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Ferromagnetic Interactions in Formazanyl–Copper Complexes

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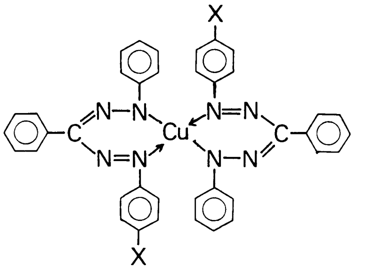
The magnetic susceptibility of four formazanyl-copper complexes have been measured by the use of a torsion balance in the range from 2 K to room temperature. Their ESR parameters have been measured on powdered samples at room temperature and the temperature of liquid nitrogen, and in solution at room temperature in order to elucidate the electronic structures of the complexes. The complexes which have shown the exchange-narrowed pattern in the spectra of powdered samples have been paramagnetic as low as 2 K. Nitro and carboxy derivatives characterized by a single, broad ESR absoption line have positive Weiss constants, indicating ferromagnetic interaction. Especially, the magnetic behavior of the carboxy derivative has been well interpreted in terms of a ground triplet-excited singlet model with the exchange parameter of 24 K. The nitro derivative showed an abnormally low magnetic moment. It has been concluded that the magnetic properties of formazanyl-copper complexes are very sensitive to substitution at the phenyl rings.

Formazans are compounds which contain a characteristic chain of atoms: -N=N-C=N-NH- and which yield tetrazolium salts upon oxidation. Since Kuhn and Jerchel drew attention to their valuable applications to biological research in 1941,[1] formazans and their tetrazolium salts have been studied extensively from various points of views.[2] In addition, it has been learned that formazans react with compounds of Cu^{2+}, Co^{2+}, and Ni^{2+} to give complexes which have two or four nitrogen atoms as ligands.[3,4] The magnetic susceptibilities of several complexes have been measured at room temperature or at three points between the temperature of liquid nitrogen and room temperature in order to ascertain the effective magnetic moments.[5,6] However, although quite a few papers have referred to the magnetic interaction among copper ions, only a few have made mention of the structures.[7] The fact that 1-(*o*-hydroxyphenyl)-3,5-diphenylformazanyl copper showed an abnormally low magnetic susceptibility was attributed to its having a binuclear form, not to its mixing of Cu^+ and Cu^{2+}.[8] 1-(*o*-carboxyphenyl)-3,5-diphenylformazanyl copper has also been presumed to be a dimer, but it showed normal magnetic susceptibility down to the temperature of liquid nitrogen.[5,8] Therefore, the dimer structure has been proposed on the basis only of the elemental analyses and the hypothetical molecular arrangement. Though it is clear from the elemental analyses that 1-(*o*-carboxyphenyl)-3,5-diphenylformazan reacts with a divalent transition-metal ion with 1:1 stoichiometry,[3,4] the structure of the complex has been an open question for a long time.

In order to clarify the problems mentioned above, four formazanyl-copper complexes have been prepared, and ESR and magnetic-susceptibility measurements have been carried out. In this paper we will report first the results of the ESR and magnetic susceptibility measurements. Second, the magnetic properties will be discussed; they will be classified into two groups, the paramagnetic species and the ferromagnetic species. Especially, the latter will be discussed theoretically based on a ferromagnetic dimer model.

Experimental

The formazans were prepared by a method described elsewhere.[1] Bis(1,3,5-triphenylformazanyl)copper as (**1**) was prepared following the method by Hunter *et al.*, but using a different solvent. Bis[1-(*p*-chlorophenyl)-3,5-diphenylformazanyl]copper (**2**), 1-(*o*-carboxyphenyl)-3,5-diphenylformazanyl copper (**3**), and the copper complex of 1-(*p*-nitrophenyl)-3,5-diphenylformazan (**4**), were prepared by a similar method. **1**, **2**, and **4** all consisted of a fine, almost black powder, while **3** was a fine, purple powder. The elemental analyses of **1** and **2** agreed well with the calculated values; those of **4** also agreed well with the calculated values assuming the 2:1 stoichiometry of formazan and copper. The hypothetical molecular structure of **4** is shown as **4′** in Fig. 1. An amount of **3** large enough for the measurements was too difficult to obtain. The **3′** used for the measurements was a sample containing some solvent molecules. In Table 1, the



1, X=H 2, X=Cl 4′, X=NO2

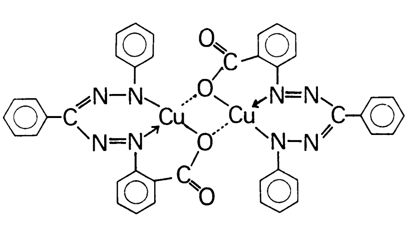


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Fig. 1. **1**; Bis(1,3,5-triphenylformazanyl)copper, **2**; Bis[1-(*p*-chlorophenyl)-3,5-diphenylformazanyl]copper, **3**; 1-(*o*-carboxyphenyl)-3,5-diphenylformazanyl copper, **4′**; Copper complex of 1-(*p*-nitrophenyl)-3,5-diphenylformazan.

TABLE 1. ANALYTICAL DATA OF COMPLEXES

Complex	Found (%)					Calcd (%)					
	C	H	N	Cl	Cu	C	H	N	Cl	Cu	
1 $(C_{19}H_{15}N_4)_2Cu$	68.8	4.6	16.6		9.9	68.9	4.5	16.4		9.6	
2 $(C_{19}H_{14}N_4Cl)_2Cu$	61.7	3.9	14.7	9.9	9.0	62.4	3.9	15.3	9.7	8.7	
3 $(C_{20}H_{14}N_4O_2)_2Cu_2$	59.0	3.6	13.5			59.3	3.5	13.8		15.2	(1:1)
$(C_{20}H_{14}N_4O_2)_2Cu$						64.2	3.7	15.0		8.5	(1:2)
3′ $(C_{20}H_{14}N_4O_2)_2Cu_2 \cdot (C_5H_5N)$	62.1	3.6	12.5		14.2	61.4	3.8	14.3		13.3	
4 $(C_{19}H_{14}N_5O_2)_2Cu$	60.5	3.7	18.6		8.6	60.7	3.7	18.6		8.4	

values calculated based on the 1 : 1 and 1 : 2 stoichiometries of copper and 1-(*o*-carboxyphenyl)-3,5-diphenylformazan are also listed for comparison. It was found that **3′** has basically the 1 : 1 stoichiometry.

The ESR spectra were observed at room temperature and at the temperature of liquid nitrogen by using an X-band ESR spectrometer(JEOL ME-3X) equipped with 100 kHz field modulation. The molar magnetic susceptibility χ_M was measured with powdered samples of about 50—70 mg in the temperature range from 2 K to room temperature by using a magnetic torsion balance described elsewhere.[10] All the data were corrected for the diamagnetic contribution calculated by the Pascal method: -341.2×10^{-6}, -331.3×10^{-6}, -288.7×10^{-6}, and -331.6×10^{-6} emu/mol for Compounds **1**, **2**, **3′**, and **4** respectively.**

Results

ESR in Solution. In order to obtain information about the isolated paramagnetic species, the ESR spectra in benzene solutions were measured at room temperature. The isotropic hyperfine structures due to the copper nuclear spin with $I=3/2$ have been observed in **1**, **2**, and **4**. Their hyperfine coupling constants are listed in Table 2. Their spectra showed a linewidth-variation effect; the linewidth in the higher field was sharper than that in the lower field. In the case of **4**, the superhyperfine splittings due to the four ligand-nitrogen nuclei(a_N) could be further observed in the absorption line of Cu^{2+} at the highest field, as is shown in Fig. 2, and a_N was equal to 5.4 G.*** On the contrary, in the benzene solution of **3**, only a single broad line with a linewidth of about 120 G was observed at room temperature, without any hyperfine splitting due to the copper nucleus. At the temperature of liquid nitrogen the ESR spectrum of **3** showed a tendency to split further into seven components. These results can be reasonably interpreted by assuming that the two copper nuclei are coupled with each other, with a strong exchange interaction. It should be noted in Table 2 that the Cu–hyperfine coupling constants (a_{Cu}) of about 41 G are abnormally small compared with those in the Cu-complexes with a planar structure. The a_N in **4**, is also much smaller than those of the usual planar complexes. These are the characteristic features of formazanyl copper complexes.

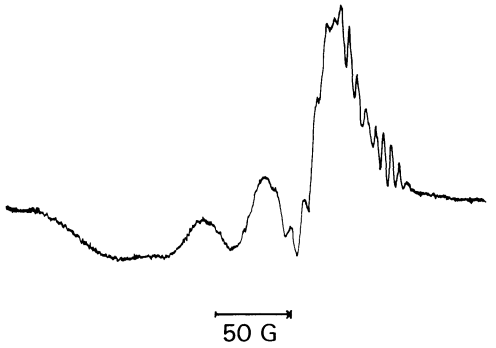

Fig. 2. ESR spectrum of 4 in benzene solution at room temperature. Note that the group at the highest field shows additional superhyperfine structure.

*Magnetic Properties of **1** and **2**.* The ESR spectra of powdered samples of four compounds are shown in Fig. 3, while their g-values are listed in Table 2. The hyperfine splitting of copper in **1** could not be observed.

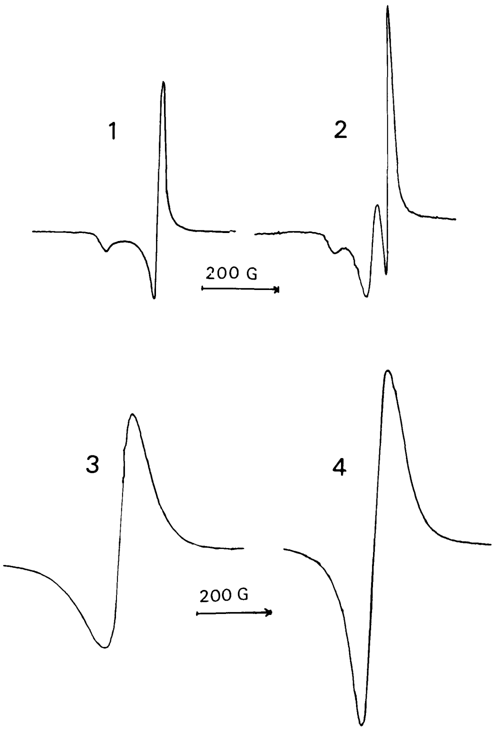

Fig. 3. ESR spectra of powdered samples at room temperature.

** The diamagnetic contribution was calculated for **4′**.

*** $1\,G=10^{-4}\,T$.

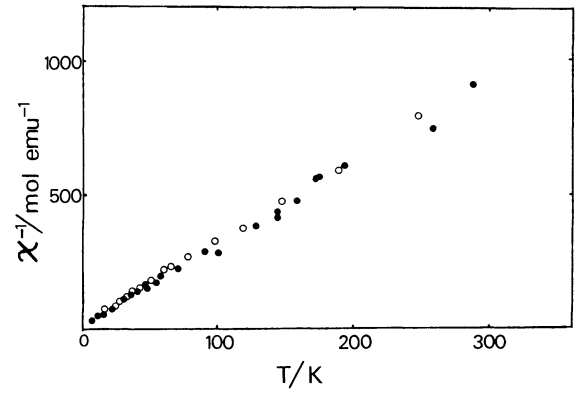

Fig. 4. The reciprocals of molar magnetic susceptibility of **1** (full circle) and **2** (open circle).

The linewidth between the halves of the absorption intensity of the parallel component, $\Delta H_{//}$, and the peak-to- peak width of that of the perpendicular component, $\Delta H_{\perp}$, were 26 and 15 G respectively. The results clearly show an exchange-narrowing effect. In Compound **2**, three components of the g-value, g_1, g_2, and g_3, were obtained. The difference in the g_{ave}-values between that at room temperature and that at the temperature of liquid nitrogen was quite small in **1** and **2**.

The reciprocal plots of χ_{M} of Compounds **1** and **2** *versus* the temperature are shown in Fig. 4. The most remarkable feature of these compounds is that both χ_{M} values follow the Curie-Weiss law described by Eq.(1):

$$\chi_{\mathrm{M}} = C/(T-\theta), \quad C = Ng^2\beta^2 S(S+1)/3k, \tag{1}$$

$$\mu_{\mathrm{eff}}/\beta = g\sqrt{S(S+1)}, \tag{2}$$

with the negative Weiss constant of −4 K. Here, the other notations have the usual meanings. This negative θ value indicates the existence of weak antiferromagnetic interaction among the magnetic species under consideration. The effective magnetic moment, μ_{eff} of **1** and **2** was estimated as 1.9β from the slopes of the $1/\chi_{\mathrm{M}}-T$ (temperature) curves. This agrees well with the μ_{eff} value (1.78β) calculated with $g=2.06$ and $S=1/2$ in Eq. (2). This can be attributed to the fact that each molecule in the system possesses an isolated magnetic moment with $S=1/2$.

Magnetic Properties of 3. The average g-value was 2.09. The ESR spectra of powdered samples of **3** and **3′** consisted of almost symmetrical broad lines without any hyperfine structure. The line shape and the g-value were almost temperature-independent.

The full circles in Fig. 5 show the experimental results of **3′**. The $1/\chi_{\mathrm{M}}$ value obeys the Curie-Weiss law in the higher-temperature region (I) above 30 K. The Weiss constant in (I) was +12 K, indicating ferromagnetic interaction. On the other hand, the $1/\chi_{\mathrm{M}}$ value in the lower-temperature region (II) deviates from the Curie-Weiss law in (I) at around 30 degrees and follows the Curie-Weiss law with a different θ value. The θ value estimated in the (II) region was almost zero. This behavior can be well interpreted in terms of the ground triplet-excited singlet model (referred to as the T-S mode),[13] as will be described later.

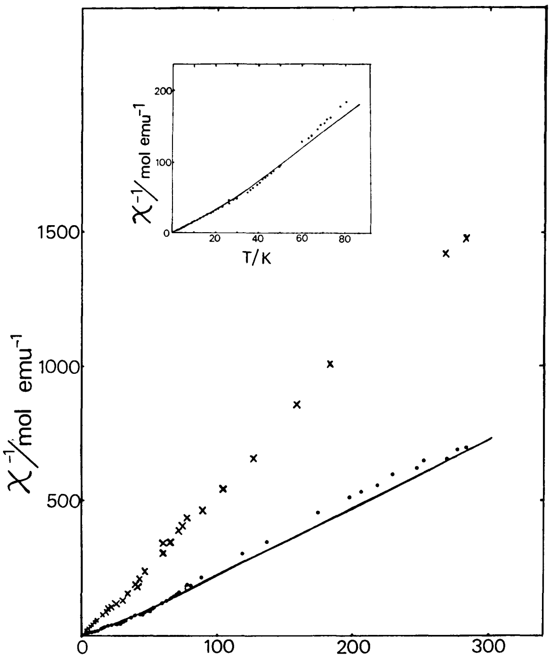

Fig. 5. The reciprocals of molar magnetic susceptibility of **3′** (full circle) and **4** (cross).
The inset shows the susceptibility of **3′** in the lower temperature region; the experimental results (full circle) and theoretical curve (solid line) based on the T-S model (see text).

Magnetic Properties of 4. The ESR spectrum observed in the powdered sample of **4** is also a single broad line which is almost symmetrical and which gives an average g-value of 2.06. This is not so much different from that of **3**. However, the stoichiometry of formazan and copper of **4** was 2 : 1, in contrast with that of **3**, 1 : 1, as is seen in the elemental analyses.

The ESR in solution and stoichiometry indicate that **4** is of a monomer type, similar to **1** and **2**. On the contrary, the ESR of the powdered sample suggests a strong interaction among the copper ions, because neither the g anisotropy nor the hyperfine splitting could be observed.

A plot of the $1/\chi_{\mathrm{M}}$ of **4** *versus* the T is also shown in Fig. 5. The Weiss constant extrapolated in the higher-temperature region(I) was +11 K, indicating that the exchange interaction in **4** is also ferromagnetic. The $1/\chi_{\mathrm{M}}$ value in the lower-temperature region(II) obeys a Curie-Weiss law, with $\theta=0$ K.

Discussion

The $g_{//}$ and $g_{\perp}$ values of **1** were similar to those of Cu-tetraphenylporphyrine ($g_{//}$=2.12, $g_{\perp}$=2.07).[11] This fact indicates that the environment of the nitrogen-bonded copper ion in the present compound is square-planar. On the other hand, the three components of the g-value in **2** demonstrate that the planarity around the copper ion is no longer kept. However, the average g-value of **2**, $g_{\mathrm{ave}}=(g_1+g_2+g_3)/3$, is not so much different from that of **1**. The slight deviation from the square-planar configulation is probably caused by the introduction of chlorine into the phenyl rings. In spite of this difference, both Compound **1** and Compound **2** showed an exchange-

Table 2. Results of ESR and magnetic susceptibility measurements

Compound	Magnetism	Weiss constant θ/K	μeff	g-value		a_{Cu}(iso)
			BM	Room temp.	Liq. nitrogen	G
1	Curie-Weiss	−4	1.9	g=2.120 g=2.031 g_{ave}=2.061	g=2.121 g=2.031 g_{ave}=2.061	41.3
2	Curie-Weiss	−4	1.9	g_1=2.032 g_2=2.061 g_3=2.123 g_{ave}=2.072	g_1=2.033 g_2=2.065 g_3=2.125 g_{ave}=2.074	41.0
3′	Ferromagnetic (T-S model)	+12	1.8	g_{ave}=2.094	g_{ave}=2.100	
4	Ferromagnetic	+11	1.0 (I) 1.3 (II)	g_{ave}=2.056	g_{ave}=2.059	41.4

(I) and (II) mean the higher- and the lower-temperature regions respectively.

narrowed pattern in ESR and obeyed the Curie-Weiss law. These results indicate that these compounds are typical paramagnetic species with small exchange interactions among the mononuclear units. On the other hand,the g_{ave} of **3**, 2.09, is the largest among the four compounds; the others have almost identical g_{ave} value, about 2.06.

The g-anisotropy of the copper ion in the powdered sample of **4** could not be seen because of the single broad line, but the copper hyperfine coupling constant of **4** in solution was almost the same as those of **1** and **2**, about 41 G, and the stoichiometry was also the same. The most remarkable difference between Compound **4** and Compounds **1** and **2** was that the χ_{M} of **4** at 288 K, 670×10^{-6} emu/mol, is abnormally small compared with the values of the others, 1200×10^{-6} emu/mol. The χ_{M} value of the isolated spin system with $S=1/2$ is calculated as 1300×10^{-6} emu/mol at 288 K on a spin-only basis. Therefore, the experimental value of χ_{M} of **4** at 288 K is about one half of the calculated value. In order to interpret these results quantitatively, we need the crystal structure of **4**. Further experiments such as ESR measurements below the temperature of liquid nitrogen and X-ray analysis are now in progress.

In conclusion, it is characteristic in formazanyl copper complexes that a subtle perturbation such as the introduction of a substituent into the phenyl rings far from the central copper ion results in changes in the symmetry of the ligand field and the magnetic properties.

Ground Triplet-excited Singlet Model. Recently, the ferromagnetic behavior in several copper complexes has been reported and discussed in relation to their molecular structures.[12] In the present case, the ferromagnetic behavior of **3′** can be well explained on the basis of the T-S model.[13] The molar magnetic susceptibility of this model is expressed by the Bleaney-Bowers equation (3):[14]

$$\chi_{\mathrm{M}}=\frac{Ng^2\beta^2}{kT}\frac{1}{3+\exp(-2J/kT)}, \tag{3}$$

where $2J$ is the energy separation between the ground triplet and the excited singlet states, and where N is the number of monomer complexes. Equation (3) indicates that the $1/\chi_{\mathrm{M}}$ ratio approaches linearly to zero with a lowing of the temperature. In the higher-temperature region, χ_{M} can be approximated by Eq. (1), with $\theta=J/2k$. Therefore, the theoretical ratio of the slope of the $1/\chi_{\mathrm{M}}$-T curve in the lower-temperature region to that in the higher-temperature region, R, can be calculated; it is equal to 0.75. The R of **3′** was found to be 0.7 ± 0.05. The θ in the higher-temperature region clearly indicates the ferromagnetic-exchange interaction. These results indicate that the ferromagnetically coupled dimeric model is adequate for **3′**. The exchange energy, J, could be estimated from the relation: $J/k=2\theta$, based on the high-temperature approximation of Eq. (3). J was equal to $24\,k$ erg**** in this case. In conformance with the above mentioned T-S model and the estimated J value, the theoretical curve of the temperature dependence of the magnetic-susceptibility behavior was drawn with the solid line in Fig. 5; it agreed with the experimental results within the limits of experimental error. Thus, the T-S model accounts well for the susceptibility behavior of **3′**. We have carried out the magnetic-susceptibility calculations based on Cubane-type models.[15,16] The experimental data fit well at the limit of the interdimer-interaction, $J'=0$. This establishes the appropriateness of the T-S model.

It is well known that the coupling of the copper ions can be ferromagnetic when the bonding angle of Cu-O-Cu is about 90°.[17] The construction of the molecular model of **3** shows that the angle of Cu-O-Cu can be about 90°. The results of the magnetic measurement give circumstantial evidence for the molecular structure of **3** shown in Fig. 1, which had been proposed only on the basis of the elemental analyses.[5]

Thus, it can be concluded that the most possible structure of **3** is the magnetic dimer, in which the triplet state is the ground state, the energy separation $2J/k$ being 48 K. Finally, it is of interest to point out that the copper complexes having such large ligands as formazan derivatives show comparatively large ferromagnetic interactions, as is visualized in **3′** and **4**. The central chain structure of formazan has a high flexibility on complexation with metal ions. This results in a variety of magnetic properties in these

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**** 1 erg = 10^{-7} J.

complexes. We are now planning to investigate such features in the other formazanyl-transition metal complexes.

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