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The Mono-, Di-, and Trinuclear Copper(II) Complexes Containing Pyrazole and Glycylglycine or Diethylenetriamine. Comparisons with Imidazole Containing Copper(II) Complexes

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Abstract

The mixed ligand copper(II) complexes with pyrazole or 3-methylpyrazole and glycylglycine (Gly·Gly) or diethylenetriamine (dien) were prepared in neutral and basic solutions. The compounds obtained in neutral solutions were mononuclear complexes, while those in basic solutions were polynuclear complexes bridged by pyrazolate (pz) or 3-methylpyrazolate (3-Mepz). The Gly·Gly- and pz-containing compounds, $Ca[Cu_2(Gly{\cdot}Gly)_2(pz)]_2{\cdot}8H_2O$ and $K_2[Cu_3(Gly{\cdot}Gly)_3(pz)_2]{\cdot}5H_2O$ were proved to be a dinuclear complex and a linear-chain trinuclear one, respectively, from their magnetic properties. In both complexes copper(II) ions are antiferromagnetically coupled ($J = -12.3$ cm^{-1} for the calcium salt complex and $J = -9.4$ cm^{-1} for the potassium salt complex). The dien-containing complexes, $[Cu_2(dien)_2(pz)]Br_3{\cdot}H_2O$ and $[Cu_2(dien)_2(pz)](ClO_4)_3{\cdot}4H_2O$ were also isolated and the existence of an antiferromagnetic exchange interaction ($J = -21.5$ cm^{-1}) between the two copper(II) ions was observed for the bromide salt complex. The magnetic properties of the perchlorate salt complex were considerably different from the corresponding bromide. Namely, the strong antiferromagnetic interaction (Weiss constant $\theta_h = -154$ K) was observed in the high-temperature range ($T > 130$ K), but was not observed apparently ($\theta_l = \sim 0$ K) in the low-temperature range ($T < 130$ K). Spectroscopic properties of these compounds were also investigated.

Introduction

The presence of copper(II)–imidazole bonding has been demonstrated for the copper proteins such as azurin [1], plastocyanin [2], and hemocyanin [3, 4] etc. Also, the existence of an imidazolate-bridged copper(II)–zinc(II) center in bovine erythrocyte superoxide dismutase was established by Richardson *et al.* [5]. A number of the copper(II) complexes containing imidazole (imH) and its derivatives have hitherto been studied in a view of the active sites of these proteins [6–15].

On the other hand, pyrazole (pzH) or pyrazolate (pz), which has the structure similar to imidazole or its anion is known to function as a potent ligand to metal ion [16–28].

We report here the preparation and characterization of monomeric and di- or trimeric copper(II) complexes containing glycylglycine or diethylenetriamine and pyrazole or pyrazolate anion. Furthermore, the results are compared with those of the corresponding imidazole-containing copper(II) complexes.

Experimental

Preparation of the Complexes

$[Cu(Gly{\cdot}Gly)(pzH)]$ *(1)*

To a mixture of glycylglycine (2.0 g, 15 mmol), pyrazole (1.0 g, 15 mmol) and water (25 cm^3) was added a copper(II) hydroxide precipitated from each aqueous solution of $CuSO_4{\cdot}5H_2O$ (4.0 g) and NaOH (1.3 g). The reaction mixture was stirred at 70–80 °C for about 15 min and then filtered. The filtrate was evaporated to dryness. The blue solid obtained was recrystallized from ethanol containing a small quantity of water.

$Ca[Cu_2(Gly{\cdot}Gly)_2(pz)]_2{\cdot}8H_2O$ *(2)*

To a mixture of glycylglycine (0.53 g, 4.0 mmol), pyrazole (0.21 g, 3.0 mmol), calcium hydroxide (0.30 g, 4.0 mmol) and methanol (20 cm^3) was added a copper(II) hydroxide obtained from $CuSO_4{\cdot}5H_2O$ (1.5 g) and NaOH (0.48 g). The reaction mixture was stirred at room temperature for 1 h and

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filtered. The filtrate was then allowed to stand for a day. Violet–blue crystalline products were deposited and recrystallized from aqueous methanol.

$K_2[Cu_3(Gly{\cdot}Gly)_3(pz)_2]{\cdot}5H_2O$ (3)

Except that KOH (0.22 g, 4.0 mmol) was used, the same procedure as that for the calcium salt described above was applied. Since the corresponding crystals could not be separated only by allowing the solution to stand, the filtrate was evaporated to dryness *in vacuo*. The violet–blue solid obtained was recrystallized from methanol–ether.

$[Cu(Gly{\cdot}Gly)(imH)]{\cdot}2H_2O$ and $Na[Cu_2(Gly{\cdot}Gly)_2(im)]{\cdot}6H_2O$

These complexes were prepared by the method given in the literature [29, 30].

$[Cu(dien)(pzH)](ClO_4)_2$ (4)

To a methanol solution (20 cm^3) of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.5 g, 4.0 mmol) were added dien (0.41 g, 4.0 mmol) and pzH (0.27 g, 4.0 mmol). The mixture was stirred for 30 min at room temperature and then cooled. The precipitate was collected by filtration, and recrystallized from aqueous ethanol to give blue–violet crystals.

$[Cu_2(dien)_2(pz)]Br_3{\cdot}H_2O$ (5)

A methanol solution of pzH (0.14 g, 2.0 mmol) and NaOH (0.08 g, 2 mmol) was added with stirring to a methanol solution (20 cm^3) of $CuBr_2$ (0.89 g, 4.0 mmol) and dien (0.41 g, 4.0 mmol). This mixture was stirred for ½ h at room temperature and then cooled in a refrigerator. Dark blue crystals were deposited, which were filtered and recrystallized from methanol.

$[Cu_2(dien)_2(pz)](ClO_4)_3{\cdot}4H_2O$ (6)

An aqueous solution of $AgClO_4{\cdot}H_2O$ (0.32 g, 1.4 mmol) was added to an aqueous solution of $[Cu_2(dien)_2(pz)]Br_3{\cdot}H_2O$ (0.30 g, 0.46 mmol). The mixture was stirred for 15 min at room temperature. After removal of precipitated silver bromide, the filtrate was evaporated to dryness *in vacuo* to give a violet–blue powder. The powder was recrystallized from ethanol containing a small quantity of water.

$[Cu_2(dien)_2(3\text{-}Mepz)]Br_3{\cdot}2H_2O$ (7)

This complex was prepared in a similar way to $[Cu_2(dien)_2(pz)]Br_3{\cdot}H_2O$ using 3-methylpyrazole in lieu of pyrazole. Recrystallization was carried out by ethanol containing a small quantity of water.

$[Cu_2(dien)_2(3\text{-}Mepz)](ClO_4)_3$ (8)

To a mixture of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.5 g, 4.0 mmol), dien (0.41 g, 4.0 mmol) and methanol (20 cm^3) was added a methanol solution of 3-methylpyrazole (0.17 g, 2.0 mmol) and NaOH (0.08 g, 2 mmol). The resulting mixture was stirred for 30 min at room temperature, and then cooled in a refrigerator. The violet crystals were filtered and washed with ethanol.

$[Cu(dien)(imH)](ClO_4)_2$ (9)

This was prepared in the same way as $[Cu(dien)(pzH)](ClO_4)_2$ using imidazole instead of pyrazole.

$[Cu_2(dien)_2(im)](ClO_4)_3$

The present binuclear complex was prepared by the method of Haddad *et al.* [31].

Analytical data for the complexes **1**–**9** are given in Table I.

Measurements

Visible absorption spectra in nujol and aqueous solutions were recorded on a Shimadzu MPS-5000 spectrophotometer and a Hitachi 200-10 double beam spectrophotometer. Magnetic susceptibility at room temperature was determined by using a Gouy magnetic apparatus. The magnetic susceptibility measurements over the range of liquid helium temperature to room temperature were carried out by the Faraday method. The X-band ESR spectra at 77 K were measured at 9.3 GHz and 100 kHz modulation frequency with a JEOL-JES-FE-1X. Aqueous ethanol (1:1 by volume) was used as a solvent. A Toa Denpa Conduct Meter CM-7B was used for conductivity measurements.

Results and Discussion

Copper(II) Complexes with Glycylglycine

The mixed ligand copper(II) complexes **1**–**3** with pyrazole and glycylglycine were prepared in neutral and basic solutions. In order to obtain detailed information on the structure of the compounds **2** and **3** formed in basic solution, the magnetic susceptibilities were measured over the temperature range 4.2–300 K (Figs. 1 and 2). The susceptibility of **2** increases with decreasing temperature until a maximum is reached at *ca.* 23 K, after which the susceptibility decreases. The magnetic parameters can be estimated as $g = 2.21$, $N\alpha = 60 \times 10^{-6}$ cgs emu mol^{-1}, and $J = -12.3$ cm^{-1} from the best fit of the χ_A values to the Bleaney–Bowers equation [32]

$$\chi_A = \frac{Ng^2\beta^2}{3kT} \times \frac{1}{1 + (1/3)\exp(-2J/kT)} + N\alpha \qquad (1)$$

where J denotes the exchange integral between copper(II) ions in binuclear copper(II) complexes. This shows that there is an antiferromagnetic exchange

TABLE I. Analytical Data for the Complexes

Complex	H(%)		C(%)		N(%)	
	found	calc.	found	calc.	found	calc.
1 [Cu(Gly•Gly)(pzH)][a]	3.94	3.96	19.51	19.38	15.86	16.15
2 $Ca[Cu_2(Gly{\cdot}Gly)_2(pz)]_2{\cdot}8H_2O$	4.21	4.25	24.28	24.17	15.36	15.38
3 $K_2[Cu_3(Gly{\cdot}Gly)_3(pz)_2]{\cdot}5H_2O$	3.92	3.89	24.87	24.47	15.83	15.86
4 $[Cu(dien)(pzH)](ClO_4)_2$	3.94	3.96	19.51	19.38	15.86	16.15
5 $[Cu_2(dien)_2(pz)]Br_3{\cdot}H_2O$	4.63	4.75	20.13	20.07	16.90	17.02
6 $[Cu_2(dien)_2(pz)](ClO_4)_3{\cdot}4H_2O$	4.38	4.85	16.90	17.14	14.26	14.54
7 $[Cu_2(dien)_2(3\text{-}Mepz)]Br_3{\cdot}2H_2O$	4.99	5.12	21.27	20.88	15.98	16.24
8 $[Cu_2(dien)_2(3\text{-}Mepz)](ClO_4)_3$	4.33	4.39	20.12	20.21	15.48	15.20
9 $[Cu(dien)(imH)](ClO_4)_2$	3.99	3.96	19.49	19.38	16.59	16.15

[a] Gly•Gly = glycylglycinate ($NH_2CH_2CONCH_2COO$).

TABLE II. Physical Properties of the Complexes

Complex	Color	μ_{eff} (K) (BM)	Vis spectra			Λ[a] (S cm^2 mol^{-1})
			Nujol (nm)	aqueous solution (nm) (log ϵ)	pH	
1 [Cu(Gly•Gly)(pzH)]	grey–blue	1.70(287.5)	575	600(1.95)[b]	7.2	2
2 $Ca[Cu_2(Gly{\cdot}Gly)_2(pz)]_2{\cdot}8H_2O$	blue–violet	1.84(291)	585	620(1.98)	9.0	161
3 $K_2[Cu_3(Gly{\cdot}Gly)_3(pz)_2]{\cdot}5H_2O$	violet–blue	1.84(290)	590	617(2.07)	8.6	–
4 $[Cu(dien)(pzH)](ClO_4)_2$	violet–blue	1.84(285)	570	605(1.90)	6.2	182
5 $[Cu_2(dien)_2(pz)]Br_3{\cdot}H_2O$	violet–blue	1.84(298)	620	606(1.90)	8.9	399
6 $[Cu_2(dien)_2(pz)](ClO_4)_3{\cdot}4H_2O$	blue–violet	1.62(282)	580	606(1.91)	8.0	410
7 $[Cu_2(dien)_2(3\text{-}Mepz)]Br_3{\cdot}2H_2O$	violet–blue	1.80(287)	605	606(1.90)	9.4	312
8 $[Cu_2(dien)_2(3\text{-}Mepz)](ClO_4)_3$	blue–violet	1.84(287)	605, 530[c]	602(2.00)	9.4	290
9 $[Cu(dien)(imH)](ClO_4)_2$	blue–violet	1.82(286)	565	582(1.94)	7.6	183
10 $[Cu_2(dien)_2(im)](ClO_4)_3$	blue–violet	1.76(288)	570	589(1.91)	9.3	331
11 $[Cu(Gly{\cdot}Gly)(imH)]{\cdot}2H_2O$	blue–violet	1.84(297)[d]	560	614(1.95)[d]	7.8[d]	8
12 $Na[Cu_2(Gly{\cdot}Gly)_2(im)]{\cdot}6H_2O$	blue–violet	1.89(295)[d]	575	618(1.94)[d]	10.2[d]	94

[a] Solvent: water. [b] Solvent: H_2O:isoProOH = 1:1. [c] Shoulder. [d] Ref. 30.

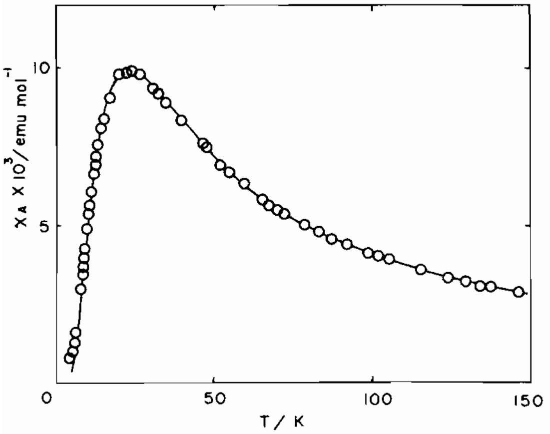


Fig. 1. Temperature-dependence of the magnetic susceptibility of **2**.

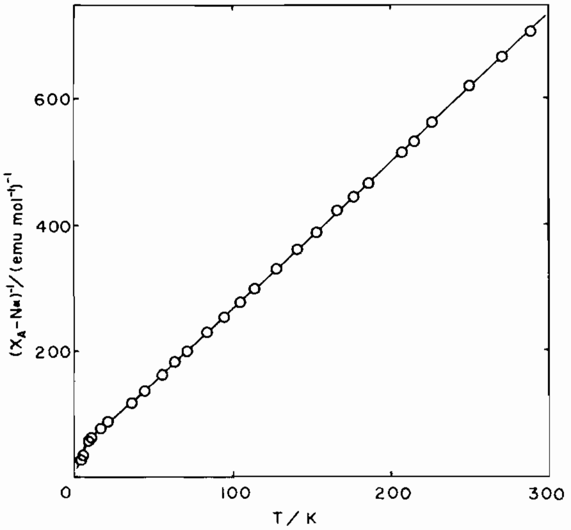
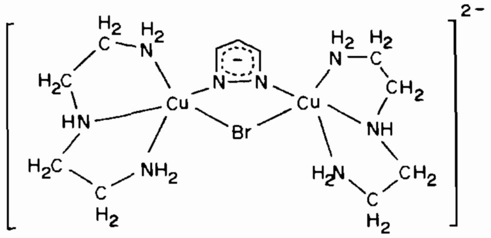


Fig. 2. Temperature-dependence of the magnetic susceptibility of **3**.

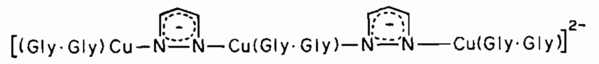


I

interaction between the two copper(II) ions in **2**. Accordingly, the structure of **2** can be proposed as the structural formula **I**. The dinuclear copper(II) complex bridged only by one pyrazolate ion has not been reported so far. The observed susceptibility for **3** obeyed the Curie–Weiss law in the temperature range $T \gtrsim 15$ K and $T \lesssim 7$ K: the Curie and Weiss constants were determined as $C_h = 0.421$ emu K mol^{-1} and $\theta_h = -13.4$ K for the high temperature range, and $C_l = 0.153$ emu K mol^{-1} and $\theta_l = -0.8$ K for the low temperature range. Furthermore, the ratio $C_h/C_l = 2.8$ suggests that a trinuclear cluster forms the magnetic unit in **3**. The theoretical susceptibility, χ_A, for a linear-chain trinuclear complex is given by a solid line in Fig. 2. The calculation of these χ_A values was carried out according to eqn. (2) [33]

$$\chi_A = \frac{Ng^2\beta^2}{12kT} \times \frac{1 + \exp(-2J/kT) + 10\exp(J/kT)}{1 + \exp(-2J/kT) + 2\exp(J/kT)} + N\alpha \tag{2}$$

where J denotes the exchange integral between three copper(II) ions as shown in Fig. 3. Magnetic parameters were as follows: $g = 2.12$, $N\alpha = 60 \times 10^{-6}$ cgs emu mol^{-1} and $J = -9.4$ cm^{-1}. Thus complex **3** is estimated to have the trinuclear structure given in **II**.



II

The color of crystals, magnetic moments at room temperature, absorption maxima for the d–d transition bands and electric conductances of these compounds are tabulated in Table II, together with those of the other pyrazole- and imidazole-containing copper(II) complexes. The λ_{max} value for **2** is in good agreement with the corresponding imidazolate-bridged complex **12** both in solid and in aqueous solution. We pointed out in the previous report [30] that the dimeric structures bridged by imidazolate in **12** are retained in basic solution (pH *ca.* 10). From the result and the electric conductance data given in Table II, we suppose that complex **2** also exists as a dinuclear complex in alkaline solution. The ESR spectra of **2** in 50% aqueous ethanol at 77 K are illustrated in Fig. 4. The spectrum at pH 9.5 (Fig. 4(a)) is typical of copper(II) dimers in a triplet state. The appearance of the seven hyperfine splitting may be caused by the inter-dimer spin-exchange interaction of $[Cu_2(Gly{\cdot}Gly)_2(pz)]^-$. The intricate spectrum at pH 5.5 (Fig. 4(b)) demonstrates that the dimeric structure bridged by pyrazolate is partly broken to monomeric species such as [Cu(Gly·Gly)(pzH)] (**1**) and [Cu(Gly·Gly)(OH$_2$)]. The ESR spectrum of **3** at pH 10.8 is identical to that of **2** at pH 9.5, indicating that **2** and **3** are present as complexes with the same structure in solution.

$$\mathrm{Cu} \overset{J}{\text{———}} \mathrm{Cu} \overset{J}{\text{———}} \mathrm{Cu}$$

Fig. 3. Spin–spin interaction in linear-chain trinuclear copper(II) complexes.

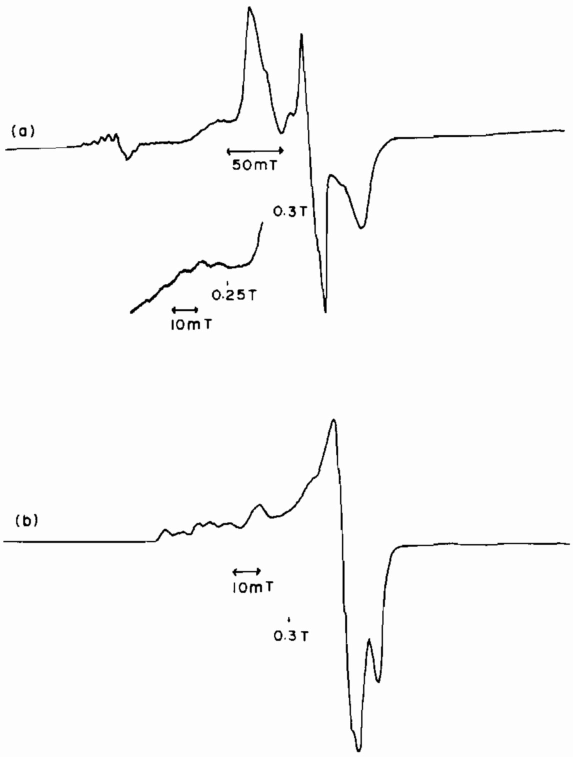


Fig. 4. ESR spectrum of **2** at 77 K.

It seems likely that **1** has a similar structure to **11** from the resemblance of the λ_{max} due to d–d transition and electric conductance data (Table II). The ESR spectrum for **1** is also characteristic of monomeric copper(II) complexes ($g_\parallel = 2.226$, $g_\perp = 2.051$, and $A_\parallel = 18.2$ mK).

Copper(II) Complexes with Diethylenetriamine

The copper(II) complexes **4–8** with diethylenetriamine and pyrazole or 3-methylpyrazole were isolated as violet–blue crystals. To obtain detailed information about the singlet–triplet splittings in complexes **5** and **6**, magnetic susceptibilities were determined as a function of temperature The

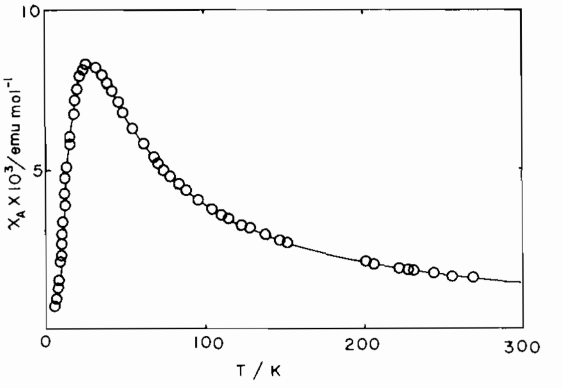


Fig. 5. Temperature-dependence of magnetic susceptibility of **5**.

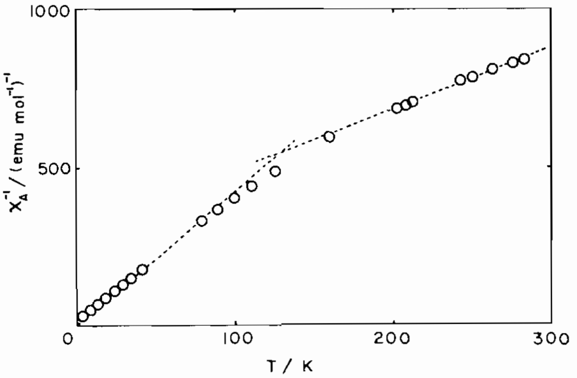
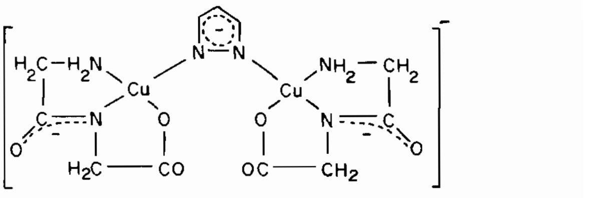


Fig. 6. Temperature-dependence of magnetic susceptibility of **6**.

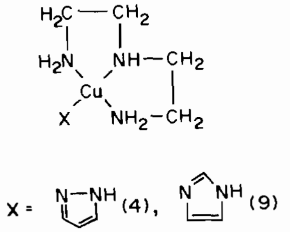
magnetic susceptibility of **5** in the 4.2–300 K region is indicated in Fig. 5. Least-squares fitting of the susceptibility data to the Bleaney–Bowers eqn. (1) [32] gives $g = 2.18$, $J = -21.5$ cm^{-1} and $N\alpha = 60 \times 10^{-6}$ cgs emu mol^{-1}. This shows that antiferromagnetic interaction is present in the dimeric complex **5**. The magnetic property of the corresponding ClO_4^- compound (**6**) is considerably different from that for **5**. The magnetic moment of **6** at room temperature was rather lower than that for the value of copper(II) complex without interaction (Table II). Figure 6 represents the temperature-dependence of the magnetic susceptibility for **6**. The fairly large Weiss constant ($\theta_h = -154$ K) is observed for high-temperature range ($T \gtrsim 130$ K), indicating the existence of strong antiferromagnetic interaction, but is not observed apparently ($\theta_l = \sim 0$ K) in the low-temperature range ($T < 130$ K). A further detailed discussion of the susceptibility and the crystal structure of complexes **5** and **6** will be reported subsequently. The magnetic moments of the 3-methylpyrazolate–bridged dinuclear copper(II) complexes **7** and **8** at room temperature are given in Table II. There is a clear difference in magnetic moments for complexes **6** and **8**, which suggests that antiferromagnetic interaction between copper(II) ions in **8** is fairly weak. This is believed to be due to a structural change owing to the substitution of methyl group into the pyrazolate moiety of **6**.

The absorption maxima for the d–d transition band of **6**, **7**, and **8** in nujol are in good agreement with each other. Evidently this is attributed to the same coordination environment around copper(II) in their complexes. Also, it is clear that the dimeric structures in the solid state of **6**–**8** are basically maintained even in aqueous solutions judging from spectral data and electric conductances given in Table II. Similar properties are seen in the corresponding imidazolate-bridged complex **10**. The absorption maximum in nujol of **5** shifts to a slightly longer wavelength region than those of **6**–**8**. Possibly this is due to the Br^- bridging as shown in structural formula **III**. But, it is considered that the structure of **5** in aqueous solution is identical to those for **6**–**8** from spectral and electric conductance data in solution (Table II).



III

As given in Table II, the magnetic and spectral properties of **4** are similar to those for corresponding imidazole-containing complex **9**. The ESR spectra of **4** and **9** are characteristic of monomeric copper(II) complexes, their parameters being analogous to each other (**4**: $g_\parallel = 2.219$, $g_\perp = 2.052$ and $A_\parallel = 20.4$ mK; **9**: $g_\parallel = 2.216$, $g_\perp = 2.052$ and $A_\parallel = 20.3$ mK). From these facts and their electric conductances (Table II), it is evident that compounds **4** and **9** are the analogous monomeric complexes, **IV**.



IV

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