baloxime complexes reflects an increase in ligand field splitting, in parallel with increased stability with respect to dissociation.[25] Interestingly, the salox and ketox nitrosyls were the least stable during the long acquisition times of our natural-abundance measurements.

The ^{59}Co data for the acacen, salen, and cobaloxime complexes with a range of axial ligands,[24,25] together with the similarities in ^{59}Co shielding for NO$^-$ and dithiocarbamato ligands, support the description of NO$^-$ as a fairly weak ligand, particularly if its nephelauxetic effect is larger than that of other nitrogen ligands such as amines (azide has been placed between Br$^-$ and I$^-$ and below dithiocarbamate in a nephelauxetic series[40]).

Table II shows a slight but consistent trend to lower ^{59}Co shielding if Me$_2$SO is used instead of chloroform for the 5-coordinate nitrosyls, and this may indicate weak coordination by Me$_2$SO. There are indications also of ^{15}N deshielding and lower NO stretching frequency with a more basic solvent; trans coordination would be expected to increase the tendency for MNO to bend.

Acknowledgment. We thank the Science and Engineering Research Council for a research studentship (B.S.) and for the provision of high-field NMR facilities, Drs. Oliver Howarth and Eirian Curzon for the 400-MHz spectra run at Warwick University, Maurice Cooper for the 180-MHz spectra run at the Physico-Chemical Measurements Unit, Harwell, and M. Saunders and R. G. Harrison for the preparation and infrared spectra of some unlabeled complexes.

Registry No. 1, 36915-19-2; **2**, 92011-01-3; **3**, 86378-38-3; **4**, 15245-34-8; **5**, 34383-67-0; **6** (R = Me), 36434-42-1; **6** (R = Et), 15684-53-4; **6** (R = *i*-Pr), 83897-62-5; ^{15}N, 14390-96-6; Co, 7440-48-4.

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Synthesis, Characterization, and X-ray Molecular Structures of Mono- and Dinuclear Copper Complexes with 2,7-Bis(2-pyridyl)-1,8-naphthyridine

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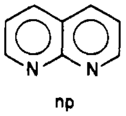
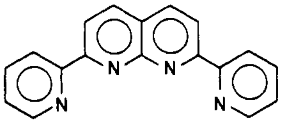
The preparation and characterization of two complexes of 2,7-bis(2-pyridyl)-1,8-naphthyridine (bpnp) with copper(II) and copper(I) are described. The X-ray molecular structure of a mononuclear Cu(I) complex, [Cu(bpnp)(PPh$_3$)$_2$]PF$_6$, was determined with full-matrix least-squares procedures to a final R index of 0.057. Crystals are monoclinic, space group $P2_1/n$, with cell dimensions a = 14.855 (6) Å, b = 21.914 (8) Å, c = 15.111 (2) Å, and V = 4862.651 Å^3 with Z = 4. The X-ray molecular structure of the dinuclear complex [Cu$_2$(bpnp)(μ-Cl)(μ-OH)Cl$_2$] was also determined to a final R index of 0.0363. The crystals are monoclinic, space group $P2_1/m$, with cell dimensions a = 7.694 (1) Å, b = 16.434 (2) Å, c = 7.921 (1) Å, and V = 952.695 Å^3 with Z = 2. In the latter complex, each Cu(II) ion is chelated by a 2,2′-bipyridine fragment of the bpnp and the two metal ions are linked by bridging chlorine and oxygen atoms. The Cu–Cu distance is 3.022 Å. The coordination geometry about each Cu(II) is approximately a square pyramid with the bridging chlorine as the apical ligand and two nitrogen atoms, one bridging oxygen atom, and a terminally bound chlorine atom as the four basal ligands of the square pyramid. Magnetic susceptibility measurements of the paramagnetic complex suggest a weak antiferromagnetic interaction ($|2J| < 200$ cm^{-1}, room-temperature magnetic moment/Cu = 1.64 μ_B), which couples the spins of the two unpaired electrons. Cyclic voltammograms of this complex in aqueous solution show reduction occurs in two one-electron transfers ($E_{1/2}$ = 0.36, 0.16 V vs. Ag/AgCl). X-ray photoelectron spectroscopy allows differentiation of bridging vs. terminal chlorine atoms with peaks at 197.2 (5) and 196.2 (2) eV, respectively. Preliminary studies show that in situ reduction of the bpnp copper(II) dimer gives solutions of bpnp copper(I) dimers that reversibly coordinate carbon monoxide.

Introduction

Binucleating ligands that can coordinate two metal centers in close proximity have been the subject of considerable experimental interest.[2] One promising dinucleating system utilizes 1,8-naphthyridine (np) as the bridging unit. However, while several dinuclear np complexes have been characterized,[3] the more common coordination of this bidentate ligand is the chelation of a single metal ion.[4] Recently, Caluwe reported the preparation of 2,7-bis(2-pyridyl)-1,8-naphthyridine (bpnp).[5] Dinuclear complexes of this relatively rigid tetradentate ligand would be crescent shaped and in principle have



np



bpnp

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minimal steric effects on the interactions between metal centers and potential substrates. Recently we reported the first synthesis of such a dinuclear "croissant complex" of bpnp, the dirhodium(II) salt $[Rh_2(\mu\text{-}O_2CCH_3)_3(bpnp)]PF_6$,[6] and also of a mononuclear rhenium(I) species, $Re(bpnp)(CO)_3Br$.[7] Here we report the synthesis and properties of several copper(I) and copper(II) bpnp complexes and the X-ray molecular structures of a mononuclear copper(I) complex, $[Cu(PPh_3)_2(bpnp)]PF_6$, and of a dinuclear copper(II) complex, $Cu_2(bpnp)(OH)Cl_3$, of this ligand. The latter species with a Cu–Cu distance of 3.022 Å demonstrates that bpnp can promote the formation of dinuclear complexes even when there is no substantive metal–metal bonding.

Experimental Section

Materials. Solvents were Mallinckrodt AR or SpectrAR quality. When higher purity was desired, the following procedures were used. Acetone was distilled from barium oxide under argon. Methylene chloride was distilled from lithium aluminum hydride under argon. Acetonitrile was distilled from calcium hydride under argon: the first fraction was discarded. Dimethylformamide (DMF) was vacuum dsitilled prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) from Aldrich was recrystallized from ethyl acetate and stored under vacuum over phosphorous pentoxide.

Cupric triflate (triflate = trifluoromethanesulfonate) was prepared by a published procedure.[8] Cupric chloride hydrate and cupric acetate were used as received from Aldrich. Cuprous triflate was prepared by the method of Solomon and Kochi.[9] Cuprous halides were used as received from Cerac. The bpnp was prepared as described.[5] Manipulation of air-sensitive compounds was accomplished by standard Schlenk techniques or in a Vacuum Atmospheres Corporation drybox with an argon atmosphere.

Physical and Analytical Methods. Electronic spectra were obtained with Cary 14 and 118 spectrophotometers. Infrared spectra were obtained on Perkin-Elmer 283 and 683 Spectrometers and calibrated vs. polystyrene. Samples were usually in KBr pellets or, when halide exchange was a possibility, as Nujol mulls between CsI plates.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories. Electron spin resonance (ESR) spectra were obtained with a Varian E-4 ESR spectrometer. Magnetic susceptibility measurements were determined with two methods: the Evans NMR method[11] and the Faraday method, with use of a Cahn-Ventron Faraday magnetic susceptibility apparatus. Conductivity measurements were obtained with a Radiometer CDM2e conductivity meter in spectral grade nitromethane or triply distilled water. NMR spectra were obtained on Varian CFT-20 and XL-100 spectrometers.

Cyclic voltammetry was performed with a Chemtrix SSP-1 unit modified in house to the specifications of the SSP-2 three-electrode system.[9] A three-compartment cell was used with a platinum-wire auxiliary electrode and a saturated sodium chloride calomel (SSCE) reference electrode. The working electrode was either a platinum ball or planar pyrolytic graphite that was cleaned prior to each run. Reversibility of the waves was determined by comparison of the separation of peak anodic–cathodic potentials to that of internal ferrocene and by the ratio of anodic to cathodic peak currents (unity for a reversible process).

X-ray photoelectron spectra were obtained at the University of California, Berkeley, CA, with a GCA/McPherson ESCA-36 photoelectron spectrometer using Mg Kα radiation (1253.6 eV) at a pressure of $<1 \times 10^{-7}$ torr. Each sample was ground to a powder and brushed onto one side of a piece of double-sided tape bonded to an aluminum plate. The plates were loaded onto an eight-position sample wheel in the spectrometer. All spectra were calibrated with use of the adventitious carbon line at 285 eV. The Cl 2p spectrum of compound II showed the presence of more than one type of chlorine atom; however, the spectra were not of sufficient resolution to separate individual lines. Therefore, NaCl, KCl, $BaCl_2$, and $CuCl_2$ were run concurrently to estimate peak parameters. The reference spectra were fit via nonlinear least-squares methods to two peaks with a mixed Gaussian–Lorentzian function. This procedure empirically accounted for the asymmetry of the peaks caused by the $^2P_{3/2}$–$^2P_{1/2}$ splitting and other satellite structure that normally accompanies core excitations in solids. The adjusted parameter included the energy separation of the peaks, the area rates, the Gaussian–Lorentzian mix ratio, and the full width at half-maximum. Spectra for compound II were computer fit to two such asymmetric peaks with the parameters found for the simple chlorides.

Preparation of Tetrachloro[2,7-bis(2-pyridyl)-1,8-napthyridine]dicopper(II). A methanol solution (5 mL) of $CuCl_2 \cdot 2H_2O$ (65 mg, 360 mmol) was quickly added to a hot butanol solution (25 mL) of bpnp (50 mg, 180 mmol). The solution turned yellow-green immediately, and within seconds, a microcrystalline precipitate formed. The suspension was cooled to −20 °C for 12 h, whereupon the yellow-green product was collected on a glass frit and washed three times with anhydrous methanol. This material was dried for 10 h in vacuo to give 95 mg of product (98% yield for $Cu_2(bpnp)Cl_4$ (I) based on bpnp). Anal. Calcd (found) for $C_{18}H_{12}N_4Cu_2Cl_4$: Cu, 22.97 (22.91); C, 39.08 (38.31); H, 2.19 (2.91); N, 10.13 (9.11). The complex was soluble in water, dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO), slightly soluble in methanol, and insoluble in less polar solvents. The infrared spectrum of the tetrachloroproduct as a Nujol mull between CsI plates showed the following absorptions (cm^{-1}): 1601 (s), 1528 (m), 1318 (m), 1269 (m), 1218 (w), 1177 (w), 1156 (m), 1055 (w), 1022 (m), 854 (m), 775 (s), 724 (m), 664 (m), 424 (w), 337 (w), 304 (w), 294 (m), 227 (m). The electronic spectrum of I in Me_2SO showed ligand $\pi\pi^*$ bands in the ultraviolet region (nm (M^{-1} cm^{-1})): 280 (3.3×10^4), 342 (2.2×10^4), 358 (2.3×10^4). A broad maximum at 860 nm ($\epsilon = 170$ M^{-1} cm^{-1}) can be attributed to a d–d transition. Recrystallization of I in the presence of water gave the dichloro(μ-chloro)(μ-hydroxo)[μ-2,7-bis(2-pyridyl)-1,8-naphthyridine]dicopper(II) complex, $Cu_2(bpnp)(OH)Cl_3$ (II), characterized by X-ray crystallography (see below).

Dichloro[2,7-bis(2-pyridyl)-1,8-naphthyridine]dicopper(I). Cuprous chloride and bpnp in acetonitrile with stirring under anaerobic conditions in a 2:1 mole ratio gave a red, air-sensitive product that was sparingly soluble in DMF and Me_2SO. Elemental analysis confirmed the proposed composition. Anal. Calcd (found) for $C_{18}H_{14}N_4Cl_2Cu_2$: C, 44.82 (45.13); H, 2.51 (2.62); N (Kjeldahl), 11.61 (11.70); Cl, 14.70 (14.61). The infrared spectrum as a Nujol mull between CsI plates showed the following absorptions (cm^{-1}): 1598 (s), 1545 (w), 1518 (m), 1380 (s), 1305 (m), 1262 (m), 1220 (m), 1150 (m), 1051 (w), 970 (w), 854 (s), 780 (s), 740 (m), 652 (w), 580 (w), 531 (w), 467 (m). In acetone solution, this material displayed a broad visible absorption band with a maximum at 535 nm and an extinction coefficient ϵ_{max} of $\sim 2.5 \times 10^3$ M^{-1} cm^{-1}. Such bands are common to Cu(I) polypyridine complexes and have been assigned as metal to ligand charge transfer in character.

Bis(triphenylphosphine)[2,7-bis(2-pyridyl)-1,8-naphthyridine]copper(I) Hexafluorophosphate. Addition of $AgPF_6$ to a stirred suspension of $Cu_2(bpnp)I_2$ (prepared by treating bpnp with CuI) in acetonitrile with 2 mol of triphenylphosphine/mol of copper under argon gave an orange solution and a silver iodide precipitate. The silver iodide was removed by filtration. Vacuum removal of solvent and cooling gave air-stable crystals of $[Cu(PPh_3)_2(bpnp)](PF_6)$ suitable for X-ray analysis.

X-ray Structure Determination: Bis(triphenylphosphine)[2,7-bis(2-pyridyl)-1,8-naphthyridine]copper(I) Hexafluorophosphate and Dichloro(μ-chloro)(μ-hydroxo)[μ-2,7-bis(2-pyridyl)-1,8-naphthyridine]dicopper(II). The crystals were mounted in capillaries under argon. Essential details of the structure operations are given in Tables I and II, and atomic coordinates are given in Tables III and IV. Key bond angles and bond lengths are summarized in Tables V and VI.

Results and Discussion

Dinuclear Copper(II) Complexes. Treatment of cupric chloride with bpnp in a 2:1 molar ratio respectively gave a nearly quantitative yield of $Cu_2(bpnp)Cl_4$ (I) (eq 1) based on either the ligand or copper as limiting reagent. This material

$$bpnp + 2CuCl_2 \rightarrow Cu_2(bpnp)Cl_4 \qquad (1)$$

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Table I. Data for X-ray Diffraction of $Cu_2(bpnp)(OH)Cl_3$ (II)

(A) Crystal Data

formula: $C_{18}H_{12}N_4OCu_2Cl_3$
cryst syst: monoclinic
space group: $P2_1/m$
$a = 7.694$ (1) Å
$b = 16.434$ (2) Å
$c = 7.921$ (1) Å

$\alpha = 90.0°$
$\beta = 107.974$ (9)°
$\gamma = 90.0°$
$V = 952.695$ Å^3
$d_c = 1.861$ g cm^{-3}
$Z = 2$
$\mu = 26.81$ cm^{-1}

(B) Solution and Refinement

reflcns measd: 2224
obsd reflcns ($I > 2.0\sigma(I)$): 1851
no. of parameters: 153
$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.0363$
$R_w = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} = 0.0454$
$w = 1/\sigma^2(F_o)$

Table II. Data for X-ray Diffraction of $[Cu(bpnp)(PPh_3)_2]PF_6$ (IV)

(A) Crystal Data

formula: $C_{54}H_{42}N_4P_3F_6Cu$
cryst syst: monoclinic
space group: $P2_1/n$
$a = 14.855$ (6) Å
$b = 21.914$ (8) Å
$c = 15.111$ (2) Å

$\alpha = 90.0°$
$\beta = 98.690$ (15)°
$\gamma = 90.0°$
$V = 4862.70$ Å^3
$d_c = 1.39$ g cm^{-3}
$Z = 4$
$\mu = 6.08$ cm^{-1}

(B) Solution and Refinement

reflcns measd: 9425
obsd reflcns ($I > 2.0\sigma(I)$): 4961
no. of parameters: 613
$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.057$
$R_w = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} = 0.066$
$w = 1/\sigma^2(F_o)$

Table III. Positional Parameters for the Atoms of $Cu_2(bpnp)(OH)Cl_3$ (II)[a] (×10^4)

atom	*x*	*y*	*z*
Cu	1855 (1)	1581 (1)	2300 (1)
Cl(1)	4762 (1)	1074 (1)	3027 (2)
Cl(2)	1673 (2)	2500	4841 (2)
O	2539 (4)	2500	1091 (5)
N(1)	747 (4)	516 (2)	2633 (4)
N(2)	−873 (4)	1791 (2)	878 (4)
C(11)	1571 (5)	−90 (2)	3738 (5)
C(12)	768 (6)	−845 (2)	3710 (6)
C(13)	−904 (5)	−999 (2)	2488 (5)
C(14)	−1772 (5)	−375 (2)	1360 (5)
C(15)	−930 (4)	382 (2)	1475 (4)
C(21)	−1789 (4)	1099 (2)	398 (4)
C(22)	−3442 (5)	1051 (2)	−1000 (5)
C(23)	−4205 (5)	1741 (2)	−1837 (5)
C(24)	−3394 (6)	2500	−1217 (6)
C(25)	−1703 (6)	2500	151 (6)
H(11)	2679 (58)	7 (27)	4425 (57)
H(12)	1348 (57)	−1209 (27)	4556 (55)
H(13)	−1453 (58)	−1521 (27)	2420 (57)
H(14)	−2853 (58)	−487 (27)	581 (55)
H(22)	−3933 (59)	612 (29)	−1313 (57)
H(23)	−5302 (59)	1755 (27)	−2894 (55)

[a] Atoms are labeled as shown in Figure 1. The estimated standard deviations of the least significant digits are given in parentheses.

was slightly soluble in DMF or Me_2SO but more soluble in water. When the reaction was performed with a 1:1 Cu(II) to bpnp ratio, I was obtained in nearly quantitative yield based on copper, but only 50% based on bpnp. The remaining bpnp was in the filtrate as determined by UV spectroscopy.

Recrystallization of I from water afforded green, block-shaped crystals. Initially these were thought to have the same composition as I (i.e., $Cu_2(bpnp)Cl_4$), but the single-crystal X-ray structure (Figure 1) demonstrated that the composition of the complex had changed to the extent that one Cl^- had been replaced by an oxygen, presumably as a hydroxide to give

Table IV. Positional Parameters for the Non-Hydrogen Atoms of $[Cu(bpnp)(Ph_3P)_2]PF_6$ (IV)[a] (×10^4)

atom	*x*	*y*	*z*
Cu	7354 (1)	4511 (1)	2811 (1)
P(1)	7732 (1)	4114 (1)	1519 (1)
P(2)	6643 (1)	5417 (1)	3002 (1)
P(3)	3257 (1)	2900 (1)	1890 (1)
P(1)	3543 (3)	2796 (2)	2932 (2)
F(2)	2594 (3)	3417 (2)	2099 (3)
F(3)	3917 (4)	2371 (2)	1701 (3)
F(4)	2508 (3)	2384 (2)	1909 (3)
F(5)	3005 (6)	2984 (2)	871 (3)
F(6)	4016 (4)	3392 (2)	1918 (4)
N(1)	6773 (3)	3862 (2)	3602 (3)
N(21)	8458 (3)	4330 (2)	3821 (3)
N(22)	9437 (3)	4987 (2)	3234 (3)
N(3)	9674 (4)	5808 (3)	1858 (4)
C(11)	5911 (4)	3667 (3)	3519 (4)
C(12)	5577 (4)	3324 (3)	4162 (4)
C(13)	6158 (5)	3160 (3)	4904 (5)
C(14)	7040 (5)	3356 (3)	5013 (4)
C(15)	7341 (4)	3691 (2)	4343 (3)
C(21)	8304 (4)	3895 (2)	4390 (3)
C(22)	9004 (4)	3630 (3)	5011 (4)
C(23)	9873 (4)	3832 (3)	5008 (4)
C(24)	10067 (4)	4285 (3)	4423 (4)
C(25)	10938 (4)	4525 (3)	4372 (4)
C(26)	11044 (4)	4951 (3)	3774 (4)
C(27)	10276 (4)	5185 (3)	3198 (4)
C(28)	9330 (3)	4548 (3)	3831 (3)
C(31)	10401 (4)	5650 (3)	2519 (4)
C(32)	11213 (3)	5900 (3)	2559 (4)
C(33)	11329 (4)	6306 (3)	1981 (5)
C(34)	10672 (5)	6518 (3)	1294 (5)
C(35)	9820 (4)	6254 (3)	1221 (4)
C(41)	7989 (3)	4690 (2)	721 (3)
C(42)	7473 (4)	5215 (3)	645 (3)
C(43)	7583 (4)	5661 (3)	28 (4)
C(44)	8241 (4)	5586 (3)	−527 (4)
C(45)	8760 (4)	5060 (3)	−459 (4)
C(46)	8642 (4)	4617 (3)	154 (4)
C(51)	8748 (4)	3633 (2)	1724 (4)
C(52)	9618 (4)	3891 (3)	1903 (4)
C(53)	10382 (4)	3532 (3)	2117 (4)
C(54)	10296 (5)	2940 (4)	2187 (6)
C(55)	9474 (6)	2656 (4)	2031 (9)
C(56)	8690 (5)	3028 (3)	1789 (7)
C(61)	6936 (4)	3616 (3)	807 (4)
C(62)	7126 (7)	3410 (5)	8 (5)
C(63)	6559 (7)	3010 (5)	−537 (5)
C(64)	5761 (5)	2842 (4)	−276 (5)
C(65)	5588 (6)	3016 (4)	526 (6)
C(66)	6163 (5)	3409 (4)	1051 (5)
C(71)	7072 (4)	6114 (3)	2527 (4)
C(72)	6565 (5)	6432 (3)	1846 (4)
C(73)	6947 (6)	6932 (4)	1499 (5)
C(74)	7820 (6)	7137 (3)	1869 (6)
C(75)	8315 (5)	6820 (3)	2534 (5)
C(76)	7954 (4)	6301 (3)	2854 (4)
C(81)	5429 (3)	5430 (3)	2568 (3)
C(82)	5090 (4)	4998 (3)	1929 (5)
C(83)	4160 (6)	4986 (4)	1603 (6)
C(84)	3574 (5)	5402 (4)	1904 (6)
C(85)	3910 (5)	5816 (4)	2524 (5)
C(86)	4822 (4)	5829 (3)	2867 (4)
C(91)	6637 (3)	5622 (2)	4176 (3)
C(92)	6377 (4)	5178 (3)	4731 (4)
C(93)	6348 (5)	5293 (3)	5630 (4)
C(94)	6580 (5)	5848 (4)	5979 (4)
C(95)	6829 (5)	6303 (3)	5443 (4)
C(96)	6859 (4)	6184 (3)	4544 (4)

[a] Atoms are labeled as shown in Figure 3. Estimated standard deviations for the least significant digits are given in parentheses.

$Cu_2(bpnp)(OH)Cl_3$ (II). The lability of the halides in aqueous solution is indicated by the conductivity properties (see below). The geometry about each copper ion of II most closely resembles that of a tetragonal pyramid. The base of the pyramid

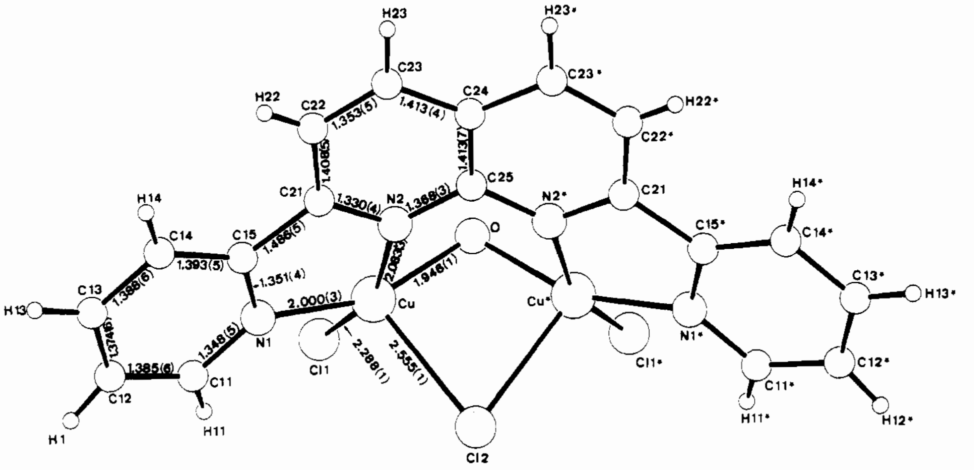


Figure 1. Perspective view and atom-numbering scheme for $Cu_2(bpnp)(OH)Cl_3$ (II).

Table V. Bond Distances (Å) and Angles (deg) for the Compound $Cu_2(bpnp)(OH)Cl_3$ (II)

Distances			
Cu-O	1.946 (1)	Cu-Cu*	3.022 (1)
Cu-Cl(1)	2.288 (1)	N(2)-N(2)*	2.330 (4)
Cu-Cl(2)	2.555 (1)	C(11)-C(12)	1.385 (6)
Cu-N(1)	2.000 (3)	C(12)-C(13)	1.374 (6)
Cu-N(2)	2.083 (3)	C(13)-C(14)	1.388 (6)
N(1)-C(11)	1.348 (5)	C(14)-C(15)	1.393 (5)
N(1)-C(15)	1.351 (4)	C(15)-C(21)	1.486 (5)
N(2)-C(25)	1.368 (3)	C(21)-C(22)	1.408 (5)
N(2)-C(21)	1.330 (4)	C(22)-C(23)	1.353 (5)
		C(23)-C(24)	1.413 (4)
		C(24)-C(25)	1.413 (7)
Angles			
Cu-O-Cu*	101.8 (2)	Cl(1)-Cu-N(1)	94.1 (1)
Cu-Cl(2)-Cu*	72.5 (1)	N(1)-Cu-N(2)	79.4 (1)
Cl(1)-Cu-Cl(2)	107.7 (1)	N(2)-Cu-O	89.2 (1)
Cl(1)-Cu-O	90.8 (1)	C(25)-N(2)-C(21)	118.1 (3)
Cl(1)-Cu-N(2)	160.2 (1)	N(2)-C(25)-N(2)*	116.9 (4)
		Cl(2)-Cu-O	91.0

Table VI. Selected Bond Distances (Å) and Angles (deg) for the Compound $[Cu(bpnp)(PPh_3)_2]PF_6$ (IV)

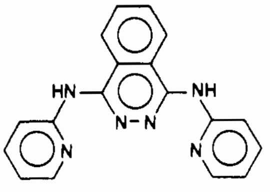
Distances			
Cu-P(1)	2.285 (1)	N(1)-C(11)	1.338 (7)
Cu-N(1)	2.125 (4)	N(1)-C(15)	1.349 (6)
Cu-N(21)	2.102 (4)	N(21)-C(21)	1.328 (7)
Cu-P(2)	2.287 (2)	N(21)-C(28)	1.378 (7)
P(1)-C(41)	1.825 (5)	N(22)-C(27)	1.328 (7)
P(1)-C(51)	1.830 (6)	N(22)-C(28)	1.346 (7)
P(1)-C(61)	1.835 (6)	N(3)-C(31)	1.400 (9)
P(2)-C(71)	1.842 (6)	N(3)-C(35)	1.412 (9)
P(2)-C(81)	1.824 (5)		
P(2)-C(91)	1.832 (5)		
Angles			
N(21)-Cu-N(1)	78.7 (2)	C(51)-P(1)-C(61)	101.4 (3)
P(2)-Cu-P(1)	128.0 (1)	C(51)-P(1)-C(41)	105.1 (2)
N(21)-Cu-P(2)	113.4 (1)	C(41)-P(1)-C(61)	101.9 (2)
N(21)-Cu-P(1)	106.5 (1)	C(71)-P(2)-Cu	118.5 (2)
N(1)-Cu-P(1)	113.6 (1)	C(81)-P(2)-Cu	114.8 (2)
N(1)-Cu-P(2)	106.0 (1)	C(91)-P(2)-Cu	113.9 (2)
C(51)-P(1)-Cu	112.2 (2)	C(71)-P(2)-C(81)	103.2 (3)
C(41)-P(1)-Cu	113.9 (2)	C(71)-P(2)-C(91)	103.1 (2)
C(61)-P(1)-Cu	120.6 (2)	C(81)-P(2)-C(91)	101.3 (2)

is formed by the two nitrogen atoms from a bipyridine-like fragment of bpnp, the bridging hydroxide, and the terminal chloride. The bridging chloride occupies the apex of each square pyramid. The dinuclear molecule posseses a plane of symmetry, which contains the bridging chlorine and oxygen atoms and two carbon atoms of the bpnp ligand. The two square pyramids about the copper ions are linked together at the edge defined by the bridging anions.

Table V gives key bond lengths and bond angles for II. The Cu-N(2) distance is significantly longer (2.083 (3) Å) than the Cu-N(1) distance (2.000 (3) Å), showing that the copper ions are displaced away from the naphthyridine fragment. This is reflective of the fact that the Cu- - -Cu* distance (3.022 (1) Å) is much greater than the distance (2.330 (4) Å) between the internal nitrogens (N(2)- - -N(2)*) of the bpnp ligand. Two of the ligand–metal–ligand angles are significantly different from 90°. The acute N(1)–Cu–N(2) angle (79.4°) reflects the small bite of the bipyridine-like fragment and is typical of the values found in copper complexes of 2,2′-bipyridine.[12] The obtuse Cl(1)–Cu–Cl(2) angle (107.7°) arises from the displacement of Cl(2) from the ideal apical position to that in the bridged complex.

The planes defined by the pyridyl rings of the bipyridine-like fragments subtend an angle of 13.7°. This angle is smaller than the analogous angle in the tetrahedral mononuclear Cu(I) complex (15.9°, vide infra) but larger than angles seen in the dirhodium(II) complex, $Rh_2(O_2CCH_3)_3(bpnp)^+$ (3.2°),[5] or the mononuclear rhenium complex, $Re(bpnp)(CO)_3Br$ (8.8°).[7]

The structure of II is similar to that recently reported[13] for $Cu^{II}_2Cl_2(\mu\text{-}Cl)(\mu\text{-}OH)(pap)$[14] (III) (pap = 1,4-bis(2-pyridylamino)phthalazine). The key similarity is that both



pap

Cu(II) ions are in square-pyramidal configurations with the OH^- bridging at basal sites and one Cl^- bridging at the apical sites. Analogous copper–ligand bond lengths are comparable, and the Cu- - -Cu* distance in III is 3.00 Å, just slightly shorter than the value (3.02 Å) found in II.

Magnetic susceptibility measurements of I as a D_2O solution (Evans method)[11] and as a powder (Faraday method) gave 1.64 ± 0.05 and 1.75 ± 0.03 μ_B (per copper) as the effective magnetic moments at room temperature. For comparison, the mononuclear Cu(II) complexes $Cu(bpy)Cl_2$ and $Cu(phen)Cl_2$ each displayed the value 1.87 μ_B at room temperature.[15] Thus,

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for $Cu_2(bpnp)Cl_4$, the magnetic moments observed both as a solid and in solution were lower than the moments observed for known monomeric species with similar ligands. The moment was lower in aqueous solution than as a solid. However, this probably reflects changes in the coordination sphere owing to the lability of the chlorides. The Curie–Weiss plot obtained for the solid $Cu_2(bpnp)Cl_4$ was linear to 120 K, the lowest temperature attainable with our apparatus. The Curie constant, C, is 0.386 and the intercept, Θ, is −4.7 K. The negative value of Θ and the low effective magnetic moment observed both in the solid state and in solution imply a small antiferromagnetic interaction between the metal centers (i.e., the ground state is a singlet).[16] The magnetic properties of both chloro-bridged and hydroxo-bridged dicopper(II) complexes have been extensively studied,[16,17] and it has been demonstrated that ability of the bridging ligand to mediate the interaction between the two centers is dependent on the nature of the bridging ligands with μ-hydroxides generally giving stronger magnetic coupling than μ-chloride. This would explain the lower magnetic moment found in aqueous solution.

The conductivity of I was found to be solvent dependent. In DMF I was a nonelectrolyte, but in aqueous solution (10^{-3} M) the molar conductivity ($\Lambda = 470$ mho cm^2/mol) was that seen for a four- or five-ion electrolyte,[19] a further indication of the lability of the coordinated chlorides. Similarly, the mononuclear complexes $Cu(bpy)Cl_2$ (bpy = 2,2′-bipyridine) and $Cu(phen)Cl_2$ (phen = 1,10-phenanthroline) were found to be nonelectrolytes in DMF but to have conductivities in the range of two- or three-ion electrolytes (Λ ca. 200 mho cm^2/mol) in aqueous solution.

Cyclic voltammetry of I in DMF showed a broad reduction wave (peak to peak separation 110 mV), $E_{1/2} = 0.22$ V vs. SSCE, possibly consistent with the presence of two overlapping, one-electron waves. By comparison, cyclic voltammetry of $Cu(bpy)Cl_2$ and $Cu(phen)Cl_2$ showed quasi-reversible single-electron reductions with the respective $E_{1/2}$ values of 0.07 and −0.02 V vs. SSCE. Thin-layer cyclic voltammetry performed in neutral aqueous solution showed a pair of overlapping, quasi-reversible waves of equal peak currents giving $E_{1/2}$ values of 0.58 and 0.38 V vs. NHE. (In comparison, aqueous $Cu(bpy)Cl_2$ underwent irreversible reduction, although a cathodic peak current at 0.35 V vs. NHE was noted.) Integration of charge passed in the thin-layer cell showed two (2.0) electrons transferred during reduction, one electron per wave. The 0.20-V separation between these reduction waves allows calculation[18] of the comproportionation constant, $K_{com} = [Cu^ICu^{II}]^2/[Cu^ICu^I][Cu^{II}Cu^{II}] \simeq 2 \times 10^3$, considerably larger than the statistical value of 4. This suggests some special stability of the mixed-valence bpnp dicopper complex under these conditions; however, the specific composition of this species in aqueous solution is uncertain.

The ESR spectrum of I as a powder showed a broad isotropic signal with $g = 2.11$ at room and liquid-nitrogen temperatures. A 10^{-3} M solution of I in a wet Me_2SO or aqueous ethylene glycol glass gave a spectrum (Figure 2) that has one component split into four lines ($g = 2.35$, $A = 118$ G) by the copper nuclei ($I = {}^3/_2$ for ^{63}Cu and ^{65}Cu) and two components nearly overlapping ($g = 2.02$, 2.01) with no hyperfine coupling resolved. The magnitude of the hyperfine coupling constant is consistent with a dinuclear species,[20] indicating that the bpnp dicopper(II) unit stays intact in solution.

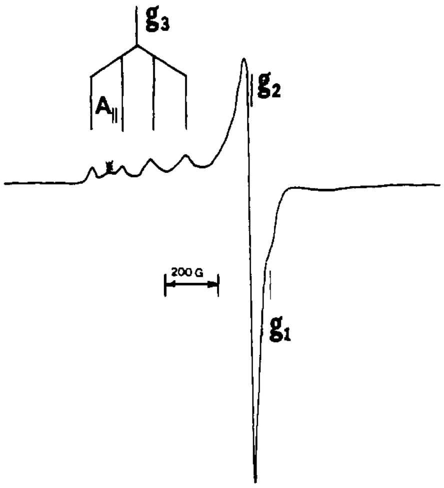

Figure 2. X-Band ESR spectrum of $Cu_2(bpnp)Cl_4$ in Me_2SO at 77 K (the asterisk denotes an impurity).

The initial indication that recrystallization of I from aqueous solution gave a new species came from an X-ray photoelectron spectral study. This technique can differentiate atoms of the same elements in different chemical environments.[21] For example, Walton and co-workers have been able to differentiate terminal and bridging halogens for a number of polynuclear complexes[22-26] such as $M_2Cl_9^{3-}$ (M = Cr, Mo, or W), for which the bridging chlorides display higher binding energies than do the terminal chlorides.[22] In the present case, the XPES spectrum of II indicated the presence of two different types of chlorides with binding energies 196.2 (2) and 197.2 (5) eV and the intensity ratio of about 2.3. We thus concluded the complex II contained two chlorides that were coordinated terminally to copper(II) ions and one that bridged the two Cu(II) centers, the latter having the higher XPES binding energy. This conclusion was later confirmed once the molecular structure of II was determined by the single-crystal X-ray diffraction studies (above).

Copper(I) Complexes. The products of the reaction between bpnp and cuprous halides were red-brown solids that were slightly soluble in polar organic solvents such as Me_2SO and DMF. The product with cuprous chloride gave the correct elemental composition for a dicopper(I) species (eq 2). The

$$2CuCl + bpnp \rightarrow Cu_2(bpnp)Cl_2 \qquad (2)$$

reaction between copper(I) and bpnp was also examined with use of tetrakis(acetonitrile)copper(I) perchlorate solutions. In methylene chloride, acetone, and methanol, an absorption band at ~530 nm characteristic of dicopper(I) bpnp complexes was observed upon mixing the colorless copper(I) and pale yellow bpnp solutions. In all three solvents, the 2:1 molar ratio of copper(I) to bpnp gave maximum absorbance (Job plots). One to one ratios gave a broader band of lower absorbance, suggesting a distribution of products, perhaps both 2:1 and 1:1 Cu(I):bpnp species.

Solutions of the dicopper(I) bpnp species in methanol or methylene chloride–acetonitrile (1:1 v/v) underwent bleaching of the visible absorption band at 535 nm (up to 95%) when

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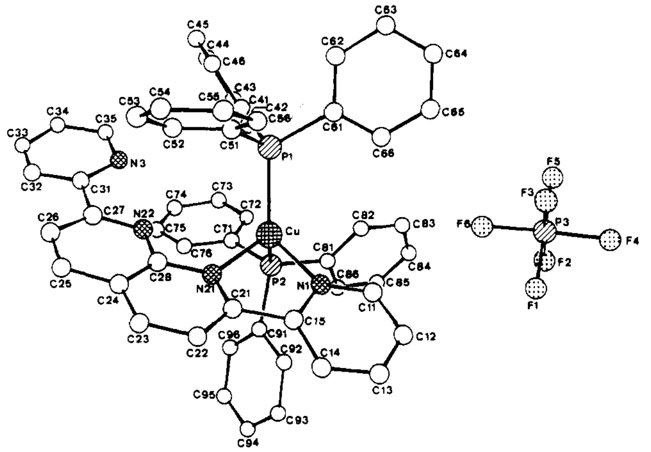

Figure 3. Perspective view and atom-numbering scheme for [Cu(bpnp)$(Ph_3P)_2$]PF_6 (IV).

stirred under an atmosphere of CO. The absorption was restored by purging with argon. Acetone solutions of the $Cu_2(bpnp)I_2$ complex were bleached only ~50% at 1 atm of CO at ambient conditions but were completely bleached at dry-ice–acetone temperatures. The infrared spectrum of the 1:1 methylene chloride/acetonitrile solutions showed an absorption at 2090 cm^{-1} under a CO atmosphere that was not present under argon. This result compares well with the value of 2070 cm^{-1} noted by Floriani[27] for a Cu(I) carbonyl complex and indicates the formation of a terminal CO adduct in the present case. Attempts to isolate these CO adducts by removing the solvent, cooling the solution, and adding other counterions were unsuccessful.

The reaction of $Cu_2(bpnp)I_2$ with silver hexafluorophosphate in dry oxygen-free acetonitrile followed by addition of triphenylphosphine (4 equiv/mol of complex) gave the mononuclear complex [Cu(bpnp)$(P(C_6H_5)_3)_2$]PF_6 (IV), which was isolated as orange needles. The structure of IV was determined by X-ray diffraction analysis (Figure 3). The unit cell consists of four discrete Cu(bpnp)$(P(C_6H_5)_3)_2^+$ cations and four PF_6^- anions. There are no intermolecular contacts suggesting cluster formation. Table VI gives key bond angles and key bond lengths for IV. The coordination about the copper ion is a distorted tetrahedron formed by the two phosphorus atoms and the two nitrogens from a bipyridyl fragment of coordinated bpnp. The copper–phosphorus distances are equal within standard deviations (Table VI), but the copper–nitrogen distances are not. The copper–naphthyridine nitrogen distance at 2.102 (4) Å is 0.023 Å shorter than the copper–pyridyl nitrogen distance of 2.125 (4) Å. The other two nitrogens of the bpnp are not bonded to the copper ion; the Cu–N(22) distance is 3.236 Å. The angle 84° between the planes defined by Cu–P(1)–P(2) and Cu–N(1)–N(21) is slightly twisted from the interplanar angle expected for a tetrahedron (90°). The small N(1)–Cu–N(21) angle reflects the fixed bite of the bipyridyl moiety while the bulk of the phosphine ligands[28] is evident in the large P–Cu–P angle of 128°, nearly 20° larger than in an ideal tetrahedron. The N–Cu–P angles are near the tetrahedral value; the average is 110 ± 4°.

The bpnp ligand is not planar in IV; the individual np and pyridyl residues are planar, but substantial angles are subtended by the separate planes. The planes defined by the np and bonded pyridyl fragments meet at a 15.97° angle, which is larger than any reported for the twisting of the pyridine fragments of coordinated bipyridine. The range for this twist in copper bipyridine complexes is 0.5–12°.[29] In fact, the Cu–N(21)–N(1) plane is not coplanar with either the bonded pyridyl plane or the naphthyridine plane; the angles are 8.74 and 11.53°, respectively. The nonbonded pyridyl ring is tilted with respect to the naphthyridine plane by 8.85°. This may be a minimization of the interactions of the backbone hydrogens on the naphthyridine and pyridyl moieties or a result of packing forces.

Summary

The above studies extend the types of metal complexes that the polydentate crescent ligand, 2,7-bis(2-pyridyl)-1,8-naphthyridine (bpnp) forms. For both copper(I) and copper(II), it is clear that bpnp promotes the formation of dinuclear complexes. In contrast to the examples of dirhodium(II)[6] and diruthenium(II)[30] bpnp complexes characterized structurally in these laboratories, the dicopper(II) bpnp complex displays little evidence of metal–metal bonding and the Cu(II)–Cu(II) distance of 3.02 Å is substantially greater than the distance between the peri nitrogen atoms of the central naphthyridine moiety. For the mononuclear Cu(I) complex, bpnp serves as a bidentate ligand binding through one of the bipyridine-like fragments. A similar bonding mode was found for the previously reported mononuclear rhenium(I) bpnp complex[7] and presumably reflects a minimization of steric interactions between the bpnp and other coordinated ligands.

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Registry No. I, 92220-38-7; II, 92220-39-8; IV, 92220-42-3; $Cu_2(bpnp)Cl_2$, 92220-40-1; $Cu_2(bpnp)I_2$, 92220-43-4.

Supplementary Material Available: Figure 4 (stereoview of $Cu_2(bpnp)(OH)Cl_3$), Tables VII and VIII (thermal parameters for non-hydrogen atoms), and Tables IX and X (observed and calculated structure factors) (32 pages). Ordering information is given on any current masthead page.

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