Monoprotic Tetradentate N_3O-Donor Ligands and Their Cu(II) and Ni(II) Complexes

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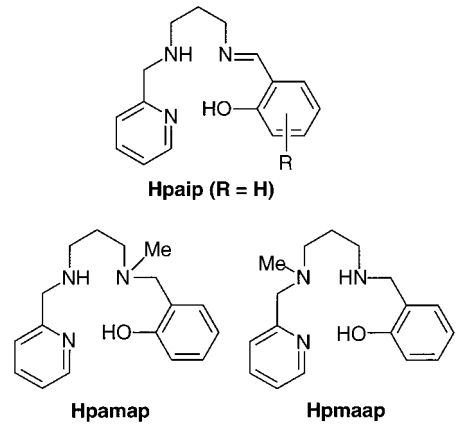
A convenient four-step procedure was developed to prepare the novel monoprotic tetradentate ligands *N*-(2-hydroxy)benzyl-*N*-methyl-*N*′-(2-pyridyl)methyl-1,3-propanediamine (Hpamap) and *N*-(2-hydroxy)benzyl-*N*′-methyl-*N*′-(2-pyridyl)methyl-1,3-propanediamine (Hpmaap), which provide an N_3O metal coordination sphere. A mononuclear copper(II) complex, [Cu(pamap)Cl] (**A**), was obtained by reaction of Hpamap with $CuCl_2 \cdot 2H_2O$. The binuclear copper(II) complexes $[Cu(pamap)]_2(BF_4)_2$ (**B**) and $[Cu(pmaap)]_2(BF_4)_2$ (**C**) were obtained when these ligands were reacted with Cu(II) in the presence of the noncoordinating BF_4^- anion. Reaction of nickel(II) with the Hpamap ligand generated the binuclear Ni(II) complex $[Ni_2(pamap)_2(NO_3)]NO_3$ (**D**). The crystal of **A** ($C_{17}H_{22}ClCuN_3O$) is orthorhombic *Pbca* (No. 61), $a = 11.837(4)$ Å, $b = 15.648(5)$ Å, $c = 11.002(11)$ Å, $Z = 8$; that of **B** ($C_{34}H_{44}B_2Cu_2F_8N_6O_2$) is triclinic $P\bar{1}$ (No. 2), $a = 9.147(0)$ Å, $b = 10.375(0)$ Å, $c = 10.535(1)$ Å, $\alpha = 107.20(0)°$, $\beta = 91.19(0)°$, $\gamma = 105.05(0)°$, $Z = 1$; that of **C** ($C_{34}H_{44}B_2Cu_2F_8N_6O_2$) is monoclinic $P2_1/c$ (No. 14), $a = 9.158(2)$ Å, $b = 10.714(2)$ Å, $c = 19.085(4)$ Å, $\beta = 90.58(2)°$, $Z = 4$; and that of **D** ($C_{34}H_{44}N_8NiO_8$) is monoclinic $C2/c$ (No. 15), $a = 13.849(0)$ Å, $b = 13.609(0)$ Å, $c = 19.558(1)$ Å, $\beta = 92.34\ (0)°$, $Z = 4$. The copper atoms of all three complexes are five-coordinate in the solid state, assuming the geometry of a distorted square pyramid with the deprotonated tetradentate ligand in the basal plane. The mononuclear complex **A** has a chloride ligand in the axial position, while each copper center in the binuclear complexes **B** and **C** has, in the axial position, a bridging phenolate O donor from the other unit of the dimer. Each nickel center in the binuclear complex **D** is six-coordinate, with the pseudo-octahedron formed by a deprotonated tetradentate ligand, a bridging nitrato oxygen atom, and a bridging phenoxy donor from the tetradentate ligand bound to the second nickel center.

Introduction

Monocationic, lipophilic copper radiopharmaceuticals are of interest for possible use in diagnostic imaging of the heart[1,2] and tumors.[3−8] Efforts to develop such agents have focused on copper(II) complexes with tetradentate bis(oxime) (N_4) ligands,[9,10] copper(I) complexes with chelating diphosphine ligands,[11] and our work with copper(II) complexes of monoprotic tetradentate ligands such as Hpaip (Chart 1).[12−14] The N_3O donor set of Hpaip provides a possible square-planar coordination sphere for Cu(II). In the solid state, a square-pyramidal Cu(II)-paip complex is formed with the tetradentate ligand in the basal plane and an elongated axial Cu−Cl bond;[12] however, in aqueous solution, the complex behaves as a cationic species.[13]

Chart 1



Extending these previous studies, we report here an easy route to new monoprotic N_3O ligands, Hpamap and Hpmaap, each of which contains one phenolate O, one pyridyl N, and two amine N donor atoms (Chart 1). While the general unsymmetric monoprotic structure of Hpaip is retained, these ligands differ by the absence of the salicylaldimine C═N double bond and

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by the presence of a methyl group on one of the amine N atoms. We also report investigation of the Cu(II) and Ni(II) coordination chemistry of these ligands.

Experimental Section

General Methods. All chemicals were reagent grade and were used as received. ^{1}H NMR spectra were recorded on 300 MHz Bruker ARX-300 or 500 MHz Varian XL 500 (^{1}H−^{1}H COSY, ^{1}H−^{13}C HETCOR, ^{1}H−^{1}H NOESY) spectrometers, with chemical shifts referenced to the protic impurity of the deuterated solvent. ^{13}C{^{1}H} NMR spectra (75.48 or 125.71 MHz) were recorded on Bruker ARX-300 or Varian XL 500 spectrometers with δ referenced to the corresponding solvent. Mass spectra were recorded with Kratos MS50 (FABMS), Bioion 20R (EI/CIMS), or Finnigan MAT LCQ (PDMS) mass spectrometers (with positive-ion detection). Infrared spectra were recorded with a Perkin-Elmer 1600 FTIR spectrophotometer. Elemental analyses were performed in the Microanalytical Service Lab in the Department of Chemistry, Purdue University.

1-Methyl-2-(2-pyridyl)hexahydropyrimidine (2). To 2-pyridinecarboxaldehyde (Aldrich Chemical Co., Milwaukee, WI) (10.71 g, 100 mmol) in a round-bottom flask in an ice bath was added *N*-methyl-1,3-propanediamine (**1**, Aldrich) (9.12 g, 100 mmol) in MeOH (13 mL). The mixture was stirred overnight and then concentrated at reduced pressure. The remaining volatiles were removed in vacuo overnight. No further purification was performed on the resultant brownish red liquid. The yield of the product was 17.86 g (99%). Anal. Calcd (found) for $C_{10}H_{15}N_3 \cdot 0.1H_2O$: C 67.08 (66.94); H 8.56 (8.47); N 23.47 (23.61). CIMS: m/e = 178 (M + 1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.58 (d, 1H, *m-H* on py), 7.64 (td, 1H, *m′-H* on py), 7.33 (d, 1H, *o′-H* on py), 7.19 (dd, 1H, *p-H* on py), 3.85 (s, 1H, C*H*py), 3.18 (dm, 1H, side-backbone CHH_e), 3.13 (dm, 1H side-backbone CHH_e), 2.76 (td, 1H, side-backbone CH_aH), 2.40 (broad s, 1H, N-*H*), 2.38 (td, 1H, side-backbone CH_aH), 2.00−1.86 (m, 5H, overlapped Me-*H* and central CHH_e), 1.61 (m, 1H, central CH_aH). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.708 MHz) δ: 159.8 (tertiary *C* on py) 150.0 (*m-C* on py), 136.5 (*m′-C* on py), 123.0 (*o′-C* on py), 122.6 (*p-C* on py); 83.2 (*C*Hpy), 56.0 (*C*H_2−N), 45.1 (*C*H_2−N), 42.3 (Me-*C*), 27.3 (central-backbone *C*H_2). IR (cm^{-1}, NaCl window): 3270 (m, ν_{NH}), 3065 (w, aromatic ν_{CH}), 3000−2690 (s, ν_{CH}, methyl and methylene groups).

***N*-Methyl-*N′*-(2-pyridyl)methyl-1,3-propanediamine (3).** 1-Methyl-2-(2-pyridyl)hexahydropyrimidine (**2**, 4.18 g, 24 mmol) was dissolved in MeOH (100 mL). To this solution was added $NaBH_4$ (5.0 g, 130 mmol) in small portions. The mixture was stirred for 4 h, and then the volatiles were removed at reduced pressure. The residue was treated with 10% NH_4OAc aqueous solution (100 mL), and then the resultant aqueous phase was extracted with $CHCl_3$ (2 × 100 mL). The organic phase was washed with H_2O (100 mL), dried over $MgSO_4$, and then condensed to a pale liquid. The identity of the product was verified by MS and ^{1}H NMR. CIMS: m/e = 180 (M + 1). EIMS: m/e = 135 (pyCH$_2$NH═CHCH$_3^+$), 121 (pyCH$_2$NH═CH$_2^+$), 93 (pyCH$_2$ + 1), 58 (MeNH═CHCH$_3^+$), 44 (MeNH═CH$_2^+$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.52 (d, 1H, *m-H* on py), 7.58 (t, 1H, *m′-H* on py), 7.22 (d, 1H, *o′-H* on py), 7.08 (dd, 1H, *p*−*H* on py), 3.85 (s, 2H, NCH_2-py), 2.70 (t, 1H, HNCH_2), 2.65 (t, 2H, CH$_3$NCH_2), 2.40 (s, 3H, NCH_3), 2.05 (broad s, 2H, N*H*s), 1.70 (q, 2H, central CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.476 MHz) δ: 159.0 (tertiary *C* on py), 149.2 (*m-C* on py), 136.6 (*m′-C* on py), 122.4 (*o′-C* on py), 122.0 (*p-C* on py), 54.5 (*C*H_2-N), 50.4 (*C*H_2-N), 47.9 (Me-*C*), 35.1 (*C*H_2py), 28.1 (central-backbone *C*H_2).

1-Methyl-2-(2-hydroxy)phenyl-3-(2-pyridyl)methylhexahydropyrimidine (4). All the crude product (**3**, ∼24 mmol) in the previous step was mixed with salicylaldehyde (3.15 g, 25.3 mmol) in MeOH (15 mL), and the mixture was stirred overnight. The volatiles were removed by rotary evaporation, and the resulting dense oil was dried at 60 °C in vacuo. The identity of the product was verified by MS and ^{1}H NMR. CIMS: m/e = 284 (M+1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.40 (d, 1H, *m-H* on py), 7.54 (t, 1H, *m′-H* on py), 7.35 (d, 1H, *o′-H* on py), 7.14 (t, 1H), 7.05 (m, 2H), 6.84 (d, 1H), 6.75 (t, 1H), 3.85 (d, $^2J_{H-H}$ = 14.0, 1H, NCHH_e-py), 3.54 (s, 1H, NC*H*-PhOH), 3.22 (d, $^2J_{H-H}$ = 14.0, 1H, NCH_aH-py), 3.08 (d, 1H, pyCH$_2$NCHH_e), 2.94 (d, 1H, pyCH$_2$NCH_aH), 2.23 (m, 2H, CH$_3$NCH$_2$), 1.95 (m, 1H, central CHH_e), 1.57 (m, 1H, central CH_aH).

***N*-(2-Hydroxy)benzyl-*N*-methyl-*N′*-(2-pyridyl)methyl-1,3-propanediamine (Hpamap) (5).** To the crude product **4** (∼24 mmol) in MeOH (200 mL) was added $NaBH_4$ (3.0 g, 79 mmol) in small portions. The mixture was stirred overnight and then evaporated to near dryness at low pressure. The residue was treated with 10% NH_4OAc (50 mL) and then extracted with $CHCl_3$ (2 × 60 mL). The organic phase was washed with H_2O (50 mL), dried over $MgSO_4$, and then concentrated to a green-yellow liquid, yield 5.06 g (76% based on **2**; overall yield: 75.5%). Anal. Calcd (found) for $C_{17}H_{23}N_3O$: C 71.55 (71.60); H 8.12 (8.05); N 14.72 (14.38). CIMS: m/e = 286 (M + 1); EIMS: m/e = 150 [(M − pyCH$_2$NH═CHCH$_3$)$^+$], 135 (pyCH$_2$NH═CHCH$_3^+$), 121 (pyCH$_2$NH═CH$_2^+$), 107 (C$_7$H$_6$O + 1), 93 (pyCH$_2$ + 1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.51 (d, 1H, *m-H* on py), 7.60 (t, 1H), 7.28 (d, 1H), 7.12 (m, 2H), 6.91 (d, 2H), 6.74 (m, 2H), 3.90 (s, 2H, NCH_2-py), 3.64 (s, 2H, NCH_2−PhOH), 2.70 (t, 2H, pyCH$_2$NCH_2), 2.56 (t, 2H, CH$_3$NCH_2), 1.80 (p, 2H, central CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.476 MHz) δ: 159.7 (tertiary *C* on py), 158.0 (tertiary *C* on PhOH), 149.2 (*m-C* on py), 136.4 (*m′-C* on py), 128.6 (*C* on PhOH), 128.3 (*C* on PhOH), 122.2 (*o′-C* on py), 121.9 (*C* on PhOH), 118.9 (*C* on PhOH), 116.0 (*C* on PhOH), 61.5 (*C*H$_2$PhOH), 55.2 (backbone *C*H$_2$-N), 54.9 (backbone *C*H$_2$-N), 47.3 (*C*H$_2$py), 41.2 (Me-*C*), 27.5 (central-backbone *C*H$_2$). IR (cm^{-1}, NaCl window): 3080 (w, aromatic ν_{CH}), 3000−2800 (m, ν_{CH}, methyl and methylene groups).

***N*-(2-Hydroxy)benzyl-*N′*-methyl-1,3-propanediamine (7).** To salicylaldehyde (6.24 g, 51.1 mmol) in a round-bottom flask in an ice bath was added **1** (4.56 g, 51.7 mmol) in MeOH (15 mL). The solution was stirred for 2 days and then was diluted with MeOH (300 mL). To this yellow solution was added $NaBH_4$ (3.0 g, 78 mmol) in small portions. The mixture was stirred for another 3 h, and then the volatiles were removed at low pressure. The residue was treated with 10% NH_4OAc aqueous solution (100 mL), and then the resultant aqueous phase was extracted with $CHCl_3$ (2 × 100 mL). The organic phase was washed with H_2O (100 mL), dried over $MgSO_4$, and then condensed to a golden liquid, which was dried in vacuo overnight. The yield of the product was 9.42 g (95%). Anal. Calcd (found) for $C_{11}H_{18}N_2O$: C 68.01 (68.16); H 9.34 (9.62); N 14.42 (14.13). CIMS: m/e = 195 (M + 1). EIMS: m/e = 136 (M − CH$_3$NH═CHCH$_3$) 122 (M − CH$_3$NH═CH$_2$), 107 (C$_7$H$_6$O + 1), 87 (M − C$_7$H$_7$O). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.14 (dt, 1H), 6.96 (d, 1H), 6.82 (d, 1H), 6.74 (dt, 1H), 4.20 (broad s, 3H, O*H* and N*H*s), 3.95 (s, 2H, NCH_2−PhOH), 2.74 (t, 1H, HNCH_2), 2.68 (t, 2H, CH$_3$NCH_2), 2.42 (s, 3H, NCH_3), 1.73 (q, 2H, central CH_2). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.476 MHz) δ: 158.3, 128.3, 122.7, 118.8, 116.2, 52.6, 50.2, 47.2, 35.5, 29.4.

1-Methyl-2-(2-hydroxy)phenyl-3-(2-pyridyl)methylhexahydropyrimidine (8). To **7** (6.01, 30.9 mmol) in MeOH (10 mL) was added 2-pyridinecarboxaldehyde (3.33 g, 31.1 mmol) in MeOH (10 mL), and the mixture was stirred for 3 h. The volatiles were removed by rotary evaporation, and the resulting solid was redissolved in MeOH (5 mL) and kept at −4 °C. A white solid was filtered out, washed with cold MeOH, and dried in vacuo. The yield of **8** was 3.73 g (43%). Anal. Calcd (found) for $C_{17}H_{21}N_3O$: C 72.06 (72.15); H 7.47 (7.41); N 14.83 (14.69). CIMS: m/e = 284 (M + 1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.57 (md, 1H, *m-H* on py), 7.72 (dt, 1H, *m′-H* on py), 7.66 (d, 1H, *o′-H* on py), 7.23 (mt, 1H, *p-H* on py), 7.06 (mt, 1H), 6.81 (d, 1H), 6.73 (dd, 1H), 6.66 (dt, 1H), 3.64 (d, $^2J_{H-H}$ = 14.0, 1H, NCHH_e-PhOH), 3.54 (s, 1H, NC*H*-py), 3.16 (m, 1H), 3.12 (d, $^2J_{H-H}$ = 14.0, 1H, NCH_aH-PhOH), 3.09 (m, 1H), 2.30 (d, 1H), 2.12 (m, 2H), 1.95 (s, 3H, CH_3), 1.65 (m, 1H, central CH_aH).

***N*-(2-Hydroxybenzyl)-*N′*-methyl-*N′*-(2-pyridyl)methyl-1,3-propanediamine (Hpmaap) (9).** To **8** (3.43, 12.1 mmol) in EtOH (180 mL) was added $NaBH_4$ (2.2 g, 58 mmol) in small portions. The mixture was refluxed overnight and then evaporated to near dryness at low pressure. The residue was treated with 10% NH_4OAc (100 mL) and then extracted with $CHCl_3$ (2 × 100 mL). The organic phase was washed with H_2O (100 mL), dried over $MgSO_4$, and then concentrated to a brown-red liquid, yielding 3.40 g of crude product. The crude **9** contained unreduced **8** as verified by MS and ^{1}H NMR. CIMS: m/e = 286 (M + 1, compound **9**, 100), 284 (M + 1, compound **8**, 5). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.51 (d, 1H, *m-H* on py), 7.60 (t, 1H),

Table 1. Crystallographic Experimental Details for [Cu(pamap)Cl] (**A**), $[Cu(pamap)]_2(BF_4)_2$ (**B**), $[Cu(pmaap)]_2(BF_4)_2$ (**C**), and $[Ni_2(pamap)_2(NO_3)]NO_3$ (**D**)

compound	**A**	**B**	**C**	**D**
formula	$C_{17}H_{22}ClCuN_3O$	$C_{34}H_{44}B_2Cu_2F_8N_6O_2$	$C_{34}H_{44}B_2Cu_2F_8N_6O_2$	$C_{34}H_{44}N_8Ni_2O_8$
formula wt	383.38	869.46	869.46	810.19
space group	*Pbca* (No. 61)	*P*$\bar{1}$ (No.2)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a, Å	11.738(3)	9.1471(4)	9.158(2)	13.8490(4)
b, Å	14.503(4)	10.3753(3)	10.741(2)	13.6093(4)
c, Å	19.731(4)	10.5352(5)	19.085(4)	19.5583(5)
α	90	107.200(3)	90	90
β	90	91.193(2)	90.582 (15)	92.336 (2)
γ	90	105.052(3)	90	90
V, Å^3	3358(2)	917.17(14)	1872.4(12)	3683.2(3)
Z	8	1	4	4
d_{calc}, g cm^{-3}	1.516	1.574	1.542	1.46
dimensions, mm	0.25 × 0.17 × 0.16	0.25 × 0.15 × 0.08	0.25 × 0.22 × 0.18	0.25 × 0.25 × 0.23
temperature, K	203	296	296	296
radiation (wavelength)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
diffractometer[a]	Enraf-Nonius CAD4	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD
h, *k*, *l* range	0−12, 0−15, −21−0	0−11, −14−12, −14−13	0−11, 0−13, −23−23	−18−18, −19−16, −25−25
2*θ* range, deg	5.08−45.34	8.94−60.78	8.00−52.71	7.43−60.94
F_{000}	1592.0	446.0	892.0	1688.0
data collected	2553	9644	7878	16240
unique data	2228	4613	3659	4870
data with $I > 2.0\sigma(I)$	1688	3306	1949	3886
number of variables	209	249	249	248
$R(F_o)$*	0.086	0.074	0.080	0.054
$R_w(F_o)$*	0.278	0.208	0.209	0.154
goodness of fit	1.183	1.040	1.012	1.093

[a] $R = \sum|F_o - F_c|/\sum F_o$, and $R_w = \mathrm{SQRT}(\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)$. The weight *w* is defined as $1/[\sigma^2(F_o^2) + (0.2000P)^2 + 0.0000P]$, $1/[\sigma^2(F_o^2) + (0.1479P)^2 + 0.5925P]$, $1/[\sigma^2(F_o^2) + (0.1337P)^2 + 0.0000P]$, or as $1/[\sigma^2(F_o^2) + (0.0673P)^2 + 8.5861P]$ for **A**, **B**, **C**, and **D**, respectively, where $P = (F_o^2 + 2F_c^2)/3$.

7.28 (d, 1H), 7.12 (m, 2H), 6.91 (d, 2H), 6.74 (m, 2H), 3.90 (s, 2H, NC*H*$_2$-py), 3.64 (s, 2H, NC*H*$_2$−PhOH), 2.70 (t, 2H, pyCH$_2$NC*H*$_2$), 2.56 (t, 2H, CH$_3$NC*H*$_2$), 1.80 (p, 2H, central C*H*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.476 MHz) *δ*: 159.7 (tertiary *C* on py), 158.0 (tertiary *C* on PhOH), 149.2 (*m*-*C* on py), 136.4 (*m*′-*C* on py), 128.6 (*C* on PhOH), 128.3 (*C* on PhOH), 122.2 (*o*′-*C* on py), 121.9 (*C* on PhOH), 118.9 (*C* on PhOH), 116.0 (*C* on PhOH), 61.5 (*C*H$_2$PhOH), 55.2 (backbone *C*H$_2$−N), 54.9 (backbone *C*H$_2$−N), 47.3 (*C*H$_2$py), 41.2 (Me-*C*), 27.5 (central-backbone *C*H$_2$).

[Cu(pamap)Cl]. To a solution of $CuCl_2 \cdot H_2O$ (0.58 g, 3.80 mmol) in 50 mL of EtOH was added Hpamap (1.00 g, 3.50 mmol) in 30 mL of EtOH. The resultant green solution was stirred and refluxed for 22 h, during which time a green precipitate was formed. The product was collected by hot filtration and dried in vacuo. No attempt was made to maximize the yield by working up the green mother liquor. The yield was 0.301 g (22.5% based on Hpamap). The product is soluble in MeOH, EtOH, and H_2O, moderately soluble in hot $CHCl_3$ and CH_2Cl_2, but insoluble in Et_2O. Anal. Calcd (Found) for $C_{17}H_{22}N_3ClCuO$: C 53.26 (53.41); H 5.78 (5.74); N 10.96 (10.98); Cl 9.25 (9.48). FABMS: $m/z = 347$ ($[Cu(pamap)]^+$). IR (cm^{-1}, KBr disk): 3110 (s, aromatic ν_{CH}), 2955−2840 (m, ν_{CH}, methyl and methylene groups).

[Cu(pamap)]$_2$(BF$_4$)$_2$. $Cu(BF_4)_2 \cdot 6H_2O$ (0.220 g, 0.637 mmol) was dissolved in a mixture of Me_2CO (20 mL) and MeOH (20 mL). This solution was filtered and added to a solution of Hpamap (0.282 g, 0.988 mmol) in 15 mL of Me_2CO. The resultant dark green solution was slowly evaporated to yield green crystals in ∼9 days. The product was collected by filtration and dried in vacuo. The yield was 0.222 g (80% based on $Cu(BF_4)_2 \cdot 6H_2O$). The product is soluble in MeOH, EtOH, $MeCO_2$, and H_2O but insoluble in Et_2O. Anal. Calcd (found) for $C_{34}H_{44}N_6Cu_2O_2B_2F_8$: C 46.97 (46.89); H 5.10 (5.11); N 9.67 (9.54). PDMS: $m/z = 347$ ($[Cu(pamap)]^+$). IR (cm^{-1}, KBr disk): 3110−3030 (w, aromatic ν_{CH}), 2980−2840 (m, ν_{CH}, methyl and methylene groups).

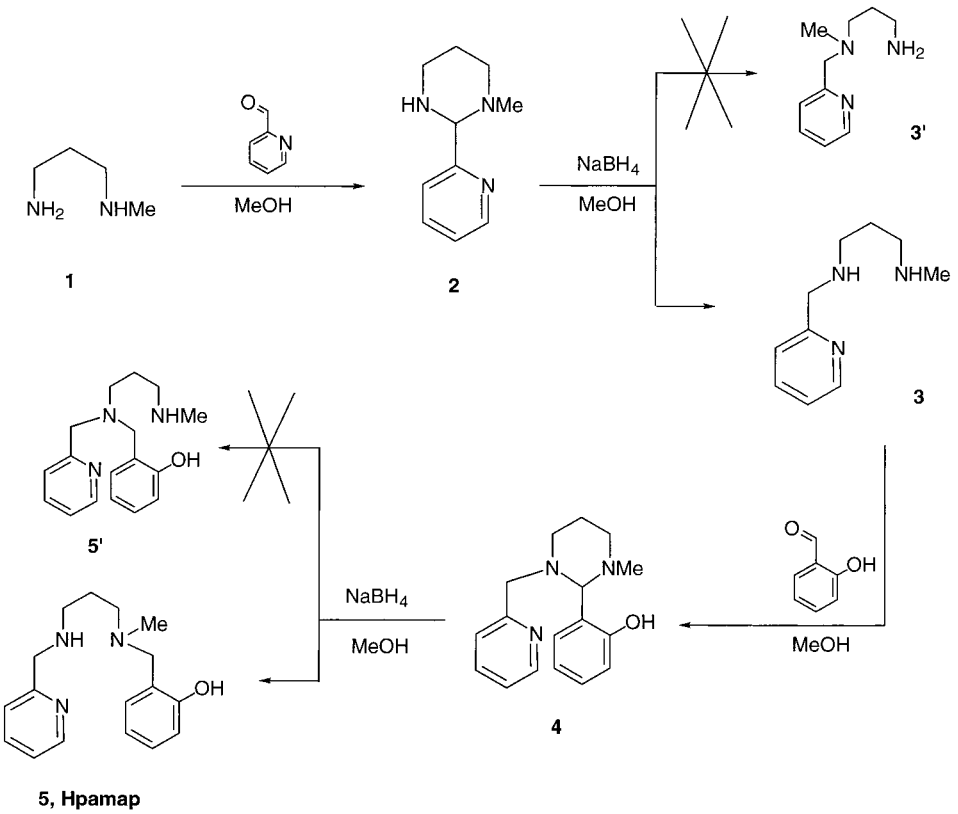
[Cu(pmaap)]$_2$(BF$_4$)$_2$. $Cu(BF_4)_2 \cdot 6H_2O$ (0.127 g, 0.368 mmol) was dissolved in a mixture of Me_2CO (10 mL) and MeOH (10 mL). This solution was filtered and added to a solution of crude Hpmaap (0.170 g) in 15 mL of Me_2CO. The resultant dark green solution was slowly evaporated to yield green crystals in ∼5 days. The product was collected by filtration, washed with minimum Me_2CO, and dried in vacuo. The yield was 0.068 g (43% based on $Cu(BF_4)_2 \cdot 6H_2O$). The product is soluble in MeOH, EtOH, Me_2CO, and H_2O but insoluble in Et_2O. Anal. Calcd (found) for $C_{34}H_{44}N_6Cu_2O_2B_2F_8$: C 46.97 (47.07); H 5.10 (5.08); N 9.67 (9.61). PDMS: $m/z = 347$ ($[Cu(pmaap)]^+$). IR (cm^{-1}, KBr disk): 3110−3000 (w, aromatic ν_{CH}), 2950−2840 (m, ν_{CH}, methyl and methylene groups).

[Ni$_2$(pamap)$_2$(NO$_3$)]NO$_3$·2.3H$_2$O. To a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.29 g, 1.0 mmol) in EtOH (20 mL) was added Hpamap (0.32 g, 1.1 mmol) in EtOH (10 mL). The resultant green solution was stirred and refluxed for 3 h, during which time a pale purple precipitate was formed. The product was collected by hot filtration, washed with Et_2O, and dried in vacuo. No attempt was made to maximize the yield by working up the blue-green mother liquor. The yield was 32.5 mg (7.6% based on Ni). The product is soluble in MeOH but insoluble in Et_2O. Anal. Calcd (found) for $C_{34}H_{48.6}N_8O_{10.3}Ni_2$: C 47.95 (48.19); H 5.75 (5.74); N 13.16 (12.83). PDMS: $m/z = 342$ ($[Ni(pamap)]^+$). IR (cm^{-1}, KBr disk): 3090−3000 (w, aromatic ν_{CH}), 2980−2840 (m, ν_{CH}, methyl and methylene groups).

X-ray Crystallographic Analyses of [Cu(pamap)Cl] (A), [Cu(pamap)]$_2$(BF$_4$)$_2$ (B), [Cu(pmaap)]$_2$(BF$_4$)$_2$ (C), and [Ni$_2$(pamap)$_2$(NO$_3$)]NO$_3$ (D). Single green crystals of [Cu(pamap)Cl] (**A**) and $[Ni_2(pamap)_2(NO_3)]NO_3$ (**D**) were obtained by slow evaporation of the solution of the corresponding sample in MeOH, while those of $[Cu(pamap)]_2(BF_4)_2$ (**B**) and $[Cu(pmaap)]_2(BF_4)_2$ (**C**) were grown similarly from MeOH/Me_2CO mixtures.

A single crystal (of **A**, **B**, **C**, or **D**) was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation ($\lambda = 0.710\ 73$ Å) on an Enraf-Nonius CAD4 (**A**) or a Nonius Kappa CCD diffractometer (**B**−**D**). The cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25, 9644, 7878, or 16240 reflections for **A**, **B**, **C**, and **D**, respectively, in the ranges specified in Table 1. For **A**, data were collected at 203 ± 1 K using variable-speed $\omega - 2\theta$ scans with the scan rate varying from 1° to 16° per minute and a maximum 2*θ* of 45.3°. A total of 2553 reflections were collected, of which 2228 were unique. For **B**−**D**, data were collected at 296 ± 1 K using variable-speed $\omega - 2\theta$ scans with a maximum 2*θ* of 60.8, 52.7, or 60.9°, respectively. A total of 9644, 7878, or 16240 reflections were collected, of which 4613, 3659, or 4870 were unique for **B**, **C**, and **D**, respectively. Lorentz and polarization corrections were applied to the data in all cases. An empirical absorption correction based on the method of Walker and

Scheme 1



Stuart (**A** and **D**),[15] or using SCALPACK (**B** and **C**),[16] was also applied. Transmission coefficients ranged from 0.568 to 0.802 with an average value of 0.748 for **A**. Transmission coefficients ranged from 0.651 to 0.905 (average 0.838), 0.611 to 0.803 (average 0.760), and 0.638 to 0.779 (average 0.741) for **B**, **C**, and **D**, respectively.

The space groups of complexes **A**−**D** were determined by the program ABSEN.[17] The structures were solved using the structure solution programs PATTY in DIRDIF92[18] for **A**−**C** and using SIR97[19] for **D**. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in refinement but restrained to ride in full-matrix least-squares planes, where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$. Scattering factors were taken from the *International Tables for Crystallography*.[20] Only reflections with intensities greater than 2.0 times their standard deviations were used in calculating R in all cases. The final refinement cycle included 209, 249, 249, and 248 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.086$, 0.074, 0.080, and 0.054, and $R_w = 0.278$, 0.208, 0.209, and 0.154, for **A**, **B**, **C**, and **D**, respectively. The standard deviation of an observation of unit weight was 1.18, 1.04, 1.01 and 1.09, respectively. The highest peak in the final difference Fourier map had a height of 1.26, 1.23, 0.61, and 1.09 e/A^3 for **A**, **B**, **C**, and **D**, respectively. Refinement was performed on an AlphaServer 2100 using SHELX-97 in each case.[21]

Results and Discussion

Ligand Synthesis and Characterization. Stoichiometric condensation of *N*-methyl-1,3-propanediamine (**1**) with 2-pyridinecarboxaldehyde brought a sole, cyclic compound, 1-methyl-2-(2-pyridyl)hexahydropyrimidine (**2**, Scheme 1), in almost quantitative yield, instead of the possible acyclic imine. This is an example of the known reaction of *N*-alkyl-1,3-propanediamines with aldehydes to give cyclic 1-alkylhexahydropyrimidines when the reactions are carried out at about 0 °C.[22−24] Such hexahydropyrimidines, or the five-membered analogue tetrahydroimidazoles, are believed to be in an equilibrium with their acyclic imine forms,[22] where the C═N bond can be further polymerized,[22] hydrolyzed,[25] or reduced.[22] Reductive hydrogenation of **2** could lead to either **3** or **3′**, both of which would be suitable intermediates for preparation of monoprotic N_3O ligands. In the present case, the cyclic compound **2** was reduced to yield exclusively **3**. The absence of **3′** (vide infra) after reduction indicates that the imine form (**2a**, Scheme 2) is preferred over iminium form (**2b**, Scheme 2) under the reaction conditions, as would be expected.

The resultant **3** was further reacted with salicylaldehyde to yield cyclic compound **4**. Borohydride reduction of **4** afforded *N*-(2-hydroxy)benzyl-*N*-methyl-*N*′-(2-pyridyl)methyl-1,3-propanediamine, a novel tetradentate ligand (**5**, or Hpamap). It has previously been reported that a five-membered imidazolidine ring was similarly reopened upon reduction of its equilibrium tautomer to yield the corresponding amine phenol chelates.[26]

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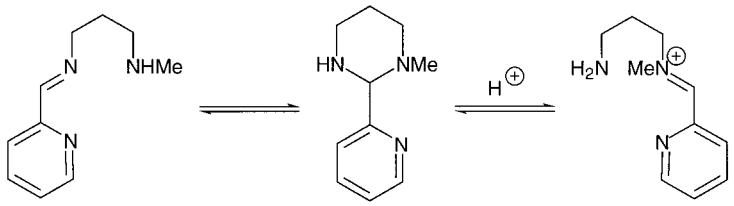
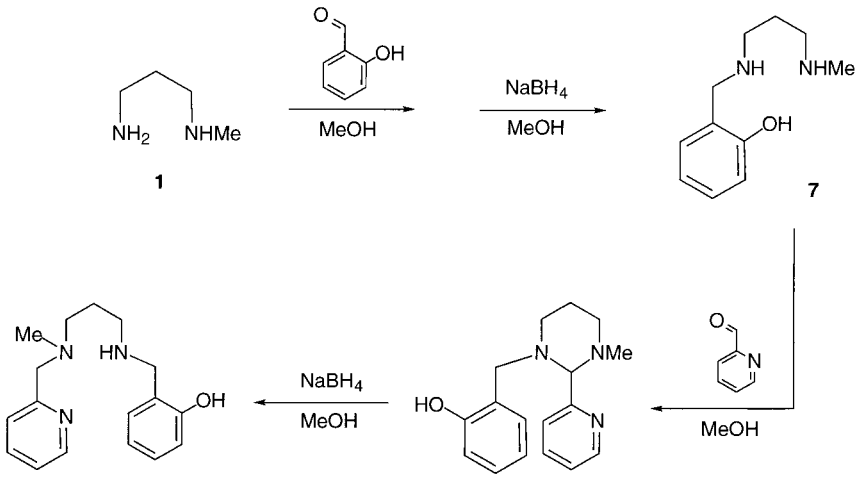
Scheme 2



2 a **2** **2 b**

Scheme 3



1 **7**

9, Hpmaap **8**

Overall, preparation of the unsymmetric, monoprotic, tetradentate (N_3O) ligand Hpamap was conveniently accomplished in moderately good yield (72%). Since in the first and third steps one could instead employ structural derivatives of the *N*-methyl-1,3-propanediamine, 2-pyridinecarboxaldehyde, and salicylaldehyde precursors, this general method appears to be suitable for generation of a diverse set of ligands that maintain the monoprotic, tetradentate (N_3O) metal coordination sphere.

In an examination of the generality of this four-step procedure, a structural analogue of Hpamap, *N*-(2-hydroxy)benzyl-*N*′-methyl-*N*′-(2-pyridyl)methyl-1,3-propanediamine (Hpmaap), was prepared by simply switching the order of addition of the aldehyde reactants (Scheme 3). In this case, the cyclic intermediate **6** was not isolated; instead the reduction was carried out in the same pot, yielding **7** in good yield. Compound **8** was precipitated from cold MeOH. However, the reduction of **8** was not complete with $NaBH_4$. The crude product Hpmaap was used in complexation without purification.

Formation of the cyclic hexahydropyrimidine, 1-methyl-2-(2-pyridyl)hexahydropyrimidine (**2**), was evidenced by the ^1H NMR spectrum, where the aliphatic region presented peaks corresponding to the unique methylene H, the methyl H, NH, as well as the tertiary CH atoms. The absence of imino hydrogen/carbon signals in $^1H/^{13}C$ NMR, and lack of a C═N band around 1595 cm^{-1} in the IR spectrum,[27] of **2** provide further evidence that the compound does not prefer the imine form.

The spectral data ($^1H/^{13}C$ NMR, IR) do not readily distinguish regioisomer **3** (a secondary amine) from **3′** (a primary amine). However, the EIMS fragmentation pattern exhibits the strongest peak at $m/e = 44$ for CH_2═$NHMe^+$, indicating that the intermediate was **3**. (Primary amine **3′** would be expected to give a series of peaks with progressively decreasing intensity at $m/z = 30, 44, 58$.)[28] The product is unambiguously established by the subsequent reaction with salicylaldehyde, which generates the cyclic hexahydropyrimidine, 1-methyl-2-(2-hydroxy)phenyl-3-(2-pyridyl)methylhexahydropyrimidine (**4**), rather than the salicylaldimine that would result from **3′**. The reduction product of **6** to **7** was established in the same manner.

The ^1H NMR spectra of **4** and **8** show resonances corresponding to the unique tertiary CH atom (singlet), the methyl CH_3 (singlet), py-methyl, or benzyl CH_2 (AB quartet), as well as the six nonequivalent multiplets corresponding to six propane backbone H atoms in the aliphatic region. The AB quartet pattern for the py-methyl or benzyl CH_2, as well as the nonequivalence for the two H atoms on each backbone C atom, are consistent with the presence of the six-membered rings in **4** and **8**.

The final Hpamap product, obtained by borohydride reduction of **4**, exhibits 14 resonances in its ^{13}C NMR spectrum and six peaks in the aliphatic region of the ^1H NMR, demonstrating that the product is not a mixture of **5** and **5′**. This product was identified as the linear tetradentate ligand **5**, rather than the possible tripodal tetradentate **5′**, based on the EI mass spectrometry fragmentation pattern. The Hpmaap product from **8** was identified similarly. There was no evidence for the parent losing CH_2═$NHMe^+$, CH_3CH═$NHMe^+$, or CH_3CH_2CH═$NHMe^+$ fragments, which would be expected from **5′** and **8′**. X-ray structures of metal complexes from the two ligands confirm the structural assignments (vide infra).

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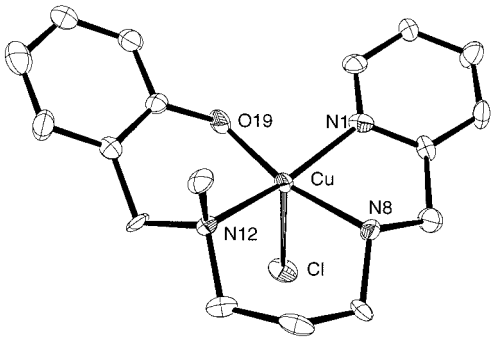

Figure 1. ORTEP drawings of [Cu(pamap)Cl] (**A**); 50% probability thermal ellipsoids are shown.

Cu and Ni Complexes. Green [Cu(pamap)Cl] (**A**) was prepared from $CuCl_2 \cdot 2H_2O$ in a fashion similar to that previously reported [Cu(paip)Cl].[12] Substitution of the noncoordinating BF_4^- anion for Cl^- led to formation of dimeric Cu(II) complexes, $[Cu(pamap)]_2(BF_4)_2$ (**B**) and $[Cu(pmaap)]_2(BF_4)_2$ (**C**), with the monodeprotonated isomeric Hpamap and Hpmaap ligands. Since isostructural complexes of nickel(II) and copper(II) can be formed from the same linear unsymmetric N_3O ligands,[29] the chemistry of Hpamap with Ni(II) was also examined. The Ni(II) reaction was carried out with $Ni(NO_3)_2 \cdot 6H_2O$, yielding a pale purple precipitate of $[Ni_2(pamap)_2(NO_3)]NO_3$ (**D**).

The analytical data for complexes **A**−**D** fit a general formula [ML]A, where A is the counteranion. Mass spectrometric analysis (FABMS or PDMS) showed no evidence for coordination of the inorganic anion following ionization in all cases; instead, the mass spectra all exhibit peaks at $m/z = 347$ or 342 for the $[ML]^+$ fragment (M = Cu or Ni, respectively). The complexes **A**−**D** were all characterized by X-ray crystallography. Data collection details, selected bond distances, and selected angles for these complexes are listed in Tables 1−3.

[Cu(pamap)Cl] (A). The coordination geometry of **A** is a distorted square pyramid with the four donor atoms (N_3O) of the tetradentate ligand in the equatorial plane (Figure 1). This is similar to the structure of [Cu(paip)Cl],[12] where the ligand presents salicyaldimine N and O donor atoms instead of the present aminophenolate N and O donors. The fifth bond in the Cu coordination sphere is formed by a chloro ligand in a slightly tilted apical position. The four donor atoms of the coordinated $pamap^{1-}$ ligand (N1, N8, N12, and O19) are less coplanar than those of the $paip^{1-}$ salicylaldimine analogue, experiencing a trigonal-bipyramidal distortion as shown by their deviations from their least-squares plane: −0.1037(72), 0.0962(72), −0.0864(64), and 0.0939(58) Å, respectively. The Cu(II) center is lifted 0.2686(10) Å above this least-squares plane toward the apical chloride ligand (Figure 1), in comparison to the value of 0.2512(4) Å in [Cu(paip)Cl].[12]

The Cu−Cl bond of **A** was found to be 2.556(2) Å, identical to that in [Cu(paip)Cl] (2.558(3) Å).[12] This Cu−Cl distance is normal for square pyramidal Cu complexes containing monoanionic basal N_3O donor sets derived from bidentate ligands (mean = 2.555 Å).[12] The Cu−O distances of **A** and [Cu(paip)Cl] are also close at 1.919(6) and 1.909(5) Å, respectively. The 2.047(7) Å $Cu-N_{H-amino}$ distance (Cu−N8) in **A** is slightly longer than the corresponding 2.030(6) Å distance in [Cu(paip)Cl], while the $Cu-N_{py}$ distance of **A** is slightly shorter than in [Cu(paip)Cl] (2.021(7) versus 2.057(7) Å). The most significant differences between **A** and [Cu(paip)Cl] occur, as expected, where the two chelates differ by presentation of either methylamine or imine nitrogen donor atoms. In **A**, the $Cu-N_{Me-amino}$ distance is 2.071(7) Å, while in [Cu(paip)Cl] the corresponding bond is an $N_{imino}-Cu$ (1.973(7) Å). This difference can be explained by availability of a favorable back-bonding of electron density from the Cu(II) center into the imine N=C π^* orbital in [Cu(paip)Cl], while this bonding is unavailable in the case of **A**.

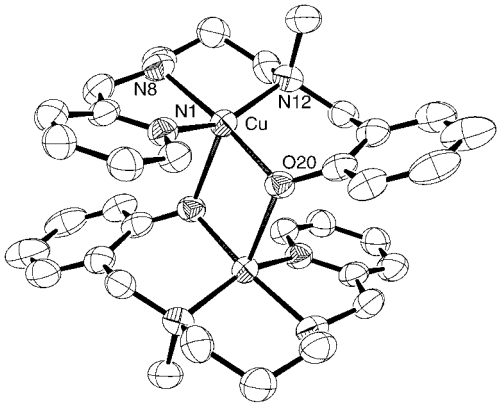

Figure 2. ORTEP drawings of $[Cu(pamap)]_2(BF_4)_2$ (**B**); 50% probability thermal ellipsoids are shown. Anions are omitted.

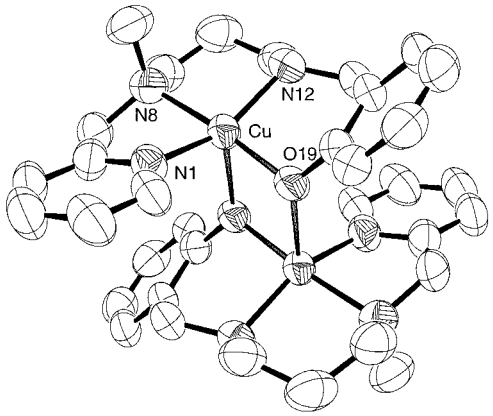

Figure 3. ORTEP drawings of $[Cu(pmaap)]_2(BF_4)_2$ (**C**); 50% probability thermal ellipsoids are shown. Anions are omitted.

The four adjacent bond angles about the Cu center in the basal plane of **A** are similar to those in [Cu(paip)Cl], as expected based on the size of the chelate rings. For the two trans bonds, while the $O_{ph}-Cu-N_{H-amino}$ in **A** remains similar to that in [Cu(paip)Cl], the $N_{Me-amino}-Cu-N_{py}$ angle (N1−Cu−N12, 159.0°) in **A** is smaller than the corresponding $N_{imino}-Cu-N_{py}$ (165.0°) in [Cu(paip)Cl]. The four X−Cu−Cl angles (X = N or O) in **A** ranged from 93.1 to 101.0, slightly narrowed from a range of 91.6 to 102.4 found in [Cu(paip)Cl].

$[Cu(pamap)]_2(BF_4)_2$ (B) and $[Cu(pmaap)]_2(BF_4)_2$ (C). Replacement of chloride with the noncoordinating BF_4^- anion resulted in dinuclear species with the $pamap^{1-}$ and $pmaap^{1-}$ ligands (Figures 2 and 3). These dimeric dications are made up by two $[Cu(II)\text{-}L]^{1+}$ units (L = $pamap^{1-}$ or $pmaap^{1-}$), which are related by an imposed center of symmetry. The two $[CuL]^+$ units are staggered, such that the two Cu centers are bridged by the pair of phenolate O atoms from the two ligands. Thus, each Cu(II) center is five-coordinate, assuming the geometry of a distorted square pyramid. The deprotonated tetradentate chelates lie in the equatorial positions, with the apical sites occupied by a bond to the phenolate O of the tetradentate ligand surrounding the second metal center.

The major distortion from a "regular" square pyramid for **B** or **C** can be viewed as a result of a trigonal-bipyramidal

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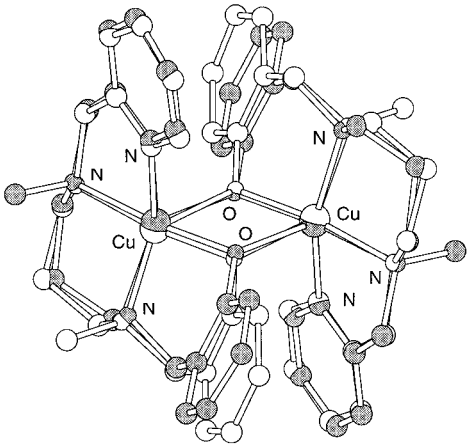
Chart 2. Overlayed Display of $[Cu(pamap)]_2^{2+}$ (○) and $[Cu(pmaap)]_2^{2+}$ (●)



distortion of the square plane of the four chelating donor atoms. The four donor atoms of $pamap^{1-}$ in **B**, or those of $pmaap^{1-}$ in **C**, are even less coplanar than those in [Cu(pamap)Cl], deviating by 0.2833(39) (N1), −0.2691(49) (N8), 0.2465(46) (N12), and −0.2607(36) (O20) Å for **B**, and 0.2407(61) (N1), −0.2339(71) (N8), 0.2165(69) (N12), and −0.2233(45) (O19) for **C**, from their respective least-squares planes. The Cu(II) atoms in **B** and **C** are setting 0.2217(6) and 0.2124(9) Å above their respective ligand N_3O least-squares planes. A similar large trigonal-bipyramidal distortion was reported with a binuclear copper(II) complex of an N_2O_2 bis(aminophenol) (reduced Schiff base) ligand.[30]

The degree of distortion from a square pyramid (SP) to a trigonal bipyramid (TBP) can be quantified on the basis of the dihedral angle between the faces of the polyhedron[31−33] or by calculation of an angular structural parameter from the two largest bond angles about the metal center.[34] Analysis by both methods reveals that all the complexes locate at positions closer to the SP in the TBP−SP spectrum. The extent of trigonal-bipyramidal distortion varies in the order [Cu(paip)Cl] < [Cu(pamap)Cl] (**A**) < $[Cu(pmaap)]_2^{2+}$ (**C**) < $[Cu(pamap)]_2^{2+}$ (**B**). The complex of Schiff base $paip^{1-}$ experiences less distortion than that of the reduced N_3O Schiff base ligands, as the former has less flexibility to adopt a TBP geometry. Dimerization of the CuL^+ units causes further distortion toward a TBP geometry, presumably to offset the steric effects.

As **B** and **C** are the complexes derived from two regioisomeric ligands, a comparative analysis of their structures is of interest (Chart 2). Comparing bond distances, corresponding $Cu-N_{py}$ and $Cu-O_{ph}$ distances are virtually the same in the Cu(II) complexes with the isomeric $pamap^{1-}$ and $pmaap^{1-}$ ligands. Corresponding $Cu-N_{amino}$ distances differ slightly (e.g., Cu−N12 is 2.064(4) Å in **B** versus 2.028(6) Å in **C**); however, it is noted that the $Cu-N_{amino}$ distances in **B** and **C** are almost identical, if amine N donor atoms bearing the same substituent (Me group or H) are compared. This observation indicates that the major factor influencing the $Cu-N_{amino}$ distances is the presence of the alkyl group on the amine N, rather than the nature of the chelate rings; the presence of a methyl group on an amine N leads to a slightly longer $Cu-N_{amine}$ bond. The axial $Cu-O'_{ph}$ distances differ for the isomeric complexes (2.367(3) in **B** and 2.325(5) in **C**), presumably due to the relative locations of the amino methyl group.

Table 2. Selected Bond Distances (Å) for [Cu(pamap)Cl] (**A**), $[Cu(pamap)]_2(BF_4)_2$ (**B**), $[Cu(pmaap)]_2(BF_4)_2$ (**C**), and $[Ni_2(pamap)_2(NO_3)]NO_3$ (**D**)

bond	**A** (M = Cu)	*a*	**B** (M = Cu)	**C** (M = Cu)	**D** (M = Ni)
M−Cl	2.556(2)	2.558(3)			
M−N1	2.021(7)	2.057(7)	2.025(4)	2.022(6)	2.064(3)
M−N8	2.047(7)	2.030(6)	2.022(4)	2.053(6)	2.086(3)
M−N12	2.071(7)	1.973(7)	2.064(4)	2.028(6)	2.138(3)
M−O19	1.919(6)	1.909(5)		1.929(4)	
M−O′19				2.325(5)	
M−O20			1.924(3)		2.007(2)
M−O′20			2.367(3)		2.089(2)
Ni−O21					2.188(2)

[a] Corresponding distances in [Cu(paip)Cl] to those in **A**. Numbers in parentheses are estimated standard deviations in the least significant digits.

The Cu−O′ distances can be taken as an indicator of the strength of the solid-state interaction of the two units of the dimers. The presence of this axial ligation of a Cu(II) center by an adjacent phenolate O, or enolate O, atom of an N_nO_{4-n} ligand is not uncommon in the solid state when there are no coordinating counteranions present.[35−37] The length of such axial Cu−O bonds has been found to vary over a wide range (2.4−3.9 Å) with binuclear Cu(II) complexes of N_3O Schiff base ligands[35−37] and N_2O_2 Schiff base ligands.[38−40] In **B** and **C**, these Cu−O′ bonds are shorter than this range; however, they are slightly longer than the 2.291(2) Å value found in binuclear Cu(II) complex of a tetradentate N_2O_2 bis(aminophenol) ligand.[30]

All the corresponding basal angles about the Cu centers of **B** and **C** are very similar, with differences less than 2.3°. However, the position of the amino methyl group does have a slight influence on the relative position of the Cu−O′ bond; comparing compounds **B** and **C**, the $N_{Me-amino}-Cu-O'$ angles of each complex are larger than the corresponding $N_{H-amino}-Cu-O'$ angles of its isomer (Table 3). This is not the result of a direct steric interaction between O′ and the methyl group, since the methyl groups are in an anti configuration with respect to the Cu−O′ bonds.

The monomeric (**A**) and the binuclear (**B**) complexes of $pamap^{1-}$ appear very similar in bonding about the Cu(II) center. For instance, three of the four equatorial bonds between the $pamap^{1-}$ ligand and Cu in **B** are identical to their counterparts in **A**, while the $Cu-N_{H-amino}$ (Cu−N8) bond is only slightly shorter in **B** than in **A** (2.022(4) Å versus 2.047(7) Å). The bite angles of the three chelate rings are also very similar in complexes **A** and **B**, with corresponding angles about the Cu(II) centers differing by less than 1.5°.

$[Ni_2(pamap)_2(NO_3)]NO_3$ (D). The structure of the nickel(II) complex (**D**) of the $pamap^{1-}$ ligand, prepared from $Ni(NO_3)_2$, differs significantly from the copper complexes of this ligand

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Table 3. Selected Bond Angles (deg) for [Cu(pamap)Cl] (**A**), $[Cu(pamap)]_2(BF_4)_2$ (**B**), $[Cu(pmaap)]_2(BF_4)_2$ (**C**), and $[Ni_2(pamap)_2(NO_3)]NO_3$ (**D**)[a]

	A	**C**		**B**, M = Cu	**D**, M = Ni
O19−Cu−N1	88.8(3)	93.4 (2)	O20−M−N1	92.42(15)	94.02(10)
O19−Cu−N8	166.6(3)	174.1(2)	O20−M−N8	172.64(14)	172.15(11)
N1−Cu−N8	80.6(3)	81.1(3)	N1−M−N8	81.52(17)	81.73(12)
O19−Cu−N12	94.0(3)	93.8(2)	O20−M−N12	95.14(15)	93.07(9)
N1−Cu−N12	159.0(3)	153.8(3)	N1−M−N12	151.55(16)	98.32(11)
N8−Cu−N12	93.0(3)	92.2(2)	N8−M−N12	92.17(17)	94.07(12)
O19−Cu−Cl	96.78(19)		N12−M−O21		87.19(10)
N1−Cu−Cl	99.3(2)		O20−M−O21		95.78(9)
N8−Cu−Cl	93.1(2)		N1− M−O21		168.49(11)
N12−Cu−Cl	100.99(19)		N8−M−O21		87.82(11)
N12−M−O′19		105.2(2)	O'20−M−N12	112.08(14)	165.02(10)
O19−M−O′19		79.00(19)	O20−M−O′20	79.08(13)	77.83(9)
N1−M−O′19		100.9(2)	N1−M−O′20	96.27(13)	94.21(10)
N8−M−O′19		99.8(2)	N8−M−O′20	97.35(14)	95.83(11)
			O20−M−O21		82.00(9)
Cu−O19−Cu′		101.00(19)	Cu−O20−Cu′	100.92(13)	
C19−O19−Cu′		114.9(3)	C19−O19−Cu	119.8(3)	
C19−O19−Cu′		135.8(4)	C19−O19−Cu′	130.2(3)	

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

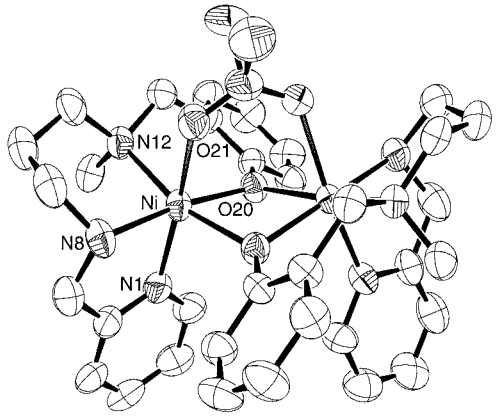

Figure 4. ORTEP drawings of $[Ni_2(pamap)_2(NO_3)]NO_3$ (**D**); 50% probability thermal ellipsoids are shown. The counteranions are omitted.

(Figure 4). The dimeric cation contains two $[Ni(pamap)]^+$ units, bridged by a μ-nitrato (O,O′) anion, and related by a 2-fold axis. Each Ni(II) center is in a pseudo-octahedral geometry. Each unit of the dimer has a $pamap^{1-}$ ligand bound to the metal center, with the two amino N atoms and phenolate O donor atom in an equatorial plane, along with a bridging phenolate O from the other unit of the dimer. The pyridyl N donor and a nitrato oxygen atom, complete the coordination sphere of each Ni center. The pair of bridging phenolate donors create a shared edge between the pseudooctrahedral metal centers. The uncoordinated O atom (O21) of the bridging NO_3^- anion is disordered.

The N_{py}−Ni bond (2.064(3) Å) is at the shorter end of a known 2.07−2.19 Å range for N_{py}−Ni distances in six-coordinate Ni(II) complexes.[41,42] The Ni−O bond (2.007(2) Å) is normal as compared to other Ni(II) complexes.[41,43,44] The Ni−$N_{Me-amino}$ bond distance (2.038(3) Å) is 0.05 Å shorter than the Ni−$N_{H-amino}$ (2.086(3) Å) distance. This is consistent with observations in a known nickel(II) complex of a N_3O ligand (2.01 versus 2.11 Å)[43] as well as observations in the copper complexes **B** and **C** (vide supra). The Ni−N_{amino} bond distances in **D** are 0.04−0.08 Å longer than the corresponding distances in **B**, consistent with the larger covalent radius of nickel(II) relative to copper(II).

The bonding angles in **D** are close to their counterparts in **B** (with differences less than 2.1°, Table 3), except for the N1−M−N12 angle where the ligand configurations differ. The N1−M−N12 in **B** is a trans angle, while it is a cis angle in **D**. The fact that the N_3O donor atoms of Hpamap can be present in either a planar or nonplanar mode demonstrates that the ligand backbone is quite flexible. A six-coordinate nickel(II) of an N_3O ligand has been reported, where the four donors bind similarly in a noncoplanar mode.[43] In that complex, however, the octahedral coordination sphere was completed by the four donors of the chelate and two oxygen atoms of the NO_3^- anion.

Conclusions

Extending previous work with the Hpaip ligand, two novel monoprotic tetradentate (N_3O) ligands, Hpamap and Hpmaap, have been synthesized in four easy steps. The Cu(II) complexes derived from reactions of $CuCl_2 \cdot 2H_2O$ with either Hpaip or Hpamap are structurally similar, with similar bond distances and angles with relatively long Cu−Cl bonds. Replacement of chloride with the noncoordinating BF_4^- anion results in dimeric Cu(II) complexes with both the $pamap^{1-}$ and $pmaap^{1-}$ ligands, where each Cu(II) center assumes a distorted square-pyramidal geometry in which the tetradentate ligand occupies the four equatorial sites and the axial site is filled by a bridging phenolate from the second Cu center. Reaction of the Hpamap ligand with $Ni(NO_3)_2 \cdot 6H_2O$ resulted in a dinuclear complex in which two pseudooctrahedral $[Ni\text{-}pamap]^{1+}$ units are linked by an edge comprised of the pair of bridging phenolate donors, as well as sharing a bridging nitrato ligand. Work remains underway to assess whether such ligands can be suitable for formulation of monocationic ^{62}Cu(II) radiopharmaceuticals.

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Supporting Information Available: Complete tables of crystallographic data, final atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles and intermolecular contacts, and least-squares planes. This material is available free of charge via the Internet at http://pubs.acs.org.

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