabbs, L. K. Royston, and W. R. Smail, *J. Chem. Soc. A*, **1969**, 291.
28 L. N. Romanenko, Yu. V. Yablokov, V. V. Gavrilov, L. N. Milkova, and A. V. Ablov, *Dokl. Akad. Nauk SSSR*, **188**, 1332 (1969),
29 F. G. Herring, B. Landa, R. C. Thompson, and C. F. Schwerdtfeger, *J. Chem. Soc. A*, **1971**, 528.
30 M. Melnik and R. Uggla, *Acta Chem. Scand.*, **26**, 4166 (1972).
31 M. Melnik and J. Mrozinski, *J. Mol. Struct.*, **57**, 135 (1979).
32 F. Cariati, L. Erre, G. Micera, L. Menabue, M. Saladini, and P. Prampolini, *Inorg. Chim. Acta*, **63**, 85 (1982).
33 J. Mrozinski and E. Heyduk, *J. Coord. Chem.*, **13**, 291 (1984).
34 Yu. V. Yablokov, V. V. Gavrilov, L. N. Milkova, and A. V. Ablov, *J. Struct. Chem. (USSR)*, **12**, 216 (1971).
35 D. B. W. Yawney, J. A. Moreland, and R. J. Doedens, *J. Am. Chem. Soc.*, **95**, 1164 (1973).
36 T. Tokii, S. Emori, and Y. Muto, *Bull. Chem. Soc. Jpn.*, **47**, 2887 (1974).
37 T. Tokii and Y. Muto, *Bull. Chem. Soc. Jpn.*, **49**, 1849 (1976).
38 M. Mikuriya, S. Kida, I. Ueda, T. Tokii, and Y. Muto, *Bull. Chem. Soc. Jpn.*, **50**, 2464 (1977).
39 A. Harada, M. Tsuchimoto, S. Ohba, K. Iwasawa, and T.

Tokii, *Acta Crystallogr., Sect. B*, **53**, 654 (1997).

40 T. Tokii, T. Ikeda, and Y. Muto, *Bull. Chem. Soc. Jpn.*, **55**, 3925 (1982).

41 T. Tokii and Y. Muto, *Bull. Chem. Soc. Jpn.*, **56**, 1549 (1983).

42 Y. Muto, A. Sasaki, T. Tokii, and M. Nakashima, *Bull. Chem. Soc. Jpn.*, **58**, 2572 (1985).

43 The values of the magnetic fields of the resonance used in obtaining the ESR parameters are deposited with the values of the parameters as Document No. 75013 at the Office of the Editor of Bull. Chem. Soc. Jpn.

44 N. D. Chasteen, *Inorg. Chem.*, **10**, 2339 (1971).

45 M. L. Boillot, Y. Journaux, A. Bencini, D. Gatteschi, and O. Kahn, *Inorg. Chem.*, **24**, 263 (1985).

46 J. A. Moreland and R. J. Doedens, *J. Chem. Soc., Chem. Commun.*, **1974**, 28.

47 J. A. Moreland and R. J. Doedens, *J. Am. Chem. Soc.*, **97**, 508 (1975),

48 Yu. A. Simonov, A. A. Dvorkii, Yu. V. Yablokov, L. N. Milkova, and A. V. Ablov, *Zh. Strukt. Khim.*, **19**, 175 (1978).

49 Yu. V. Yablokov, A. V. Ablov, L. N. Milkova, and L. N. Romanenko, *Dokl. Akad. Nauk SSSR*, **180**, 659 (1968).

50 Yu. V. Yablokov, L. N. Mosina, Yu. A. Simonov, L. N. Milkova, A. V. Ablov, and V. I. Ivanov, *Zh. Strukt. Khim.*, **19**, 42 (1978).

51 H. Uekusa, S. Ohba, T. Tokii, Y. Muto, M. Kato, S. Husebye, O. W. Steward, S-C. Chang, J. P. Rose, J. F. Pletcher, and I. Suzuki, *Acta Crystallogr., Sect. B*, **48**, 650 (1992).

52 Yu. A. Simonov, V. I. Ivanov, A. V. Ablov, L. N. Milkova, and T. I. Malinovskii, *Zh, Strukt. Khim.*, **17**, 516 (1976).

53 G. Dovey and F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, **1970**, 2803.

54 M. Nakashima, T. Tokii, Y. Muto, S. Ohba, O. W. Steward, M. Kato, and I. Suzuki, 30th International Conference on Coordination Chemistry, Kyoto, July 1994, *Abstr.*, PS2–52.

55 D can be approximated by the first term in Eq. 2 as

$$D \fallingdotseq -1/16\,(g_{//} - 2)^2\, J_{xy,\,x^2-y^2}.$$

This approximation is based on the fact that D^{dip} is comparatively small and the second term in Eq. 2 is negligible owing to the quantity $(g_{\perp} - 2)$ being small.[57,58]

56 V. K. Voronkova, M. V. Eremin, L. V. Mosina, and Yu. V. Yablokov, *Mol. Phys.*, **50**, 379 (1983).

57 O. Kahn, *Angew. Chem. Int. Ed. Engl.*, **24**, 834 (1985).

58 O. W. Steward, M. Kato, S-C. Chang, M. Sax, C-H. Chang, C. F. Jury, Y. Muto, T. Tokii, T. Taura, J. F. Pletcher, and C. S. Yoo, *Bull. Chem. Soc. Jpn.*, **64**, 3046 (1991).

59 M. Yamanaka, S. Ohba, T. Tokii, C. F. Jury, O. W. Steward, and M. Kato, *Acta Crystallogr., Sect. C*, **49**, 1469 (1993).

60 T. Fujita, S. Ohba, M. Nagamatsu, T. Tokii, C. F. Jury, O. W. Steward, and M. Kato, *Acta Crystallogr., Sect. C*, **49**, 2095 (1993).

61 F. A. Cotton, G. Wilkinson and P. L. Gaus, "Basic Inorganic Chemistry," 3rd ed, John Wiley & Sons, New York (1995).

62 E. I. Solomon, M. J. Baldwin, and M. D. Lowery, *Chem. Rev.*, **92**, 521 (1992).

63 A. E. Palmer, D. W. Randall, F. Xu, and E. I. Solomon, *J. Am. Chem. Soc.*, **121**, 7138 (1999).