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Inorganica Chimica Acta 361 (2008) 365–372
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Note

Synthesis and characterization of an *N*-coordinated amidate copper(II) complex of deprotonated *N*-(2,6-diisopropylphenyl)-2-(bis-(2-pyridylmethyl))aminoethanamide

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Received 6 April 2007; accepted 2 June 2007
Available online 12 June 2007

Abstract

The title ligand, *N*-(2,6-diisopropylphenyl)-2-(bis-(2-pyridylmethyl))aminoethanamide (DIPMAE-H), was prepared by a nucleophilic substitution reaction between *N*-(2,6-diisopropyl)phenyl-2-bromoethanamide and bis-(2-pyridylmethyl)amine. An analogous ligand (TBPMAE-H) in which the 2,6-diisopropylphenyl group was substituted for a *tert*-butyl group was also prepared in this manner. Then, $[(DIPMAE\text{-}H)CuBr]^{+}Br^{-}$ and $[(TBPMAE\text{-}H)CuBr]^{+}Br^{-}$ were prepared by heating one equivalent of ligand and $CuBr_2$ in CH_3CN. In both compounds the geometry about the copper center is square pyramidal with distortions due to the geometrical constraints of the ligand. The amide oxygen occupies the axial position, and the three amine nitrogens and the bromide ligand form the basal plane of the square pyramid. Pairs of complexes in the unit cell are associated via weak donation of a lone pair on the bromide ligand of one complex to the copper center of another (Cu···Br distances in the range of 3.3576–3.4022 Å).

The title compound, (DIPMAE)CuBr, was prepared by deprotonation of $[(DIPMAE\text{-}H)CuBr]^{+}Br^{-}$ using NaH. The key feature of (DIPMAE)CuBr is the amidate group η^1- and *N*-coordinated to the copper center. The compound also exhibits distorted trigonal bipyramidal coordination geometry with the bromide and tertiary amine donors occupying the axial sites and the amidate and pyridyl donors occupying the equatorial positions. The copper atom is displaced from the trigonal plane towards the bromide donor apex due to the geometrical demands of the ligand.

Keywords: Tetradentate ligand; Distorted square pyramidal Cu(II) complex; Distorted trigonal pyramidal Cu(II) complex; η^1- and *N*-Coordinated amidate ligand

1. Introduction

Copper (I) and (II) coordination complexes of polydentate ligands play key roles in the chemistry of atom transfer radical addition (ATRA) [1–7] and atom transfer radical polymerization (ATRP) [8–12]. These methods are catalytic processes that mediate single radical additions to various alkenes, as in the case of ATRA, and multiple additions to alkene monomers, as in the case of ATRP. Furthermore, these types of coordination complexes have been studied as analogs of active centers in metalloproteins that mediate dioxygen activation, electron transfer, and transport processes [13].

Copper-based ATRA and ATRP involve atom transfer from an organic halide to a copper(I) complex to yield a reactive free-radical and a copper(II) complex, also called the deactivator. The free radicals can be used for productive addition reactions with little or no accompanying self-termination by coupling or disproportionation due to the persistent radical effect [14–17]. Consequently, it is important to identify factors that make copper(I) complexes efficient at abstracting halogen atoms and copper(II) complexes proficient at halogen atom donation. Prior studies on copper(I) and copper(II) complexes with tripodal tetradentate amines showed that variations in several structural parameters, such

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0020-1693/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2007.06.003

as chelate ring size and the nature of the donor group, were found to have dramatic effects upon the structure, redox potential and spectroscopic features of the corresponding complexes [18–22]. Many copper(I) complexes of multidentate amines and their derivatives are effective catalysts for ATRP [23,24], and changes in the ligand sphere affect the polymerization kinetics and molecular weight control in ways that are often unexpected and just understood qualitatively [25–31]. A better understanding of the inorganic chemistry side of ATRP can be gained through knowledge about the structure, solution dynamics, and chemistry of the copper centers involved in the atom transfer step, and current efforts are directed at developing methods to quantify the effects of catalyst structure on the chemistry of ATRP [32–34].

Recently, an atom transfer catalyst system based on a monoanionic, tripodal tetradentate ligand design was reported, and the copper(I) and (II) complexes of this ligand exhibited simple solution structures that mirrored their solid-state structures [35]. The ligand design imparted stability to the complex structure via maximization of the chelate effect and incorporation of electrostatic attraction between the ligand and metal center. This catalyst system provides the opportunity to develop quantitative correlations between the structures and chemical characteristics of the atom transfer complexes and their reactivity in polymerizations or other organic transformations. During the course of searching for effective ligand systems, the coordination chemistry of *N*-(2,6-diisopropylphenyl)-2-(bis-(2-pyridylmethyl))aminoethanamide (DIPMAE-H), a bis(picolyl)amine-based ligand containing a C-linked amidate donor group, with copper(II) was studied. The synthesis and structural characterization of copper(II) complexes of neutral and deprotonated DIPMAE-H and the related *tert*-butyl derivative *N*-(*tert*-butyl)-2-(bis-2-pyridylmethyl)-aminoethanamide (TBPMAE-H) are reported here. The copper coordination chemistry of different, yet comparable ligand systems were also investigated recently [35–40].

2. Experimental

2.1. Materials

Tetrahydrofuran was distilled from sodium and benzophenone just prior to use. Chloroform, methylene chloride, methylene chloride-d_2 and acetonitrile were stirred over P_2O_5, distilled and degassed. Triethylamine was stirred over CaH_2, distilled and degassed. Bis-(2-methylpyridyl)-amine was prepared as described previously. Alumina gel used for column chromatography was Acros aluminum oxide, which was activated and neutral (50–200 μm). Analytical TLC was performed on commercial EM Science plates coated with aluminum oxide 60 F_{254}, neutral (0.2 mm thick). Unless stated otherwise, all materials were purchased from commercial sources and used without further purification. Reagents were handled under nitrogen atmosphere using standard drybox and Schlenk techniques.

2.2. Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Inova 400 instrument or a Varian Mercury 300 NMR spectrometer. Chemical shifts, δ (ppm), were referenced to the proton or carbon signal of the NMR solvent. FTIR spectra were obtained with a Mattson Galaxy Series FTIR 3000. UV–Vis spectra were recorded on an HP 8452A Spectrophotometer in THF solvent. Elemental analyses were performed by Midwest Microlabs.

2.3. X-ray structure determinations

Diffraction data for DIPMAE were collected on a Siemens P4 diffractometer employing Cu Kα radiation and a nitrogen cold stream provided by a Siemens LT-2 apparatus. No absorption correction was applied. Data for complex **2** were collected using a Siemens P3 diffractometer, Mo Kα radiation, and a locally modified Siemens LT-1 apparatus. An empirical absorption correction (XABS) was applied. Diffraction data for complexes **1** and **3** were collected with a Bruker SMART 1000 diffractometer, graphite-monochromated Mo Kα radiation, and a nitrogen cold stream provided by a CRYO Industries apparatus. Corrections for absorption were applied using the program SADABS-2.03 [41]. The structures were solved by direct methods (SHELXS-97) [42] and refined by full-matrix least-squares on F^2 (SHELXL-97) [42]. All non-hydrogen atoms at full occupancy were refined with anisotropic thermal parameters. Certain disordered solvate molecules are present in the structures of complexes **1**, **2**, and **3**. Crystal data and refinement details for the complexes are shown in Table 1. Additional experimental information, including atomic positional parameters, and a description of the disorder are supplied in CIF format as described in Supplementary material.

2.4. N-(2,6-Diisopropyl)phenyl-2-bromoethanamide

A solution of 4.00 ml (21.2 mmol) of 2,6-diisopropylaniline and 3.00 ml (21.2 mmol) of triethylamine in 50 ml of dry CH_2Cl_2 was added dropwise to 1.84 ml (21.2 mmol) of bromoacetyl bromide in 50 ml of dry CH_2Cl_2 stirred in an ice bath. The reaction was stirred overnight. The solution was then washed with $NaHCO_3$ (50 ml), H_2O (50 ml), diluted HCl (50 ml) and H_2O (50 ml). The CH_2Cl_2 layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting white powder was recrystallized from toluene, yielding 5.37 g (85%). m.p. = 166–168 °C; ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 7.7 (s, 1H), 7.3 (m, 2H), 4.1 (s, 2H), 3.0 (m, $J = 6.9$ Hz, 2H), 1.2 (d, $J = 6.9$ Hz, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ (ppm) 160.1, 159.7, 146.0, 128.8, 123.6, 29.4, 28.9, 23.7; IR (CH_2Cl_2): ν (cm^{-1}) 3392, 1676, 1500. *Anal.* Calc. for $C_{14}H_{19}NOBr$: C, 56.56; H, 6.45; N, 4.71. Found: C, 56.46; H, 6.76; N, 4.68%.

Table 1
Crystal data for DIPMAE and complexes **1**, **2** and **3**

Compound	DIPMAE	[CuBr(DIPMAE-H)]Br · 0.125acetone · 0.125toluene · 0.375H_2O (**1**)	[CuBr(TBMAE-H)]Br · 2.59H_2O · 0.41CH_3OH (**2**)	[CuBr(DIPMAE)] · 0.25H_2O (**3**)
Formula	$C_{26}H_{32}N_4O$	$C_{27.25}H_{34.50}Br_2CuN_4O_{1.5}$	$C_{18.41}H_{26.80}Br_2CuN_4O_4$	$C_{26}H_{31.5}$ $BrCuN_4O_{1.25}$
Formula weight	416.56	665.45	591.52	563.50
Space group	$Pca2_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	10.8433(10)	15.420(3)	7.8338(17)	9.8522(14)
b (Å)	12.8258(10)	15.671(3)	11.254(2)	12.0835(17)
c (Å)	16.2960(14)	25.552(4)	14.309(3)	21.988(3)
α (°)	90	88.490(11)	85.087(18)	90
β (°)	90	82.958(9)	76.438(18)	101.837(5)
γ (°)	90	89.354(9)	82.257(18)	90
V (Å^3)	2266.4(3)	6125.9(18)	1213.3(5)	2562.0(6)
T (K)	130(2)	91(2)	130(2)	91(2)
Z	4	8	2	4
D_{calc} (Mg m^{-3})	1.221	1.443	1.619	1.465
μ (mm^{-1})	0.592 (Cu Kα)	3.349 (Mo Kα)	4.223 (Mo Kα)	2.439 (Mo Kα)
Range of transmission factors	0.842–0.965	0.569–0.753	0.408–0.567	0.775–0.867
wR_2[a] (all data)	0.0671	0.2792	0.1763	0.1134
R_1[b] [$I > 2\sigma(I)$ data]	0.0274	0.1065	0.0718	0.0437

[a] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.
[b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

2.5. *N*-(2,6-Diisopropylphenyl)-2-(bis-2-pyridylmethyl)aminoethanamide (DIPMAE-H)

To 20 ml of degassed toluene, 1.53 g (7.69 mmol) of bis-(2-pyridylmethyl) amide was added. Then, 2.30 g (7.67 mmol) of *N*-(2,6-diisopropyl)phenyl-2-bromoethanamide was added. The reaction was stirred at 80 °C for 3 days. The solution was then extracted with (3 × 50 ml) 10% HCl. The acidic layers were combined, and the pH was adjusted to >9 with 10% NaOH. The resulting solution was then extracted with (4 × 100 ml) CH_2Cl_2. The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified using alumina column chromatography, eluted with 5% Et_3N in EtOAc. The fractions containing the product were combined and concentrated, and volatile materials were removed under vacuum, yielding 1.36 g (42%) of an orange solid. ^{1}H NMR (300 MHz, CD_3CN): δ (ppm) 10.0 (s, 1H), 8.5 (d, $J = 3.6$ Hz, 2H), 7.7 (m, 2H), 7.4 (d, $J = 5.7$ Hz, 2H), 7.2 (m, 3H), 7.1 (d, $J = 3.7$ Hz, 2H), 3.9 (s, 4H), 3.4 (s, 2H), 2.9 (m, $J = 5.1$ Hz, 2H), 1.1 (d, $J = 5.4$ Hz, 12H); ^{13}C NMR (75 MHz, CD_3CN): δ (ppm) 171.7, 158.9, 149.4, 146.7, 136.8, 133.4, 128.0, 123.4, 123.3, 122.6, 60.5, 57.9, 28.8, 23.2; IR (CH_2Cl_2): ν (cm^{-1}) 3435, 2962, 1678, 1592, 1494. *Anal*. Calc. for $C_{26}H_{32}N_4O$: C, 74.97; H, 7.74; N, 13.45. Found: C, 75.11; H, 7.71; N, 13.44%.

2.6. *N*-(tert-Butyl)-2-bromoethanamide

A similar procedure was followed as in the synthesis of *N*-(2,6-diisopropyl)phenyl-2-bromoethanamide, substituting an equivalent molar amount of *tert*-butyl amine for 2,6-diisopropylaniline. Yield: 3.54 g (64%) of white crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.3 (s, 1H), 3.8 (s, 2H), 1.4 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 165.3, 52.2, 30.3, 28.8; IR (CH_2Cl_2): ν (cm^{-1}) 3320, 1675, 1550.

2.7. *N*-(tert-Butyl)-2-(bis-2-pyridylmethyl)aminoethanamide (TBPMAE-H)

A similar procedure was followed as in the synthesis of DIPMAE except for the following changes. An equivalent molar amount of *N*-*tert*-butyl-2-bromoethanamide was substituted for *N*-(2,6-diisopropyl)phenyl-2-bromoethanamide. The acid extraction step was omitted, and instead the concentrated crude product was purified using alumina column chromatography, eluted with 5% Et_3N in EtOAc. The fractions containing the product were combined and concentrated, and volatile materials were removed under vacuum, yielding 0.213 g (38%) of an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.6 (d, $J = 4.8$ Hz, 2H), 8.3 (s, 1H), 7.6 (m, 2H), 7.3 (d, $J = 5.7$ Hz, 2H), 7.17 (m, 2H), 3.8 (s, 4H), 3.2 (s, 2H), 1.4 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 170.4, 158.3, 149.4, 136.8, 123.4, 122.6, 60.9, 59.1, 51.0, 29.1.

2.8. (DIPMAE-H)$CuBr_2$

A solution of 1.07 g (2.57 mmol) of DIPMAE-H in 35 ml of dry CH_3CN was transferred via a cannula onto 0.59 g (2.64 mmol) of $CuBr_2$. The solution was heated at reflux for 10 min and then cooled. Volatile materials were removed by rotary evaporation, and the resulting blue-

green solid was recrystallized from acetone/toluene to yield 1.08 g (65%) of blue crystals. IR (CH_2Cl_2): ν (cm^{-1}) 3428, 1652, 1608, 1504, 1446; UV–Vis: $\lambda_{max} = 805$ nm, $\varepsilon = 208\ nm^{-1}\ cm^{-1}$; *Anal.* Calc. for $C_{26}H_{32}N_4OCuBr_2$: C, 48.79; H, 5.05; N, 8.75. Found: C, 49.50; H, 5.22; N, 8.18%.

2.9. (TBPMAE-H)$CuBr_2$

A similar procedure was followed as in the synthesis of (DIPMAE-H)$CuBr_2$, except that the resulting solid was recrystallized from CH_3OH.

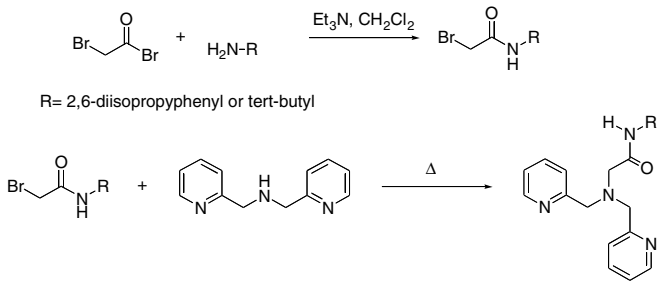
2.10. (DIPMAE)CuBr

A solution of 0.414 g (0.647 mmol) of (DIPMAE-H)$CuBr_2$ in 30 ml of dry THF was transferred via a cannula onto 17.4 mg (0.725 mmol) of NaH. The solution was heated at reflux for 1 h and then stirred at room temperature for 2 days. The solution was hot filtered, and green/orange crystals formed when the filtrate cooled. The crystals were isolated by filtration and any remaining volatile materials were removed under vacuum to yield 0.290 g (63%) of green crystals.

3. Results and discussion

The ligand in this study was *N*-(2,6-diisopropylphenyl)-2-(bis-2-pyridylmethyl)aminoethanamide (DIPMAE-H), and it was prepared in two steps. First, *N*-(2,6-diisopropyl)phenyl-2-bromoethanamide was prepared by the addition–elimination reaction of 2,6-diisopropyl aniline with bromoacetyl bromide. Then, bis-(2-pyridylmethyl)amine was added to the product via a nucleophilic substitution process (Scheme 1). An analogous ligand (TBPMAE-H) in which the 2,6-diisopropylphenyl group was substituted for a *tert*-butyl group was also prepared in this manner starting with *tert*-butyl amine. Purified DIPMAE-H readily formed crystals suitable for X-ray analysis from a THF/CH_2Cl_2 solvent system, so X-ray structural analysis was performed. The molecular structure is shown in Fig. 1, and the crystal data are contained in Table 1.

The title complex was formed in two steps. First, one equivalent of DIPMAE-H was added to $CuBr_2$ in CH_3CN, and the solution was heated at reflux (Eq. (1)). Evaporation of the solvent and recrystallization from acetone/toluene



Scheme 1. Synthetic route for the preparation of DIPMAE-H.

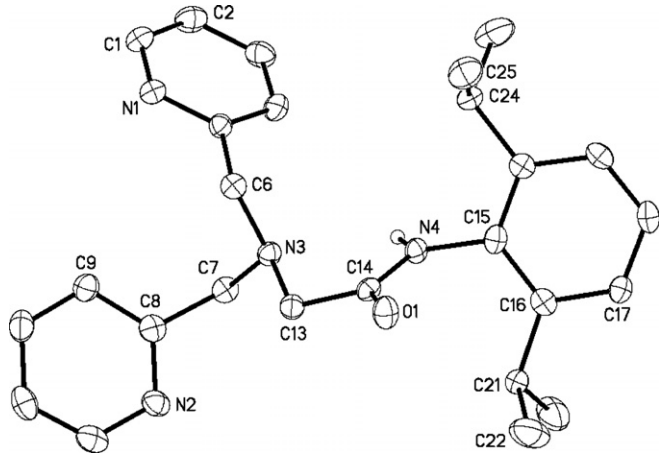
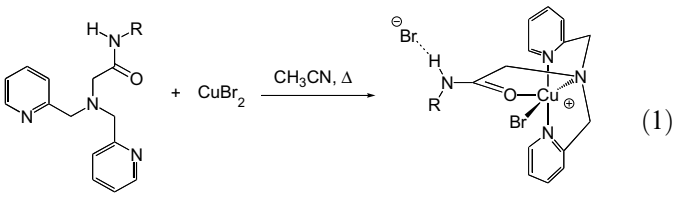


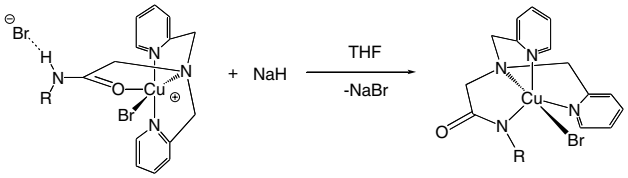
Fig. 1. The molecular structure of DIPAME-H, probability ellipsoids are set to 50%.

yielded blue crystals, complex **1**. In a similar manner, a complex between TBPMAE-H and $CuBr_2$ was prepared, complex **2**. The molecular structures are shown in Figs. 2 and 3, and the crystal data are contained in Table 1.



(1)

R = 2,6-diisopropyphenyl or tert-butyl



(2)

Complex **1** crystallized in the space group $P\bar{1}$, and the unit cell contained fractional occupancies of the solvent system used to grow the crystals. The geometry about the copper center is square pyramidal with distortions due to the geometrical constraints of the ligand. Tables 2 and 3 show key bond distance and bond angle data, respectively, for complex **1** as well as for DIPMAE-H and the other complexes studied. There are two complex dimers in the unit cell related to two others by an inversion center, for a total of four unique molecular structures and eight complexes overall. For each structure, the amide oxygen occupies the axial position, and the three amine nitrogens and the bromide ligand form the basal plane of the square pyramid. The copper center has only one negatively charged donor and therefore carries a formal positive charge. A bromide anion (such as Br5) is present to maintain overall charge neutrality, and it is involved in an N–H···Br hydro-

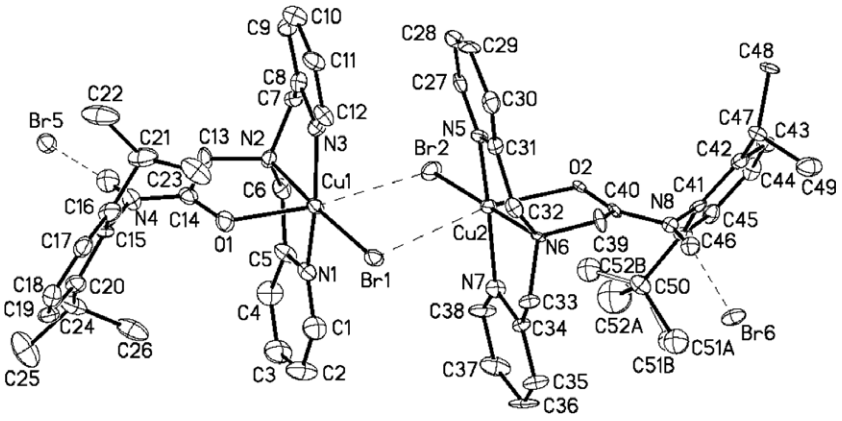


Fig. 2. The molecular structure of complex **1**, probability ellipsoids are set to 50%.

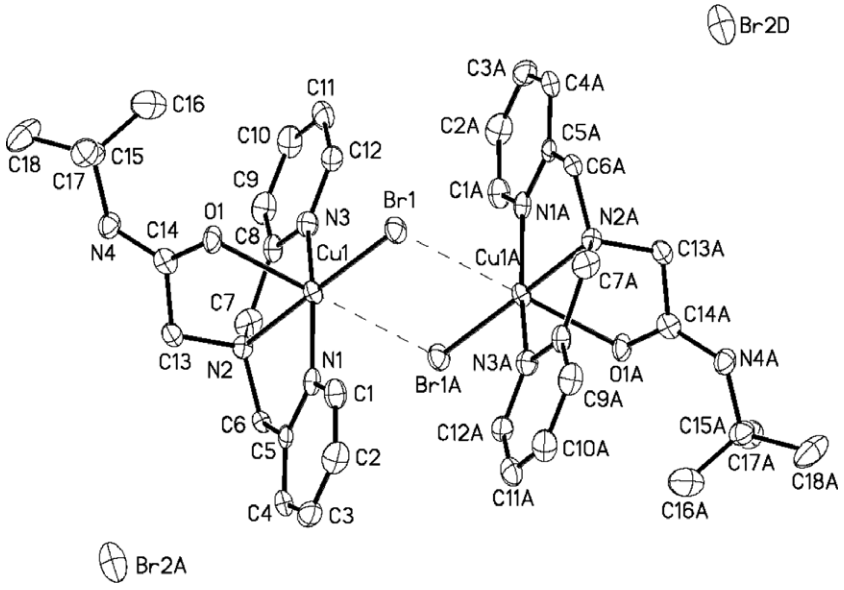


Fig. 3. The molecular structure of complex **2**, probability ellipsoids are set to 50%.

gen bond to the amide hydrogen of the ligand. (This hydrogen bonding pattern was not observed in the structure of complex **2**.) The angles between the central nitrogen of the ligand (N2) and the other nitrogens (N1 and N3) and oxygen (O1) of the ligand are all 8–9° less than the ideal square pyramidal geometry of 90° due to the bite angles of the ligand. Consequently, the copper center is displaced from the center of the basal plane towards the bromide ligand Fig. 4.

When compared to the bond distances of DIPMAE-H, the shorter amide C–N and longer amide C═O distances indicate more resonance delocalization consistent with a greater partial negative charge on the donor oxygen atom coordinated to the copper center. The two complexes of the dimer are associated via weak donation of a lone pair on the bromide ligand of one complex to the copper center of another (Cu···Br distances in the range of 3.3576–3.4022 Å). The bridging bromide occupies the coordination site opposite to the axial oxygen, so the geometry of each complex might also be considered to be octahedral with a severe axial elongation distortion. The pyridyl C–C and C–N bond lengths are within the range found for the parent ligand, and the Cu–N and Cu–Br bond distances reveal no other unusual features. The structural features of complex **2** are very similar to those of complex **1** with no notable differences other than the aforementioned absence of hydrogen bonding to the bromide counterion.

The next step involved deprotonation of the ligand to prepare the neutral complex. One equivalent of (DIPMAE-H)$CuBr_2$ dissolved in dry THF was transferred onto a small excess of NaH. The solution was heated at reflux for 1 h and then stirred at room temperature for 2 days. The solution was then heated at reflux again and hot filtered. Upon cooling green-orange crystals formed, complex **3**. Complex **3** crystallized in the space group $P2_1/n$ with four symmetry-related molecules, and the unit cell contained fractional occupancies of the solvent system used to grow the crystals. Tables 2 and 3

Table 2
Selected bond lengths for DIPMAE and complexes **1**, **2**, and **3**

Compound	DIPMAE	[CuBr(DIPMAE-H)]Br · 0.125acetone · 0.125toluene · 0.375H_2O (**1**)	[CuBr(TBMAE-H)]Br · 2.59H_2O · 0.41CH_3OH (**2**)	[CuBr(DIPMAE)] · 0.25H_2O (**3**)
Bond lengths (Å)				
Amide C–N	1.347(3)	1.321(13), 1.315(15), 1.317(14), 1.350(12)	1.317(11)	1.333(6)
Amide C═O	1.227(3)	1.258(13), 1.225(12), 1.242(14), 1.243(12)	1.254(10)	1.243(6)
N2–Cu1		2.094(9), 2.092(8), 2.083(9), 2.080(9)	2.065(7)	2.030(4)
N1–Cu1		2.008(9), 1.992(9), 2.001(11), 1.991(10)	2.012(7)	2.118(4)
N3–Cu1		2.015(10), 2.011(9), 2.011(10), 2.014(9)	2.014(8)	2.165(4)
Cu1–N4				1.987(4)
Cu1–O1		2.228(8)	2.291(6)	
Bond angles (°)				
N–H···O	3.213(3)			
N–H···Br		3.319(10), 3.309(9), 3.329(10), 3.270(9)		
Cu1–Br1		2.4125(16), 2.3857(17), 2.3875(16), 2.3959(16)	2.4100(15)	2.3755(7)
Cu1···Br2		3.4022(14), 3.3576(14), 3.3653(13), 3.3887(14)	3.1384(15)	

Table 3
Selected bond angles for DIPMAE and complexes **1**, **2**, and **3**

Compound	DIPMAE	[CuBr(DIPMAE-H)]Br · 0.125acetone · 0.125toluene · 0.375H_2O (**1**)	[CuBr(TBMAE-H)]Br · 2.59H_2O · 0.41CH_3OH (**2**)	[CuBr(DIPMAE)] · 0.25H_2O (**3**)
Amide N–C–O	123.9(2)	122.7(10), 125.4(9), 124.9(9), 125.2(11)	124.5(8)	128.2(4)
Br1–Cu1–N1		97.9(3), 97.7(3), 97.4(3), 97.1(3)	97.6(2)	99.10(10)
Br1–Cu1–N2		176.6(2), 179.5(2), 178.3(3), 176.2(2)	179.1(2)	175.78(11)
Br1–Cu1–N3		97.8(2), 96.8(3), 97.0(3), 96.4(3)	98.2(2)	97.40(10)
Br1–Cu1–O1		101.5(2), 98.81(19), 99.3(2), 102.37(19)	98.97(15)	
Br1–Cu1–N4				100.84(11)
N2–Cu1–N1		82.8(4), 81.9(3), 83.4(4), 83.3(4)	81.7(3)	80.61(14)
N2–Cu1–N3		81.8(4), 83.6(3), 82.0(4), 82.5(4)	82.5(3)	78.64(14)
N2–Cu1–O1		81.8(3), 81.3(3), 82.1(3), 81.4(3)	81.6(2)	
N2–Cu1–N4				82.62(15)
N3–Cu1–O1		90.2(3), 89.8(3), 96.7(3), 100.4(3)	84.6(3)	
O1–Cu1–N1		92.0(3), 98.8(3), 89.2(4), 88.3(3)	101.8(3)	
N3–Cu1–N1		163.3(4), 161.8(4), 163.3(4), 162.0(4)	161.8(3)	
N4–Cu1–N1				126.00(15)
N1–Cu1–N3				104.05(15)
N3–Cu1–N4				122.18(15)
Cu1–O1–C14		109.9(7), 106.6(6), 108.5(7), 107.6(6)	105.3(5)	
Cu1–N4–C14				114.8(3)
N–H···Br		169.6, 170.6, 172.5, 174.3		
N–H···O	134(2)			

show key bond distance and bond angle data, respectively, for complex **3**.

The key feature of complex **3** is the amidate group η^1- and *N*-coordinated to the copper center. The bromide counterion as found in complexes **1** and **2** is not observed in the unit cell, which is consistent with the DIPMAE ligand having been deprotonated during the reaction. The amide C–N (1.333(6) Å) and C–O (1.243(6) Å) bond lengths were very similar to those found for a recently reported *N*-coordinated amidate–copper(I) complex [38] and are consistent with substantial localization of the formal negative charge of the amidate group on the nitrogen atom. The pyridyl C–C and C–N bond lengths are within the range found for complexes **1** and **2**. The Cu–N and Cu–Br bond distances reveal no other unusual features.

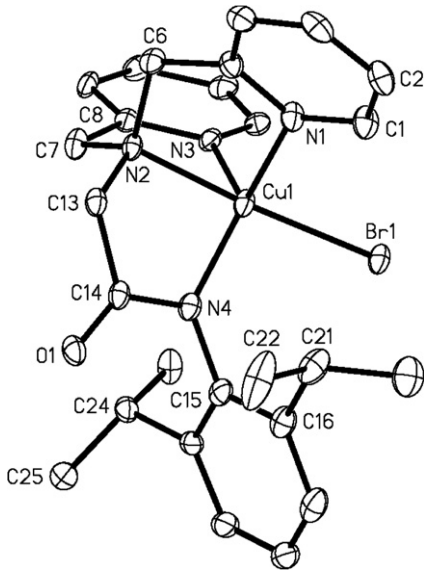


Fig. 4. The molecular structure of complex **3**, probability ellipsoids are set to 35%.

The geometry about the copper center is trigonal bipyramidal and is somewhat distorted towards square pyramidal. The axial coordination sites are occupied by the bromide ligand and the central nitrogen atom of DIPMAE, while the equatorial coordination sites contain the two pyridyl donor nitrogen atoms and the amidate nitrogen. Two of the angles made between the equatorial donors and the copper atom are greater than 120° and one is less than 120°. The angle between the axial donors and the copper atom is a few degrees less than 180°. The angles between the axial donors and the equatorial donors are all greater than 90° for the bromide axial ligand and are less than 90° for the central nitrogen axial donor. As a result, the copper atom is displaced from the trigonal plane towards the bromide ligand. All of these angular distortions are likely due to the mismatch between the bite angle constraints of the ligand and ideal trigonal bipyramidal geometry.

In summary, a coordination complex was formed from $CuBr_2$ and DIPMAE-H, complex **1**; the *tert*-butyl analogue, complex **2**, was formed as well. Complex **1** was then deprotonated using NaH to yield Cu(DIPMAE)Br, complex **3**. The latter compound features an amidate group η^1- and *N*-coordinated to the copper center. Complex **3** exhibits distorted trigonal bipyramidal coordination geometry with the bromide and tertiary amine donors occupying the axial sites and the amidate and pyridyl donors occupying the equatorial positions. The copper atom is displaced from the trigonal plane towards the bromide donor apex due to the geometrical demands of the ligand.

Acknowledgements

The donors of the Petroleum Research Fund, administered by the American Chemical Society, are acknowledged for support of this research (Grant #35150-AC7).

Appendix A. Supplementary material

CCDC 642628, 642629, 642631 and 642630 contain the supplementary crystallographic data (excluding structure factors) for DIPMAE, **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.06.003.

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