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Comparison of ESR Signal Intensities of Some Binuclear Copper Complexes

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ESR signal intensities of two kinds of binuclear copper complex were measured by the two-step integral method with a multi-mode resonator cavity. The intensities standardized with $CuSO_4 \cdot 5H_2O$ are the proper values for these substances, and can be compared with each other. The intensities of oxamide type complexes (A-group) were a few tens of percent of the intensity of $CuSO_4 \cdot 5H_2O$, while the intensities of binuclear complexes having a bridge of two oxygens (B-group) were less than one percent. This suggests that the two coppers in each binuclear molecule interact, and that the magnitude of the interaction of the B-group can be considered to be much greater than that of the A-group.

Although the electron spin resonance (ESR) spectra of many substances have been determined, there are not so many examples of quantitative measurements of ESR signal intensity. An ESR signal is usually recorded in derivative shape of an absorption curve, and there are some instances of quantitative analysis by using the peak-to-peak height of the signal.$^{1-15)}$ However, the peak-to-peak height method cannot be used except in the case of sharp and symmetrical signals. Hence, the two-step integration method was attempted for quantitative measurements and gave good results for general signals.$^{16,17)}$ After this, a few instances of the integration method have been seen.$^{18-21)}$ The wave height of a two-step integral curve, however, varies with changes in the measuring conditions; and it cannot be normalized for the microwave output power, although normalization for the other measuring conditions is possible.$^{22)}$ Moreover, the Q-value of a sample varies in its signal intensity, and thus the signal intensities of samples having different Q-values cannot be compared with each other even if determined under the same measuring conditions. To make such comparison between different species possible two-step integral method using a multi-mode resonator (double cavity) was devices.$^{23)}$

A sample and a standard substance were put into each hole of two sample holes of the double cavity, and the wave heights of two-step integral were measured under same-phase and anti-phase of magnetic modulation. This method made it possible to obtain the proper ESR signal intensities of various substances. These proper values can be considered to have the same sort of significance as that of such properties as molar absorption coefficient, magnetic moment and molar heat. The ESR signal intensities of some binuclear copper complexes are reported in the present paper.

Experimental

Apparatus. The ESR apparatus used was a JES-ME3X (Japan Electron Optics Laboratory Co. Ltd.) which had been partially modified in its phase sensitive detector circuit.$^{24)}$ The multi-mode cavity resonator was a TE_{105} mode type (JES-MCX-1, JEOL). Its cavity had two sample holes and in each hole was set a quartz adapter to minimize the variation of sample position by reinsertion.$^{24)}$ Into one of two holes was inserted a sample and into the other a standard. Magnetic modulation applied to the two holes could be switched to the same-phase or to the anti-phase.

A signal was integrated by a hand-made integrator in which two operational amplifiers were employed.$^{16)}$ The wave height of the two-step integral curve was measured by a process similar to the method for measuring limiting current in polarography. Quartz tubes of 5 mm outside diameter to just fit the adapter were used for the sample tube.

Materials. The binuclear copper complexes were synthesized by one of the present authors.$^{25-30)}$ The complexes measured and their symbols are listed in Table 1. From a few mg to about 20 mg of $CuSO_4 \cdot 5H_2O$ were used as standards. Mononuclear copper complexes measured for comparison were extra pure grade or were prepared from extra pure reagents. The samples used for measurements were fine grain or powder.

Measurements. Figure 1 shows each signal example of A-group and B-group. They were measured with a single cavity. As B-4 was measured under ten-fold greater sensitivity than A-6, the signal of B-4 was much smaller than that of A-6.

The method of calculation was as follows. Sample a and sample b are inserted into the two holes, hole 1 and hole 2, of the double cavity, respectively. When the magnetic modulation of the two holes is in the same phase, the wave heights of the two-step integral curve is represented as h_s, and when in the anti phase, it is represented as h_a, then,

$$h_s = I_a + \alpha I_b \qquad (1)$$

$$h_a = \beta(I_a - \alpha I_b) \qquad (2)$$

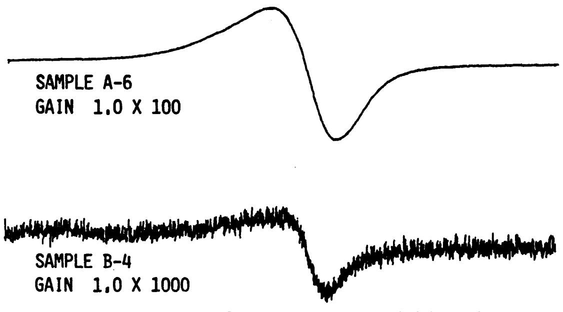


Fig. 1. Examples of ESR signal of binuclear copper complexes. Magnetic field: 3100±1000 gauss, magnetic moduration width: 6.06 gauss, microwave frequency: 9.42 GHz, microwave output power: 6.0 mW, crystal current: 0.4 mA, sweep time: 10 min, at room temperature.

Table 1. Binuclear Copper Complexes and Their Symbols

Symbol	Complex	Lit.
A- 1	μ-[*N*,*N*′-Bis(2-pyridylmethyl)oxamido]dichlorodicopper(II)	25)
A- 2	μ-[*N*,*N*′-Bis(3-dimethylaminopropyl)oxamido]dichlorodicopper(II)	26)
A- 3	μ-[*N*,*N*′-Bis(2-pyridylethyl)oxamido]dichlorodicopper(II)	25)
A- 4	μ-[*N*,*N*′-Bis[2-(2-pyridyl)ethyl]oxamido]-(1,10-phenanthroline)dicopper(II) nitrate	a)
A- 5	μ-[*N*,*N*′-Bis[2-(2-pyridyl)ethyl]oxamido]-(2,2′-bipyridine)dicopper(II) nitrate	27)
A- 6	μ-[*N*,*N*′-Bis(2-pyridylethyl)oxamido]-(2,2′-bipyridine)dicopper(II) nitrate	b)
A-10	μ-[*N*,*N*′-Bis(2-pyridylmethyl)oxamido]-bis(γ-picoline)dicopper(II) nitrate	b)
A-16	μ-[*N*,*N*′-Bis(2-pyridylmethyl)oxamido]-(2,2′-bipyridine)dicopper(II) nitrate	27)
A-18	μ-[*N*,*N*′-Bis[2-(2-pyridyl)ethyl]oxamido]-bis(γ-picoline)dicopper(II) nitrate	b)
A-33	μ-[*N*,*N*′-Bis(2-dimethylaminoethyl)oxamido]dicopper(II) chloride	26)
A-34	μ-[*N*,*N*′-Bis[2-(3-dimethylaminopropylamino)ethyl]oxamido]dicopper(II) chloride	26)
A-35	μ-[*N*,*N*′-Bis[3-(2-dimethylaminoethylamino)propyl]oxamido]dicopper(II) chloride	26)
A-36	μ-[*N*,*N*′-Bis[3-(3-dimethylaminopropylamino)propyl]oxamido]dicopper(II) chloride	26)
A-37	μ-[*N*,*N*′-Bis[4-(2-dimethylaminoethylamino)butyl]oxamido]dicopper(II) chloride	26)
A-38	μ-[*N*,*N*′-Bis[4-(3-dimethylaminopropylamino)butyl]oxamido]dicopper(II) chloride	26)
A-39	μ-[*N*,*N*′-Bis[6-(2-dimethylaminoethylamino)hexyl]oxamido]dicopper(II) chloride	26)
A-40	μ-[*N*,*N*′-Bis[6-(3-dimethylaminopropylamino)hexyl]oxamido]dicopper(II) chloride	26)
A-41	μ-[*N*,*N*′-Bis[2-(2-dimethylaminoethylamino)ethyl]oxamido]dicopper(II) perchlorate	26)
A-42	μ-[*N*,*N*′-Bis[2-(3-dimethylaminopropylamino)ethyl]oxamido]dicopper(II) perchlorate	26)
A-43	μ-[*N*,*N*′-Bis[3-(2-dimethylaminoethylamino)propyl]oxamido]dicopper(II) perchlorate	26)
A-44	μ-[*N*,*N*′-Bis[3-(3-dimethylaminopropylamino)propyl]oxamido]dicopper(II) perchlorate	26)
A-45	μ-[*N*,*N*′-Bis[4-(2-dimethylaminoethylamino)butyl]oxamido]dicopper(II) perchlorate	26)
A-46	μ-[*N*,*N*′-Bis[4-(3-dimethylaminopropylamino)butyl]oxamido]dicopper(II) perchlorate	26)
A-47	μ-[*N*,*N*′-Bis[6-(2-dimethylaminoethylamino)hexyl]oxamido]dicopper(II) perchlorate	26)
B- 1	μ-Bis[*N*-(3-hydroxopropyl)-*N*′-methylglycinamido]dicopper(II)	28)
B- 2	μ-Bis[*N*-(3-hydroxopropyl)-*N*′,*N*′-dimethylglycinamido]dicopper(II)	28)
B- 3	μ-Bis[*N*-(3-hydroxopropyl)glycinamido]dicopper(II)	28)
B- 4	μ-Bis[*N*-(3-hydroxopropyl)picolinamido]dicopper(II)	29)
B- 6	μ-Bis[*N*-(3-methylaminopropyl)hydroxoacetamido]dicopper(II)	30)
B- 7	μ-Bis[*N*-(3-dimethylaminopropyl)hydroxoacetamido]dicopper(II)	30)
B- 8	μ-Bis[*N*-(2-pyridylethyl)hydroxoacetamido]dicopper(II)	26)
B- 9	μ-Bis[*N*-(2-pyridylmethyl)hydroxoacetamido]dicopper(II)	26)

a) Obtained similarly to the complex A-5 using 1,10-phenanthroline instead of 2,2′-bipyridine in the complex A-5. b) Derived from the complex A-1 or A-3 using pyridine- or 4-methylpyridine.

while I_a and I_b are respectively the wave heights of sample a and sample b in hole 1 in the same phase, α is the ratio of the wave heights in hole 1 and hole 2, and β is the ratio of the wave heights of the same sample in the same phase and in the anti phase. Figure 2 shows an example of an original curve (1), the 1st step integral curve (2), and the 2nd step integral curve (3), and the determination of h_s and h_a are also shown in the figure.

The following equation is obtained from Eqs. 1 and 2.

$$\frac{I_a}{I_b} = \frac{\alpha(h_s + h_a/\beta)}{h_s - h_a/\beta} \tag{3}$$

I_a and I_b vary considerably with changes in the measuring conditions and in the *Q*-value of the sample; however, the ratio I_a/I_b is maintained almost constant. Therefore, if sample b is a standard, the signal intensity of sample a can be obtained by Eq. 3.

$CuSO_4 \cdot 5H_2O$ was employed as the standard substance in the present experiments. If n mg of $CuSO_4 \cdot 5H_2O$ are taken as a standard and m mg of binuclear complex are taken as a sample, the ratio γ of copper atoms to those in the standard is

$$\gamma = \frac{2m}{M} \cdot \frac{249.7}{n} \tag{4}$$

M: molecular weight of the binuclear complex.

The ESR signal intensity of copper in the sample is given by

$$I = \frac{1}{\gamma} \cdot \frac{I_a}{I_b} \tag{5}$$

All measurements were carried out at room temperature. Measuring conditions of the spectrometer were as follows: Sweep width of the magnetic field was 3100±1000 gauss, sweep time was 1 min, magnetic modulation width was 6.06 gauss, the microwave frequency was 9.4 GHz and its output power was 6.0 mW, and the crystal current was 0.4 mA. The cavity constants, α and β, were revaluated when the cavity and the adapters were reset.

The relative standard deviation of repeated measurements of a sample was generally within a few %, when the shape of the signal was favorable. However, when the signal was very small, as in the B-type complex, the number of significant figures of the intensity I was only one. Moreover, when the two wings of a signal curve did not coincide with the base line, the precision decreased. However, noise with short periods scarcely affected the precision, since it was canceled out by integration. The relative standard deviations of the signal intensities obtained in the present work except for the B-group were within a few %, and even the maximum deviation was less than 10%.

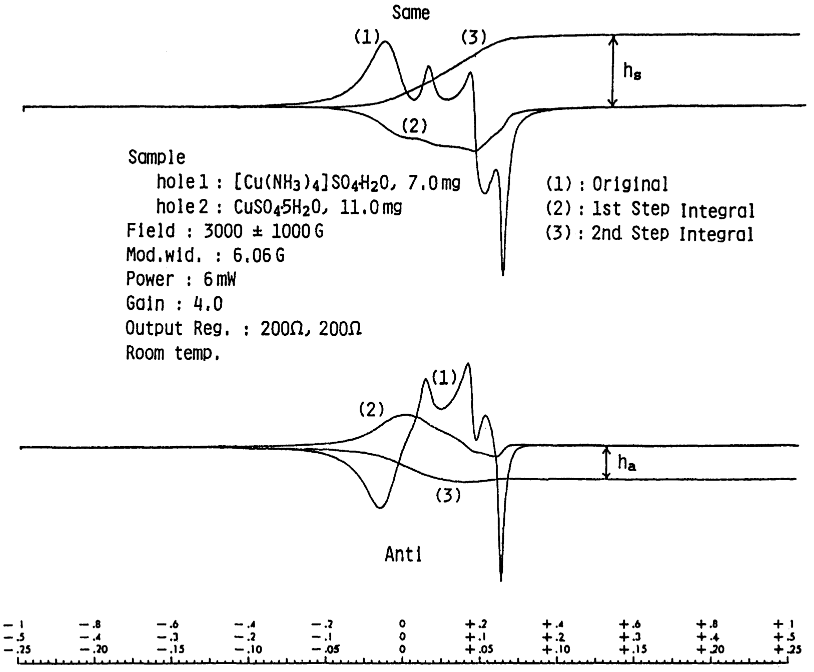


Fig. 2. An example of integrated curves of ESR signal with double cavity.
h_s: Wave height in same phase. h_a: Wave height in anti phase.

Results and Discussion

The results obtained for the ESR signal intensities *I* standardized with $CuSO_4 \cdot 5H_2O$ are tabulated in Table 2. The table also includes the magnetic moment μ measured previously by one of the present authors. In addition, the signal intensities of a few mononuclear copper complexes are also listed. The data are compiled and presented in Fig. 3; and when roughly classified, they show that, although the intensities of mononuclear complexes are almost 1, those of the A-group are a few tens of % and those of B-group under 1% of the copper sulfate crystals. This suggests that the two unpaired electrons of the two copper atoms in a molecule partly make a pair through bridging atoms. The interaction can be considered to be stronger in the B-group (two-oxygen bridge) than in the A-group (oxamide bridge).

With respect to the compounds A-1 to A-18, those whose chelate ring adjacent to the bridging ring has fine members have about half the *I* value of those having six members. Thus, it can be considered that the copper–copper interaction of a five-membered ring is stronger than that of a six-membered ring, since the larger strain of the six-membered ring more strongly affects the delocalization of π-electrons through the bridging atoms. The same tendency can be seen in the compounds from A-33 to A-47, that is, the *I* values of the compounds of l=2 (five-membered ring) are smaller than those of l=3 (six-membered ring). However, that the values of l=6 (nine-membered ring) are smaller than those of l=3 may suggest that the structural strain is rather smaller than in the six-membered ring. The number of members of the chelate ring on the opposite side of the bridging ring does not seem to have obvious effect on its signal intensity.

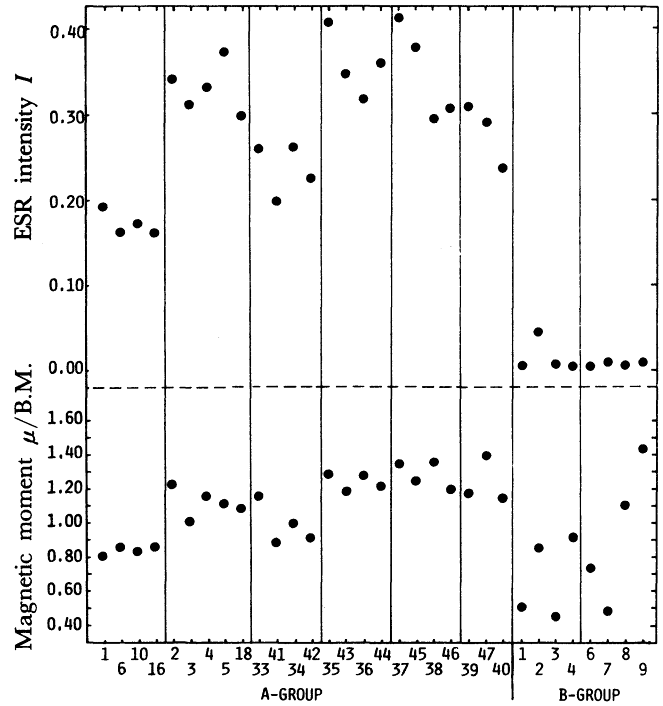
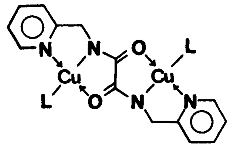


Fig. 3. ESR signal intensities and magnetic moments of binuclear copper complexes.

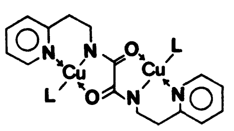
The values of magnetic moment μ of binuclear complexes shown in Fig. 3 are smaller than the value of

Table 2. ESR Signal Intensities and Magnetic Moments of Binuclear Cu Complexes

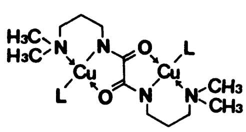
Complex	$CuCl_2 \cdot 2H_2O$	$[Cu(NH_3)_4] \cdot (NO_3)_2$	$[Cu(acac)_2]$	$[Na_2Cu(edta)] \cdot 4H_2O$
Intensity	0.945	1.017	0.932	1.025



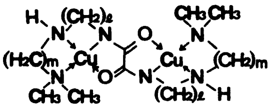
	A-1	A-6	A-10	A-16
2L	2Cl trans	2N⟨◯⟩ trans	2N⟨◯⟩CH_3 trans	bipy cis
Anion	—	$(NO_3)_2$	$(NO_3)_2$	$(NO_3)_2$
H_2O	—	—	—	—
I	0.190	0.158	0.171	0.159
μ(B.M.)	0.81	0.87	0.84	0.87



	A-3	A-4	A-5	A-18
2L	2Cl trans	phen cis	bipy cis	2N⟨◯⟩CH_3 trans
Anion	—	$(NO_3)_2$	$(NO_3)_2$	$(NO_3)_2$
H_2O	0.5	2	3	—
I	0.309	0.329	0.369	0.291
μ(B.M.)	1.21	1.01	1.16	1.12

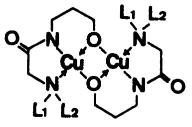


	A-2
2L	2Cl trans
Anion	—
H_2O	—
I	0.388
μ(B.M.)	1.23

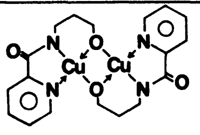


No.	A-33	A-41	A-34	A-42	A-35	A-43
ℓ	2	2	2	2	3	3
m	2	2	3	3	2	2
Anion	Cl	ClO_4	Cl	ClO_4	Cl	ClO_4
H_2O	5/2	—	1	2	1/4	—
I	0.258	0.198	0.259	0.213	0.404	0.345
μ	1.16	0.89	1.00	0.92	1.29	1.19

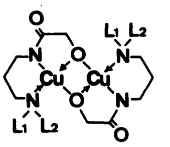
No.	A-36	A-44	A-37	A-45	A-38	A-46	A-39	A-47	A-40
ℓ	3	3	4	4	4	4	6	6	6
m	3	3	2	2	3	3	2	2	3
Anion	Cl	ClO_4	Cl	ClO_4	Cl	ClO_4	Cl	ClO_4	Cl
H_2O	1/2	2	2	1/4	1/2	1	5/4	2	—
I	0.315	0.358	0.410	0.376	0.293	0.304	0.306	0.287	0.235
μ	1.28	1.22	1.35	1.25	1.36	1.20	1.18	1.40	1.15



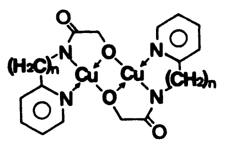
	B-1	B-2	B-3
L_1	H	CH_3	H
L_2	CH_3	CH_3	H
I	0.005	0.043	0.007
μ	0.51	0.86	0.46



	B-4
I	0.003
μ	0.78



	B-6	B-7
L_1	H	CH_3
L_2	CH_3	CH_3
I	0.003	0.006
μ	0.74	0.49



	B-8	B-9
n	2	1
I	0.004	0.007
μ	1.11	1.44

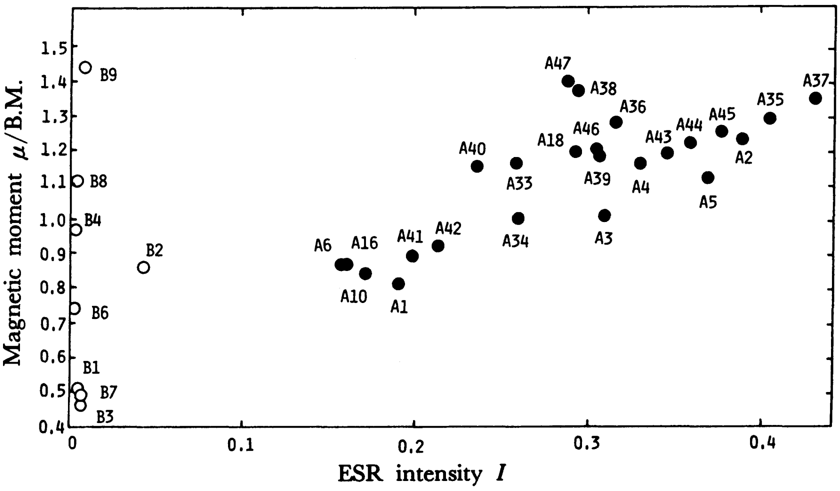


Fig. 4. Relationship between the ESR signal intensities and the magnetic moments of binuclear copper complexes.

the general mononuclear copper complex, which is about 1.9. Although the values of five-membered rings are smaller than those of six-membered rings as in the relationship in the case of ESR signal intensity, no significant difference between six or seven-membered ring and nine-membered rings can be seen. Moreover, although the ESR intensities of the B-group are much smaller than those of the A-group, there is no great difference in the magnetic moments of the A-group and B-group. The relationship between the signal intensities and magnetic moments is shown in Fig. 4. A considerable correlation is exhibited between I and μ in the A-group, but such correlation cannot be seen in the B-group. The reason for this is not yet understood.

Conclusion

The two-step integral method using a multimode cavity made it possible to obtain the intensities of ESR signals of samples relative to a standard substance, regardless of the measuring conditions and the Q-values of the samples. It can be considered that the accurate determination of an ESR signal intensity as a proper value of a species is very important. In the present work the ESR signal intensities of some binuclear copper complexes were measured as the first examples. The results showed that the intensities of the binuclear copper complexes of the A-group (oxamide type) were a few tens of percent of the intensity of copper sulfate crystals, while those of B-group (binuclear complexes bridged with two oxygen atoms) were less than one percent of copper sulfate. This difference may have been caused by the magnitude of interaction between the two copper atoms in binuclear molecule. On the other hand, the difference in the magnetic moments between the A-group and B-group was not notable. However, as the interaction between the two copper atoms of a B-group compound is generally supposed to be stronger than that of an A-group compound due to their structures, the ESR signal intensity can be considered to be more useful than the magnetic moment for estimating the interaction between these atoms.

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