Inorganica Chimica Acta, *74* (1983) 159–167

Monomeric and Dimeric Copper(II) Complexes Composed of some Terdentate Schiff Bases and Oxalate, Oxamate, Azide, Thiocyanate or Cyanate Ions

YASUO NAKAO, MITSUHIRO YAMAZAKI
Chemical Laboratory, Faculty of Education, Okayama University, Okayama 700, Japan
SHINNICHIRO SUZUKI, WASUKE MORI, AKITSUGU NAKAHARA
Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan
KEIJI MATSUMOTO and SHUN'ICHIRO OOI
Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Received February 25, 1983

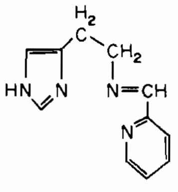
Monomeric and dimeric copper(II) complexes containing the Schiff bases derived from 2-pyridinecarbaldehyde and histamine (2-Pca=Hist), 2-(2-aminoethyl)pyridine (2-Pca=2-Aep), or β-alanine (2-Pca=β-Ala), and oxalate (ox), oxamate (om), azide, thiocyanate, or cyanate ions have been prepared and characterized based on their electronic, infrared and electron spin resonance spectra, and magnetic susceptibilities.

The structure of the monomeric copper(II) complex, $[Cu(2\text{-}Pca{=}Hist)(N_3)_2]$ *has been determined by the X-ray diffraction method. The crystal of* $[Cu(2\text{-}Pca{=}Hist)(N_3)_2]$ *is triclinic, with* $a = 10.262(8)$, $b = 9.177(6)$, $c = 7.688(5)$ Å, $\alpha = 104.42(4)$, $\beta = 94.09(4)$, $\gamma = 92.64(4)^\circ$, $Z = 2$, *and space group* $P\bar{1}$. *The five-coordinate geometry around copper(II) ion is intermediate between trigonal-bipyramid and square-pyramid.*

The half-field absorption in the $\Delta M_s = 2$ *region of powdered X-band ESR spectra was scarcely observed for* $[Cu(2\text{-}Pca{=}2\text{-}Aep)(N_3)_2]$, $[Cu(2\text{-}Pca{=}2\text{-}Aep)(NCS)_2]$, $[Cu(2\text{-}Pca{=}2\text{-}Aep)(NCO)_2]$ *and* $[Cu(2\text{-}Pca{=}Hist(N_3)_2]$. *The compounds* $[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_3]Cl\cdot 2H_2O$ *and* $[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_2](ClO_4)_2$ *which are considered to have a dimeric structure exhibited the half-field absorption in the same region. However, an exchange interaction was hardly observed down to 4.2 °K in the magnetic susceptibility measurement for* $[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_3]Cl\cdot 2H_2O$. *The susceptibility of an oxalate-bridged copper(II) complex,* $[Cu_2(2\text{-}Pca{=}Hist)_2(ox)](ClO_4)_2$, *showed an antiferromagnetic interaction* ($J = -21.5$ cm^{-1}) *and the X-band ESR spectrum for the powdered sample showed a very weak absorption for the triplet state of such a dimer in the* $\Delta M_s = 2$ *region.*

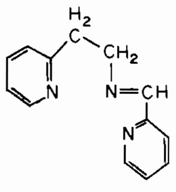
Introduction

A number of azide or oxalate-bridged binuclear copper(II) complexes have hitherto been studied with a view to understanding the strongly coupled binuclear copper(II) sites in some copper proteins [1–13]. These studies indicate that the magnitude of the antiferromagnetic exchange interaction depends strongly upon the geometry around copper(II) ions. Recently we studied the preparation and characterization of monomeric and dimeric copper(II) complexes containing the Schiff bases (I–III) derived from 2-pyridinecarbaldehyde and histamine, (2-Pca=Hist), 2-(2-aminoethyl)pyridine, (2-Pca=2-Aep), or β-alanine, (2-Pca=β-Ala), and oxalate (ox), oxamate (om), azide, thiocyanate or cyanate ions.



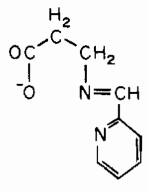
2-Pca=Hist

I



2-Pca=2-Aep

II



2-Pca=β-Ala

III

This paper also describes the crystal and molecular structure of the monomeric copper(II) complex with the Schiff base composed of 2-pyridinecarbaldehyde and histamine, and two azide ions, $[Cu(2\text{-}Pca{=}Hist)(N_3)_2]$.

Experimental

Preparation of Copper(II) Complexes

$[Cu_2(2\text{-}Pca{=}Hist)_2(ox)](ClO_4)_2$, 1

To a mixture of 2-pyridinecarbaldehyde (1.07 g, 10 mmol), histamine dihydrochloride (1.84 g, 10 mmol) and copper(II) perchlorate hexahydrate (3.70 g, 10 mmol) in 10 cm^3 of water was added a saturated aqueous solution of oxalic acid dihydrate (1.26 g,

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10 mmol). The resulting mixture was adjusted to pH 6 by NaOH aqueous solution and stirred at room temperature for 1 h. After cooling a dark green crystalline product was isolated by filtration. Recrystallization from water gave blue-green crystals of *1*.

$[Cu_2(2\text{-}Pca{=}2\text{-}Aep)_2(ox)](ClO_4)_2$, 2

This complex was prepared according to a similar procedure as described for the complex *1*, by using 2-pyridinecarbaldehyde (0.54 g, 5.0 mmol), 2-(2-aminoethyl)pyridine (0.61 g, 5.0 mmol), copper(II) perchlorate hexahydrate (1.85 g, 5.0 mmol) and oxalic acid dihydrate (1.26 g, 10 mmol). Recrystallization from water gave blue crystals of *2*.

$[Cu_2(2\text{-}Pca{=}\beta\text{-}Ala)_2(ox)]\cdot 3H_2O$, 3

To a mixture of 2-pyridinecarbaldehyde (0.54 g, 5.0 mmol), β-alanine (0.45 g, 5.0 mmol), and copper(II) nitrate trihydrate (1.2 g, 5.0 mmol) in 10 cm^3 of water was added a saturated aqueous solution of oxalic acid dihydrate (0.63 g, 5.0 mmol), being adjusted to pH 6 by NaOH aqueous solution. The reaction mixture was then stirred at room temperature for 30 min. After it had been filtered, the filtrate was evaporated to dryness. The green solid obtained was recrystallized from water–ethanol (1:1 by volume).

$[Cu_2(2\text{-}Pca{=}Hist)_2(om)](ClO_4)_2\cdot H_2O$, 4

To a mixture of 2-pyridinecarbaldehyde (0.54 g, 5.0 mmol), histamine dihydrochloride (0.92 g, 5.0 mmol), and oxamic acid (0.22 g, 2.5 mmol) in 100 cm^3 of warm water (50 °C) was added copper(II) perchlorate hexahydrate (1.85 g, 5.0 mmol). The resulting mixture was adjusted to pH 7 by NaOH aqueous solution and stirred at 60–70 °C for 1 h. After filtration, the filtrate was evaporated to dryness to give a green-blue crystalline product, which was recrystallized from water–ethanol (2:1 by volume).

$[Cu_2(2\text{-}Pca{=}2\text{-}Aep)_2(om)](ClO_4)_2$, 5

This complex was obtained as described for *4* using 2-(2-aminoethyl)pyridine (0.61 g, 5.0 mmol) instead of histamine dihydrochloride. Recrystallization was carried out by using aqueous ethanol (1:1 by volume).

$[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_3]Cl\cdot 2H_2O$, 6

2-Pyridinecarbaldehyde (0.54 g, 5.0 mmol), histamine dihydrochloride (0.92 g, 5.0 mmol), copper(II) nitrate trihydrate (1.2 g, 5.0 mmol) and a saturated aqueous solution of sodium azide (1.6 g, 25 mmol) were mixed in water (10 cm^3), and the resulting solution was adjusted to pH 6 with NaOH aqueous solution. The reaction mixture was stirred at room temperature for 30 min to give a yellow-green product, which was recrystallized from water.

$[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_3]Br\cdot 1.5H_2O$, 7

2-Pyridinecarbaldehyde (0.38 g, 3.5 mmol), histamine (0.40 g, 3.5 mmol), copper(II) bromide (0.78 g, 3.5 mmol), a saturated aqueous solution of sodium azide (0.46 g, 7.0 mmol) and 10 cm^3 of water were mixed together and stirred at room temperature for 30 min. The product was filtered and recrystallized from water.

$[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_3]N_3\cdot 1.5H_2O$, 8

2-Pyridinecarbaldehyde (0.38 g, 3.5 mmol), histamine (0.40 g, 3.5 mmol), copper(II) nitrate trihydrate (0.85 g, 3.5 mmol) and a saturated aqueous solution of sodium azide (1.14 g, 17.5 mmol) were mixed together in water (10 cm^3) and stirred at room temperature for 30 min. The isolated product was recrystallized from water.

$[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_2](ClO_4)_2$, 9

2-Pyridinecarbaldehyde (0.54 g, 5.0 mmol), histamine dihydrochloride (0.92 g, 5.0 mmol), copper(II) perchlorate hexahydrate (1.85 g, 5.0 mmol) and a saturated solution of sodium azide (0.65 g, 10 mmol) were mixed together in water (10 cm^3), being adjusted to pH 6 with NaOH aqueous solution. The reaction mixture was stirred at room temperature for 30 min to give a green product which was recrystallized from water.

$[Cu(2\text{-}Pca{=}Hist)(N_3)_2]$, 10

Except that a saturated aqueous solution of 0.65 g (10 mmol) of sodium azide was used, a similar procedure to that in the preparation of complex *6* was adopted. Recrystallization was carried out using water.

$[Cu(2\text{-}Pca{=}2\text{-}Aep)(N_3)](ClO_4$, 11

This was prepared in the same way as *9*, by using 2-(2-aminoethyl)pyridine instead of histamine dihydrochloride.

$[Cu(2\text{-}Pca{=}2\text{-}Aep)(N_3)_2]$, 12 *and* $[Cu(2\text{-}Pca{=}\beta\text{-}Ala)(N_3)]\cdot H_2O$, 13

These were prepared by the same method as *10* using 2-(2-aminoethyl)pyridine and β-alanine, respectively, instead of histamine dihydrochloride.

$[Cu_2(2\text{-}Pca{=}Hist)_2(NCS)_3]NCS$, 14

This was prepared by the same method as *6* using sodium thiocyanate.

$[Cu(2\text{-}Pca{=}Hist)(NCS)]3/4ClO_4\cdot 1/4NCS$, 15 *and* $[Cu(2\text{-}Pca{=}2\text{-}Aep)(NCS)]3/4ClO_4\cdot 1/4NCS$, 16

These were prepared by the same method as *9*.

$[Cu(2\text{-}Pca{=}2\text{-}Aep)(NCS)_2]$, 17 *and* $[Cu(2\text{-}Pca{=}\beta\text{-}Ala)(NCS)]\cdot H_2O$, 18

These were prepared by the same method as *10* using 2-(2-aminoethyl)pyridine or β-alanine respectively, and sodium thiocyanate.

[Cu(2-Pca=β-Ala)(NCO)], 22

This was obtained in the same way as *9* by use of cyanate instead of azide.

[Cu(2-Pca=Hist)(NCO)$_2$], 20

This was prepared by the similar way as *10* by using 2-(2-aminoethyl)pyridine.

[Cu(2-Pca=2-Aep)(NCO)]ClO$_4$·1/2H$_2$O, 21

This was obtained in the same way as *9*. Recrystallization was carried out using aqueous ethanol.

[Cu(2-Pca=c-Ala)(NCO)], 22

To a mixture of 2-pyridinecarbaldehyde (0.54 g, 5.0 mmol), β-alanine (0.45 g, 5.0 mmol) and copper(II) nitrate trihydrate (1.2 g, 5.0 mmol) in 10 cm^3 of water was added a saturated solution of sodium azide (0.65 g, 10 mmol). The resulting mixture was adjusted to pH 7 by NaOH aqueous solution and stirred at room temperature for 30 min. After filtration, the filtrate was evaporated to dryness. The green-blue product obtained as a syrup was rubbed with ethanol, and the resulting crystal was filtered. This was recrystallized from aqueous ethanol.

The analytical data for the compounds described above are listed in Table I.

Measurements

IR spectra were obtained with a Hitachi EPI-2 infrared spectrophotometer with KBr disk. Visible absorption spectra in nujol were recorded on a Shimadzu MPS-5000 spectrophotometer. Magnetic measurements at room temperature were carried out by employing the Gouy method. The magnetic susceptibility measurements over the range of liquid helium to room temperature were carried out as described in a previous paper [14]. The powdered X-band ESR spectra at room temperature were recorded at 9.5 GHz microwave irradiation, 6.3 G modulation amplitude, and 100 KHz modulation frequency with a JEOL JES-FE1X. The g values were calibrated based on Li·TCNQ (g = 2.0025).

Crystal Data of [Cu(2-Pca=Hist)(N$_3$)$_2$], 10

[CuC$_{11}$H$_{12}$N$_{10}$], F. W. = 347.9, triclinic, a = 10.262 (8), b = 9.177(6), c = 7.688(5) Å, α = 104.42(4), β = 94.09(4), γ = 92.64(4)°, U = 697.9(8) Å^3, F(000) = 354, Z = 2, D_m = 1.64 g cm^{-3}, D_c = 1.66, space group P$\bar{1}$, μ(MoKα) = 16.4 cm^{-1}, λ(MoKα) = 0.7107 Å.

X-Ray Data Collection of 10

The crystal chosen for data collection and lattice constants had dimensions of 0.26 × 0.29 × 0.38 mm.

TABLE I. Analytical Data for the Complexes.

	Compound	C(%)	H(%)	N(%)
		Found (Calcd.)	Found (Calcd.)	Found (Calcd.)
1	$[Cu_2(2\text{-}Pca{=}Hist)_2(ox)](ClO_4)_2$	35.43 (35.39)	2.93 (2.97)	13.91 (13.76)
2	$[Cu_2(2\text{-}Pca{=}2\text{-}Aep)_2(ox)](ClO_4)_2$	40.31 (40.20)	3.13 (3.14)	10.19 (10.05)
3	$[Cu_2(2\text{-}Pca{=}\beta\text{-}Ala)_2(ox)]\cdot 3H_2O$	38.37 (38.52)	3.62 (3.89)	9.17 (8.99)
4	$[Cu_2(2\text{-}Pca{=}Hist)_2(om)](ClO_4)_2\cdot H_2O$	34.74 (34.66)	3.17 (3.27)	15.11 (15.16)
5	$[Cu_2(2\text{-}Pca{=}2\text{-}Aep)_2(om)](ClO_4)_2$	40.28 (40.24)	3.34 (3.26)	11.53 (11.74)
6	$[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_3]Cl\cdot 2H_2O$	36.74 (36.43)	3.91 (3.90)	32.78 (32.84)
7	$[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_3]Br\cdot 1.5H_2O$	34.65 (34.74)	3.62 (3.59)	31.48 (31.31)
8	$[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_3]N_3\cdot 1.5H_2O$	36.46 (36.56)	3.79 (3.77)	38.80 (38.78)
9	$[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_2](ClO_4)_2$	32.91 (32.60)	2.94 (2.99)	24.84 (24.20)
10	$[Cu(2\text{-}Pca{=}Hist)(N_3)_2]$	38.27 (37.98)	3.56 (3.48)	40.54 (40.27)
11	$[Cu(2\text{-}Pca{=}2\text{-}Aep)(N_3)]ClO_4$	37.55 (37.50)	3.05 (3.15)	20.29 (20.19)
12	$[Cu(2\text{-}Pca{=}2\text{-}Aep)(N_3)_2]$	43.57 (43.50)	3.65 (3.66)	35.27 (35.13)
13	$[Cu(2\text{-}Pca{=}\beta\text{-}Ala)(N_3)]\cdot H_2O$	35.93 (35.94)	3.69 (3.69)	23.27 (23.27)
14	$[Cu_2(2\text{-}Pca{=}Hist)_2(NCS)_3]NCS$	41.11 (41.09)	3.12 (3.19)	21.83 (22.12)
15	$[Cu(2\text{-}Pca{=}Hist)(NCS)]3/4ClO_4\cdot 1/4\ NCS$	35.70 (35.80)	2.94 (2.95)	18.09 (17.90)
16	$[Cu(2\text{-}Pca{=}2\text{-}Aep)(NCS)]3/4ClO_4\cdot 1/4NCS$	40.75 (40.55)	3.13 (3.11)	14.18 (14.11)
17	$[Cu(2\text{-}Pca{=}2\text{-}Aep)(NCS)_2]$	45.84 (46.07)	3.31 (3.36)	17.61 (17.92)
18	$[Cu(2\text{-}Pca{=}\beta\text{-}Ala)(NCS)]\cdot H_2O$	37.66 (37.91)	3.43 (3.19)	13.31 (13.27)
19	$[Cu(2\text{-}Pca{=}Hist)(NCO)]ClO_4$	35.34 (35.56)	2.89 (2.99)	16.89 (17.28)
20	$[Cu(2\text{-}Pca{=}2\text{-}Aep)(NCO)_2]$	50.17 (50.20)	3.64 (3.66)	19.73 (19.52)
21	$[Cu(2\text{-}Pca{=}2\text{-}Aep)(NCO)]ClO_4\cdot 1/2H_2O$	39.81 (39.53)	3.02 (3.32)	13.22 (13.13)
22	$[Cu(2\text{-}Pca{=}\beta\text{-}Ala)(NCO)]$	42.30 (42.47)	3.22 (3.21)	14.87 (14.86)

It was mounted in an arbitrary orientation on a Philips PW1100 automated diffractometer. The PW1100 programs obtained 15 accurately centered reflections and an orientation matrix, and then identified a triclinic cell. The space group P$\bar{1}$ was assumed throughout the structure analysis and confirmed by the successful refinement of the structure. The intensity data ($2\theta \leq 50°$) were collected at room temperature by the use of graphite-monochromated MoKα radiation. The ω-scan mode was employed. The scan range was $(1.0 + 0.2 \tan\theta)°$ and the scan speed $0.033° \text{ s}^{-1}$; the background was counted for 15 s at each side of the scan range. During the data collection, the intensities of three standard reflections were monitored every 4 h in order to check the orientation and stability of the crystal. The compound remained quite stable. A total of 2164 reflections having $F_o^2 \geq 3\sigma(F_o^2)$ were considered as observed. The intensities were corrected for Lorenz polarization effects but not for absorption [15].

Structure Solution and Refinement

The Cu atom was located from a Patterson synthesis. The other non-hydrogen atom positions were obtained from successive difference-Fourier syntheses. The block-diagonal least-squares refinement with anisotropic temperature factors for all the non-hydrogen atoms gave $R = 0.041$ and $R' = [\Sigma w \Delta F^2/\Sigma w F_o^2]^{1/2} = 0.065$. The hydrogen atoms defined by the geometry of the complex were found at calculated positions (N–H, C–H = 1.0 Å). Continued refinement converged at $R = 0.023$ and $R' = 0.034$. In the final cycles of the refinement, the hydrogen atoms were included with a common isotropic temperature factor $B = 4.0$ Å^2, but their parameters were not refined. The function minimized was $\Sigma w(F_o - |F|_c)^2$, where $w = 1/\sigma^2(F_o)$ was used. All the parameter shifts were less than 0.5σ. The atomic scattering factors for Cu, N, C and H atoms were taken from Ref. 16, with correction for anomalous scattering for the Cu atom. The final difference Fourier map was featureless and showed no peaks greater than 0.3 e·Å^{-3}. Observed and calculated structure factors, thermal parameters, and hydrogen atom coordinates are available from the authors. Final atomic coordinates for non-hydrogen atoms are given in Table II. The computer programs used in the calculations were a local version of UNICS [17]. Figures were drawn by the use of ORTEP [18]. Calculations were performed on a FACOM 230-60 computer at Osaka City University and on a ACOS-700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

TABLE II. Atomic Coordinates ($\times 10^5$ for Cu and $\times 10^4$ for others) of Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses.

Atom	x	y	z	B$_{eq}$*
Cu	31646(3)	18223(3)	21658(4)	22
N(1)	1973(2)	694(3)	6675(3)	31
N(2)	2295(2)	1338(2)	4171(3)	25
N(3)	1905(2)	3494(3)	2056(3)	27
N(4)	3914(2)	2648(3)	223(3)	24
N(5)	4933(2)	1339(3)	3111(3)	33
N(6)	5829(2)	2251(3)	3531(3)	31
N(7)	6747(3)	3099(3)	3988(4)	50
N(8)	2295(3)	−105(3)	80(3)	31
N(9)	1857(2)	−1231(3)	392(3)	28
N(10)	1426(3)	−2339(3)	653(4)	47
C(1)	907(3)	1424(3)	6274(4)	32
C(2)	2786(3)	662(3)	5393(4)	28
C(3)	1087(3)	1802(3)	4714(4)	27
C(4)	199(3)	2513(3)	3596(4)	34
C(5)	835(3)	3920(3)	3204(4)	35
C(6)	2091(3)	4135(2)	794(4)	31
C(7)	3205(3)	3698(3)	−277(4)	27
C(8)	3509(3)	4308(3)	−1676(4)	33
C(9)	4598(3)	3832(3)	−2574(4)	36
C(10)	5319(3)	2777(3)	−2064(3)	32
C(11)	4959(3)	2196(3)	−659(3)	28

*Equivalent isotropic temperature factors (×10); W. C. Hamilton, *Acta Crystallogr.*, *12*, 609 (1959).

Results and Discussion

Copper(II) Complexes with ox or om

The copper(II) complexes containing ox or om as bridging ligands were prepared by treating copper(II) perchlorate or nitrate with the respective reagents to form Schiff bases and oxalic or oxamic acid in water. The color of crystals, absorption maxima for the d–d transition band in nujor and IR data for $\nu_{C=O}$ absorptions of these compounds are tabulated in Table III. The magnetic moment of complex *1* was 1.84 B.M. at room temperature (288 °K), which is close to the value for copper(II) complexes without interaction. The temperature-dependence of the magnetic susceptibility for this complex is represented in Fig. 1. The susceptibility increased with decreasing temperature until it reached a maximum at *ca.* 26 °K, and then decreased. The magnetic parameters can be estimated as g = 2.14, Nα = 60 × 10^{-6} cgs emu and J = −21.5 cm^{-1} from the best fit of the χ_A values to the Bleaney–Bowers equation [19],

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

where J denotes the exchange integral between copper(II) ions in binuclear copper(II) complexes. This indicates that there is an antiferromagnetic exchange interaction between the two copper(II) ions in the complex *1*. Although the half-field absorption of the $\Delta M_s = 2$ region in the powdered X-band ESR

TABLE III. Colors, Electronic and IR Spectra of the Complexes.

Complex No.	Color	λ_{max}(nm)	IR (cm^{-1})		
			$\nu_{C=O}$	$\nu_{asym}(N_3^-)$	$\nu_{C\equiv N}$
1	blue-green	720	1630		
2	blue	680	1640, 1650		
3	blue-green	695	1630		
4	blue	675	1630–1640		
5	blue	708	1630–1640		
6	green	680		2120, 2070	
7	green	678		2100, 2060	
8	green	683		2120, 2070	
9	brown-green	640		2100	
10	brown-green	710		2100	
11	dark green	613, 720 (sh)		2080	
12	yellow-green	765		2080	
13	dark green	660		2100	
14	green-blue	640			2150, 2090
15	blue	597			2120
16	blue	650			2130
17	yellow-green	693			2140
18	blue-green	710			2160
19	grey-blue	605			2250
20	green	735			2240
21	blue	640			2230
22	dark blue-green	657			2260

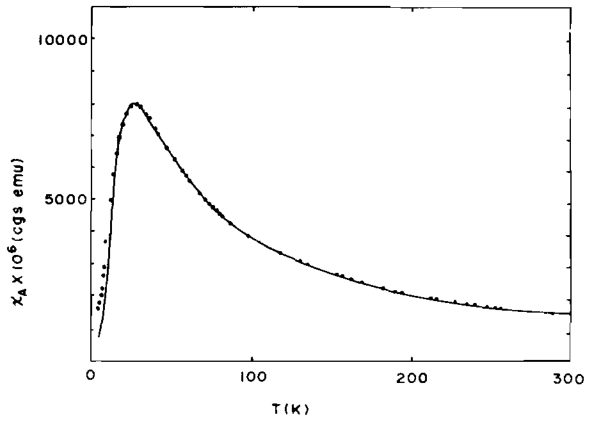
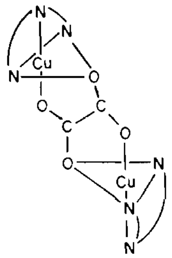
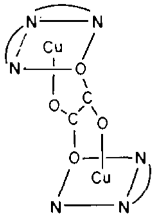


Fig. 1. The temperature-dependence of magnetic susceptibility of copper(II) complex *1*. The solid line shows the theoretical susceptibility calculated by eqn. 1 with the parameters described in the text.

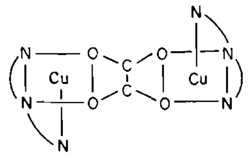
spectrum was rarely observed, the interaction of the two copper(II) ions is expected to be rather strong as inferred from the J value (–21.5 cm^{-1}). An observation of this kind was reported for the imidazolate-bridged binuclear complex, Na[Cu_2Gly·Gly)$_2$(im)] · 6H_2O, in which the J value was –19 cm^{-1} [20]. These magnetic susceptibility and ESR data suggest that the oxalate dianion in complex *1* bridges two copper(II) ions in a bis-bidentate fashion. The result of elemental analyses also supports the above presumption. Felthouse *et al.* previously proposed three types of structures for the μ-oxalato copper(II) dimers with tridentate ligands containing N, N and N (or O) donor atoms [8]:



IV



V



VI

The copper(II) complexes of type VI show subnormal magnetic moments at room temperature [11], while those of type V are known to exhibit a weak antiferromagnetic exchange interaction between two copper(II) ions. Accordingly, the structure of the complex *1* (J = –21.5 cm^{-1}) is supposed to be IV or an intermediate of IV and V, although the ESR spectrum (Fig. 2) at $\Delta M_s = 1$ region shows that the geometry around each copper(II) ion appears to be square-pyramidal with $d_{x^2-y^2}$ ground state ($g_{\parallel} = 2.23$, $g_{\perp} = 2.10$) [21, 22].

The ESR spectra in the $\Delta M_s = 2$ region of the other copper(II) complexes (*2–5*) containing ox or om exhibit a signal comparable with that of complex *1*. These complexes *2–5* are also expected to have

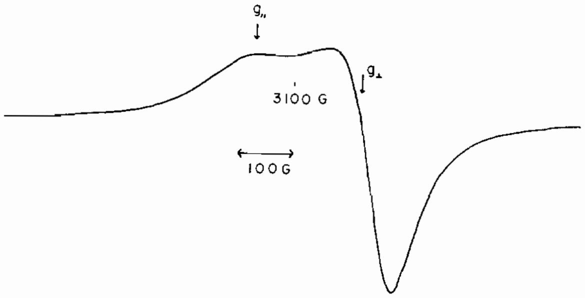


Fig. 2. ESR spectrum for copper(II) complex *1* at room temperature: power 3 mW, amplitude 5.

dimeric structures bridged by ox or om, and the coordination geometry around each copper(II) ion can be regarded as intermediates between a trigonal-bipyramid, IV and a square-pyramid, V.

Copper(II) Complexes with Azide, Thiocyanate or Cyanate Ion

A comparison of spectroscopic data for the complexes with azide, thiocyanate or cyanate (*6–22*) is represented in Table III. Among these, the compound *10* is a five-coordinate monomeric copper(II) complex, of which the geometry around copper(II) has been determined as an intermediate structure between trigonal-bipyramid and square-pyramid (Fig. 7) as will be mentioned in the following section. The ESR spectrum of a powdered sample of complex *10* is given in Fig. 3. The $\Delta M_s = 1$ region indicates the rhombic ESR spectrum with $g_1 = 2.23$, $g_2 = 2.12$ and $g_3 = 2.04$ and the $\Delta M_s = 2$ region does not exhibit the half-field absorption. A similar phenomenon is also observed for complexes, $[Cu(2\text{-}Pca{=}2\text{-}Aep)(N_3)_2]$ (*12*), $[Cu(2\text{-}Pca{=}2\text{-}Aep)(NCS)_2]$ (*17*), and $[Cu(2\text{-}Pca{=}2\text{-}Aep)(NCO)_2]$ (*20*), hence these are concluded to have monomeric structures. The IR spectra of the monomeric azide-containing complexes *10* and *12* exhibit one $\nu_{asym}(N_3^-)$ absorption at 2080–2100 cm^{-1}. In the cases of *17* and *20*, one C–N stretching vibration of thiocyanate or cyanate group was found in the region 2140–2240 cm^{-1}.

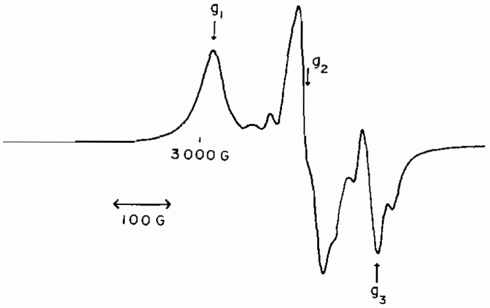


Fig. 3. ESR spectrum for copper(II) complex *10* at room temperature: power 5 mW, amplitude 1.

On the other hand, the IR spectra of compound *6* and *7* show two $\nu_{asym}(N_3^-)$ absorption in the 2060–2120 cm^{-1}, suggesting that there are two kinds of azide groups with different bonding modes in their structures. The half-field $\Delta M_s = 2$ transitions at *ca.* ~1500 G were observed for *6* and *7* in the ESR spectra. This implies the presence of an exchange interaction between the two copper(II) ions, though the magnetic susceptibility data (Fig. 4) down to 4.2 °K for the compound *6* showed only a very small exchange interaction ($0 > J \geqq -0.5$ cm^{-1}). Based on elemental analysis, IR and ESR spectra and magnetic susceptibility data, the structure for the cations in $[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_3]Cl\cdot 2H_2O$ (*6*) and $[Cu_2(2\text{-}Pca{=}Hist)_2(N_3)_3]Br\cdot 1.5H_2O$ (*7*) can be proposed as structure VII. The ESR spectra ($d_{x^2-y^2}$ ground states) at $\Delta M_s = 1$ region of these complexes may support this structure (Fig. 5). It seems likely that the compound *8* has also the same structure VII from the facts that a $\Delta M_s = 2$ signal can be seen at ~1500 G and λ_{max} due to d–d transition is similar to those for *6* and *7* (Table III).

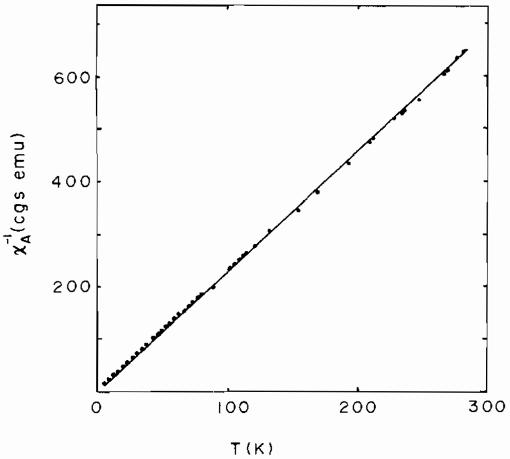
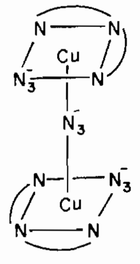


Fig. 4. The temperature-dependence of magnetic susceptibility of copper(II) complex, *6*.



VII

The IR spectrum of the complex *9* exhibited a strong $\nu_{asym}(N_3^-)$ band (Table III), and the magnetic moment per copper(II) ion was estimated to be 1.84 B.M. at room temperature (291 °K). The $\Delta M_s = 2$ transition was observed at half-field, as illustrated in

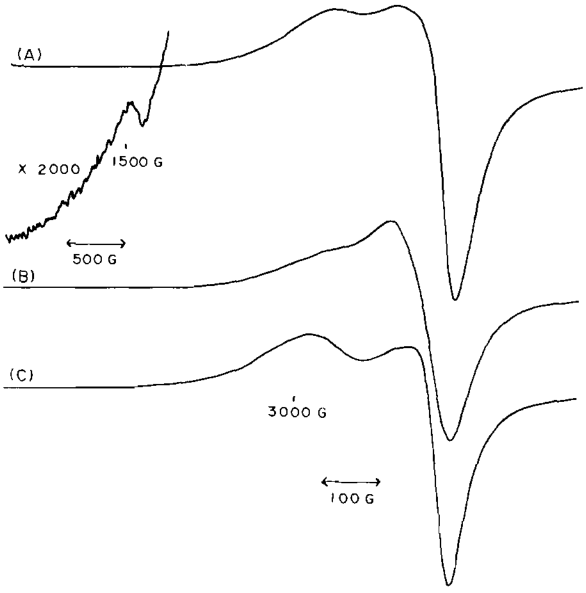


Fig. 5. ESR spectra of copper(II) complexes, *6* (A), *7* (B), and *8* (C) at room temperature.

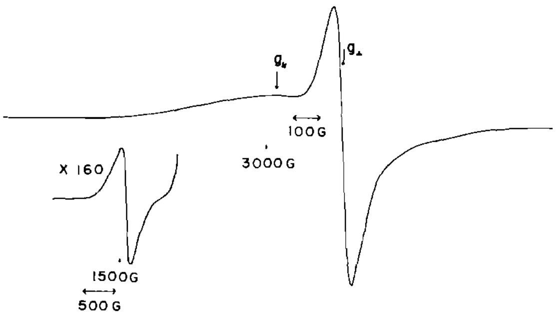


Fig. 6. ESR spectrum for copper(II) complex *9* at room temperature: power 5 mW, amplitude 2 ($\Delta M_s = 1$ signal) and 320 ($\Delta M_s = 2$ signal).

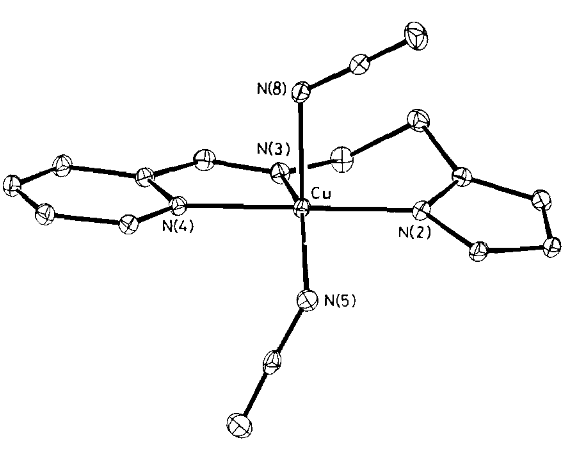
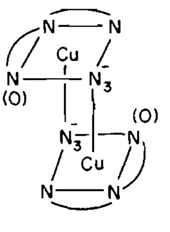


Fig. 7. The molecular structure of [Cu(2-Pca=Hist)$(N_3)_2$], *10*.

Fig. 6. Based on these data and the ESR spectrum (Fig. 6, $g_{\parallel} = 2.22$, $g_{\perp} = 2.06$), at $\Delta M_s = 1$ region, the structure for the complex *9* is considered to be a dimer as illustrated in the structural formula VIII.



VIII

The complex [Cu(2-Pca=2-Aep)(N_3)]$(ClO_4)_2$, *11* showed $\Delta M_s = 2$ signal of a weaker intensity than that for the complex *9*. However, the ground state of the compound *11* seems to be d_{z^2}, hence the local geometry around copper(II) ion of this complex is considered to have a distorted trigonal-bipyramidal structure. The copper(II) complex *13* containing 2-Pca=β-Ala and azide ion did not show the $\Delta M_s = 2$ signal at ~1500 G. The magnetic moment of this complex was 1.87 B.M. at room temperature (290 °K). From the behavior in $\Delta M_s = 1$ signal ($d_{x^2-y^2}$ ground state) and the preliminary experiment [23] on variable-temperature magnetic susceptibility as well as the above results, compound *13* is considered to have the dimeric structure indicated in VIII.

The ESR spectra of the complexes (*14*, *15*, *16*, *18*, *19*, *21*, and *22*) with Schiff base I, II, or III and thiocyanate or cyanate ion indicate the $d_{x^2-y^2}$ ground state, and the $\Delta M_s = 2$ signals have hardly found except for *18* and *19*. The IR spectrum of *14* is similar to that for [Cu_2(2-Pca=Hist)$_2(N_3)_3$]$N_3 \cdot 1.5H_2O$ (*8*). Thus, the complex *14* is considered to have the dimeric structure VII like the complexes *6–8*. Although there are no other evidences for dimeric structure of the other complexes (*15*, *16*, *18*, *19*, *21* and *22*) except the very weak $\Delta M_s = 2$ signals in ESR spectra, we suppose that these compounds also have a binuclear structure similar to *9*.

The Crystal and Molecular Structure of Monomeric Copper(II) Complex [Cu(2-Pca=Hist)$(N_3)_2$], 10

Figure 8 shows a perspective view of the complex. Selected interatomic distances and angles are given in Table IV. The complex is best described as an intermediate between a trigonal bipyramid and a square pyramid. From the trigonal bipyramidal viewpoint, N(2) and N(4) atoms occupy the apical positions. The Cu atom deviated 0.11 Å toward N(2) from the equatorial plane defined by the N(3), N(5), and N(8) atoms. One of the equatorial bond (Cu–N (8) = 2.176 Å) is longer than the other two and the N–Cu–N angles in the equatorial plane are 109.64°, 146.00°, and 103.45°. The N(2)–Cu–N(4) angle is 170.46°. The Cu–N(2) bond and the equatorial plane

TABLE IV. Interatomic Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

Cu–N(2)	1.968(2) Å	N(2)–Cu–N(3)	91.17(8)°
Cu–N(3)	2.065(2)	N(2)–Cu–N(4)	170.46(8)
Cu–N(4)	2.017(2)	N(2)–Cu–N(5)	92.69(8)
Cu–N(5)	2.015(3)	N(2)–Cu–N(8)	96.47(8)
Cu–N(8)	2.176(3)	N(3)–Cu–N(4)	79.80(8)
N(1)–C(1)	1.365(4)	N(3)–Cu–N(5)	146.00(8)
N(1)–C(2)	1.332(3)	N(3)–Cu–N(8)	103.45(8)
N(2)–C(2)	1.332(3)	N(4)–Cu–N(5)	93.12(8)
N(2)–C(3)	1.388(3)	N(4)–Cu–N(8)	88.69(8)
C(3)–C(4)	1.489(4)	N(5)–Cu–N(8)	109.64(8)
C(4)–C(5)	1.526(4)	Cu–N(2)–C(3)	125.8(2)
N(3)–C(5)	1.464(4)	N(2)–C(3)–C(4)	121.5(2)
N(3)–C(6)	1.274(4)	C(3)–C(4)–C(5)	112.9(3)
C(6)–C(7)	1.469(4)	N(3)–C(5)–C(4)	109.5(3)
N(4)–C(7)	1.347(3)	Cu–N(3)–C(5)	126.3(2)
N(4)–C(11)	1.337(3)	Cu–N(3)–C(6)	113.6(2)
C(7)–C(8)	1.378(4)	N(3)–C(6)–C(7)	117.6(3)
C(8)–C(9)	1.386(4)	N(4)–C(7)–C(6)	114.4(2)
C(9)–C(10)	1.361(4)	Cu–N(4)–C(7)	114.1(2)
C(10)–C(11)	1.383(4)	Cu–N(5)–N(6)	122.4(2)
N(5)–N(6)	1.184(3)	N(5)–N(6)–N(7)	176.5(3)
N(6)–N(7)	1.169(4)	Cu–N(8)–N(9)	123.2(2)
N(8)–N(9)	1.192(3)	N(8)–N(9)–N(10)	178.4(3)
N(9)–N(10)	1.159(4)		

Short contact distances (Å)

N(8)···N(1) ($x, y, -1+z$)	2.890(3) Å
C(7)···N(1) ($x, y, -1+z$)	3.276(3)
C(1)···C(1) ($-x, -y, 1-z$)	3.258(5)

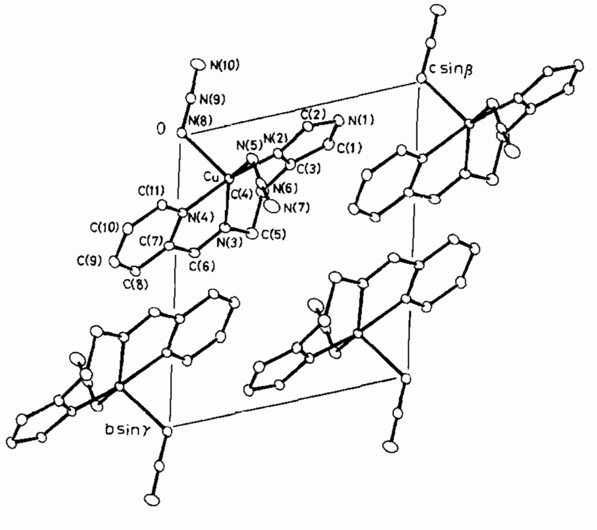


Fig. 8. The crystal structure of [Cu(2-Pca=Hist)$(N_3)_2$] viewed along the c axis.

make an angle of 86.22°, while the Cu–N(4) bond and the plane make an angle of 82.76°. In the square pyramidal approximation, the apical position is occupied by the N(8) atom, whereas the basal plane is defined by the N(2), N(3), N(4), and N(5) atoms, the deviations of the atoms from the plane being N(2) 0.27, N(3) –0.21, N(4) 0.27, and N(5) –0.26 Å. The Cu–N(8) apical bond is longer than the four basal bonds. No atom approaches the Cu atom within 4.0 Å on the opposite side of the pyramid.

The pyridine and imidazole rings are planar within ±0.005 Å. The [Cu, N(3), N(4), C(6), C(7)] ring is also nearly planar (maximum deviation of atom is 0.042 Å). The angle between this plane and the pyridine ring is 3.2°. The [Cu, N(2), N(3), C(3), C(4), C(5)] ring is of the boat conformation.

Within the azide groups the N–N bonds close to the Cu atom are longer than the other more distant N–N bonds [24]. The Cu–N–N and N–N–N angles are 122.8° and 177.4°.

Figure 8 gives the projection of the crystal structure viewed along the c axis. The crystal consists of discrete [Cu(2-Pca=Hist)$(N_3)_2$] complexes. Short contact distances less than 3.3 Å are given in Table IV.

Acknowledgements

We thank Miss Reiko Kobayashi for her collaboration in the preparation of some of the compounds.

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