2212 © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 2212—2217 (1990) [Vol. 63, No. 8

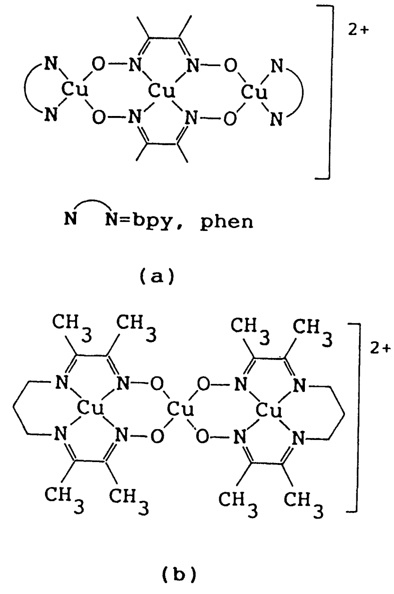
Synthesis, Structure, and Magnetism of Binuclear Cu(II)Cu(II), Cu(II)Ni(II), and Ni(II)Ni(II) Complexes Doubly Bridged by Oxymate Groups

Dominique Luneau,†† Hiroki Oshio, Hisashi Ōkawa,*,† Masayuki Koikawa,† and Sigeo Kida†
Institute for Molecular Science, Myodaiji, Okazaki 444
†Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812

(Received March 31, 1990)

Binuclear complexes, $[Cu(L)Cu(L')(H_2O)_2]X_2$ (H_2L=3,3′-trimethylenedinitrilobis(2-butanoneoxime) (H_2dopn) or 3,3′-ethylenedinitrilobis(2-butanoneoxime) (H_2doen); L′=2,2′-bipyridyl (bpy) or 1,10-phenanthroline (phen); X=ClO_4 or NO_3), $[Ni(dopn)Cu(bpy)(H_2O)](ClO_4)_2$, and $[Ni(dopn)Ni(bpy)_2](ClO_4)_2$, have been prepared and characterized. The structure of $[Cu(dopn)Cu(phen)(CH_3OH)_2](ClO_4)_2$ (di-methanol adduct) has been determined by single crystal X-ray method. The Cu(dopn) molecule coordinates to the second copper(II) ion through the deprotonated oximate oxygens to afford a binuclear structure doubly bridged by the oximate groups in the cis arrangement. The binuclear cation is bent at the oxymate oxygens with a dihedral angle of 26.7(2)°. The binuclear copper(II) complexes show a characteristic visible band of significant intensity (ε 2700—2900 $dm^3\,mol^{-1}\,cm^{-1}$) near 22000 cm^{-1} and a strong intramolecular antiferromagnetic spin-exchange interaction. The exchange integrals (J) are evaluated to be −413.3—−433.0 cm^{-1}. The magnetic moment (per molecule) of the nickel(II)-copper(II) complex is 1.80 μ_B at room temperature and the moment of the binuclear nickel(II) complex is 2.94 μ_B, demonstrating that the Ni(dopn) entity of these complexes is diamagnetic.

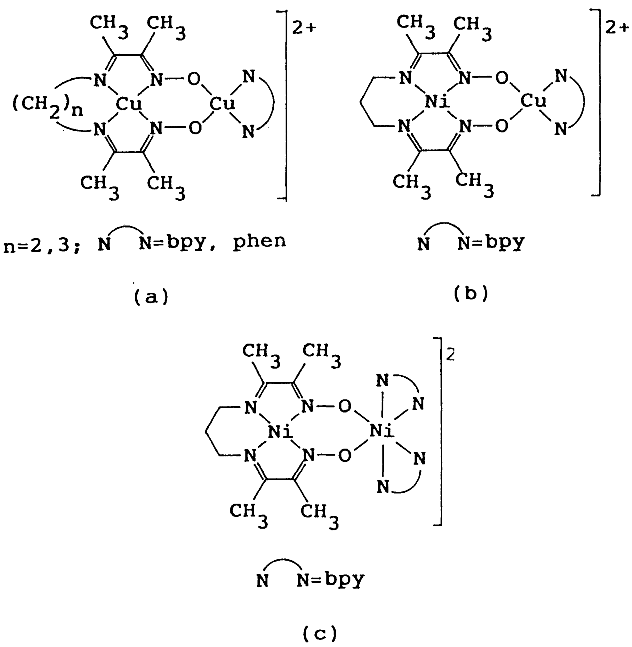
Studies on spin exchange in polynuclear metal complexes in view of the nature of the bridging group and stereochemical factors are continuing subjects in the field of coordination chemistry.[1,2] Recently we have reported the trinuclear copper(II) complexes of the general formula $[Cu(dioxim)_2\{CuL\}_2]X_2$[3] ($H_2$-dioxim=dimethylglyoxime, diphenylglyoxime, or o-benzoquinonedioxime; L=2,2′-dipyridyl (bpy) or 1,10-phenanthroline (phen); X=NO_3^- or ClO_4^-) where $Cu(dioxim)_2^{2-}$ functions as a bridge to combine two CuL^{2+} entities through its deprotonated oximate oxygens to afford linear trinuclear skeleton (see Fig. 1 (a)). Those complexes show a very strong antiferromagnetic spin-exchange through the dioximate-bridge in cis arrangement so as to cause complete spin-coupling even at room temperature. In a related trinuclear complex $[Cu\{Cu(dopn)\}_2](ClO_4)_2$[4] of 3,3′-trimethylenedinitrilobis(2-butanoneoxime) (H_2dopn) (see Fig. 1 (b)) the configuration around the central copper is significantly distorted to tetrahedron and the trinuclear cation is bent at the edges of the bridging oximate oxygens to afford a butterfly shape to the cation. In spite of such large distortions this complex shows a



(a)

(b)

Fig. 1. Chemical structures of $[Cu(dioxim)_2(CuL)_2]^{2+}$ (a) and $[Cu\{Cu(dopn)\}_2]^{2+}$ (b).



(a) (b)

(c)

Fig. 2. Chemical structures of Cu(II)Cu(II) (a), Ni(II)Cu(II) (b), and Ni(II)Ni(II) (c) complexes.

---

†† Present address: Centre d'Etudes Nucleaires de Grenoble, Departement de Recherche Fondamentale, Laboratoire de Chimie, 38041 Grenoble Cedex, France.

Table 1. Elemental Analysis of Dinuclear Complexes **1** to **7**

Complex	Found % (Calcd %)				
	C	H	N	Cu[a]	Ni[a]
[Cu(dopn)Cu(bpy)(H_2O)$_2$](ClO_4)$_2$	33.39	4.10	11.20	16.92	—
(**1**)	(33.34)	(3.99)	(11.11)	(16.80)	—
[Cu(dopn)Cu(phen)(H_2O)$_2$](ClO_4)$_2$	35.02	4.19	10.82	16.30	—
(**2**)	(35.39)	(3.87)	(10.64)	(16.28)	—
[Cu(doen)Cu(bpy)(H_2O)$_2$](NO_3)$_2$	36.72	4.33	16.57	18.81	—
(**3**)	(37.00)	(4.44)	(16.44)	(18.64)	—
[Cu(doen)Cu(bpy)(H_2O)$_2$](ClO_4)$_2$	32.39	3.70	11.26	17.22	—
(**4**)	(32.35)	(3.80)	(11.32)	(17.16)	—
[Cu(doen)Cu(phen)(H_2O)$_2$](ClO_4)$_2$	35.36	4.11	10.58	16.55	—
(**5**)	(35.39)	(3.87)	(10.77)	(16.28)	—
[Ni(dopn)Cu(bpy)(H_2O)](ClO_4)$_2$	34.70	3.72	11.56	8.75	8.17
(**6**)	(34.38)	(3.87)	(11.45)	(8.66)	(8.00)
[Ni(dopn)Ni(bpy)$_2$](ClO_4)$_2$	42.66	3.97	12.56	—	13.68
(**7**)	(42.94)	(3.95)	(12.93)	—	(13.54)

a) Determined by atomic absorption.

Table 2. Summary of Crystal Data, Intensity Data Collections, and Structure Refinements

Formula	$C_{25}H_{34}N_6O_{12}Cl_2Cu_2$
F.W.	804.48
Crystal system	Triclinic
Space group	P1
a/Å	13.948(2)
b/Å	14.076(2)
c/Å	8.381(2)
α/°	99.90(1)
β/°	95.79(1)
γ/°	89.49(1)
V/Å^3	1612.4(5)
z	2
D_x/g cm^{-3}	1.665
D_m/g cm^{-3}	1.658
μ (Mo $K\alpha$)/cm^{-1}	16.07
Crystal size /mm	0.43×0.24×0.18
Temperature/K	200
Diffractometer	Rigaku AFC-5
Scan type	$\theta-2\theta$
Scan width/°	$1.2+0.4\tan\theta$
Scan speed/° min^{-1}	3
$2\theta_{max}$/°	60
Octant measd.	$+h, \pm k, \pm l$
No. of refl. measd.	8228
No. of unique refl. with ($\|F_o\|>3\sigma(F_o)$)	4971
No. of refl. per parameter	7.6
Max. min. residual electron density/(eÅ^3)	2.6, −0.9
Max (shift/e.s.d.)	0.3
Weighting scheme (w)	$[\sigma_c^2+(0.03\|F\|)^2]^{-1}$
R	0.051
R_w	0.060

strong antiferromagnetic spin-exchange through the dioximate-bridge in cis arrangement so as to cause perfect spin-coupling at 170 K.

In order to gain further evidences for the effective spin-coupling in such cis dioximate bridging system, we have synthesized binuclear Cu(II)Cu(II), Cu(II)-Ni(II), and Ni(II)Ni(II) complexes of the types given in Fig. 2 by the use of H_2dopn and 3,3′-ethylenedinitrilobis(2-butanoneoxime) (H_2doen). This paper deals with the synthesis, structure, and magnetic and spectral properties of the complexes.

Experimental

Materials. All chemicals were of reagent grade and were used as commercially obtained. H_2dopn, H_2doen, [Cu(H-dopn)]$ClO_4\cdot H_2O$, [Cu(Hdoen)]$ClO_4\cdot H_2O$, and [Ni(H-dopn)]ClO_4 were prepared according to the literature methods.[5,6]

Preparations of Complexes. Following seven complexes have been synthesized in this study: [Cu(dopn)Cu(bpy)-(H_2O)$_2$](ClO_4)$_2$ (**1**), [Cu(dopn)Cu(phen)(H_2O)$_2$](ClO_4)$_2$ (**2**), [Cu(doen)Cu(bpy)(H_2O)$_2$](NO_3)$_2$ (**3**), [Cu(doen)Cu(bpy)-(H_2O)$_2$](ClO_4)$_2$ (**4**), [Cu(doen)Cu(phen)(H_2O)$_2$](ClO_4)$_2$ (**5**), [Ni(dopn)Cu(bpy)(H_2O)](ClO_4)$_2$ (**6**), and [Ni(dopn)Ni-(bpy)$_2$(ClO_4)$_2$ (**7**). Some typical examples of synthetic methods are shown below.

Complex 1. A mixture of [Cu(Hdopn)]$ClO_4\cdot H_2O$ (0.5 mmol), copper(II) perchlorate hexahydrate (0.5 mmol), and bpy (0.5 mmol) in methanol (30 cm^3) was refluxed for 1 hour. The resulted red solution was filtered while hot and concentrated slowly to a small portion to give red crystals.

Complexes **2** and **3** were obtained in a way similar to that of complex **1**.

Complex 4. A solution of copper(II) perchlorate hexahydrate (0.5 mmol) in methanol (10 cm^3) was added to a hot solution of H_2doen (0.5 mmol) in methanol (10 cm^3), and the mixture was refluxed for 30 minutes. Then a hot solution of copper(II) perchlorate hexahydrate (0.5 mmol) and bpy (0.5 mmol) in methanol (10 cm^3) was added and the mixture was refluxed for one hour. The resulting red solution was once filtered while hot and slowly concentrated to a small portion to give purple crystals.

In a similar way complex **5** was obtained as purple crystals.

Complex 6. A solution of [Ni(Hdopn)]ClO_4 (0.5 mmol), copper(II) perchlorate hexahydrate (0.5 mmol), and bpy (0.5 mmol) in methanol (30 cm^3) was refluxed for one hour and the resulting reddish solution was filtered while hot. A methanolic solution of NaOH (0.5 mmol) was added to the filtrate, and the mixture was allowed to stand at room temperature to give an orange microcrystalline powder.

Complex 7. A solution of [Ni(Hdopn)]ClO_4 (0.5 mmol), nickel(II) perchlorate hexahydrate (0.5 mmol), and bpy (1 mmol) in methanol (30 cm^3) was refluxed for 1 hour and filtered while hot. The addition of a methanolic solution of NaOH (0.5 mmol) to the filtrate resulted in the precipitation of yellow microcrystals.

The analytical results for **1**—**7** are given in Table 1.

X-Ray Crystal Structure Analysis of 2. Crystal data and the details of experimental conditions are given in Table 2. In our preliminary experiments at room temperature, the crystal effloresced in the course of data collection. Thus, the intensity data were collected at 200 K on a Rigaku AFC-5 four-circle diffractometer equipped with a Mo $K\alpha$ X-ray tube and a graphite monochromator. Peak profile study for one reflection upon cooling the crystal showed no deterioration. Three reference intensities were recorded periodically throughout the data collection and the results showed no sign of deterioration. Cell constants were obtained from a least-squares fit of 50 reflections. The intensity data were corrected for Lorentz and polarization effects and for absorption and were reduced by the use of UNICS III program[7] system of the Computer Centre of the Institute for Molecular Science.

The location of the copper atoms and the coordinated atoms were based on direct method using MULTAN package.[8] The remaining non-hydrogen atoms were located in a succession of difference Fourier synthesis. After anisotropic refinement the hydrogen atoms were located in difference Fourier synthesis and refined with isotropic thermal parameters. During the structure determination one of the perchlorate ions was found to be disordered. Thus, three oxygens of the perchlorate ion were refined with two sets of positions each with occupation factor 0.5. The atomic scattering factors were taken from International Tables.[9] The final block diagonal least-squares refinement converged at $R=0.051$ and $R_w=0.060$.

Atomic parameters for non-hydrogen atoms are listed in Table 3. Non-hydrogen anisotropic parameters, hydrogen atomic parameters, F_o-F_c tables, and full bond lengths and angles are deposited as Document No. 8934 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Other Physical Measurements. Electronic spectra were recorded on a Hitachi 3400 UV Spectrometer in DMF solutions. Magnetic susceptibilities were determined with a Faraday balance designed in Kyushu University, in the range from liquid nitrogen temperature to room temperature. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$[10] and diamagnetic corrections were made by the use of Pascal's constants.[11]

Table 3. Atomic Parameters for Non-Hydrogen Atoms

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
Cu(1)	0.20076(5)	0.19854(4)	0.34081(8)	2.3
Cu(2)	0.35234(4)	0.41245(4)	0.36040(8)	2.0
O(1)	0.3892(2)	0.2811(2)	0.2945(5)	2.8
O(2)	0.2539(2)	0.4023(2)	0.5021(4)	2.4
N(1)	0.3329(3)	0.2037(3)	0.2829(5)	2.2
N(2)	0.2131(3)	0.0622(3)	0.2422(6)	3.1
N(3)	0.0723(3)	0.1848(3)	0.4151(5)	2.7
N(4)	0.1907(3)	0.3299(3)	0.4737(5)	2.0
N(5)	0.4713(3)	0.4479(3)	0.2583(5)	2.6
N(6)	0.3526(3)	0.5597(3)	0.4359(5)	2.5
C(1)	0.3685(4)	0.1207(4)	0.2240(6)	2.6
C(2)	0.4686(5)	0.1089(5)	0.1748(9)	4.7
C(3)	0.2993(5)	0.0396(4)	0.2072(7)	3.2
C(4)	0.3311(6)	−0.0618(5)	0.1468(9)	5.5
C(5)	0.1378(5)	−0.0123(4)	0.2295(9)	4.8
C(6)	0.0398(5)	0.0327(5)	0.2230(8)	4.4
C(7)	0.0137(5)	0.0964(5)	0.3745(9)	4.7
C(8)	0.0470(4)	0.2575(4)	0.5150(7)	2.7
C(9)	−0.0429(4)	0.0624(5)	0.5983(9)	4.8
C(10)	0.1138(4)	0.3409(4)	0.5529(6)	2.4
C(11)	0.0978(4)	0.4304(5)	0.6691(8)	4.5
C(12)	0.5300(4)	0.3897(5)	0.1733(7)	3.4
C(13)	0.6091(4)	0.4241(5)	0.1046(7)	4.1
C(14)	0.6256(4)	0.5215(5)	0.1277(8)	4.3
C(15)	0.5643(4)	0.5863(5)	0.2174(7)	3.6
C(16)	0.4876(4)	0.5453(4)	0.2823(7)	2.9
C(17)	0.4230(4)	0.6055(4)	0.3743(7)	2.6
C(18)	0.4331(4)	0.7065(4)	0.3999(7)	3.6
C(19)	0.3669(5)	0.7613(4)	0.4938(8)	4.1
C(20)	0.2971(4)	0.7150(4)	0.5582(8)	3.7
C(21)	0.2927(4)	0.6139(4)	0.5268(7)	2.8
C(22)	0.5122(5)	0.7458(5)	0.3316(8)	4.5
C(23)	0.5745(5)	0.6897(5)	0.2477(8)	4.6
O(ml)	0.1413(3)	0.2483(3)	0.0869(4)	3.1
C(ml)	0.1667(5)	0.1998(5)	−0.0638(8)	4.4
O(m2)	0.2359(3)	0.4204(3)	0.1429(4)	3.0
C(m2)	0.1610(5)	0.4913(5)	0.1671(9)	4.5
Cl(1)	0.3019(1)	0.0388(1)	0.6579(2)	4.0
O(3)	0.2547(4)	0.1237(4)	0.6191(6)	5.9
O(4)	0.3738(4)	0.0097(3)	0.5464(6)	5.4
O(5)	0.3479(4)	0.0606(4)	0.8181(6)	7.2
O(6)	0.2348(5)	−0.0347(4)	0.643(1)	10.4
Cl(2)	0.8816(1)	0.2880(1)	0.071(2)	4.6
O(7)	0.8031(4)	0.2860(5)	−0.048(1)	10.0
O(8)	0.9543(7)	0.3597(7)	0.043(1)	6.1
O(9)	0.9349(9)	0.2034(7)	0.046(1)	7.0
O(10)	0.867(1)	0.318(1)	0.234(2)	11.9
O(8′)	0.871(1)	0.1971(8)	0.136(1)	9.1
O(9′)	0.883(2)	0.349(1)	0.194(2)	19.8
O(10′)	0.9522(9)	0.275(2)	−0.013(2)	16.3

The isotropic equivalent thermal parameter is given as $B_{eq}=4/3\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\boldsymbol{a}_j$.

Results and Discussion

Crystal Structure of 2. An ORTEP diagram of the complex is shown in Fig. 3. Relevant bond distances and angles are given in Table 4. The crystal used for X-ray structure analysis contains two methanol molecules though the elemental analysis made on a effloresced polycrystalline sample indicated the presence of two water molecules. It appears that the methanol molecules are readily replaced with atmospheric water molecules.

The complex consists of a dinuclear cation $[Cu(dopn)Cu(phen)(CH_3OH)_2]^{2+}$ and perchlorate ions. The Cu(dopn) molecule coordinates to the second copper(II) ion through the deprotonated oximate oxygens to afford a dinuclear skeleton doubly bridged by oximate groups in cis arrangement. The copper(II) ion Cu(1) is planarly surrounded by four nitrogen atoms of dopn^{2-}. The deviations of the

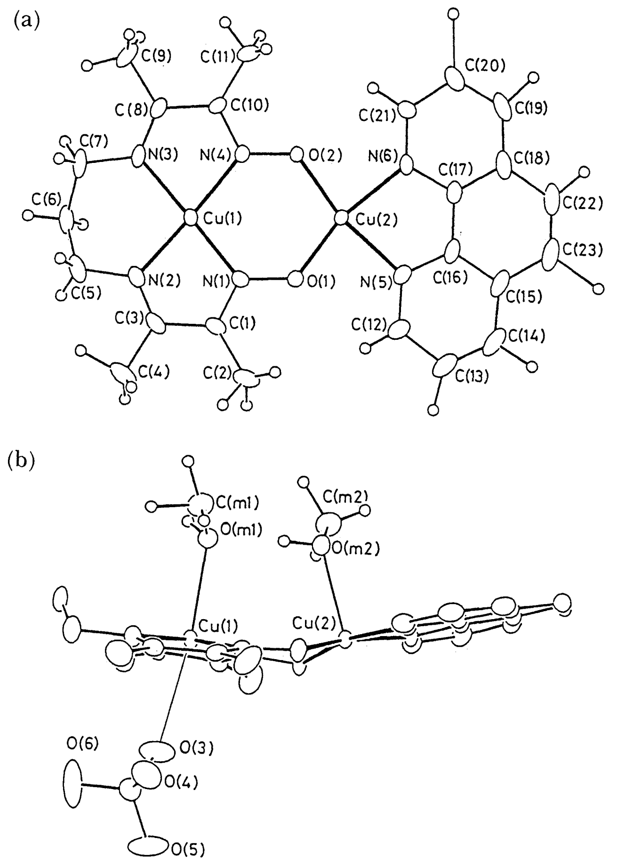


Fig. 3. ORTEP views of **2** (di-methanol adduct) with the numbering system: Projection onto the coordination plane (a) and edge view (b). In the ORTEP diagram (a) the methanol molecules and the perchlorate ion are eliminated for clarity.

Table 4. Relevant Bond Lengths/Å and Angles/°

Cu(1)-N(1)	1.958(4)	Cu(1)-N(2)	1.968(4)
Cu(1)-N(3)	1.977(5)	Cu(1)-N(4)	1.992(4)
Cu(1)-O(ml)	2.420(4)	Cu(1)-O(3)	2.756(5)
Cu(2)-O(1)	1.917(3)	Cu(2)-O(2)	1.926(4)
Cu(2)-N(5)	2.044(5)	Cu(2)-N(6)	2.060(4)
Cu(2)-O(m2)	2.333(4)	Cu(1)—Cu(2)	3.666(1)
N(1)-Cu(1)-N(2)	81.7(2)	N(1)-Cu(1)-N(3)	174.2(2)
N(1)-Cu(1)-N(4)	100.5(2)	N(2)-Cu(1)-N(3)	95.9(2)
N(2)-Cu(1)-N(4)	171.1(2)	N(3)-Cu(1)-N(4)	81.1(2)
N(1)-Cu(1)-O(ml)	89.9(2)	N(2)-Cu(1)-O(ml)	94.2(2)
N(3)-Cu(1)-O(ml)	95.6(2)	N(4)-Cu(1)-O(ml)	94.5(2)
N(1)-Cu(1)-O(3)	93.8(2)	N(2)-Cu(1)-O(3)	95.9(2)
N(3)-Cu(1)-O(3)	80.6(2)	N(4)-Cu(1)-O(3)	90.2(2)
O(3)-Cu(1)-O(ml)	173.4(1)	O(1)-Cu(2)-O(2)	103.3(2)
O(1)-Cu(2)-N(5)	85.7(2)	O(2)-Cu(2)-N(6)	164.4(2)
O(1)-Cu(2)-O(m2)	97.4(1)	O(2)-Cu(2)-N(5)	165.7(2)
O(2)-Cu(2)-N(6)	88.5(2)	O(2)-Cu(2)-O(m2)	90.9(2)
N(5)-Cu(2)-N(6)	80.8(2)	N(5)-Cu(2)-O(m2)	99.0(2)
N(6)-Cu(2)-O(m2)	92.6(2)	Cu(1)-N(1)-O(1)	128.1(3)
Cu(1)-N(4)-O(2)	129.2(3)	Cu(2)-O(1)-N(1)	125.9(3)
Cu(2)-O(2)-N(4)	122.1(3)		

nitrogen atoms from the N_4 least-squares plane fall within ±0.03 Å. The Cu-N bond lengths fall in the range 1.958(4)—1.992(4) Å which are slightly elongated compared with the Cu-N bonds of [Cu(dopn)]ClO_4 (1.937(5)—1.961(5) Å). One of the methanol molelcules weakly coordinates to Cu(1) with the Cu(1)-O(ml) distance of 2.420(4) Å. Further, one of the perchlorate ions is more weakly bonded to Cu(1) with the Cu(1)-O(3) distance of 2.756(5) Å. Thus, the configuration around Cu(1) can be regarded as a distorted octahedron where Cu(1) is slightly displaced from the N_4 plane (0.120(2) Å) towards the methanol oxygen O(ml). The other perchlorate ion is free from coordination and disordered.

The coordination geometry around Cu(2) is a distorted square-pyramid with two oximate oxygens and two nitrogens of the phen ligand on the basal plane and a methanol oxygen at the apical position. The Cu(2)-N(5) and Cu(2)-N(6) bond distances (2.044(5) and 2.060(4) Å, respectively) and Cu(2)-O(1) and Cu(2)-O(2) distances (1.917(3) and 1.926(4) Å, respectively) are common for in-plane bonds whereas the Cu(2)-O(m2) distance (2.333(4) Å) is elongated. The deviation of Cu(2) from the N_2O_2 plane is 0.168(2) Å.

The binuclear cation is not coplanar and bent at the edge with the oximate oxygens. The dihedral angle between the plane defined by N(1), N(4), O(1), and O(2) and the plane defined by Cu(2), O(1), and O(2) is 26.7(2)°. A similar deviation has been found for trinuclear [Cu{Cu(dopn)}$_2$](ClO_4)$_2$$^{4)}$ but the dihedral angle found for the present complex is much small compared with those (55.88(9)°) found for the trinuclear complex. Because of the bent structure the Cu(1)—Cu(2) distance (3.665(1) Å) is significantly short compared with the corresponding distance (3.74—3.75 Å) of [Cu(dioxim)(CuL)$_2$]$^{2+}$ (see Fig. 1(a)) which adopts a coplanar trinuclear skeleton.$^{3)}$

Electronic Spectra., The electronic spectra of **1**—**7** were determined in DMF solutions in the range 10000—37000 cm^{-1}. Electronic spectra of [Cu(dopn)]$ClO_4\cdot H_2O$, [Ni(dopn)]ClO_4, and [Cu{Cu(dopn)}$_2$](ClO_4)$_2$$^{4)}$ were also recorded for comparison. All the spectra obey Beer's law in the concentration range 1×10^{-3}—1×10^{-4} mole dm^{-3}. The numerical data are summarized in Table 5.

The most characteristic feature of the electronic spectra of the binuclear copper(II) complexes **1**—**5** is a discrete absorption band (ε~2800 $dm^3\,mol^{-1}\,cm^{-1}$) near 22000 cm^{-1} (see Fig. 4). This band cannot be assigned to a d-d transition band judging from its extinction coefficient. A similar absorption band was observed for [Cu{Cu(dopn)}$_2$](ClO_4)$_2$$^{4)}$ but not for **6** (Ni(II)Cu(II)) and **7** (Ni(II)Ni(II)). Further, such an absorption band is not seen for [Cu(Hdopn)]ClO_4. Thus, the visible band found for **1**—**5** (and also for [Cu{Cu(dopn)}$_2$](ClO_4)$_2$) can be ascribed to the Cu(dopn) and Cu(doen) chromophores. In fact the extinction coefficient (per molecule) of the band for [Cu{Cu(dopn)}$_2$](ClO_4)$_2$ is approximately twice of that for **1**—**5**. In the previous paper$^{3)}$ we have reported that trinuclear complexes [Cu(dioxim)$_2$\{CuL\}$_2$]X_2

Table 5. Electronic Spectral Data in DMF

Complex	$\tilde{\nu}/10^3$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})				
1	16.5(600)		22.8(2700)	30.0(9600) 33.1(23500)	32.1(22700) 34.5(20400)
2	16.5(670)		22.8(2820)	30.8(12300) 36.8(35700)	33.9(21050)
3	16.8(610)		22.9(2760)	30.0(9800) 33.1(20600)	32.0(20000) 34.5(17200)
4	15.6(710)		20.7(2810)	29.5(9300) 33.1(25100)	32.1(22600) 34.5(22200)
5	15.8(730)		20.5(2900)	30.3(11300) 37.0(38100)	33.9(21900)
6	16.6(225) 21.7(750)	18.7(520)	25.3(3630)	32.3(21700) 34.5(22000)	33.2(24200)
7	17.2(1020) 20.8(1710)	18.5(1310)	26.2(4050)	32.8(30800) 34.5(28800)	33.6(32700)
[Cu{Cu(dopn)}$_2$](ClO$_4$)$_2$$^{a)}$	16.7(1500)		22.1(5100)	29.4(21400)	33.5(25100)
[Cu(Hdopn)]ClO$_4$	18.0(220)				
[Ni(Hdopn)]ClO$_4$	16.7(410)	20.0(760)	26.0(3200)	30.8(2910)	33.9(3950)

a) Ref. 4.

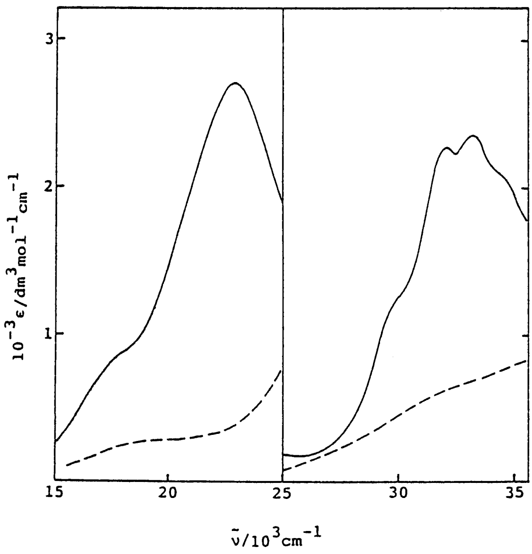


Fig. 4. Electronic absorption spectra of **1** (——) and [Cu(Hdopn)]ClO$_4$ (----) in methanol.

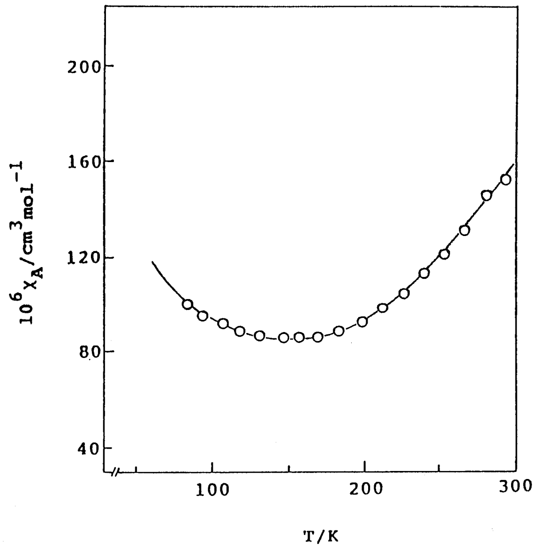


Fig. 5. Temperature-variation of magnetic susceptibility of **1**. The trace is drawn based on the equation given in the text by the use of magnetic parameters given in Table 6.

show a characteristic band near 21000 cm^{-1} (ε=4000—5000 dm^3 mol^{-1} cm^{-1}). This band is probably the same in origin as the visible band found for the present complexes **1**—**5**. The d-d bands for **1**—**5** appear as a superposed band near 16000 cm^{-1}. The complex **6** shows three bands at 17200, 18700, and 21700 cm^{-1}. The latter two bands may be assigned to the d-d transition bands of the planar Ni(dopn) chromophore. The complex **7** shows three d-d bands in the region 16000—21000 cm^{-1} which are assigned to the d-d transition bands of the nickel(II) ions. The intense absorption bands in the near ultraviolet to ultraviolet region may be assigned to intraligand transition and charge-transfer bands.

Magnetic Properties. All the dicopper(II) complexes **1**—**5** show a subnormal magnetic moment (0.60—0.70 μ_B per copper) at room temperature, suggesting the operation of an antiferromagnetic spin-exchange within each molecule. The susceptibilities were measured over the temperature range 80—300 K and a typical example is shown in Fig. 5. The susceptibility decreases with lowering of temperature, reaches a plateau (85×10^{-6} cm^3 mol^{-1}) at 160 K and then again tends to increase below 140 K. The increase of the susceptibility at lower temperature

Table 6. Magnetic Data for Complexes **1**—**7**

Complex	μ_{eff}[a] (T/K)	$-J$ $\mathrm{cm^{-1}}$	g	$N_\alpha \times 10^6$ $\mathrm{cm^3\,mol^{-1}}$	$p \times 10^2$
1	0.64 (295.6)	426.6	2.13	56	0.9
2	0.69 (296.3)	433.0	2.10	60	1.1
3	0.72 (295.0)	420.8	2.12	63	1.3
4	0.52 (297.2)	413.3	2.10	55	0.5
5	0.48 (295.6)	417.7	2.11	62	0.3
6	1.84 (296.8)				
7	3.01 (297.5)				

a) Calculated by the equation $\mu_{\mathrm{eff}}=2.828\,(\chi_A T)^{1/2}$ for **1**—**5** and by the equation $\mu_{\mathrm{eff}}=2.828\,(\chi_M T)^{1/2}$ for **6**—**7**.

suggests the presence of a small amount of paramagnetic impurities. Thus, the magnetic analyses have been made by the use of modified Bleaney-Bowers equation[13] including a correcting term for the paramagnetic impurities,

$$\chi_A = (Ng^2\beta^2/3kT)\{1+[\exp(-2J/kT)]/3\}^{-1}(1-p) + 0.45p/T + N\alpha,$$

where p is the mole fraction of the paramagnetic contaminant and other symbols have their usual meanings. The magnetic properties of **1**—**5** can be simulated with this equation as shown by the trace in Fig. 5. The magnetic parameters determined by the best fit technique are summarized in Table 6. The exchange integrals ($-J$) fall in the range 413.3—433.0 $\mathrm{cm^{-1}}$ and demonstrate a very strong antiferromagnetic spin-exchange in **1**—**5** through the double oxymate bridge in the cis arrangement. However, it should be mentioned that the interaction through the double oximate-bridges in **1**—**5** is even weaker compared with some binuclear and trinuclear copper(II) complexes showing a complete spin-coupling even at room temperature.[3,14—19] It is reasonable to ascribe the reason for the weakened spin-exchange of the present complexes to the bent structure at the edge as demonstrated for complex **2**.

The heteronuclear complex **6** shows a magnetic moment corresponding to one unpaired electron (1.80 μ_B per molecule) at room temperature. Further, the magnetic moment is constant in the range from room temperature to liquid nitrogen temperature. The result clearly demonstrates that the nickel(II) ion of the Ni(dopn) entity is of low-spin, in line with the previous report[5] that [Ni(Hdopn)]ClO$_4$ is diamagnetic. In accord with this the binuclear nickel(II) complex **7** shows a magnetic moment corresponding to two unpaired electrons at room temperature (2.94 μ_B per molecule). Thus, this complex is a mixed-spin binuclear complex comprised of a high-spin and a low-spin nickel(II) ions.

References

1) R. D. Willet, D. Gatteschi, and O. Kahn, "Magneto-Structural Correlations in Exchange-Coupled Systems, NATO ASI Series," Riedel-Dordrecht, Holland (1985), p. 399.

2) O. Kahn, *Angew. Chem., Int. Ed. Engl.*, **24**, 834 (1985); *Struct. Bonding (Berlin)*, **68**, 89 (1987).

3) D. Luneau, H. Oshio, H. Ōkawa, and S. Kida, *Chem. Lett.*, **1989**, 443; H. Ōkawa, D. Luneau, H. Oshio, M. Koikawa, and S. Kida, *J. Chem. Soc., Dalton Trans.*, **1990**, 469.

4) D. Luneau, H. Oshio, H. Ōkawa, and S. Kida, *J. Chem. Soc., Dalton Trans.*, in press.

5) R. Gagné, *J. Am. Chem. Soc.*, **98**, 6709 (1976).

6) E. Uhlig and M. Friedrich, *Z. Anorg. Allg. Chem.*, **343**, 299 (1966).

7) T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Rev.*, **55**, 69 (1979).

8) P. Main, S. E. Hull, L. Lessinger, G. Germian, J. P. Declercq, M. H. Woolfson, MULTAN 78, Universities of York, England, and Louvain, Belgium (1978).

9) D. T. Cromer, International Tables for X-Ray Crystallography, The Kynoch Press, Birmingham (1974), Vol. 4.

10) N. F. Curtis, *J. Chem. Soc.*, **1961**, 3147.

11) E. A. Bourdeaux and L. N. Mulay, "Theory and Application of Molecular Paramagnetism," John Wiley, New York (1976), p. 491.

12) J. A. Bertrand, J. N. Smith, and D. G. VanDerveer, *Inorg. Chem.*, **16**, 1484 (1977).

13) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

14) J. A. Bertrand, J. N. Smith, and P. Garyeller, *Inorg. Chem.*, **13**, 1649 (1974).

15) G. A. Nicholson, C. R. Lazarus, and B. J. McCormick, *Inorg. Chem.*, **19**, 192 (1980); G. A. Nicholson, J. L. Petersen, and B. J. McComick, *ibid.*, **19**, 195 (1980).

16) S. Baral and A. Chakravorty, *Inorg. Chim. Acta*, **39**, 1 (1980); S. Baral, R. P. Singh, J. G. Mohanty, and A. Chakravorty, *Inorg. Nucl. Chem. Lett.*, **10**, 655 (1974).

17) J. E. Young and R. K. Murmann, *J. Phys. Chem.*, **67**, 2647 (1963); P. F. Ross, R. K. Murmann, and E. O. Schlemper, *Acta Crystallogr. Sect. B*, **30B**, 1120 (1974).

18) R. Beckett, R. Colton, B. F. Hoskins, R. L. Martin, and D. G. Vince, *Aust. J. Chem.*, **22**, 2527 (1969); R. Beckett and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, **1972**, 291.

19) R. J. Butcher, J. O'Connor, and E. Sinn, *Inorg. Chem.*, **18**, 1913 (1979).