Synthesis, Properties and Crystal Structures of Dicopper(I) and Disilver(I) Complexes with 1,8-Naphthyridine (napy): $[Cu_2(napy)_2](ClO_4)_2$ and $[Ag_2(napy)_2](ClO_4)_2$

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Abstract

Binuclear copper(I) and binuclear silver(I) complexes with 1,8-naphthyridine (napy) have been prepared. The crystal structures of $[Cu_2(napy)_2](ClO_4)_2$ (1) and $[Ag_2(napy)_2](ClO_4)_2$ (2) have been determined by using single crystal X-ray diffraction methods.

Compound 1 crystallizes in space group $P\bar{1}$, with $a = 8.245(2)$, $b = 10.376(2)$, $c = 5.886(1)$ Å, $\alpha = 84.06(2)$, $\beta = 98.73(2)$, $\gamma = 108.53(2)°$ and $Z = 1$; $R = 0.047$ for 1247 reflections. The cation of 1, $[Cu_2(napy)_2]^{2+}$, is binuclear with two napy ligands bridging the two metals. The geometry of each Cu atom is nearly linear. Compound 1, having a short Cu···Cu distance of 2.506(2) Å, reversibly reacts with CO, acetylene and ethylene.

Crystals of 2 are monoclinic space group $P2_1/n$ with $a = 16.017(7)$, $b = 10.427(4)$, $c = 5.752(2)$ Å, $\beta = 99.90(3)°$ and $Z = 2$; $R = 0.088$ for 1321 reflections. The structure of 2 is essentially the same as that of 1. The Ag···Ag distance of 2.748(2) Å is short compared with the corresponding distance in metallic silver 2.88 Å.

Introduction

A three-coordinate binuclear copper(I) complex with amine and pyridine nitrogen donor atoms reacts with dioxygen resulting in oxygenation of the ligand of the complex [1]. Carbon monoxide in the dicopper(I) complex $[Cu_2(tmen)_2(\mu\text{-}CO)(PhCO_2)]BPh_4$ displays a bridging bonding mode which is one of the prerequisites for facilitating its metal-promoted reduction [2]. Thus, binuclear copper(I) complexes have been of interest in a novel catalysis since they can provide two sites for binding to small molecules.

Metal–metal bonds are well known in clusters of Mo, W, Re, Ru and Os, and there has been remarkable gains in understanding the metal–metal bonds owing to both theoretical work and various kinds of physical measurements [3]. On the other hand, the metal–metal interaction is still ambiguous in polynuclear copper(I) and silver(I) compounds. Dicopper(I) complexes having short copper···copper distances have been of interest in recent years, because an extremely close Cu(I)···Cu(I) contact (2.371 Å) has been found in $[Cu_2(H)_2(CH_3C(CH_2PPh_2)_3)_2]$ and is considered to correspond to a metal–metal interaction [4].

Bis(diphenylphosphino)methane [5a], acetate [5b], benzoate [2], halides [5c], and sulfur-containing ligands [5d] and 2-vinylpyridine [5e] have been used as bridging ligands. 1,8-Naphthyridine (napy) and its derivatives are interesting ligands because they can function as either a monodentate, bidentate or binuclear bidentate ligand. Examples of derivatives acting as a monodentate are found in $[Cu(napy)_2Cl_2]$ [6a], $[Pt(napy)(PEt_3)_2Cl]BF_4$ [6b], $[Hg_2(napy)_2](ClO_4)_2$ [6c] and $[Cu(2,7\text{-}Me_2napy)_2Cl_2]$ [6d]; as a bidentate in $[Cd(napy)_4](ClO_4)_2$ [7a], $[Hg(napy)_3(ClO_4)](ClO_4)$ [7a], $[Fe(napy)_4](ClO_4)_2$ [7b, 7c]; and as a binuclear bidentate in $[Rh_2(napy)_2(nbd)_2](ClO_4)_2\cdot H_2O$ (nbd = norbonadiene) [8a], $[Cu_2(napy)_2Cl_4]$ [8b], $[Ni_2(napy)_2Br_2]BPh_4$ [8c], $[Cu_2(2,7\text{-}py_2\text{-}napy)(OH)Cl_3]$ [7d], $[Rh_2(2\text{-}py\text{-}napy)_3Cl_2](PF_6)_2$ [8d], $[Rh_2(2,7\text{-}py_2\text{-}napy)(CH_3CO_2)_3](PF_6)$ [8e] and $[Ni(2,7\text{-}Ac_2\text{-}napy)_3]$ [8f].

No binuclear copper(I) and silver(I) complexes with napy have been synthesized so far. We have now found that dicopper(I) and disilver(I) complexes with napy are formed, in which both have relatively short metal···metal distances and the former reversibly reacts with carbon monoxide, olefins and alkynes. Here we report the synthesis, and X-ray molecular structures and reactivity of the dimetal complexes.

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Experimental

Materials

Tetrakis(acetonitrile)copper(I) hexafluorophosphate was prepared in the usual way [9]. 1,8-Naphthyridine was purchased from Tokyo Kasei Kogyou Co. Ltd. Acetone treated with potassium permanganate was dried over potassium carbonate and then fractionally distilled from molecular sieves before use. Methanol was dried and distilled before use.

Physical Meausrements

Electronic spectra were obtained with a Hitachi 200-10 spectrometer. The instrument is easily thermostated to better than ±0.2 °C. Infrared spectra were recorded on a Hitachi 260-10 spectrometer and calibrated versus polystyrene. Solution samples were measured as 0.1 M $[Cu_2(napy)_2]^{2+}$ in potassium chloride cavity cells and solid samples were measured as KBr pellets. ^1H NMR spectra were recorded on a JEOL GSX 270 FT NMR spectrometer. Sample concentration was $5 \sim 10$ mM. The transients of $300 \sim 500$ were accumulated using 4.0 μs pulses (45°) and 16 K data points were collected over a band width of 3500 Hz. The temperature was set at 23 and −90 °C. Tetramethylsilane was used as an internal standard.

X-ray Data Collection, Structure Solution and Refinement

Crystals suitable for diffraction studies were obtained for both compounds by cooling a methanol or acetone solution of the complex. Diffraction data were obtained on a Rigaku AFC-6B four-circle diffractometer at ambient temperature. Crystal data and details of measurements for complexes $[Cu_2(napy)_2](ClO_4)_2$ and $[Ag_2(napy)_2](ClO_4)_2$ are summarized in Table 1. Three standard reflections were monitored every 56 measurements and their intensities showed no decay. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.

Both structures were solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by block-diagonal least-squares calculations. Reliability factors are defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = \{\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2\}^{1/2}$. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV. Hydrogen atoms were included in the last cycle; their position were obtained from difference Fourier synthesis, and their temperature factors were assumed to be isotropic. The final R and R_w values were 0.047 and 0.051 for $[Cu_2(napy)_2](ClO_4)_2$ and 0.088 and 0.102 for $[Ag_2(napy)_2](ClO_4)_2$. The final difference Fourier maps were featureless. The calculations were carried out on the FACOM 780 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY [10].

TABLE 1. Crystal data for 1 and 2

	1	2
Formula	$Cu_2Cl_2O_8C_{16}N_4H_{12}$	$Ag_2Cl_2O_8C_{16}N_4H_{12}$
Molecular weight	586.3	674.9
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Cell constants		
a (Å)	8.245(2)	16.017(7)
b (Å)	10.376(2)	10.427(4)
c (Å)	5.886(1)	5.752(2)
α (°)	84.06(2)	90.00(0)
β (°)	98.73(2)	99.90(3)
γ (°)	108.53(2)	90.00(0)
U (Å^3)	471.1	946.3
Z	1	2
D_c (g cm^{-3})	2.066	2.368
F(000)	292	656
μ (Cu Kα) (cm^{-1})	59.64	201.55
Colour	brown	white
Crystal size (mm)	*c.* 0.2 × 0.2 × 0.2	*c.* 0.3 × 0.3 × 0.2
Radiation	Cu Kα	Cu Kα
δ(Cu Kα) (Å)	$\lambda = 1.54178$	$\lambda = 1.54178$
Scan mode	$\omega-2\theta$	$\omega-2\theta$
Scan speed (°/min)	8	8
Scan width (°)	1	1
2θ range (°)	2–120	2–120
Total reflections	1566	1683
Reflection used in refinement	1247 $(\|F\| \geqslant 3\sigma\|F_o\|)$	1321 $(\|F\| \geqslant 3\sigma\|F_o\|)$
R^a	0.047	0.088
$R_w{}^b$	0.051	0.102

$^aR = \Sigma[(|F_o| - |F_c|)/\Sigma|F_o|]$. $^bR_w = \{\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|\}^{1/2}$.

Bis(1,8-naphthyridine)dicopper(I) Diperchlorate

Copper(II) diperchlorate hexahydrate (18.5 mg, 0.05 mmol) was reduced with copper wire to copper(I) in methanol (5.0 ml) under ethylene. Addition of 1,8-naphthyridine (13.0 mg, 0.10 mmol) in methanol (5.0 ml) to this solution gave an orange solution. After ethylene was replaced with Ar, the solution was filtered. The filtrate was sealed in a 7 mm diameter glass tube under Ar and after 4 days the brown crystals were obtained at −20 °C (yield = 12 mg, 41%).

Bis(1,8-naphthyridine)disilver(I) Diperchlorate

Silver(I) perchlorate (20.7 mg, 0.10 mmol) was added to 1,8-naphthyridine (13.0 mg, 0.10 mmol) in acetone (100 ml) under Ar. The clear solution was sealed in a 7 mm diameter glass tube covered by aluminum foil under Ar and after 2 days white needle crystals were obtained at ambient temperature in a dark room (yield = 25 mg, 74%).

Bis(1,8-naphthyridine)(carbon monoxide)bis(acetonitrile)dicopper(I) Dihexafluorophosphate

$[Cu(CH_3CN)_4]PF_6$ (55.9 mg, 0.15 mmol) was added to 1,8-naphthyridine (19.5 mg, 0.15 mmol) in acetone (5 ml) under CO. After passing CO through the solution for 2 h, pale brown crystals were separated from the solution by filtration. (Yield = 18 mg, 30%). *Anal.* Found: C, 32.54; H, 2.77; N, 9.52. Calc. for $C_{21}H_{18}N_6OP_2F_{12}Cu_2$: C, 32.15; H, 2.31; N, 10.71%.

Results and Discussion

Structure of [Cu_2(napy)$_2$](ClO_4)$_2$

The structure of $[Cu_2(napy)_2](ClO_4)_2$ shown in Fig. 1 consists of perchlorate anions and a dimeric cation molecule where the two copper atoms are bridged by the two napy molecules. The perchlorate anions are not coordinated to the coppers, the distances of Cu···O(4) being 2.683(7) Å. Each copper atom is coordinated by the two nitrogen atoms of different napy molecule. Atomic coordinates of non-hydrogen atoms are given in Table 2 and selected intramolecular bond distances and angles in Table 3. The coppers and four nitrogens are coplanar within 0.01 Å. Both angles N(1)–Cu–N(2′) and N(2)–Cu′–N(1′) are 174.15(25)°.

The copper–nitrogen distances of 1.908(5) and 1.909(5) Å are within those reported for two-coordinate copper(I) with nitrogen atoms (1.871(4)–1.966(5) Å); $[Cu_2(EDTB)]$ (1.873(4) Å) [11a], [Cu(1-Me-pz)$_2$] (1.876(3) Å) [11b], [Cu(1,3,5-Me$_3$-pz)$_2$] (1.871(4) Å) [11b], [Cu(BBDH)] (1.918(4) Å) [11c], [Cu(2,6-Me$_2$-py)$_2$](ClO_4) (1.936(5) Å) [11d], [Cu(2,6-Me$_2$-py$_2$)$_2$](NO_3) (1.956(5), 1.966(5) Å) [11d] and [Cu(2,4-Me$_2$-py)$_2$]ClO_4 (1.86(1) Å) [11d]. The distances are shorter than those (2.02–2.07 Å) of four-coordinate copper(I) complexes; [Cu(py)$_4$](ClO_4) (2.05 Å) [12a], [Cu(bpy)$_2$](ClO_4) (2.021(11) Å) [12b], [Cu(dmbpy)$_2$](BF_4) (2.034(1) Å) [12c], [Cu(dmpy)$_2$] (2.071(8) Å) [12d]. The angle of N(1)–C(8)–N(2) of napy molecules 117.5(6)° is almost the same as that of 116(1)° of bridging napy for [Rh$_2$(napy)$_2$(nbd)$_2$](ClO_4)$_2$·H_2O [8a],

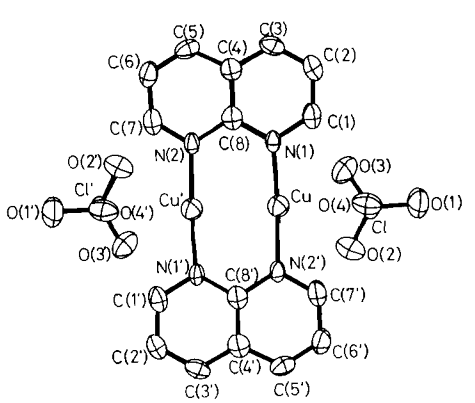

Fig. 1. Molecular structures of $[Cu_2(napy)_2](ClO_4)_2$. The atoms are represented by their 50% probability ellipsoids for thermal motion.

TABLE 2. Atomic parameters for non-hydrogen atoms in $[Cu_2(napy)_2](ClO_4)_2$

Atom	x	y	z	B_{eq}
Cu	0.0357(1)	0.8995(1)	0.9455(2)	3.72(4)
Cl	0.6711(2)	1.2816(2)	0.9173(3)	3.62(7)
C(1)	0.2290(8)	0.9642(6)	0.5747(13)	3.46(26)
C(2)	0.3160(8)	1.0395(7)	0.3950(13)	3.76(29)
C(3)	0.3334(8)	1.1724(9)	0.3646(13)	3.87(30)
C(4)	0.2623(8)	1.2350(6)	0.5047(13)	3.38(25)
C(5)	0.2748(9)	1.3719(7)	0.4844(13)	3.87(27)
C(6)	0.2073(9)	1.4257(6)	0.6295(14)	4.13(30)
C(7)	0.1240(8)	1.3392(6)	0.8021(13)	3.79(29)
C(8)	0.1761(7)	1.1527(6)	0.6833(12)	3.15(25)
N(1)	0.1584(6)	1.0173(5)	0.7154(10)	3.02(20)
N(2)	0.1027(6)	1.2074(5)	0.8291(10)	3.15(22)
O(1)	0.5960(7)	1.3824(5)	0.9483(11)	5.73(27)
O(2)	0.7196(7)	1.2962(5)	0.6927(10)	5.21(24)
O(3)	0.5543(7)	1.1503(5)	0.9547(10)	5.17(23)
O(4)	0.8211(7)	1.2957(6)	1.0868(10)	5.41(25)

TABLE 3. Selected bond distances (Å) and angles (°) in [Cu$_2$(napy)$_2$](ClO_4)$_2$

Cu···Cu′	2.506(2)	C(1)–C(2)	1.395(10)
Cu–N(1)	1.908(5)	C(2)–C(3)	1.336(10)
Cu–N(2′)	1.909(5)	C(3)–C(4)	1.395(12)
N(1)···N(2)	2.343(8)	C(4)–C(5)	1.385(10)
N(1)–C(1)	1.331(10)	C(5)–C(6)	1.338(12)
N(1)–C(8)	1.362(8)	C(6)–C(7)	1.393(10)
N(2)–C(7)	1.318(8)	C(4)–C(8)	1.412(9)
N(2)–C(8)	1.379(10)	Cu···O(4)	2.683(7)
Cu′–Cu–N(1)	87.46(19)		
Cu′–Cu–N(2′)	87.59(18)		
N(1)–Cu–N(2′)	174.15(25)		
Cu–N(1)–C(1)	118.4(4)		
Cu–N(1)–C(8)	123.9(5)		
N(1)–C(1)–C(2)	123.3(6)		
N(1)–C(8)–C(4)	122.0(7)		
N(2)–C(7)–C(6)	124.7(7)		
N(2)–C(8)–C(4)	120.4(6)		
C(1)–C(2)–C(3)	118.8(8)		
C(2)–C(3)–C(4)	121.1(7)		
C(3)–C(4)–C(8)	117.1(6)		
C(3)–C(4)–C(5)	124.6(7)		
C(8)–C(4)–C(5)	118.3(7)		
C(4)–C(5)–C(6)	121.3(7)		
C(5)–C(6)–C(7)	117.7(6)		
N(1)–C(8)–N(2)	117.5(6)		
C(1)–N(1)–C(8)	117.7(6)		
C(7)–N(2)–C(8)	117.5(6)		

TABLE 4. Cu···Cu distances of polynuclear copper(I) complexes

Complexes	Cu···Cu distance (Å)	Reference
$[Cu_2(H)_2(CH_3C(CH_2PPh_2)_3)_2]$	2.371(2)	4
$[Cu_2(tmen)_2(CO)(PhCO_2)]BPh_4$	2.410(2)	2
$[Cu_2(CH_3CO_2)_2]$	2.491(3), 2.556(2)	5b, 14
$[Cu_2((tolyl)NCHN(tolyl))_2]$	2.497(2)	17
$[Cu_2(napy)_2](ClO_4)_2$	2.506(2)	this work
$[Cu_2\{HB(3,5\text{-}Me_2pz)_3\}_2]$	2.506(1)	18
$[Cu_2I_2(Me_4pip)_4]$	2.535(9)	19
$[Cu_3((tolyl)N_5(tolyl))_3]$	2.348(2), 2.358(2)	20
$[Cu_3I_4](NPr_4)$	2.461(5)	21
$[Cu_4(CH_2SiMe_3)_4]$	2.417	22
$[Cu_3(Mes)(PhCO_2)_2]$	2.421(2), 2.888(2)	23
$[Cu_4(MeC_6H_3CH_2NMe_2)_4]$	2.38	24
$[Cu_4(Mes)_4(C_4H_8S)_2]$	2.441(3)–2.449(2)	25
$[Cu_4(C{\equiv}CPh)_4(PMe_3)_4]$	2.45	26
$[Cu_5(Mes)_5]$	2.437(8)–2.469(9)	25
$[Cu_6(H)_6(PPh_3)_6]$	2.494(6)–2.674(5)	27
$[Cu_6(H)_6\{P(NMe_2)_3\}_6]$	2.508(2)–2.804(3)	28

whereas it is larger than the angle of 113(1)° of bidentate napy for $[Pr(napy)_6](ClO_4)_2$ [13]. This reflects the fact that the N(1)···N(2) distance (2.343(8) Å) of napy for $[Cu_2(napy)_2](ClO_4)_2$ is longer than that (2.257(12) Å) of $[Pr(napy)_6](ClO_4)_2$. These facts show that the framework of napy is still flexible, depending on the mode of its coordination. The Cu···Cu distance of 2.506(2) Å is at the short end of values (2.35–3.6 Å) found so far in dinuclear copper(I) complexes and is short compared with the corresponding distance in metallic copper 2.56 Å. The complexes having a short Cu···Cu distance have been rapidly accumulated in the polynuclear copper(I) complexes in recent years. The Cu···Cu distances less than 2.56 Å are summarized in Table 4 [14, 17–28].

Although the Cu···Cu interaction is still not fully defined, molecular orbital calculations on Cu_n^{n+} ($n = 2 \sim 4$) indicate that with Cu 4s and 4p orbitals there is an attractive interaction between two copper(I) centers approaching one another [15]. The force constant and the mean amplitude for the Cu(I)–Cu(I) bond in gaseous dicopper(I) complex $[Cu_2(CH_3COO)_2]$ also indicate weak Cu(I)–Cu(I) interaction, where the Cu(I)···Cu(I) distance is 2.490 Å [14a]. The Cu(I)···Cu(I) distances of 2.348 and 2.358 Å in $[Cu_3((tolyl)N_5(tolyl))_3]$ are short enough to suggest the possibility of a metal–metal interaction [16]. On the other hand, more recently it has been reported that there is little or no direct metal–metal bonding in the $M_2(form)_2$ complex (M = Cu(I), Ag(I); form = (tolyl)NCHN(tolyl)) by the SCF-Xα-SW molecular orbital calculation [17], where the Cu···Cu and Ag···Ag distances are 2.497(2) and 2.705(1) Å, respectively.

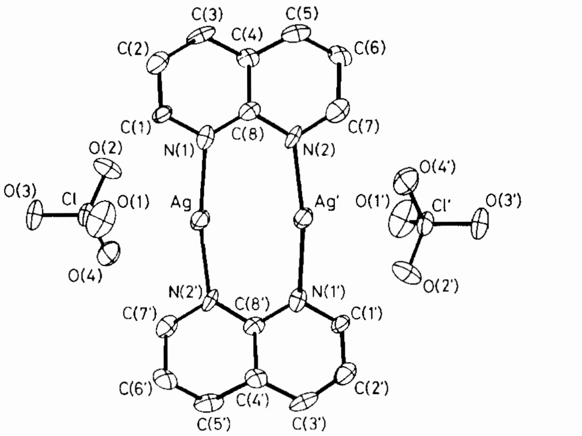

Fig. 2. Molecular structures of $[Ag_2(napy)_2](ClO_4)_2$. The atoms are represented by their 50% probability ellipsoids for thermal motion.

Structure of $[Ag_2(napy)_2](ClO_4)_2$

The structure of $[Ag_2(napy)_2](ClO_4)_2$ shown in Fig. 2 is very similar to that observed in the corresponding dimeric copper(I) complex. The silvers are coordinated by two nitrogen donor atoms of two different napy molecules. Atomic coordinates of non-hydrogen atoms are given in Table 5. Selected bond distances and angles are given in Table 6. The angle N(1)–Ag–N(2′) is 167.82(50)° less than that (174.15(25)°) of the copper(I) analogue. The departure from linearity suggests a weak $Ag–ClO_4$ interaction is considered, since the $Ag\cdots ClO_4$ distance is 2.64 Å. Large departures have been reported in other two-coordinate silver(I) complexes: the angles N–Ag–N of 164.1(2)° in $[Ag_2$-

TABLE 5. Atomic parameters for non-hydrogen atoms in $[Ag_2(napy)_2](ClO_4)_2$

Atom	x	y	z	B_{eq}
Ag	0.0298(1)	0.3790(1)	0.5618(3)	2.93(7)
Cl	0.1620(3)	0.1148(4)	0.5899(9)	2.58(18)
C(1)	−0.0516(11)	0.1957(17)	0.1845(37)	2.67(77)
C(2)	−0.0882(12)	0.1413(19)	−0.0235(40)	3.17(84)
C(3)	−0.1274(12)	0.2192(20)	−0.1942(38)	3.06(85)
C(4)	−0.1301(10)	0.3508(17)	−0.1567(34)	2.28(70)
C(5)	−0.1725(11)	0.4423(21)	−0.3172(38)	3.03(86)
C(6)	−0.1745(11)	0.5655(19)	−0.2752(38)	2.94(85)
C(7)	−0.1340(11)	0.6074(19)	−0.0475(39)	2.92(80)
C(8)	−0.0914(10)	0.4004(17)	0.0620(35)	2.18(71)
N(1)	−0.0511(9)	0.3187(13)	0.2288(30)	2.29(62)
N(2)	−0.0917(8)	0.5264(13)	0.1166(30)	2.20(60)
O(1)	0.0832(9)	0.1455(16)	0.6733(34)	4.98(80)
O(2)	0.1452(9)	0.1270(16)	0.3320(25)	4.15(69)
O(3)	0.1871(10)	−0.0108(12)	0.6556(31)	4.18(68)
O(4)	0.2238(9)	0.2077(14)	0.6880(29)	4.00(66)

TABLE 6. Selected bond distances (Å) and angles (°) in $[Ag_2(napy)_2](ClO_4)_2$

Ag···Ag′	2.748(2)	C(1)–C(2)	1.362(28)
Ag–N(1)	2.211(15)	C(2)–C(3)	1.344(29)
Ag–N(2′)	2.179(15)	C(3)–C(4)	1.391(27)
N(1)···N(2)	2.321(8)	C(4)–C(5)	1.417(27)
N(1)–C(1)	1.307(23)	C(5)–C(6)	1.309(30)
N(1)–C(8)	1.360(23)	C(6)–C(7)	1.427(29)
N(2)–C(7)	1.358(24)	C(4)–C(8)	1.402(26)
N(2)–C(8)	1.351(23)	Ag···O(1)	2.623(17)

Ag′–Ag–N(1)	84.91(36)
Ag′–Ag–N(2′)	83.75(36)
N(1)–Ag–N(2′)	167.82(50)
Ag–N(1)–C(1)	115.5(12)
Ag–N(1)–C(8)	124.7(11)
N(1)–C(1)–C(2)	124.5(18)
N(1)–C(8)–C(4)	119.0(16)
N(2)–C(7)–C(6)	122.8(18)
N(2)–C(8)–C(4)	123.3(16)
C(1)–C(2)–C(3)	117.8(19)
C(2)–C(3)–C(4)	120.4(19)
C(3)–C(4)–C(8)	118.8(16)
C(3)–C(4)–C(5)	126.0(17)
C(8)–C(4)–C(5)	115.1(17)
C(4)–C(5)–C(6)	124.4(19)
C(5)–C(6)–C(7)	116.6(18)
N(1)–C(8)–N(2)	117.7(16)
C(1)–N(1)–C(8)	119.4(16)
C(7)–N(2)–C(8)	117.7(16)

(adeninum)$_2$] [29] and O–Ag–O of 161.6(8)° in $[Ag_2(\beta\text{-ala})_2](NO_3)_2$ [30] have been reported. The chelate plane defined by Ag, Ag′ N(1), N(2), N(1′) and N(2′) is nearly coplanar to two napy rings. The Ag–N distances of 2.211(15) and 2.179(15) Å are comparable to those found in the two-coordinate silver(I) complexes with adeninum (2.155(10), 2.195(10) Å) [29] and 2,6-dimethylpyridine (2.166-(4) Å) [11d], but are longer than those in the complex with succinimide (2.079(5) and 2.067(5) Å) [31]. The difference of 0.286(5) Å between Cu–N and Ag–N distances is almost the same as in $[M(py)_4]ClO_4$ (M = Cu(I) and Ag(I)) (0.276(6) Å) [32], $[M_4I_4(C_5H_{11}N)_4]_4$ (0.278(5) Å) [33], $[M(NC(CH_2)_4CN)_2]^+$ (0.30(1) Å) [34] and $[M_2(form)_2]$ (0.232(8) Å) [17]. The Ag···Ag separation of 2.748(2) Å is 0.14 Å shorter than in metallic silver (2.889(6) Å). Short Ag···Ag distances have often been observed and the range is from 2.654(1) to 3.493(1) Å. Silver(I) complexes having the Ag···Ag distances less than 2.9 Å are summarized in Table 7 [35–40]. Silver–silver bonding in the compounds with thiocarbamates and other ligands has been discussed by Jennische and Hesse, who concluded that the metal···metal distance is probably determined by ligand geometry rather than Ag–Ag bonding [41]. It has been reported that the Ag···Ag distance of 2.654(1) Å is possibly short enough for some Ag–Ag bonding [35]. On the other hand, no direct Ag–Ag bonding is considered to exist when the Ag···Ag distance is 2.705(1) Å as described above [17].

Reaction of $[Cu_2(napy)_2]^{2+}$ with O_2, CO, C_2H_4 and C_2H_2

The complex is sparingly in soluble chloroform and non-polar solvents, the best one being acetone. Four-coordinate copper(I) complexes having conjugated organic ligands exhibit a charge transfer band which is usually assigned to Cu(dπ)→ ligand(π^*). For example, the charge transfer bands of $[Cu(py)_4]^+$ and $[Cu(bpy)_2]^+$ appear at 330 nm (ϵ = 5250) [42] and 440 nm (ϵ = 4800) [43], re-

TABLE 7. Ag···Ag distances of polynuclear silver(I) complexes

Complexes	Ag···Ag distance (Å)	Reference
$[Ag_2\{py\text{-}C(SiMe_3)_2\}_2]$	2.654(1)	35
$[Ag_2(PhN_3Ph)_2]$	2.669	36
$[Ag_2((tolyl)NCHN(tolyl))_2]$	2.705(1)	17
$[Ag_2(napy)_2](ClO_4)_2$	2.748(2)	this work
$[Ag_2(C_{16}H_{21}O_3)_2]\cdot 2H_2O$	2.778(5), 2.834(5)	37
$[Ag_2(py)_2(PhCO_2)_2]$	2.85(2), 2.90(2)	38
$[Ag_2(\beta\text{-alanine})_2](NO_3)_2$	2.855(4)	30
$[Ag_4(Mes)_4]$	2.733(3)	39
$[Ag_4\{SCH_2(SiMe_3)\}_3]_n(OCH_3)_n$	2.892(8)–3.350(7)	40

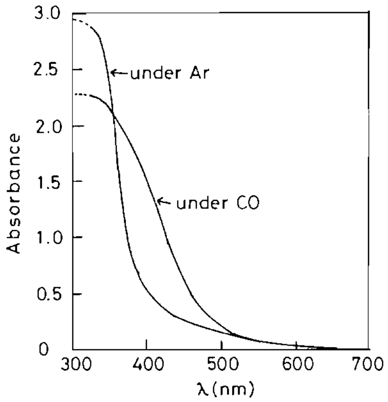

Fig. 3. Electronic spectra of $[Cu_2(napy)_2](ClO_4)_2$ in acetone under Ar and CO at 23 °C. $[Cu_2(napy)_2](ClO_4)_2 = 5.0 \times 10^{-4}$ M.

spectively. Such a charge transfer band has not been found so far in two-coordinate copper(I) complexes. It is noteworthy that $[Cu_2(napy)_2]^{2+}$ exhibits the charge transfer band at *c.* 335 nm (ϵ = 5700) in acetone, as shown in Fig. 3. In the methanol solution of $[Cu_2(napy)_2]^{2+}$, the charge transfer band appears at *c.* 340 nm (ϵ = 5600).

Generally, copper(I) complexes easily react with dioxygen to give the corresponding copper(II) complexes. It was found that two-coordinate coppers(I) of $[Cu_2(napy)_2]^{2+}$ did not react with O_2 because the intensity of the charge transfer band did not decrease in acetone when exposed to O_2 for 1 h. On the other hand, the complex quickly reacts with dioxygen in the presence of ligands such as ethylenediamine and sodium phthalate, which coordinate to the coppers to form four-coordinate copper complex. This fact indicates that two-coordinate copper(I) complex cannot be oxidized by O_2 if it is not guaranted that the copper gives at least a four-coordinate copper(II) complex.

When CO gas was passed through the acetone solution of $[Cu_2(napy)_2]^{2+}$, the intensity of the charge transfer band decreased, and simultaneously, a new charge transfer band appeared at *c.* 360 nm. Then, the intensity was completely restored by passing Ar gas through the solution. This suggests the formation of the carbonyl complex because the same phenomenon is observed for the charge transfer band of the binuclear complexes $[Cu_2(bpy)_2X_2]$ (bpy = 2,2′-bipyridine; X = Cl^-, Br^- and I^-) which reversibly react with CO to give the carbonyl complexes [43]. The coordination of CO to $[Cu_2(napy)_2]^{2+}$ is also supported by the fact that the ^1H NMR signals shift upfield in the presence of CO. The infrared spectrum of the complex in acetone was measured under CO in the region of CO stretching frequencies. Figure 4 demonstrates the appearance of a $\nu(CO)$ signal (1993 cm^{-1}) of CO coordinated to a Cu(I) atom. This type of signal in this region was not observed in the absence of CO. The carbonyl complex containing two acetonitrile molecules $[Cu_2(napy)_2(CO)(CH_3CN)_2](PF_6)_2$ which gives $\nu(CO)$ at 1999 cm^{-1} was isolated using tetrakis(acetonitrile)copper(I) hexafluorophosphate as the starting material of copper(I) in acetone. The $\nu(CO)$ values of 1993 and 1999 cm^{-1} are lower than those found for terminally coordinated CO, 2062 ~ 2110 cm^{-1} [44]. If CO forms a bridge between two metals, its $\nu(CO)$ (1930 ~ 1800 cm^{-1}) is much lower than that of the terminal CO group. An example of the bridging coordination of CO to two coppers is found

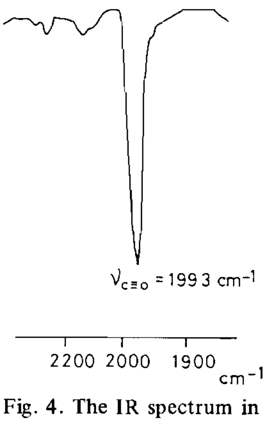

Fig. 4. The IR spectrum in acetone solution of the carbonyl complex of $[Cu_2(napy)_2](ClO_4)_2$ in the 2400 ~ 1800 cm^{-1} region.

in $[Cu_2(tmen)_2(\mu\text{-}CO)(PhCO_2)](BPh_4)_2$ (ν(CO) = 1930 cm^{-1}) of which the Cu···Cu distance of 2.410 Å is short. Thus, the ν(CO) values of 1993 and 1999 cm^{-1} are between those of the terminal coordination of CO and bridging coordination of CO.

The charge transfer band of $[Cu_2(napy)_2]^{2+}$ disappeared by passing C_2H_4 and C_2H_2 gasses through the methanol and acetone solutions and then restored by passing Ar gas through the solution. This demonstrates that $[Cu_2(napy)_2]^{2+}$ reversibly reacts with C_2H_4 and C_2H_2.

The ^1H NMR spectrum of $[Ag_2(napy)_2]^{2+}$ was not changed by bubbling CO and C_2H_4 through the solution.

Conclusions

The copper(I) and silver(I) dinuclear complexes with napy, $[Cu_2(napy)_2](ClO_4)_2$ and $[Ag_2(napy)_2](ClO_4)_2$ were synthesized. The two metal atoms are bridged by the two napy molecules with nearly linear geometry. The copper···copper distance of 2.506(2) Å is shorter than that (2.659(4) Å) of dicopper(II) complex $[Cu_2(napy)_2Cl_4]$. It is noted that the copper···copper distance (2.386(4) Å) of the mixed-valence copper complex with 4-methyl-1,8-naphthyridine, $[Cu^ICu^{II}(4\text{-}Me\text{-}napy)_2Cl_3]$ [45] is significantly shorter than those of the dinuclear copper(I) and dinuclear copper(II) complexes. A short metal···metal distance of 2.42 Å has been found for the mixed-valence nickel complex with napy $[Ni_2(napy)_2Br_2]BPh_4$ [8c]. The Ag···Ag separation of 2.748(2) Å for $[Ag_2(napy)_2](ClO_4)_2$ is shorter than in metallic silver. Thus, napy promotes the formation of the dinuclear complex of which the metal ions are two-coordinate, whereas it serves as a bidentate ligand for Cd(II), Fe(II) and Hg(II) and acts as a monodentate ligand for Hg(I) and Au(I). An important feature of $[Cu_2(napy)_2]^+$ is that it does not react with O_2 in acetone whereas it reacts with CO, olefins and alkynes to give the carbonyl, olefin and alkyne complexes, respectively. The carbonyl complex exhibits a significantly low ν(CO) value compared with those of other copper(I) carbonyl complexes.

Supplementary Material

For $[Cu_2(napy)_2](ClO_4)_2$ and $[Ag_2(napy)_2](ClO_4)_2$: tables of fractional coordinates, isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond angles, bond distances, torsion angles and observed and calculated structure factors are available from the authors on request.

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References

1 (a) K. D. Karlin, P. L. Dahlstrom, S. N. Cozzette, P. M. Scensny and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, (1981) 881; (b) K. D. Karlin, Y. Gultneh, J. P. Huchinson and J. Zubieta, *J. Am. Chem. Soc., 104* (1982) 5240.

2 (a) M. Pasquali and C. Floriani, *J. Am. Chem. Soc., 103* (1981) 185; (b) M. Pasquali, C. Floriani, G. Ventri, A. Graetani-Manfredotti and A. Chiesi-Villa, *J. Am. Chem. Soc., 104* (1982) 4092.

3 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Wiley, New York, 1982.

4 G. V. Goeden, J. C. Huffman and K. G. Caulton, *Inorg. Chem., 25* (1986) 2484.

5 (a) X. L. R. Fontaine, S. J. Higgins, B. L. Shaw, M. Thornton-Pett and W. Yichang, *J. Chem. Soc., Dalton Trans.*, (1987) 1501; (b) R. D. Mounts, T. Ogura and Q. Fernando, *Inorg. Chem., 13* (1974) 802; (c) M. W. Churchill, B. G. Deboer and D. J. Donovan, *Inorg. Chem., 14* (1975) 617; (d) S. Gamborotta, C. Floriani, A. Chiesi-Villa and C. Guastimi, *J. Chem. Soc., Chem. Commun.*, (1983) 1156; (e) M. Munakata, S. Kitagawa, H. Simono, T. Emori and H. Masuda, *J. Chem. Soc., Chem. Commun.*, (1988) 1798.

6 (a) E. L. Enwall and K. Emerson, *Acta Crystallogr., Sect. B 35* (1979) 2562; (b) G. W. Bushnell, K. R. Dixon and M. A. Khan, *Can. J. Chem., 56* (1978) 450; (c) J. C. Dewan, D. L. Kepert and A. H. White, *J. Chem. Soc., Dalton Trans.*, (1975) 490; (d) C. Mealli and L. Sacconi, *Acta Crystallogr., Sect. B, 33* (1977) 710.

7 (a) J. M. Epstein, J. C. Dewan, D. L. Kepert and A. H. White, *J. Chem. Soc., Dalton Trans.*, (1974) 1949; (b) A. Clearfield and P. Singh, *J. Chem. Soc., Chem. Commun.*, (1970) 389; (c) P. Singh, A. Clearfield and I. Bernal, *J. Coord. Chem., 1* (1971) 29; (d) W. R. Tikkanen, C. Kruger, K. D. Bomben, W. L. Jolly, W. C. Kaska and P. C. Ford, *Inorg. Chem., 23* (1984) 3633.

8 (a) A. Tiripicchio, M. T. Camellini, R. Uson, L. A. Oro, M. A. Ciriano and F. Viguri, *J. Chem. Soc., Dalton Trans.*, (1984) 125; (b) C. Mealli and F. Zanobini, *J. Chem. Soc., Chem. Commun.*, (1982) 97; (c) D. Gatteschi, C. Mealli and L. Sacconi, *J. Am. Chem. Soc., 95* (1973) 2736; (d) A. T. Baker, W. R. Tikkanen, W. C. Kaska and P. C. Ford, *Inorg. Chem., 23* (1984) 3254; (e) W. R. Tikkanen, E. Binamira-Soriaga, W. C. Kaska and P. C. Ford, *Inorg. Chem., 22* (1983) 1147; *23* (1984) 141; (f) H. Aghabozorg, R. C. Palenik and G. J. Palenik, *Inorg. Chem., 24* (1985) 4214.

9 D. F. Shriver, *Inorganic Syntheses*, Vol. 19, Wiley-Interscience, New York, 1979, p. 90.

10 T. Taga, T. Higashi and H. Iizuka, *KPPXRAY*, Kyoto program for X-ray cyrstal structure analysis, University of Kyoto, Japan, 1985.

11 (a) H. M. J. Hendriks, P. J. M. W. L. Birker, J. van Rijn, G. C. Verschoor and J. Reedijk, *J. Am. Chem. Soc., 104* (1982) 3607; (b) T. N. Sorrell and D. L. Jameson, *J. Am. Chem. Soc., 105* (1983) 6013; (c) M. J. Shilstra, P. J. M. W. L. Birker, G. C. Verschoor and J. Reedijk, *Inorg. Chem., 21* (1982) 2637; (d) L. M. Engelhard, C. Paka-

watchai, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, (1985) 117.

12 (a) A. H. Lewin, R. J. Michl, P. Ganis, U. Lepore and G. Avitable, *J. Chem. Soc., Chem. Commun.*, (1971) 1400; (b) M. Munakata, S. Kitagawa, A. Asahara and H. Masuda, *Bull. Chem. Soc. Jpn.*, *60* (1987) 1927; (c) P. J. Burke, D. R. McMillin and W. R. Robinson, *Inorg. Chem.*, *19* (1980) 1211; (d) R. Haemaelaeinen, M. Ahlgren, U. Turpeinen and T. Raikas, *Cryst. Struct. Commun.*, *8* (1979) 75.

13 A. Clearfield, R. Gopal and R. W. Olsen, *Inorg. Chem.*, *16* (1977) 911.

14 K. Iijima, T. Itoh and S. Shibata, *J. Chem. Soc., Dalton Trans.*, (1985) 2555.

15 P. K. Mehrotra and R. Hoffmann, *Inorg. Chem.*, *17* (1978) 2187.

16 K. M. Merz and R. Hoffmann, *Inorg. Chem.*, *27* (1988) 2120.

17 F. A. Cotton, X. Feng, M. Matusz and R. Poli, *J. Am. Chem. Soc.*, *110* (1988) 7077.

18 C. Mealli, C. S. Arcus, J. L. Wilkinson, T. J. Marks and J. A. Ibers, *J. Am. Chem. Soc.*, *98* (1976) 711.

19 P. C. Healy, C. Pakawatchao and A. H. White, *J. Chem. Soc., Dalton Trans.*, (1983) 1917.

20 J. Beck and J. Strahle, *Angew. Chem., Int. Ed. Engl.*, *24* (1985) 409.

21 H. Hartl and F. Z. Mahdjour-Hassan-Abadi, *Z. Naturforsch., Teil B*, *39* (1985) 149.

22 J. A. J. Jarvis, B. T. Kilbourn, R. Pearce and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, (1973) 475.

23 H. L. Aalten, G. V. Koten, K. Goubitz and C. H. Stam, *J. Chem. Soc., Chem. Commun.*, (1985) 1252.

24 G. V. Koten and J. G. Noltes, *J. Organomet. Chem.*, *84* (1975) 129.

25 S. Gamborotta, C. Floriani, A. Chiesi-Villa and C. Guastimi, *J. Chem. Soc., Chem. Commun.*, (1983) 1156.

26 P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, *21* (1966) 957.

27 M. R. Churchill, S. A. Bezman, J. A. Osborn and J. Wormald, *Inorg. Chem.*, *11* (1972) 1818.

28 T. H. Lemmen, K. Folting, T. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, *107* (1985) 7774.

29 C. Gagnon, J. Hubert, R. Rivest and A. L. Beauchamp, *Inorg. Chem.*, *16* (1977) 2469.

30 M. E. Kamwaya, E. Papavinasam, S. G. Teoh and R. K. Rajaram, *Acta Crystallogr., Sect. C*, *40* (1984) 1318.

31 J. Perron and A. L. Beauchamp, *Inorg. Chem.*, *23* (1984) 2853.

32 K. Nilsson and A. Oskarsson, *Acta Chem. Scand., Ser. A*, *36* (1982) 605.

33 (a) V. Schramm, *Inorg. Chem.*, *17* (1978) 714; (b) G. B. Ansell, *J. Chem. Soc. B*, (1971) 443.

34 (a) Y. Kinoshita, I. Matsubara, T. Higuchi and Y. Saito, *Bull. Chem. Soc. Jpn.*, *32* (1959) 1221; (b) D. M. Barnhardt, C. N. Caughlan and Mazhar-Ul-Haque, *Inorg. Chem.*, *8* (1969) 2768.

35 R. I. Papasergio, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, (1984) 612.

36 J. Beck and J. Straehle, *Z. Naturforsch., Teil B*, *41* (1986) 4.

37 P. Coggon and A. T. McPhail, *J. Chem. Soc., Chem. Commun.*, (1972) 91.

38 V. M. Hedrich and H. Hartl, *Acta Crystallogr., Sect. C*, *39* (1983) 533.

39 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, (1983) 1087.

40 K. Tang, M. Aslam, E. Block, T. Nicholson and J. Zubieta, *Inorg. Chem.*, *26* (1987) 1488.

41 P. Jennische and R. Hesse, *Acta Chem. Scand.*, *25* (1971) 423.

42 S. Kitagawa, M. Munakata and A. Hiagashie, *Inorg. Chim. Acta*, *59* (1982) 219.

43 S. Kitagawa and M. Munakata, *Inorg. Chem.*, *20* (1981) 2261.

44 (a) T. Tsuda, H. Habu, S. Horiguchi and T. Saegusa, *J. Am. Chem. Soc.*, *96* (1974) 5930; (b) R. R. Gagne, J. L. Allison, R. S. Gall and C. A. Koval, *J. Am. Chem. Soc.*, *99* (1977) 7170; (c) Y. Souma, J. Iyoda and H. Sano, *Inorg. chem.*, *15* (1976) 968; (d) R. R. Gagne, R. S. Gall, G. C. Lisensky and R. E. Marsh, *Inorg. Chem.*, *18* (1979) 771; (e) M. Pasquali, G. Marini, C. Floriani, A. Gaetani-Manfredotti and C. Guastini, *Inorg. Chem.*, *19* (1980) 2525; (f) M. Pasquali, C. Floriani and A. Gaetani-Manfredotti, *Inorg. Chem.*, *19* (1980) 1191; (g) M. Pasquali, F. Marchetti and C. Floriani, *Inorg. Chem.*, *17* (1978) 1684; (h) G. M. Villacorta and S. J. Lippard, *Inorg. Chem.*, *26* (1987) 3672; (i) M. Munakata, S. Kitagawa and K. Goto, *J. Inorg. Biochem.*, *16* (1982) 319; (j) S. Kitagawa and M. Munakata, *Bull. Chem. Soc. Jpn.*, *59* (1986) 2743.

45 D. Gatteschi, C. Mealli and L. Sacconi, *Inorg. Chem.*, *15* (1976) 2774.