September, 1986] © 1986 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 59, 2755—2760 (1986) 2755

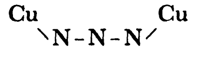
Azide-, Thiocyanate- or Cyanate-Bridged Di- and Trinuclear Copper(II) Complexes with *N,N,N′,N′*-Tetramethylethylenediamine, *N,N*-Diethylethylenediamine, 2,2′-Bipyridyl or 1,10-Phenanthroline

Yasuo Nakao,* Hideo Nakamura, Wasuke Mori,[†] Takeshi Sakurai,[†]
Shinnichiro Suzuki,[†] and Akitsugu Nakahara[†]
Chemical Laboratory, Faculty of Education, Okayama University, Okayama 700
[†]Institute of Chemistry, College of General Education, Osaka University,
Toyonaka, Osaka 560

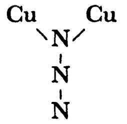
(Received December 26, 1985)

A series of di- and trinuclear copper(II) complexes containing *N,N,N′,N′*-tetramethylethylenediamine (tmen), *N,N*-diethylethylenediamine(deen), 2,2′-bipyridyl(bpy) or 1,10-phenanthroline(phen) and azide, thiocyanate or cyanate ions have been prepared and characterized by their magnetic susceptibilities, infrared, electronic, and ESR spectra, and electric conductances. Magnetic susceptibility data for the dimeric complex $[Cu_2(tmen)_2(N_3)_2](ClO_4)_2$ shows the presence of a ferromagnetic interaction (Weiss constant $\theta=+30$ K) above 150 K, whereas the two copper(II) ions are apparently non-coupled below 150 K. On the other hand, the dimeric complex $[Cu_2(bpy)_2(N_3)_2](ClO_4)_2$ shows the presence of a large antiferromagnetic exchange interaction ($\mu_{eff}<0.6$ B.M. at room temperature). The complex $[Cu_3(tmen)_3(NCS)_3](ClO_4)_3\cdot 1.5H_2O$ is estimated to have the trimeric structure; the temperature-dependence of the magnetic susceptibility for this compound indicates the existence of an antiferromagnetic exchange interaction with a J value of $-175\ cm^{-1}$.

It is well-known that azide, thiocyanate, and cyanate ions act as a bridging ligand between metal atoms. The azide ligand can bridge two metal ions in an end-to-end fashion as in (1) or in an end-on fashion as in (2).[1—22] On the other hand,

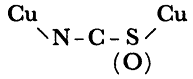


(1)

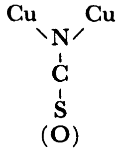


(2)

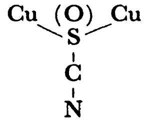
three bridging modes are available for the thiocyanate and cyanate ions ((3)—(5)).[15,23—29] Some dimeric copper complexes



(3)



(4)



(5)

containing these bridging groups are of particular interest as synthetic models for the natural dinuclear copper proteins and their derivatives.[9,11,12,20]

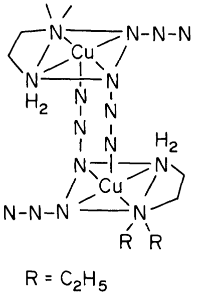
In this paper we report the preparation and characterization of dimeric and trimeric copper(II) complexes containing *N,N,N′,N′*-tetramethylethylenediamine(tmen), *N,N*-diethylethylenediamine (deen), 2,2′-bipyridyl(bpy) or 1,10-phenanthroline(phen) and azide, thiocyanate or cyanate anions.

Experimental

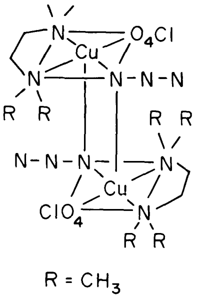
Preparation of Copper(II) Complexes. $Cu_2(tmen)_2X_4\cdot nH_2O$ (X=N_3, NCS, and NCO), 1, 4, and 6. To a mixture of $Cu(ClO_4)_2\cdot 6H_2O$ (1.85 g, 5 mmol) and 20 cm^3 of ethanol were added tmen(0.58 g, 5 mmol) and NaX(X=N_3, NCS, or NCO, 10 mmol). The reaction mixture was stirred at room temperature for 1 h, and then allowed to stand for several hours in a refrigerator. After it had been filtered off, the precipitate was recrystallized from ethanol.

$Cu_2(deen)_2X_4\cdot nH_2O$(X=$N_3$, NCS, and NCO), 7, 9, and 10. These complexes were also prepared in the same way as that for $Cu_2(tmen)_2X_4\cdot nH_2O$, and then recrystallized from ethanol.

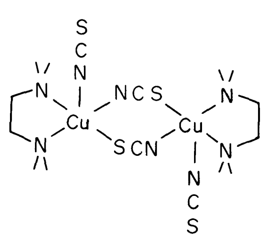
$Cu_2(tmen)_2(N_3)_2(ClO_4)_2$, 2 and $Cu_3(tmen)_3(NCS)_3(ClO_4)_3\cdot 1.5H_2O$, 5. Except that 4 mmol of NaX(X=N_3 or NCS) was used, the same procedure as that for the preparation of $Cu_2(tmen)_2X_4\cdot nH_2O$ was adopted. The products obtained were washed by ethanol.



I



II



III

Table 1. Analytical Data for the Complexes

No.	Complex	H(%)		C(%)		N(%)	
		Found	Calcd	Found	Calcd	Found	Calcd
1	$Cu_2(tmen)_2(N_3)_4$	6.07	6.12	27.56	27.31	42.45	42.48
2	$Cu_2(tmen)_2(N_3)_2(ClO_4)_2$	5.15	5.03	22.70	22.43	21.95	21.80
3	$Cu_2(tmen)_2(N_3)_2(NO_3)_2 \cdot 2.5H_2O$	5.70	6.10	23.16	23.52	27.74	27.44
4	$Cu_2(tmen)_2(NCS)_4$	5.31	5.46	32.12	32.46	18.72	18.94
5	$Cu_3(tmen)_3(NCS)_3(ClO_4)_3 \cdot 1.5H_2O$	5.09	4.96	24.30	24.27	11.90	12.14
6	$Cu_2(tmen)_2(NCO)_4 \cdot 1.5H_2O$	6.03	6.37	35.08	34.64	19.81	20.21
7	$Cu_2(deen)_2(N_3)_4$	5.90	6.12	26.82	27.31	42.52	42.48
8	$Cu_2(deen)_2(N_3)_2(ClO_4)_2$	4.88	5.03	22.14	22.43	21.74	21.80
9	$Cu_2(deen)_2(NCS)_4 \cdot 0.5H_2O$	5.21	5.55	31.61	31.98	18.61	18.65
10	$Cu_2(deen)_2(NCO)_4$	6.10	6.13	36.26	36.42	20.95	21.24
11	$Cu_2(bpy)_2(N_3)_4$	2.68	2.66	39.54	39.53	36.61	36.89
12	$Cu_2(bpy)_2(N_3)_2(ClO_4)_2$	2.36	2.24	34.14	33.25	19.17	19.39
13	$Cu_2(bpy)_2(NCS)_4$	2.47	2.41	43.00	42.90	16.63	16.68
14	$Cu_2(bpy)_2(NCO)_4$	2.67	2.66	47.19	47.44	17.95	18.45
15	$Cu_2(phen)_2(N_3)_4$	2.51	2.46	44.03	43.96	33.71	34.19

The complex $Cu_2(tmen)_2(N_3)_2(NO_3)_2 \cdot 2.5H_2O$, **3** was isolated by the same way using $Cu(NO_3)_2 \cdot 3H_2O$.

$Cu_2(deen)_2(N_3)_2(ClO_4)_2$, 8. This was obtained by the same method as **2** by use of deen.

$Cu_2(bpy)_2X_4$(X=N_3, NCS, and NCO), and $Cu_2(phen)_2(N_3)_4$, 11, 13, 14, and 15. These were prepared by the same method as **1** using bpy or phen instead of tmen. Recrystallization was carried out using aqueous ethanol (1:1 by volume).

$Cu_2(bpy)_2(N_3)_2(ClO_4)_2$, 12. Except that 5 mmol of NaN_3 was used, the same method as that for the preparation of **11** was adopted. The purification was carried out by washing with ethanol.

The analytical data for the compounds described above are collected in Table 1.

Measurements. Infrared absorption spectra were measured with a JASCO A-102 infrared spectrophotometer with KBr disk. Visible absorption spectra of DMF solutions were recorded on 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 Faraday method. The instrument was calibrated with $CuSO_4 \cdot 5H_2O$. The X-band ESR spectra of powdered sample at 77 K were recorded at 9.3 GHz and 100 kHz modulation frequency with a JEOL JES-FE-1X. The g values were calibrated based on Li-TCNQ (g= 2.0025). The X-ray powder patterns were recorded by the use of a Rigaku RAD-1B diffractometer at room temperature, with the Cu-$K\alpha$ line filtered through nickel. The differential scanning calorimetry measurement was carried out by the use of Rigaku DSC 8230. A Toa Denpa Conduct Meter CM-7B was used for conductivity measurements.

Results and Discussion

Copper(II) Complexes with tmen and deen. The dimeric copper(II) complex **1** had already been prepared and characterized by Bkouche-Waksman et al.[13] The similar type of complexes (**1**—**10**) bridged by N_3^-, NCS^-, and NCO^- were newly prepared by the method described in the Experimental section. The color of crystals, magnetic moments at room temperature, IR spectral and electric conductance data are given in Table 2. The complex **1** has centrosymmetric dimeric units with two asymmetric end-to-end azide bridges.[13] However, it has been pointed out that the two copper(II) ions are magnetically non-coupled in the complex **1**.[13] The complex **7** shows the similar magnetic moment and λ_{max} due to d-d transition(Table 3) as those for **1**, hence this compound is estimated to have the dimeric structure I like the corresponding complex **1**. The magnetic moments of the complexes **2** and **8** at room temperature are higher than that of copper(II) complex having no interaction. In order to obtain detailed information on the structure of these complexes, the magnetic susceptibility of **2** was measured over the temperature range 4.2—300 K. Figure 1 shows the temperature-dependence of the magnetic susceptibility. The χ_A^{-1}—T profile in this Figure curves at about 150 K, indicating the possibility of phase transition. The differential scanning calorimetry(DSC) curve for **2** showed the existence of a single broad endotherm at ca. 138 K. These results for **2** suggest that there is a ferromagnetic exchange interaction(Weiss constant θ=+30 K) between the two copper(II) ions above ca. 150 K. However, the two copper(II) ions are essentially non-coupled below 150 K. The similar behavior was recently observed for complexes $[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_2](ClO_4)_2$[31] and $[Cu_2(2\text{-}Pca{=}\beta\text{-}Ala)_2(N_3)_2] \cdot 2H_2O$.[31] Thus, the complex **2** is considered to have the dimeric structure II like $[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_2]$ $(ClO_4)_2$ with the end-on azide bridging. The splitting of ClO_4^- vibration(1090, 1115, and 1145 cm^{-1}) in IR spectrum supports the validity of this structure. The structure of **8** is

Table 2. Physical Properties of the Complexes

Complex No.	Color	μ_{eff}/BM(K)	IR	Λ
			$\nu_{\mathrm{asym}}(N_3^-)$ or $\nu(C{\equiv}N)$/cm^{-1}	S cm^2 mol^{-1}
1	Dark green	1.85 (286)	2025 vs, 2080 vs, 2100 vw	14
2	Grey blue	2.02 (287)	2050 vs, 2080 vs	133
3	Dark green	1.92 (299)	2080 vs, 2100 vs	143
4	Dark green	1.90 (287)	2080 vs, 2110 vs	73
5	Dark green	1.34 (286)	2110 vs, 2140 vw	255
6	Blue violet	1.78 (285.5)	2190 vs, 2230 vs	35
7	Dark green	1.81 (288.5)	2015 vw, 2030 vs, 2050 vs, 2075 vw	9
8	Dark green	1.99 (287.5)	2070 vs, 2110 w	141
9	Green	1.87 (288)	2100 vs, 2125 vs	66
10	Violet blue	1.83 (288)	2190 vs, 2205 vw	10
11	Dark green	1.89 (293)	2020 s, 2070 vs	6
12	Brown green	<0.6 (288)	2070 vw, 2100 vs	136
13	Green	1.90 (293)	2100 vs, 2125 vs	61
14	Blue	1.86 (296)	2190 s, 2210 vs	13
15	Brown green	1.87 (289.5)	2030 vs, 2060 vs	6

Table 3. Electronic Spectral Data of the Complexes[a)]

Complex No.	λ_{max}/nm(log ε/mol^{-1} dm^3 cm^{-1})
1	615 (2.53), 450 sh (3.2)[b)] 390 (3.46)
2	656 (2.27), 394 (3.40)
3	656 (2.34), 394 (3.51)
4	656 (2.18), 374 (3.16)
5	664 (2.06), 372 (3.01)
6	641 (2.06), 330 sh (3.4)[b)]
7	608 (2.58), 384 (3.60)
8	672 (2.40), 386 (3.48)
9	673 (2.20), 363 (3.10)
10	654 (2.04), 315 sh (3.4)[b)]
11	628 (2.49), 448 sh (3.4)[b)] 393 (3.54)
12	678 (2.28), 398 (3.47)
13	680 (2.05), 388 (3.02)
14	655 (1.89), 335 sh (3.4)[b)] 318 (3.51)
15	636 (2.51), 450 (3.40) 395 (3.57)

a) Solvent: DMF. b) sh=shoulder.

expected to be analogous to that of **2** because of its similar magnetic moment and the splitting mode of ClO_4^- (1090, 1120, and 1145 cm^{-1}) in IR spectrum. The above structures are also born out by the ESR parameters of both the complexes **2** ($g_{/\!/}=2.18$ and $g_{\perp}=2.07$) and **8** ($g_{/\!/}=2.15$ and $g_{\perp}=2.05$). Further, the signals due to triplet state were found at $g=3.0$ and $g=1.2$ for **8** (Fig. 2), which exhibits that the complex is a dinuclear copper(II) complex. The spectral lines in the $\Delta M_s=1$ region of Fig. 2 are not easily interpreted. Because the sample **8** is a good crystalline solid, we consider that the amount of impurities (probably the copper(II) monomers of unknown composition) is very slight. However, the $\Delta M_s=1$ signal in Fig. 2 may be attributed to some contaminants.

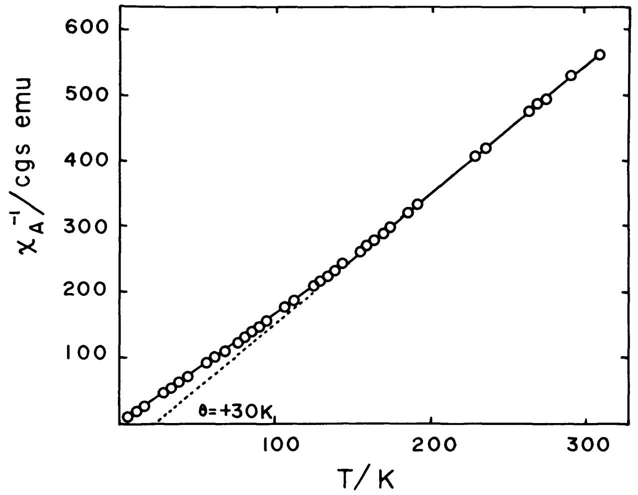


Fig. 1. Temperature-dependence of the magnetic susceptibility of **2**.

The room-temperature magnetic moments of the thiocyanate containing complexes **4** and **9** were close to the values for non-interacting or weakly interacting copper(II) complexes. The IR spectra of these complexes showed two C–N stretching vibrations of thiocyanato group in the region 2080—2125 cm^{-1} (Table 2). This suggests that there are two kinds of thiocyanato group of different bonding modes in each complex. It is pointed out that the complexes bridged by thiocyanate exhibit ν(CN) above 2100 cm^{-1}.[24)] In addition, the wavenumbers of the two ν(CN) vibrations for **4** and **9** are close to those for α- and β-$[Cu_2(NCS)_4(dmtp)_4]$[28)] which have the skeleton  $\mathrm{Cu}\overset{\diagup\mathrm{NCS}\diagdown}{\underset{\diagdown\mathrm{SCN}\diagup}{\quad}}\mathrm{Cu}$, hence two Cu–NCS bonds. Thus the

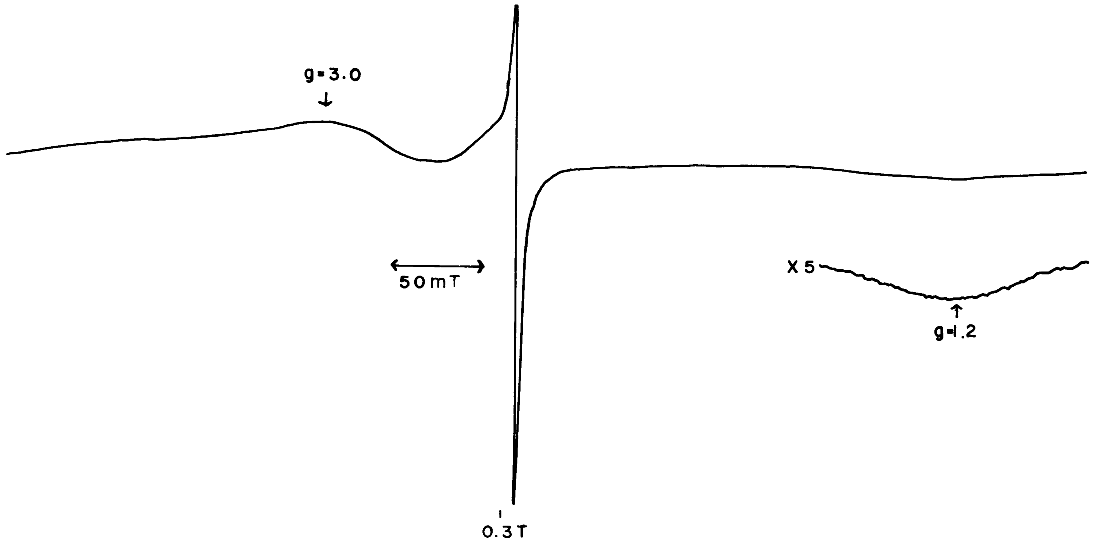


Fig. 2. ESR spectrum of **8** at 77 K.

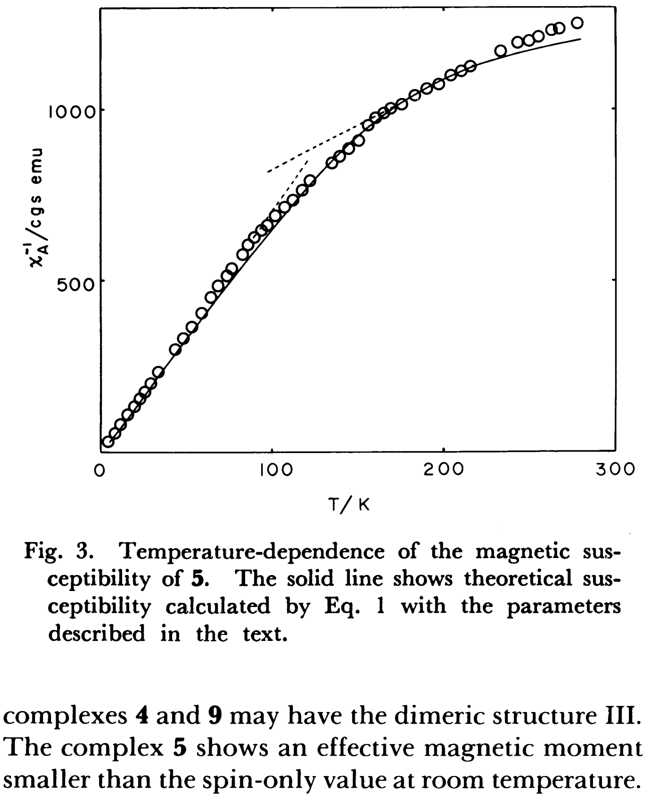


Fig. 3. Temperature-dependence of the magnetic susceptibility of **5**. The solid line shows theoretical susceptibility calculated by Eq. 1 with the parameters described in the text.

complexes **4** and **9** may have the dimeric structure III. The complex **5** shows an effective magnetic moment smaller than the spin-only value at room temperature. The magnetic susceptibility was measured over the range from liquid helium temperature to room temperature. Figure 3 represents the temperature-dependence of the magnetic susceptibility. The observed susceptibility obeyed the Curie–Weiss law in the temperature range $T \gtrsim 160$ K and $T \lesssim 90$ K: the Curie and Weiss constants were determined as $C_h = 0.38$ emu K mol^{-1} and $\theta_h = -210$ K for the high temperature range, and $C_l = 0.143$ emu K mol^{-1} and $\theta_l = 0$ K for the low temperature range. Furthermore, the ratio C_h/C_l is 2.7. This magnetic behavior indicates that the complex **5** is the compound

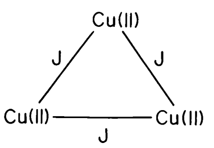


Fig. 4. Spin-spin interaction in triangular trinuclear copper(II) complexes.

containing three copper(II) ions magnetically interacted. The theoretical susceptibility, χ_A, for triangular trinuclear complex is given by a solid line in Fig. 3. The calculation of these χ_A values was carried out according to the Eq. 1[30]

$$\chi_A = \frac{Ng^2\mu_B^2}{12kT} \times \frac{1+10\exp(3J/kT)}{1+2\exp(3J/kT)} + N\alpha, \tag{1}$$

where J denotes the exchange integral between copper(II) ions as indicated in Fig. 4. Magnetic parameters were as follows: $g=2.16$, $N\alpha = 60 \times 10^{-6}$ cgs emu mol^{-1}, $J = -175$ cm^{-1}. Thus the complex **5** is considered to have the triangular trimeric structure bridged by thiocyanate ions. This complex indicates the rhombic ESR spectrum with $g_1=2.18$, $g_2=2.13$, and $g_3=2.07$ in the $\Delta M_s=1$ region.

The $\Delta M_s=2$ transition in the X-band ESR spectra for cyanate containing complexes **6** and **10** was not observed at half-field. The same results were found for the thiocyanato complexes **4** and **9**. Although there are no other evidences for dimeric structure of **6** and **10**, these compounds are also supposed to have a dinuclear structure similar to III proposed for thiocyanato complexes.

The electric conductances (Table 2) of **1**, **7**, and **10** show that these complexes are non-electrolytes in DMF solutions. Accordingly, the structures in the solid state of **1**, **7**, and **10** are supposed to be maintained in DMF. The molar conductances of **2**, **3**, and **8** are in the range found for 1:2 electrolytes, suggesting that these compounds undergo significant structural changes upon dissolution. Also, a partial dissociation of NCS^- for **4** and **9** takes place in DMF.

All of the azido complexes display an intense band at 380—390 nm(log ε, ca. 3.5) (Table 3). These bands are assigned to azide to copper CT transitions.[32,33] The CT bands are also observed for the thiocyanato complexes around 370 nm (Table 3).[33] The similar $N_3^- \rightarrow$ and $SCN^- \rightarrow Cu$ CT bands are observed in metazido- and metthiocyanato-hemocyanin in which the peroxide of oxy-hemocyanin is displaced by N_3^- and NCS^-, respectively.[33]

Copper(II) Complexes with bpy and phen. The copper(II) complexes **11**—**15** were prepared by the same method as that for **1**—**10** by using 2,2′-bipyridyl or 1,10-phenanthroline. The complexes with same compositions with ours, $[Cu(bpy)(N_3)_2]$, $[Cu(bpy)(NCS)_2]$, and $[Cu(phen)(N_3)_2]$ were described by Dutta and De.[34] Bushnell and Kahn[6] reported the crystal and molecular structure of $[Cu(bpy)(N_3)_2]$,[34] which has the polymeric structure with asymmetric end-on azide bridges. No difference was observed in IR spectra of $[Cu(bpy)(N_3)_2]$ and **11**. However, the low-angle lines of X-ray powder diffraction patterns (Fig. 5) for both complexes are fairly different in location and relative intensity. This indicates a somewhat different

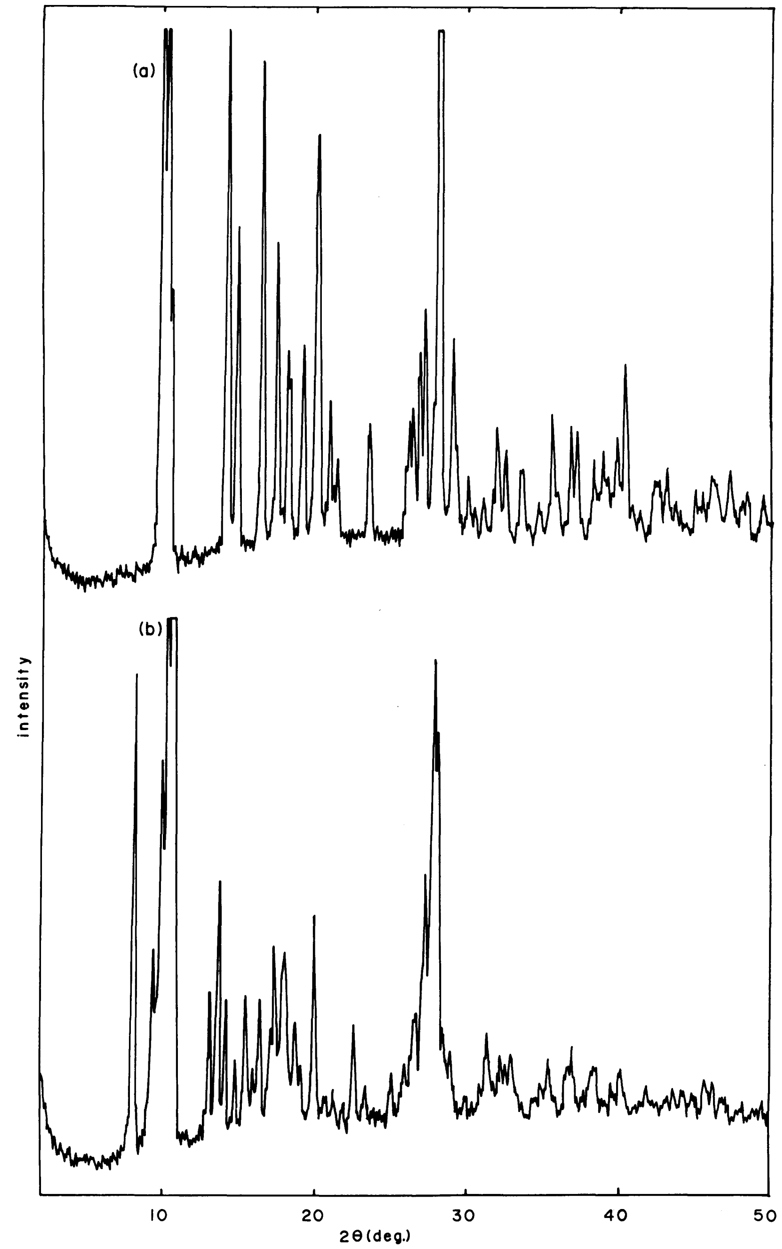
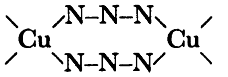
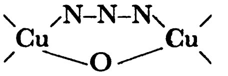


Fig. 5. Comparison of X-ray powder diffraction patterns for **11** (a) and $[Cu(bpy)(N_3)_2]$ (b).

packing arrangement in the unit cells of $[\mathrm{Cu(bpy)(N_3)_2}]$6) and **11**. Although more precise measurements of magnetic susceptibilities and the determination of the crystal structure of **11** will be required for elucidating the difference between $[\mathrm{Cu(bpy)(N_3)_2}]$6) and **11**, it may be suggested that **11** has a dimeric structure similar to **1**. The magnetic moment of **12** at room temperature shows 0.6 B.M. However, we consider that the compound **12** has a property near diamagnetism, since the presence of several % of paramagnetic impurities in the solid sample **12** is confirmed from the experiment on variable-temperature magnetic susceptibility. Antiferromagnetic interactions have been found in many copper(II) complexes containing end-to-end azide bridges.8,9,11,13,22) The complex **12** is, therefore, considered to have the structure with end-to-end azide bridging. Also, we imagine that the two copper(II) coordination planes are nearly coplanar and the azide ions bridge the two copper(II) ions in the coordination planes, because the large spin–spin interaction usually operates only when the coplanality of the bridging group  is attained.8,9,11,13,22) Thus, we consider that the diamagnetic metazido-hemocyanins35,36) derived from the hemocyanins of *Busycon canaliculatum* and *Limulus polyphemus* contain  plane. These complexes **11**—**15** exhibit the similar behaviors as **1**—**10** in electronic spectra and electric conductances (Tables 2 and 3).

We thank Miss Sachiyo Nishi for her collaboration in the preparation of compounds. We also indebted to Dr. Isao Kusachi of Okayama University for obtaining the results of the X-ray diffraction and Mr. Sakira Kaneko of Rigaku Denki Co. for DSC measurement and his valuable disscussion. This work was supported in part by a Grant-in-Aid for Scientific Reserch (C) (No. 58540389) from the Ministry of Education, Science and Culture.

References

1) I. Agrell, *Acta Chem. Scand.*, **21**, 2647 (1967).

2) I. Agrell and S. Lamnevik, *Acta Chem. Scand.*, **22**, 2038 (1968).

3) J. Drummond and J. S. Wood, *J. Chem. Soc., Chem. Commun.*, **1969**, 1373.

4) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **12**, 2422 (1973).

5) C. G. Barraclough, R. W. Brookes, and R. L. Martin, *Aust. J. Chem.*, **27**, 1843 (1974).

6) G. W. Bushnell and M. A. Kahn, *Can. J. Chem.*, **52**, 3125 (1974).

7) G. R. Hall, D. M. Duggan, and D. N. Hendrickson, *Inorg. Chem.*, **14**, 1956 (1975).

8) T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, **17**, 444 (1978).

9) Y. Agnus, R. Louis, and R. Weiss, *J. Am. Chem. Soc.*, **101**, 3381 (1979).

10) M. G. B. Drew, M. McCann, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, **1979**, 481.

11) V. McKee, J. V. Dagdigian, R. Bau, and C. A. Reed, *J. Am. Chem. Soc.*, **103**, 7000 (1981).

12) J. Comarmond, P. Plumere, J.-M. Lehn, Y. Agnus, R. Louis, R. Weiss, O. Kahn, and I. Morgenstern-Badarau, *J. Am. Chem. Soc.*, **104**, 6330 (1982).

13) I. Bkouche-Waksman, S. Sikorav, and O. Kahn, *J. Cryst. Spect. Res.*, **13**, 303 (1983).

14) O. Kahn, S. Sikorav, J. Gouteron, S. Jeannin, and Y. Jeannin, *Inorg. Chem.*, **22**, 2877 (1983).

15) Y. Nakao, M. Yamazaki, S. Suzuki, W. Mori, A. Nakahara, K. Matsumoto, and S. Ooi, *Inorg. Chim. Acta*, **74**, 159 (1983).

16) S. Sikorav, I. Bkouche-Waksman, and O. Kahn, *Inorg. Chem.*, **23**, 490 (1984).

17) Y. Agnus, R. Louis, J.-P. Gisselbrecht, R. Weiss, *J. Am. Chem. Soc.*, **106**, 93 (1984).

18) M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta*, **85**, 117 (1984).

19) I. Bkouche-Waksman, M.-L. Boillot, O. Kahn, and S. Sikorav, *Inorg. Chem.*, **23**, 4454 (1984).

20) V. McKee, M. Zvagulis, J. V. Dagdigian, M. G. Patch, and C. A. Reed, *J. Am. Chem. Soc.*, **106**, 4765 (1984).

21) M.-L. Boillot, O. Kahn, C. J. O'Connor, J. Gouteron, S. Jeannin, and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, **1985**, 178.

22) K. Matsumoto, S. Ooi, K. Nakatsuka, W. Mori, S. Suzuki, A. Nakahara, and Y. Nakao, *J. Chem. Soc., Dalton Trans.*, **1985**, 2095.

23) E. J. Laskowski, D. M. Duggan, and D. N. Hendrickson, *Inorg. Chem.*, **14**, 2449 (1975).

24) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," Wiley, New York (1977), p. 270.

25) M. G. B. Drew, M. McCann, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, **1981**, 1868.

26) S. M. Nelson and F. S. Esho, *J. Chem. Soc., Chem. Commun.*, **1981**, 388.

27) M. Nelson, F. S. Esho, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, **1982**, 407.

28) J. G. Haasnoot, W. L. Driessen, and J. Reedijk, *Inorg. Chem.*, **23**, 2803 (1984). The ligand, dmtp, represents 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine.

29) M.-L. Boillot, O. Kahn, C. J. O'Connor, J. Gouteron, S. Jeannin, and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, **1985**, 178.

30) "Theory and Applications of Molecular Paramagnetism," ed by E. A. Boudreaux and L. M. Mulay, John Wiley, New York (1976).

31) These complexes are described in a previous paper.22) The ligands, 2-Pca=Hist and 2-Pca=β-Ala, represent Schiff bases derived from 2-pyridinecarbaldehyde and histamine, and 2-pyridinecarbaldehyde and β-alanine, respectively.

32) S. Masatatsu, H. Kanatomi, Y. Demura, and I. Murase, *Bull. Chem. Soc. Jpn.*, **57**, 1003 (1984).

33) R. S. Himmelwright, N. C. Eickman, C. D. LuBien, and E. I. Solomon, *J. Am. Chem. Soc.*, **102**, 5378 (1980).

34) R. L. Dutta and D. De, *J. Indian Chem. Soc.*, **46**, 1 (1969).

35) G. L. Woolery, L. Powers, M. Winkler, E. I. Solomon, and T. G. Spiro, *J. Am. Chem. Soc.*, **106**, 86 (1984).

36) D. E. Wilcox, J. R. Long, and E. I. Solomon, *J. Am. Chem. Soc.*, **106**, 2186 (1984).