Structural variation in copper(I) complexes with pyridylmethylamide ligands: structural analysis with a new four-coordinate geometry index, τ_4†

Lei Yang, Douglas R. Powell and Robert P. Houser*

Four Cu(I) complexes were synthesized with a family of pyridylmethylamide ligands, HL^R [$HL^R = $ N-(2-pyridylmethyl)acetamide, R = null; 2,2-dimethyl-N-(2-pyridylmethyl)propionamide, R = Me$_3$; 2,2,2-triphenyl-N-(2-pyridylmethyl)acetamide, R = Ph$_3$]. Complexes **1–3** were synthesized from the respective ligand and [Cu(CH$_3$CN)$_4$]PF$_6$ in a 2 : 1 molar ratio: [Cu(HL)$_2$]PF$_6$ (**1**), [Cu$_2$(HL^{Me3})$_4$](PF$_6$)$_2$ (**2**), [Cu(HL^{Ph3})$_2$]PF$_6$ (**3**). Complex **4**, [Cu(HL)(CH$_3$CN)(PPh$_3$)]PF$_6$, was synthesized from the reaction of HL with [Cu(CH$_3$CN)$_4$]PF$_6$ and PPh$_3$ in a 1 : 1 : 1 molar ratio. X-Ray crystal structures reveal that complexes **1**, **3** and **4** are mononuclear Cu(I) species, while complex **2** is a Cu(I) dimer. The copper ions are four-coordinate with geometries ranging from distorted tetrahedral to seesaw in **1**, **2**, and **4**. Complexes **1** and **2** are very air sensitive and they display similar electrochemical properties. The coordination geometry of complex **3** is nearly linear, two-coordinate. Complex **3** is exceptionally stable with respect to oxidation in the air, and its cyclic voltammetry shows no oxidation wave in the range of 0–1.5 V. The unusual inertness of complex **3** towards oxidation is attributed to the protection from bulky triphenyl substituent of the HL^{Ph3} ligand. A new geometric parameter for four-coordinate compounds, τ_4, is proposed as an improved, simple metric for quantitatively evaluating the geometry of four-coordinate complexes and compounds.

Introduction

Control of the coordination environment in transition metal complexes continues to be the pivotal objective in designing molecules and materials in varied fields of inorganic chemistry, including bioinorganic modeling, catalysis, supramolecular self-assembly, and coordination polymers. The coordination environment provided by ligands can impart unique and useful properties on their transition metal complexes. The design and synthesis of new molecules to be used as ligands is and will continue to be an important part of inorganic chemistry. At the same time, relatively simple ligands can, under judicious synthetic conditions, give rise to complexes of import and interest. One such class of ligands that we have been investigating in our laboratory is the pyridylmethylamide ligand system.

The ongoing interest in pyridylmethylamide ligands can be attributed to their ability to pre-organize and tune the structural properties of their transition metal complexes. Much effort has been devoted to the investigation of the influence of substituents, base, and stoichiometry on the coordination modes of the ligand, the geometric conformation of the metal centers and the different properties of the complexes.[1,2] Some of the transition metal complexes with pyridylamide ligands have been used specifically as biomimetic models,[3,4] while others exhibited interesting supramolecular and/or polymeric structural properties.[2,5]

As a part of our ongoing research on the design and synthesis of new copper complexes with pyridylamide ligands,

we have employed a new polydentate pyridylmethylamide ligand family (HL^R; R = H, Me$_3$, Ph and Ph$_3$) with different substituents on the amide, and probed their complexation properties with Cu(II) and Cu(I).[4,6–9] Novel copper clusters—([Cu$_8$L$_8$(OH)$_4$]$^{4+}$ and [Cu$_4$(L^{Ph})$_4$(OH)$_2$]$^{2+}$)—and methoxide-bridged dimers—([Cu$_2$(HL^{Me3})$_2$(OMe)$_2$]$^{4+}$ and [Cu$_2$(HL^{Ph3})$_2$(OMe)$_2$]$^{4+}$)—were synthesized and characterized.[6,8] We established that not only can the protonation or deprotonation of the amide nitrogen control the metal nuclearity and stability of complexes formed, but the substituent groups, R, also turn out to be an important factor to the coordination geometry of the metal center and the chemical properties of their copper complexes.

The pyridylmethylamide ligand, HL^R, has three potential donor atoms, the N and O atoms from the amide group and a pyridyl N atom. The coordination modes of copper complexes formed by these three donor atoms can be modulated by the steric effect of the substituents, the use of base, or the use of different copper salt starting materials. When HL^R coordinates in its neutral form, the pyridyl N and O from the amide group will chelate to the copper atom in a bidentate fashion, and form mononuclear or dinuclear species.[6,8] If CuCl is used, only the pyridyl N donor will coordinate to the copper center in a monodentate fashion, and mononuclear, dinuclear or one dimensional polymer complexes can be synthesized.[9] With the application of base, a tridentate bridging coordination mode can be observed. The pyridyl and amidate N donors chelate to the same copper atom and the amidate O atom bridges to a second copper atom. Illustrating this coordination mode, the reaction of Cu(ClO$_4$)$_2$·6H$_2$O, HL and Et$_3$N leads to the formation of a novel octanuclear copper cluster, in which two pseudosymmetric tetranuclear copper clusters are linked by four bidentate bridging ligands, L$^-$, and two μ$_3$-hydroxo

Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Norman, Oklahoma, 73019, USA. E-mail: houser@ou.edu; Fax: +1 (405) 325-6111; Tel: +1 (405) 325-3551
† The HTML version of this article has been enhanced with colour images.

ligands.[8] When the methyl group on the amide is replaced by a benzyl group, the increased steric effect leads to the formation of tetranuclear cluster $[Cu_4(L^{Ph})_4(OH)_2](ClO_4)_2$.[6]

Because Cu(I) complexes, especially those with coordinatively unsaturated Cu(I) centers, play an important role in the understanding of metal properties in various biosystems, we are very interested in the complexation properties of ligands HL^R with Cu(I) ions. Herein, we report the synthesis and characterization of four new Cu(I) complexes with HL, HL^{Me3}, and HL^{Ph3}. The increasing steric effects of substituent groups in these ligands lead to the different nuclearities of the copper complexes and different coordination geometries of the copper centers. The interesting electrochemical properties exhibited by these complexes are consistent with their structural properties. Because of its two-coordinate, linear coordination geometry and the protective effect from the bulky triphenyl groups, complex **3** $[Cu(HL^{Ph3})_2]PF_6$ is remarkably stable in open air, even in coordinating solvents.

Finally, in this paper we introduce a new four-coordinate metrical parameter. The coordination number of all of the complexes reported in this paper is four or less. Of the four-coordinate complexes, several display geometries that are difficult to objectively describe, being neither close to tetrahedral or square planar. We propose a new parameter, τ_4, which can be used to quantify the geometry of four-coordinate species. The formula is very simple, and can be calculated by hand using only the bond angles of the metal coordination sphere.

Results and discussion

The syntheses of complexes **1–4**, summarized in Scheme 1, were all carried out using $[Cu(CH_3CN)_4]PF_6$ with the appropriate ligand(s) in dichloromethane under anaerobic conditions. Complex **1**, characterized by elemental analysis and X-ray diffractometry as $[Cu(HL)_2]PF_6$, differs from **4**, which was synthesized from $[Cu(CH_3CN)_4]PF_6$, HL and PPh$_3$ and characterized as $[Cu(HL)(CH_3CN)(PPh_3)]PF_6$, only in that **1** contains two ligands HL, while **4** contains one ligand HL, one PPh$_3$, and one coordinated acetonitrile molecule. Finally, on the basis of their elemental analyses and X-ray structural analysis, complexes **2** and **3** were characterized as $[Cu_2(HL^{Me3})_4](PF_6)_2$ and $[Cu(HL^{Ph3})_2]PF_6$, respectively.

Complexes **1** and **2** are relatively stable in the solid state when stored under N$_2$, but the yellow crystals of the two complexes are oxidized to green powder within 24 h when exposed to open air. The light yellow solutions of complexes **1** and **2** are very air sensitive, as indicated by the rapid color change to light blue, and the reaction of complex **1** with the oxidant S$_8$ gave the simple oxidation product $[Cu(HL)_2](PF_6)_2$, which was characterized by X-ray crystallography. Further characterization of the resultant green Cu(II) species from the oxidation of complex **2** is currently under investigation.

In contrast, a remarkable and interesting feature of complex **3** is its unusually high stability towards oxidation. No oxidations of
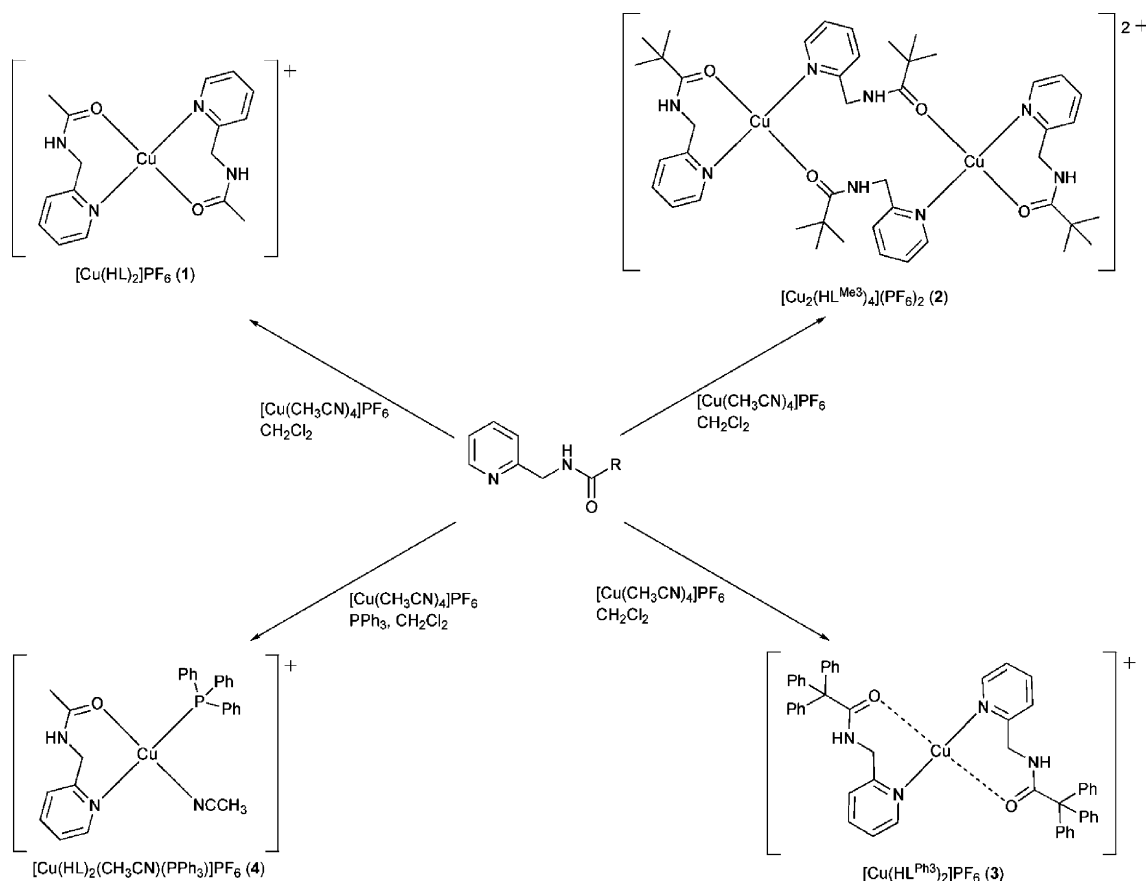
Scheme 1 Synthesis and structure representation of complexes **1–4**.

complex **3** were observed even if the colorless solid was exposed to open air for months. More interestingly, colorless CH_2Cl_2 or CH_3CN solutions of complex **3** were also very stable in open air, with no observable color changes within 8 weeks. Although examples of linear, two-coordinate Cu(I) species have been reported, structurally characterized two-coordinate Cu(I) complexes with nitrogen donor ligands are relatively rare.[10] Furthermore, only one two-coordinate, linear Cu(I) complex with monodentate ligands having similar stability towards oxidation has been reported.[11]

Electrochemistry

Cyclic voltammetry was performed on solutions of **1–3** in CH_2Cl_2 or CH_3CN containing 0.1 M n-Bu$_4$NPF$_6$ as the supporting electrolyte. Ferrocene was added to the solution as an internal standard and potentials are reported *vs.* Ag/AgCl. Complexes **1** and **2** exhibit similar electrochemical properties in CH_2Cl_2. Both undergo one partially reversible reduction at −0.3 V, assigned to the Cu^I/Cu^0 reduction. One irreversible oxidation process can also be observed in the CVs of both complexes, but the wave positions are different for **1** and **2**, with 0.54 V for complex **1** and 0.69 V for complex **2**. The higher stability towards oxidation of complex **2** with respect to complex **1** can be interpreted in terms of the solution conformations of the two complexes. On the basis of the ESI mass spectrometry of **1** and **2** in CH_2Cl_2, they both exist in solution as similar mononuclear species, $[Cu(HL)_2]^+$ and $[Cu(HL^{Me3})_2]^+$. The protection to Cu(I) provided by the bulky *tert*-butyl groups of ligand HL^{Me3} may result in the anodic shift of the oxidation wave for $[Cu(HL^{Me3})_2]^+$.

The cyclic voltammetry of complex **3** in CH_2Cl_2 or CH_3CN only displays an irreversible reduction at −0.63 V, which we assign to the Cu^I/Cu^0 couple. This cathodic shift of the reduction wave indicates that complex **3** is harder to reduce than complexes **1** and **2**. More interestingly, no oxidation was observed in the range of 0 to 1.5 V. It has been established that reactivity of Cu(I) species possessing linear geometries with O_2 and CO is unfavorable.[12,13] However, two-coordinate Cu(I) complexes are still very air sensitive if the ligand is sterically unhindered.[11,12,14] The complex reported by Banthia and Samanta[11] has a coordination environment similar to complex **3**, and it is also stable in open air. However, the oxidation of Samanta's complex can still be observed at ∼1.15 V, and its inertness is due to the electronic factors from ligand and perchlorate anions. The cyclic voltammetry of ligand HL^{Ph3} shows no oxidation or reduction within +1.5 V to −1.5 V, and the PF$_6^-$ anion has no close interactions with the copper center in complex **3**. Therefore the steric hindrance provided by the bulky triphenyl groups to the linear copper center exerts the greatest influence to the exceptional stability of this complex. To our knowledge, complex **3** is the most stable Cu(I) complex with a two-coordinate linear copper center.

Our previous results showed that the amide group of the HL^R ligands is quite flexible, and hydrogen bonding involving the carbonyl and N–H groups can stabilize the complex significantly.[9] The crystal structure of complex **3** (*vide infra*) shows weak interactions between the Cu atom and the carbonyl O atoms, so the two triphenyl groups are "pulled" close to the Cu(I) center and protect the Cu(I) from oxidation. ESI mass spectrometry also shows that the mononuclear cationic portion of **3** exists in the

solution, which helps explain the unusual stability of solutions of **3** in the open air.

X-Ray crystal structures

[Cu(HL)$_2$]PF$_6$ (1). Crystallographic analysis of mononuclear **1** indicates that it consists of one Cu(I) ion, two neutral HL ligands, and a PF$_6$ anion (Fig. 1). The pyridyl N atom and amide O atom from both ligands chelate to the same copper ion with the pyridyl groups *trans* to each other. The dihedral angle formed by the two pyridyl rings is only 8.9°, and the copper center lies out of these two pyridyl ring planes by an average distance of 0.195 Å. One interesting structural feature of this complex is that the two amide groups stay on the same side of two pyridyl rings with an O1–Cu1–O2 angle of 101.21(5)° (see Table 1). The two Cu–O bonds pull the copper out of the two pyridyl ring planes with a N1–Cu1–N3 bond angle of 161.96(6)°. This very distorted tetrahedral geometry of the Cu(I) center can be better described as a seesaw structure, with the nearly linear N1–Cu1–N3 forming the plank and the O1–Cu1–O2 forming the pivot. The N1–Cu–N3 and O1–Cu1–O2 planes are nearly perpendicular, with a dihedral angle of about 92.2°.
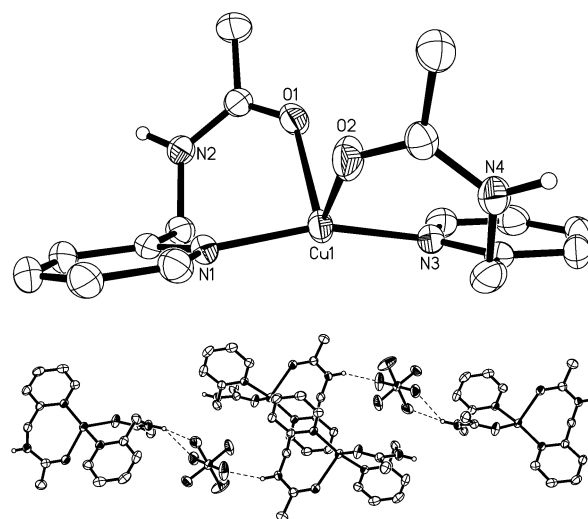

Fig. 1 X-Ray crystal structure (top) and packing diagram (bottom) for [Cu(HL)$_2$]PF$_6$ (**1**) with thermal ellipsoids at the 50% probability level.

Very few examples of mononuclear Cu(I) complexes with a similar N_2O_2 coordination environment have been reported,[15–17] and the examples structurally characterized as seesaw structures are even more rare.[15,17] The average Cu–N distance of 1.931 Å and the average Cu–O distance of 2.298 Å for complex **1** are comparable to the reported examples. The seesaw structure is different from the square planar geometry of the Cu(II) center in the similar mononuclear Cu(II) complex, [Cu(HL)$_2$](ClO$_4$)$_2$, reported previously by our group.[8]

In supramolecular chemistry, weak interactions such as π–π stacking and hydrogen bonding contribute significantly to the self-assembly and molecular recognition processes. For aromatic nitrogen heterocycles, π–π interactions are commonly defined by interplanar distances of about 3.3–3.8 Å.[18] Results of a search of the Cambridge Structural Database (CSD) indicate that most π–π interactions of pyridine or quinoline rings exist with a

Table 1 Selected bond distances (Å) and bond angles (°) of complexes **1–4**

1			
Cu1–N1	1.9308(15)	Cu1–O2	2.2892(15)
Cu1–N3	1.9320(15)	Cu1–O1	2.3077(14)
N1–Cu1–N3	161.96(6)	N3–Cu1–O2	99.05(6)
N1–Cu1–O2	92.85(6)	N1–Cu1–O1	95.93(6)
N3–Cu1–O1	95.01(6)	O1–Cu1–O2	101.21(5)
2			
Cu1–N1	1.9519(10)	Cu1–N2	1.9470(10)
Cu1–O1	2.2810(9)	Cu1–O4	2.2235(9)
Cu2–N4	1.9442(11)	Cu2–N5	1.9454(11)
Cu2–O2	2.1869(9)	Cu2–O3	2.3169(9)
N1–Cu1–N2	152.47(4)	N4–Cu2–O2	102.39(4)
N2–Cu1–O4	101.29(4)	N4–Cu2–N5	150.59(4)
N2–Cu1–O1	95.20(4)	N5–Cu2–O2	99.63(4)
N1–Cu1–O1	95.40(4)	N4–Cu2–O3	91.70(4)
O4–Cu1–O1	111.73(4)	N5–Cu2–O3	99.90(4)
N1–Cu1–O4	98.22(4)	O2–Cu2–O3	107.77(4)
3			
Cu1–N1	1.935(3)	Cu1–N3	1.921(3)
Cu1···O1	2.448(25)	Cu1···O2	2.835(21)
N1–Cu1–N3	170.64(11)	N3–Cu1–O2	78.45(8)
N1–Cu1–O2	93.21(9)	N1–Cu1–O1	103.18(10)
N3–Cu1–O1	86.02(9)	O1–Cu1–O2	157.13(7)
4			
Cu1–N1	2.067(3)	Cu1–O1	2.159(2)
Cu1–N3	2.031(3)	Cu1–P1	2.1975(10)
N3–Cu1–N1	100.36(10)	N3–Cu1–P1	114.48(8)
N3–Cu1–O1	102.59(10)	N1–Cu1–P1	128.39(8)
N1–Cu1–O1	90.99(9)	O1–Cu1–P1	115.30(7)

centroid–centroid distance of about 3.80 Å and displacement angle up to 20°.[18] In complex **1**, two mononuclear units stack in an offset face-to-face fashion and the four pyridyl rings are nearly parallel to each other with an average interplanar angle of only 4.45°. Although the mean centroid–centroid distance of 5.30 Å and displacement angle of 52.3° indicate very weak interactions, the average interplanar distances of 3.43 Å and closest atom–atom contacts of 3.75 Å are still acceptable for π–π interactions.[18] The π–π stacking arrangement in **1** contributes to the large N1–Cu1–N3 bond angle of 161.96(6)°, and the coplanar structure of the pyridyl rings. This is the driving force for the formation of the seesaw structure of complex **1**. A second, weaker interaction in complex **1** is the intermolecular hydrogen bonding interactions involving amide N–H groups and the neighboring PF6⁻ anions. These hydrogen-bonding interactions extend to form 1-D chains of anionic and cationic units, and stabilize the complex in the solid state (Fig. 1).

[Cu₂(HLᴹᵉ³)₄](PF₆)₂ (2). The steric effects of substituents on the end of the amide group are essential to the structural conformation of their copper complexes. For complexes **1** and **2**, although the reaction stoichiometry is the same 2 : 1 ratio, the structures are quite different. When the methyl group in HL is replaced by a *tert*-butyl group, instead of forming a mononuclear species similar to **1**, the reaction of two equivalents of ligand HLᴹᵉ³ with one equivalent of [Cu(CH₃CN)₄]PF₆ produces a dinuclear copper complex, [Cu₂(HLᴹᵉ³)₄](PF₆)₂ (**2**, Fig. 2). For each copper ion, one HLᴹᵉ³ chelates the copper *via* the pyridyl N and amide O atoms, and the two copper ions are bridged by two additional ligands. The copper coordination sphere is made up by the amide O atom and pyridyl N atom from the bridging ligands combined

with the chelating ligand. The tetrahedral geometry of the copper centers are compressed from the N–Cu–N side, resulting in an average N–Cu–N bond angle of 151.5° that is greater than the average O–Cu–O bond angle of 109.75° (Table 1). The distorted tetrahedral structure at each copper in **2** is at least partially due to the spatial orientation of the bridging ligands, with some steric interactions between the *tert*-butyl groups and pyridyl rings.
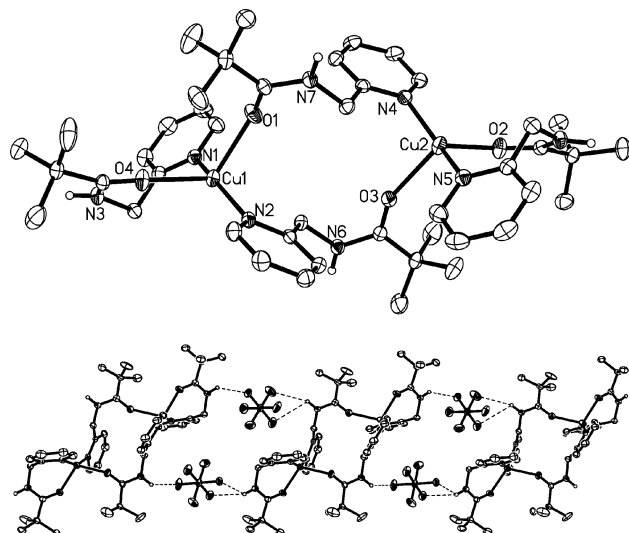

Fig. 2 X-Ray crystal structure (top) and hydrogen bonding (bottom) for [Cu₂(HLᴹᵉ³)₄](PF₆)₂ (**2**) with thermal ellipsoids at the 50% probability level.

The two bridging ligands and the two copper atoms form a fourteen-membered ring, and the Cu···Cu distance is about 6.7 Å. The hollow cavity in complex **2** clearly demonstrates that the bulky *tert*-butyl group of HLᴹᵉ³ exerts a large influence on the structure of the complex. So far, the known coordination modes of HLᴿ ligands to copper include tridentate, bidentate, and monodentate.[4,6,8,9,19] The two HLᴹᵉ³ bridging ligands in **2** exhibit a new bridging coordination mode for the pyridylmethylamide ligand system. The intermolecular interactions of the cationic portion of **2** are also interesting. The hydrogen bonding between the N–H groups of HLᴹᵉ³ and neighboring PF₆⁻ anions extend to form a double stranded polymeric ladder, which helps to stabilize complex **2** in the solid state (Fig. 2).

[Cu(HLᴾʰ³)₂]PF₆ (3). Changing the *tert*-butyl substituent to a triphenyl group can further modulate the copper center geometry and resulting structure. A 2 : 1 reaction ratio between ligand HLᴾʰ³ and [Cu(CH₃CN)₄]PF₆ leads to the formation of mononuclear **3**, which possesses a linear coordination geometry (Fig. 3 and 4). The copper center is only coordinated by the two pyridyl N atoms with a N1–Cu1–N3 bond angle of 170.64(11)° (Table 1). Although the C=O groups of the two HLᴾʰ³ ligands are oriented toward the metal center, the very bulky groups on the free amide arms prevents the formation of Cu–O bonds. The Cu···O distances of 2.45 Å and 2.84 Å in **3** suggest only weak, non-bonding interactions between the Cu and O atoms. If these long Cu···O interactions are viewed as bonds, the O1–Cu1–O2 bond angle of 157.1° suggests a four-coordinate geometry around Cu1 that is distorted square planar. The average distance of the two pyridyl N and two amide O atoms from their least squares plane is about 0.327 Å, and
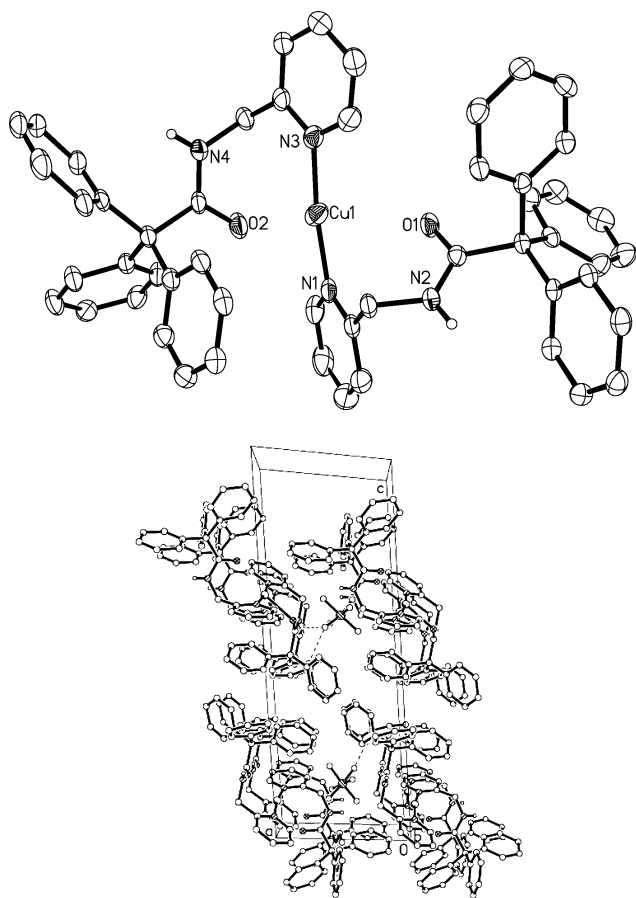
Fig. 3 X-Ray crystal structure (top) and packing structure diagram (bottom) for [Cu(HL^{Ph3})$_2$]PF$_6$ (**3**) with thermal ellipsoids at the 50% probability level.
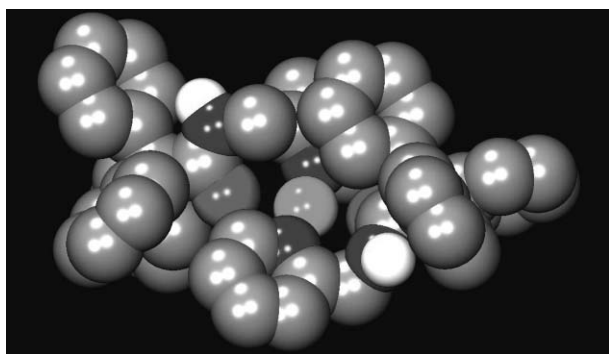

Fig. 4 Space-filling representation of [Cu(HL^{Ph3})$_2$]PF$_6$ (**3**).

the copper atom lies 0.599 Å out of this plane. Because of the spatial orientation of the two ligands and the steric effects of their bulky triphenyl groups, the dihedral angle between the two pyridyl rings is about 23.1°. The Cu1–N1 and Cu1–N3 bond distances of 1.935(3) Å and 1.921(3) Å, respectively, are longer than those previously reported for Cu(I) complexes with N donor ligand systems possessing linear geometry (1.83–1.89 Å).[11–14]

The HL^{Ph3} N–H groups are involved in intermolecular hydrogen bonding with the neighboring PF$_6^-$ anions with a H···F distance of 2.52 Å and an N–H···F angle of 122°. The space-filling diagram of the cationic portion of **3** shown in Fig. 4 clearly shows

the shielding effect provided by the two bulky triphenyl groups. The copper atom sits in the center of the cavity formed by the pyridyl aromatic rings and the amide groups, and is further encased by the six phenyl aromatic rings of HL^{Ph3}. The closest distance of a phenyl ring to the Cu(I) atom is the intermolecular Cu···phenyl ring centroid distance of about 3.34 Å. This intermolecular interaction may further protect the copper center. In the previously reported two-coordinate Cu(I) complexes with imidazole and pyrazole ligands, the steric effect of methyl, ethyl and benzyl substituents towards reactivity of Cu(I) complexes was discussed.[13,20] Complex **3** represents the first time that a triphenyl group has been used to protect the Cu(I) center successfully.

A structural comparison of complexes **1–3** clearly demonstrates that increasing steric effects can lead to the formation of different structural motifs. For ligand HL, the small methyl group allows the formation of a mononuclear Cu(I) complex, **1**, in which the pyridyl N and O atoms of both ligands coordinate to the same copper center. For ligand HL^{Me3}, instead of forming a similar mononuclear complex, the *tert*-butyl groups force the carbonyl O atom of the second ligand to bridge to another copper atom and form a dinuclear Cu(I) complex, **2**. Further increasing the steric effect by the use of the triphenyl group changes the coordination mode of the ligand from bidentate to monodentate, and the coordination of two pyridyl N atoms leads to the linear two-coordinate, mononuclear Cu(I) complex, **3**, which possesses extraordinary resistance to oxidation. Cu(I) complexes with 1,2-bis(2-pyridylethynyl)benzene ligands reported by Kawano also illustrate the importance of substituent groups on ligands in the self-organization of supramolecular structures.[21,22] Similar to complex **2**, the introduction of a bulky menthyl substituent to the 1,2-bis(2-pyridylethynyl)benzene ligand led to the formation of binuclear Cu(I) complexes with a distorted tetrahedral geometry at each copper.[21] Surprisingly, Cu(I) complexes with the less bulky, unsubstituted 1,2-bis(2-pyridylethynyl)benzene ligand produced mononuclear, linear two-coordinate species much like **3**.[22] While the specifics differ in each case, they all point to the significance of the presence and/or absence of bulky ligand substituent groups in the modulation of the metal center geometry, the structures of the complexes, and more importantly, the reactivity of the compounds.

[Cu(HL)(CH$_3$CN)(PPh$_3$)]PF$_6$ (4). The Cu(I)–phosphine complex, [Cu(HL)(CH$_3$CN)(PPh$_3$)]PF$_6$ (**4**), displays a distorted tetrahedral structure in which the copper atom is coordinated by the pyridyl N and amide O atoms from HL, the PPh$_3$ and one acetonitrile (Fig. 5). The steric crowding from the PPh$_3$ results in the elongation of the N1–Cu1 bond length (2.067 Å, Table 1) relative to complexes **1–3**. In addition, the chelate angle of HL (N1–Cu1–O1 = 90.99°) is smaller than those in complexes **1** and **2**. To our knowledge, only two examples in which a Cu(I) ion possesses the same N$_2$OP coordination environment have been reported.[23,24] The Cu–P bond distance (2.198 Å) in complex **4** is quite comparable with these two examples, but is somewhat less than that in most other previously reported Cu(I)–PPh$_3$ complexes.[25]

τ_4—A new four-coordinate geometry index

Describing the structures of four-coordinate copper(I) and copper(II) species can be a subjective endeavor, particularly when the structure is intermediate between the two most common
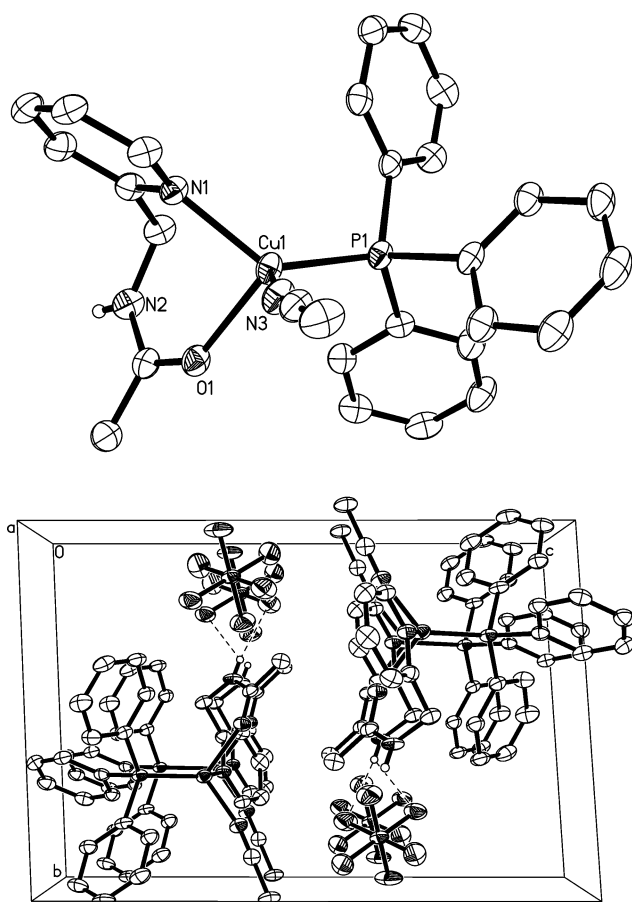
Fig. 5 X-Ray crystal structure (top) and packing structure diagram (bottom) for $[Cu(HL)(CH_3CN)(PPh_3)](PF_6)_2$ (**4**) with thermal ellipsoids at the 50% probability level.

tetrahedral	trigonal pyramidal	see-saw	square planar
T_d	C_{3v}	C_{2v}	D_{4h}
$\theta_{1-6} = 109.5°$	$\theta_{1-3} = 120°$	$\theta_1 = 180°$	$\theta_{1-2} = 180°$
	$\theta_{4-6} = 90°$	$\theta_{2-5} = 90°$	$\theta_{3-6} = 90°$
		$90 < \theta_6 < 180°$	

Scheme 2

four-coordinate geometries, tetrahedral and square planar. In copper complexes, the oxidation state plays a leading role in the geometry formed—d^{10} copper(I) complexes prefer four-coordinate tetrahedral geometries due to the lack of any ligand field stabilization energy, while d^9 copper(II) prefers square planar four-coordinate, or higher coordination numbers (square pyramidal, trigonal bipyramidal, or axially elongated six-coordinate). However, ligand constraints can play an overpowering role and force unusual geometries onto copper(I) or copper(II) centers. An excellent example of this effect is seen in the blue copper electron transfer proteins, where coordination geometry, constrained by the protein entatic state, has an influence on their redox properties. Structures of four-coordinate blue copper sites span distorted tetrahedral to trigonal pyramidal.[26]

Four-coordinate transition metal complexes and metalloprotein sites can be described in subjective terms by placing an adjective, *e.g.* "distorted", in front of one of the geometric forms shown in Scheme 2: distorted tetrahedral, distorted trigonal pyramidal, distorted seesaw, or distorted square planar. The advantages of using a more objective method of analyzing geometry have been apparent for many years. For example, Muetterties and Guggenberger proposed a quantitative measure of shape, not only for four-coordinate systems, but cluster and coordination compound classes for all *x*-atom families, that uses the dihedral angles formed by the normals to the adjacent polytopal faces.[27] Symmetry has
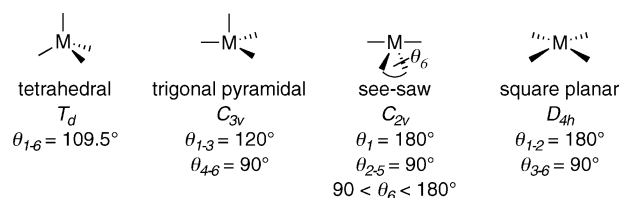
also been used to analyze tetrahedral/planar distortions in seminal work by Dunitz and coworkers,[28] and more recently by Keinan and Avnir.[29] While all of these approaches provide a wealth of information that has contributed to our understanding of correlations between structure and physical, chemical and spectroscopic properties,[30] the calculations are nontrivial at best, and in many cases quite complex. A simple metric for molecular shape in four-coordinate complexes would be tremendously useful.

The utility of a simple metric to assess molecular shape is exemplified best by the τ parameter for five-coordinate transition metal complexes (henceforth τ_5), introduced by Addison, Reedijk and coworkers in 1984 on the pages of this journal.[31] The angular structural parameter, τ_5 (eqn (1)),

$$\tau_5 = \frac{\beta - \alpha}{60} \qquad (1)$$

can be easily calculated using the two largest bond angles in the five-coordinate complex to give an index of the degree of trigonality. Hence, a trigonal bipyramidal structure with D_{3h} symmetry has a $\tau_5 = 1$, while a square pyramidal structure with C_{4v} symmetry has $\tau_5 = 0$. The simplicity and utility of the formula in its ability to gauge the structures of five-coordinate complexes with geometries not easily definable, are reflected in the use of the formula in perhaps thousands of papers.[32]

Similar formulas for four-coordinate compounds and complexes that are simpler than the aforementioned approaches have been proposed. Toyota and Oki defined the tetrahedral character (*THC*) parameter for boron complexes with coordinative $N \rightarrow B$ bonds using the three bond angles that do not include the $N \rightarrow B$ bond.[33] Later Höpfl generalized the formula to include all six bond angles (eqn (2)).[34]

$$THC_{DA} = \left(1 - \frac{\sum_{n=1-6} |109.5° - \theta_n|}{90°}\right) \times 100 \qquad (2)$$

The THC_{DA} index is useful for the analysis of the tetrahedral and trigonal pyramidal extremes expected for $N \rightarrow B$ complexes. A perfect tetrahedral structure generates $THC_{DA} = 100$ while a perfect trigonal pyramidal structure generates $THC_{DA} = 0$. However, other four-coordinate geometries relevant to transition metal chemistry, *e.g.* square planar and seesaw, produce negative values (Table 2). A formula proposed by Holland and coworkers for the analysis of the belt iron atoms of the iron–molybdenum cofactor of nitrogenase can also be effectively used to analyze structures between tetrahedral and trigonal pyramidal.[35]

Since the THC_{DA} formula and Holland's formula were designed for species with structures intermediate between T_d and C_{3v}, the utility for the analysis of four-coordinate transition metal complexes is limited. Furthermore, the formulas require multiple steps and, while a simple matter for a computer program to

This journal is © The Royal Society of Chemistry 2007

Table 2 Four-coordinate geometry indices for ideal geometrical shapes

	τ_4	$THC_{DA}/100^{34}$	$FCGP/100^{36}$
Tetrahedral (T_d)	1.00	1.00	0.00
Trigonal pyramidal (C_{3v})	0.85	0.00	1.00
Seesaw (C_{2v}, $\theta_6 = 90°$)	0.64	−0.87	1.00
Seesaw (C_{2v}, $\theta_6 = 109.5°$)	0.50	−0.65	0.70
Seesaw (C_{2v}, $\theta_6 = 154.4°$)	0.18	−1.15	0.00
Seesaw (C_{2v}, $\theta_6 = 170°$)	0.07	−1.32	−0.24
Square planar (D_{4h})	0.00	−1.43	−0.40

calculate, are significantly more complex than the parameter we propose.

Another formula designed for main group complexes was proposed by Hutchison and coworkers.[36] Their so-called four-coordinate geometric parameter (*FCGP*) defines "faces" as the sum of the angles involved in each polytopal face of the four-coordinate structure. Inserting the largest face value and the sum of the remaining angles into the formula produces the *FCGP* parameter (eqn (3)).

$$FCGP = \left[\frac{\text{largest face} - (\sum \text{remaining } 3°)(5.61) + 1515.15}{360}\right] \times 100 \quad (3)$$

Serious drawbacks with the *FCGP* parameter include the need to visually assign the polytopal faces (*e.g.* one cannot generate the *FCGP* from a table of the six θ angles without visually inspecting the structure), and the illogical range of negative values for structures between D_{4h} and C_{2v} (see Table 2). The authors designed the *FCGP* parameter to deal specifically with four-coordinate Group 13 compounds ranging from tetrahedral to trigonal pyramidal, so the nonsensical results for other geometries make it unacceptable for transition metal four-coordinate species with a wider range of structural possibilities.

We propose a very simple geometry index for four-coordinate complexes, τ_4 (eqn (4)),

$$\tau_4 = \frac{360° - (\alpha + \beta)}{141°} \quad (4)$$

inspired by Addison and Reedijk's five-coordinate τ_5 index. The formula for our four-coordinate τ_4 index is simply the sum of angles α and β—the two largest θ angles in the four-coordinate species—subtracted from 360°, all divided by 141°. The calculation can be done with pen and paper or on a calculator without visually analyzing the structure, simply by choosing the two largest θ values from a table of bond angles. The values of τ_4 will range from 1.00 for a perfect tetrahedral geometry, since $360 - 2(109.5) = 141$, to zero for a perfect square planar geometry, since $360 - 2(180) = 0$ (see Table 2). Intermediate structures, including trigonal pyramidal and seesaw, fall within the range of 0 to 1.00.

The τ_4 parameter is particularly good for four-coordinate transition metal complexes since square planar and tetrahedral geometries are the extremes. A comparison of τ_4, THC_{DA}, and *FCGP* are summarized in Tables 2 and 3. Table 2 compares the values of the three parameters for ideal geometries. The geometries, shown graphically in Scheme 2, proceed from tetrahedral to square planar. τ_4 nicely tracks from 1.00 for tetrahedral, to 0.85 for a perfect trigonal pyramid, through a series of values for C_{2v} seesaw structures that get smaller as the angle θ_6 (see Scheme 2) gets larger. When θ_6 is 180°, the geometry is square planar, and τ_4 is 0.00. From Table 2 it can be seen that THC_{DA} also decreases

as structures change from tetrahedral to square planar, but not smoothly. There is a sharp decrease going from trigonal pyramidal to seesaw with $\theta_6 = 90°$, followed by an anomalous increase before decreasing again. This is an inherent flaw in the THC_{DA} formula when used for transition metal complexes. *FCGP* starts at 0.00 for tetrahedral and increases to 1.00 for trigonal pyramidal, but then decreases again. Several disparate structures in Table 2 have the same *FCGP* values: tetrahedral and seesaw with $\theta_6 = 154.4°$ have *FCGP* = 0.00, and trigonal pyramidal and seesaw with $\theta_6 = 90°$ have *FCGP* = 1.00. Furthermore, *FCGP* values greater than 1.00 are possible (*vide infra*, see Table 3).

Four-coordinate structural parameters for complexes **1**–**4** are listed in Table 3, along with parameters for other four-coordinate copper and transition metal complexes. The τ_4 parameters nicely compliment and support the structural descriptions made previously in this paper on the basis of the bond angles and visual inspection of the structures. Complexes **1** and **2**, with structures described previously in this paper as seesaw, have τ_4 values of ∼0.70 ± 0.02, which fits with a seesaw description. Complex **3**, which was described as linear two-coordinate, has Cu⋯O interactions that are close to being within bonding range. When the Cu–O bonds are included, the four-coordinate geometry around the copper is close to square planar, and the τ_4 value of 0.23 accurately reflects this description. Complex **4**, which is closer to trigonal pyramidal, has a τ_4 value of 0.82, supporting an assignment of distorted trigonal pyramidal geometry. Other four-coordinate copper complexes that were described earlier in the paper in comparison to **1**–**4**, as well as a representative sampling of other four-coordinate transition metal complexes, are also summarized in Table 3, illustrating the universality of τ_4. Table 3 also illustrates the limitations inherent to the THC_{DA} and *FCGP* parameters.

Experimental

General

All reagents were purchased from commercial suppliers and used as received without further purification, unless otherwise stated. Ligands *N*-(2-pyridylmethyl)acetamide (HL), 2,2-dimethyl-*N*-(2-pyridylmethyl)propionamide (HL^Me3), and 2,2,2-triphenyl-*N*-(2-pyridylmethyl)acetamide (HL^Ph3) were synthesized according to procedures previously reported.[4,6] All solvents were dried under nitrogen using standard methods and distilled before use. FTIR spectra were collected on a NEXUS 470 FTIR spectrometer using the KBr pellet technique. Mass spectra were recorded on a Q-TOF quadrupole time-of-flight mass spectrometer (Micromass, Manchester, UK) equipped with a Z-spray electrospray ionization (ESI) source. ^{1}H NMR spectra were recorded on a Varian 300 MHz spectrometer using deuterated solvent as an internal standard. Elemental analyses were carried out by Atlantic Microlabs, Norcross, GA. Electrochemical measurements were performed with a C-3 CV-50W instrument (Bioanalytical Systems Inc.). Ferrocene (Fc) was added to the solution as an internal standard and potentials are reported *vs.* Ag/AgCl and the potentials of complexes (∼+0.46 V *vs.* Ag/AgCl).[42] Cyclic voltammetry was performed on complexes **1**–**3** in CH_2Cl_2 or CH_3CN solutions containing 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte at a Pt disk (3 mm diameter) working electrode and Ag/AgCl reference electrode.

Table 3 Four-coordinate geometry indices for **1–4** and representative examples from the literature

	Geometry[a]	τ_4	$THC_{DA}/100^{34}$	$FCGP/100^{36}$	Reference
1	Seesaw	0.69	−0.29	0.64	This work
2 (Cu1)	Seesaw	0.68	−0.03	0.48	This work
2 (Cu2)	Seesaw	0.72	0.03	0.53	This work
3	Dist. square planar	0.23	−1.07	0.09	This work
4	Dist. trigonal pyramidal	0.82	0.29	0.35	This work
$(Et_4N)[Fe(S^tBu)_3(NO)]$	Tetrahedral	0.93	0.74	0.06	37
$[Cu_2(XYL\text{-}O\text{–})(PPh_3)_2]PF_6{}^b$	Psuedotetrahedral	0.81, 0.83	0.31, 0.30	0.36, 0.39	23
Psuedoazurin	Dist. tetrahedral	0.79	0.28	0.39	38
Azurin	Trigonal pyramidal	0.73	−0.03	0.81	39
$[Cu(Tpms)(PPh_3)]^c$	Trigonally dist. tetrahedral	0.67	−0.35	0.81	24
$[Cu(10\text{-methylisoalloxazine})_2]ClO_4$	None given	0.60	−0.61	0.73	15
$[Cu((C_5H_5)Fe(C_5H_4CH_2N(CH_3)(CH_2)_2\text{–}))_2]OTf$	Dist. tetrahedral	0.56	−0.90	1.16	17
$[Cu_2(\mathbf{L2})_2](PF_6)_2{}^d$	Dist. tetrahedral	0.55	−0.76	0.68	21
$[\{[2,6\text{-}(i\text{-}Pr)_2PhN=C(Me)]_2(C_5H_3N)\}Mn(CH_2SiMe_3)][Li(OEt_2)_4]$	Dist. square planar	0.47	−0.64	0.58	40
$[Au^I(\mu\text{-}\{CH_2\}_2PPh_2)_2Au^{III}(C{\equiv}CPh)_2]$	Square planar	0.03	−1.39	−0.36	41

[a] Geometry as described in the text of this paper or the paper from which the structural data was retrieved. [b] XYL-O– is the deprotonated form of XYL–OH. XYL–OH is bis(2-(2-pyridyl)ethyl)ethyl)amine). [c] Tpms is tris(pyrazolyl)methanesulfonate. [d] **L2** is 1,2-bis(2-pyridylethynyl)benzene.

Syntheses

[Cu(HL)$_2$]PF$_6$ (1). A solution of HL (0.075 g, 0.5 mmol) in CH_2Cl_2 (2 mL) was added to a stirred solution of $[Cu(CH_3CN)_4]PF_6$ (0.093 g, 0.25 mmol) in CH_2Cl_2 (2 mL). The reaction was stirred for 20 h, during which the color changed to light yellow. The solution was filtered and diffusion of diethyl ether into the filtrate produced crystals suitable for crystallographic characterization (0.104 g, 82.0%). Found: C, 38.0; H, 3.95; N, 11.0. Calc. for $C_{16}H_{20}CuF_6N_4O_2P$: C, 37.8; H, 4.0; N, 11.0%. FTIR (KBr): 3445, 3425, 3285, 3062, 1645, 1603, 1539, 1482, 1440, 1373, 1358, 1292, 1234, 1032, 842, 834, 765, 751, 615, 559, 510 cm^{-1}. ^{1}H NMR (300 MHz, DMSO): δ = 1.94 (s, 3H); 4.49 (s, 2H); 7.47 (m, 3H), 7.95 (t, 1H); 8.63 (s, 1H) ppm. ESI-MS (CH$_3$CN): m/z = 363.1 [Cu(HL)$_2$]$^+$; 254.1 [Cu(HL)CH$_3$CN]$^+$; 213.0 [Cu(HL)]$^+$.

[Cu$_2$(HL^{Me3})$_4$](PF$_6$)$_2$ (2). A solution of HL^{Me3} (0.192 g, 1.0 mmol) in CH_2Cl_2 (1 mL) was added to a stirred solution of $[Cu(CH_3CN)_4]PF_6$ (0.186 g, 0.5 mmol) in CH_2Cl_2 (1 mL). The reaction was stirred for 4 h, during which the color changes to light yellow. The solution was filtered and layering of diethyl ether onto the filtrate produced light yellow crystals suitable for crystallographic characterization (0.263 g, 89.0%). Found: C, 45.1; H, 5.55; N, 9.6. Calc. for $C_{44}H_{64}Cu_2F_{12}N_8O_4P_2$: C, 44. 6; H, 5.4; N, 9.45%. FTIR (KBr): 3447, 2970, 2873, 1628, 1605, 1571, 1525, 1481, 1444, 1408, 1367, 1294, 1227, 1203, 1160, 1108, 1058, 1013, 992, 828, 772, 740, 716, 625, 558, 530, 481, 445, 423 cm^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 1.16–1.24 (m, 9H); 4.83 (d, 2H); 7.08 (s, 1H); 7.51 (t, 1H); 7.69 (d, 1H); 8.03 (t, 1H); 8.82 (d, 1H) ppm. ESI-MS (CH$_3$CN): m/z = 446.2 [Cu(HL^{Me3})$_2$]$^+$; 255.1 [Cu(HL^{Me3})]$^+$; 193.13 [H$_2$L^{Me3}]$^+$.

[Cu(HL^{Ph3})$_2$]PF$_6$ (3). A solution of HL^{Ph3} (0.0946 g, 0.25 mmol) in CH_2Cl_2 (2 mL) was added to a stirred solution of $[Cu(CH_3CN)_4]PF_6$ (0.0465 g, 0.125 mmol) in CH_2Cl_2 (2 mL). The reaction was stirred for 24 h, during which the color changed to light yellow. The solution was filtered and layering of diethyl ether onto the filtrate produced colorless crystals suitable for crystallographic characterization (0.085 g, 70.4%). Found: C, 64.55; H, 4.7; N, 6.0. Calc. for $C_{52}H_{44}CuF_6N_4O_2P$: C, 64.7; H, 4.6; N, 5.8%. FTIR (KBr): 3418, 3057, 3032, 2940, 1635, 1608, 1571, 1490, 1444, 1356, 1324, 1258, 1243, 1226, 1188, 1161, 1109, 1085, 1066, 1034, 1001, 974, 934, 836, 767, 740, 700, 671, 638, 558, 521, 431 cm^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 4.51 (d, 2H); 7.05 (s, 1H); 7.08 (s, 1H); 7.20 (s, 1H); 7.31 (m, 15 H); 7.64 (t, 1H); 8.41 (d, 1H) ppm. ESI-MS (CH$_3$CN): m/z = 819.4 [Cu(HL^{Ph3})$_2$]$^+$; 482.2 [Cu(HL^{Ph3})CH$_3$CN]$^+$; 441.2 [Cu(HL^{Ph3})]$^+$; 379.2 [H$_2$L^{Ph3}]$^+$.

[Cu(HL)(CH$_3$CN)(PPh$_3$)]PF$_6$ (4). A solution of HL (0.075 g, 0.5 mmol) in CH_2Cl_2 (1 mL) was added to a stirred solution of $[Cu(CH_3CN)_4]PF_6$ (0.186 g, 0.5 mmol) in CH_2Cl_2 (2 mL). A solution of PPh$_3$ (0.1311 g, 0.5 mmol) in 1 mL CH$_2$Cl$_2$ (1 mL) was subsequently added to the mixture. The reaction was stirred for 14 h, during which the color changed to light yellow. The solution was filtered and diffusion of diethyl ether into the filtrate produced colorless crystals suitable for crystallographic characterization (0.231 g, 83.8%). Found: C, 47.4; H, 4.1; N, 5.7. Calc. for $C_{29}H_{30}Cl_2CuF_6N_3OP_2$: C, 46.6; H, 4.05; N, 5.6%. FTIR (KBr): 3426, 3056, 1649, 1603, 1539, 1480, 1435, 1373, 1295, 1234, 1183, 1158, 1095, 1056, 1028, 998, 841, 773, 748, 695, 641, 607, 558, 525, 507, 443 cm^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 1.96 (m, 6H); 4.41 (d, 2H); 6.99 (s, 1H); 7.24 (t, 1H); 7.42 (m, 16 H); 7.73 (t, 1H); 8.53 (s, 1H) ppm. ESI-MS (CH$_3$CN): m/z = 587.1 [Cu(PPh$_3$)$_2$]$^+$; 475.1 [Cu(HL)(PPh$_3$)]$^+$; 366.0 [Cu(CH$_3$CN)(PPh$_3$)]$^+$; 254.0 [Cu(HL)(CH$_3$CN)]$^+$; 213.0 [Cu(HL]$^+$.

X-Ray crystal structure determination

Single crystals of **1–4** were obtained by vapor diffusion or layering of Et$_2$O into solutions of the complex. Data for **1–4** were collected on a Bruker Apex CCD area detector diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. For complexes **1–4**, cell parameters were determined from a non-linear least squares fit of the data. The data of these four complexes were corrected for absorption by the semi-empirical method. The structures were solved by direct methods by use of the SHELXTL program, and refined by full-matrix least-squares on F^2 by use of all reflections.[43] Hydrogen atom positions were

Table 4 Summary of crystal data and refinement parameters for complexes **1–4**

	1	**2**	**3**	**4**
Formula	$C_{16}H_{20}CuF_6N_4O_2P$	$C_{44}H_{64}Cu_2F_{12}N_8O_4P_2$	$C_{52}H_{44}CuF_6N_4O_2P$	$C_{29}H_{30}Cl_2CuF_6N_3OP_2$
M	508.87	1186.05	965.42	746.94
T/K	87(2)	110(2)	294(2)	97(2)
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	9.5739(16)	15.2619(8)	9.336(3)	8.008(2)
b/Å	8.5420(14)	19.9179(11)	9.732(3)	11.738(4)
c/Å	25.145(4)	18.4954(10)	25.406(8)	17.289(5)
α/°	90	90	82.221(5)	86.917(5)
β/°	99.355(5)	110.1750(10)	81.962(5)	89.583(5)
γ/°	90	90	74.409(5)	84.150(5)
Z	4	4	2	2
V/Å³	2029.0(6)	5277.4(5)	2190.0(12)	1614.3(8)
ρ_{calcd}/g cm³	1.666	1.493	1.464	1.537
μ/mm⁻¹	1.230	0.957	0.609	1.005
$R1$ [$I > 2\sigma(I)$]	0.0259	0.0271	0.0527	0.0474
$wR2$[$I > 2\sigma(I)$]	0.0733	0.0766	0.1376	0.1268
GOF on F^2	1.007	1.025	1.009	1.050

initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. In complexes **1** and **3**, the PF_6^- anion was disordered and was modeled in three and two orientations, respectively, and restraints on the positional and displacement parameters of the anion were required. For complex **1**, the occupancies of the anion were refined to 0.403(8), 0.308(4), and 0.289(7) for the unprimed, primed, and double primed atoms. For complex **3**, the occupancies of the anion were refined 0.882(3) and 0.118(3) for the unprimed and primed atoms. In addition, for complex **3**, a large residual peak was located near the metal in the final difference map that is believed to be due to a small contribution of complete translational disorder of the cation. Crystal data for **1–4** are summarized in Table 4, and selected bond lengths and angles are listed in Table 2.

CCDC reference numbers 627606 (**1**), 627605 (**2**), 627607 (**3**), and 627608 (**4**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617136b

Conclusions

Four new Cu(I) complexes with a set of pyridylmethylamide ligands, HL^R, were synthesized and characterized by X-ray crystallography, NMR, FT-IR, ESI-MS and cyclic voltammetry. A new bidentate bridging coordination mode for HL^R is observed in complex **2**, where two HL^{Me3} ligands bridge between two copper centers. The ligand, or more specifically the functional substituent group R, influences the chemical and electrochemical properties of **1–4**. Complexes **1** and **2** are very reactive with oxygen, and the cyclic voltammetry shows irreversible oxidation processes at 0.54 V and 0.69 V, respectively. In contrast, complex **3** is unusually inert towards oxidation, and no oxidation waves are observed in the range 0 to +1.5 V. The remarkable stability of **3** is attributed to the protection provided by the bulky triphenyl group. The substituent group R on HL^R also influences the metal center geometry of these complexes. The steric effect of the R group, which increases in the order of H < Me$_3$ < Ph$_3$, contributes to the variety of copper center geometries, ranging from distorted tetrahedral geometry (**4**) to seesaw (**1**, **2**) to linear geometry (**3**). Consequently, the substituents

are crucial to the formation of different molecular structures of these copper complexes. To assist in the structural analysis of **1–4**, the new four-coordinate metrical parameter τ_4 was proposed. Like its five-coordinate inspiration,[31] τ_4 is a simple formula that can be used to gauge the geometries of four-coordinate transition metal complexes and main group compounds.

References

1 D. S. Cati and H. Stoeckli-Evans, *Acta Crystallogr., Sect. E*, 2004, **60**, M174–M176; D. Z. Gao, H. K. Lin and S. R. Zhu, *Acta Crystallogr., Sect. E*, 2005, **61**, M2359–M2361; B. W. Lee, K. S. Min and M. K. Doh, *Inorg. Chem. Commun.*, 2002, **5**, 163–165; M. Nonoyama, *Inorg. Chim. Acta*, 1975, **13**, 5–10; M. Nonoyama, S. Tomita and K. Yamasaki, *Inorg. Chim. Acta*, 1975, **12**, 33–37; J. M. Rowland, M. M. Olmstead and P. K. Mascharak, *Inorg. Chem.*, 2000, **39**, 5326–5332; P. J. Toscano, K. A. Belsky, L. M. Engelhardt, K. J. Fordon and A. H. White, *Inorg. Chem.*, 1990, **29**, 1357–1359; P. J. Toscano, K. A. Belsky, T.-C. Hsieh, T. Nicholson and J. Zubieta, *Polyhedron*, 1991, **10**, 977–991; P. J. Toscano, K. J. Fordon, D. Macherone, S. Liu and J. Zubieta, *Polyhedron*, 1990, **9**, 2375–2383; N. Tounsi, L. Dupont, A. Mohamadou, C. Cadiou, M. Aplincourt, R. Plantier-Royon, F. Massicot and C. Portella, *New J. Chem.*, 2004, **28**, 785–792.
2 K. Uemura, S. Kitagawa, K. Fukui and K. Saito, *J. Am. Chem. Soc.*, 2004, **126**, 3817–3828; K. Uemura, S. Kitagawa, M. Kondo, K. Fukui, R. Kitaura, H.-C. Chang and T. Mizutani, *Chem.–Eur. J.*, 2002, **8**, 3587–3600.
3 T. C. Harrop, M. M. Olmstead and P. K. Mascharak, *Inorg. Chem.*, 2005, **44**, 9527–9533; S. R. Zhu, W. W. Brennessel, R. G. Harrison and L. Que, *Inorg. Chim. Acta*, 2002, **337**, 32–38.
4 E. L. Klein, M. A. Khan and R. P. Houser, *Inorg. Chem.*, 2004, **43**, 7272–7274.
5 D. S. Cati, J. Ribas, J. Ribas-Arino and H. Stoeckli-Evans, *Inorg. Chem.*, 2004, **43**, 1021–1030; J. Hausmann, G. B. Jameson and S. Brooker, *Chem. Commun.*, 2003, 2992–2993; Z. Q. Qin, M. C. Jennings, R. J. Puddephatt and K. W. Muir, *Inorg. Chem.*, 2002, **41**, 5174–5186.
6 U. Pal Chaudhuri, L. R. Whiteaker, L. Yang and R. P. Houser, *Dalton Trans.*, 2006, 1902–1908.

7 J. T. Michels, B. G. O'Malley, E. L. Klein, L. Yang, A. Grohmann and R. P. Houser, *Acta Crystallogr., Sect. E*, 2005, **61**, O3834–O3836.

8 A. Mondal, Y. Li, M. A. Khan, J. H. Ross and R. P. Houser, *Inorg. Chem.*, 2004, **43**, 7075–7082.

9 L. Yang and R. P. Houser, *Inorg. Chem.*, 2006, **45**, 9416–9422.

10 L. M. Engelhardt, C. Pakawatchai, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1985, 117–123; A. Habiyakare, E. A. C. Lucken and G. Bernardinelli, *J. Chem. Soc., Dalton Trans.*, 1991, 2269–2273; D. Hagrman, C. Sangregorio, C. J. O'Connor and J. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1998, 3707–3709; P. C. Healy, J. D. Kildea, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1989, **42**, 115–136; T. Kawano, J. Kuwana and I. Ueda, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 789–797; B. Liu and Q. Yuan, *Inorg. Chem. Commun.*, 2005, **8**, 1022–1024; S. Lopez and S. W. Keller, *Inorg. Chem.*, 1999, **38**, 1883–1888; R. E. Marsh, *Acta Crystallogr., Sect. B*, 1997, **53**, 317–322; M. Munakata, S. Kitagawa, H. Shimono and H. Masuda, *Inorg. Chim. Acta*, 1989, **158**, 217–220; M. Munakata, M. Maekawa, S. Kitagawa, M. Adachi and H. Masuda, *Inorg. Chim. Acta*, 1990, **167**, 181–188; Y. P. Ren, X. J. Kong, L. S. Long, R. B. Huang and L. S. Zheng, *Cryst. Growth Des.*, 2006, **6**, 572–576; X.-S. Wang, H. Zhao, Z.-R. Qu, Q. Ye, J. Zhang, R.-G. Xiong, X.-Z. You and H.-k. Fun, *Inorg. Chem.*, 2003, **42**, 5786–5788.

11 S. Banthia and A. Samanta, *Inorg. Chem.*, 2004, **43**, 6890–6892.

12 I. Sanyal, K. D. Karlin, R. W. Strange and N. J. Blackburn, *J. Am. Chem. Soc.*, 1993, **115**, 11259–11270.

13 T. N. Sorrell and D. L. Jameson, *J. Am. Chem. Soc.*, 1983, **105**, 6013–6018.

14 L. Le Clainche, M. Giorgi and O. Reinaud, *Eur. J. Inorg. Chem.*, 2000, 1931–1933.

15 M. W. Yu and C. J. Fritchie, *J. Biol. Chem.*, 1975, **250**, 946–951.

16 M. A. S. Goher, F. A. Mautner, A. K. Hafez and A. A. Youssef, *Polyhedron*, 2003, **22**, 515–520; L. P. Wu, T. Yamamoto, T. KurodaSowa, M. Maekawa, Y. Suenaga and M. Munakata, *J. Chem. Soc., Dalton Trans.*, 1996, 2031–2037.

17 C. DelavauxNicot, A. Bigeard, A. Bousseksou, B. Donnadieu and G. Commenges, *Inorg. Chem.*, 1997, **36**, 4789–4797.

18 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885–3896.

19 L. R. Whiteaker, U. Pal Chaudhuri, D. R. Powell and R. P. Houser, *Acta Crystallogr., Sect. E*, 2006, **62**, o3337–o3338; L. R. Whiteaker, U. Pal Chaudhuri, D. R. Powell and R. P. Houser, *Acta Crystallogr., Sect. E*, 2006, **62**, o3339–o3340.

20 F. Khajenhouri, S. Motallebi and E. A. C. Lucken, *J. Mol. Struct.*, 1995, **345**, 277–281.

21 T. Kawano, J. Kuwana, C. X. Du and I. Ueda, *Inorg. Chem.*, 2002, **41**, 4078–4080.

22 T. Kawano, J. Kuwana, T. Shinomaru, C. X. Du and I. Ueda, *Chem. Lett.*, 2001, 1230–1231.

23 K. D. Karlin, R. W. Cruse, Y. Gultneh, A. Farooq, J. C. Hayes and J. Zubieta, *J. Am. Chem. Soc.*, 1987, **109**, 2668–2679.

24 C. Santini, M. Pellei, G. G. Lobbia, A. Cingolani, R. Spagna and M. Camalli, *Inorg. Chem. Commun.*, 2002, **5**, 430–433.

25 D. G. Cuttell, S. M. Kuang, P. E. Fanwick, D. R. McMillin and R. A. Walton, *J. Am. Chem. Soc.*, 2002, **124**, 6–7; S. L. Howell, B. J. Matthewson, M. I. J. Polson, A. K. Burrell and K. C. Gordon, *Inorg. Chem.*, 2004, **43**, 2876–2887; W. L. Jia, T. McCormick, Y. Tao, J. P. Lu and S. N. Wang, *Inorg. Chem.*, 2005, **44**, 5706–5712; L. Kovbasyuk, H. Pritzkow and R. Kramer, *Eur. J. Inorg. Chem.*, 2005, 894–900; S. M. Kuang, D. G. Cuttell, D. R. McMillin, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 2002, **41**, 3313–3322; P. Manikandan, B. Varghese and P. T. Manoharan, *J. Chem. Soc., Dalton Trans.*, 1996, 371–376; M. Schwach, H. D. Hausen and W. Kaim, *Inorg. Chem.*, 1999, **38**, 2242–2243.

26 E. I. Solomon, *Inorg. Chem.*, 2006, **45**, 8012–8025.

27 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748–1756.

28 P. Murrayrust, H. B. Burgi and J. D. Dunitz, *J. Am. Chem. Soc.*, 1975, **97**, 921–922.

29 S. Keinan and D. Avnir, *J. Chem. Soc., Dalton Trans.*, 2001, 941–947; S. Keinan and D. Avnir, *Inorg. Chem.*, 2001, **40**, 318–323.

30 H. B. Burgi and J. D. Dunitz, in *Structure Correlation*, ed. H. B. Burgi and J. D. Dunitz, VCH, Weinheim, 1994, vol. 1, pp. 163–204; T. Auf der Heyde, in *Structure Correlation*, ed. H. B. Burgi and J. D. Dunitz, VCH, Wienheim, 1994, vol. 1, pp. 337–368.

31 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.

32 As of November 2006, reference 31 had been cited 1445 times (ISI Web of Knowledge: Science Citation Index Expanded, http://portal.isiknowledge.com, 15 November 2006). While every citation is not necessarily associated with the τ_5 index, it is also likely that many papers have used the τ_5 index without citing the paper.

33 S. Toyota and M. Oki, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1832–1840.

34 H. Höpfl, *J. Organomet. Chem.*, 1999, **581**, 129–149.

35 J. Vela, S. Stoian, C. J. Flaschenriem, E. Munck and P. L. Holland, *J. Am. Chem. Soc.*, 2004, **126**, 4522–4523; J. Vela, J. Cirera, J. M. Smith, R. J. Lachiocotte, C. J. Flaschenriem, S. Alvarez and P. L. Holland, *Inorg. Chem.*, 2007, DOI: 10.1021/ic0609148.

36 A. R. Hutchison, A. Mitra and D. A. Atwood, *Main Group Chem.*, 2005, **4**, 187–200.

37 T. C. Harrop, D. T. Song and S. J. Lippard, *J. Am. Chem. Soc.*, 2006, **128**, 3528–3529.

38 K. Petratos, Z. Dauter and K. S. Wilson, *Acta Crystallogr., Sect. B*, 1988, **44**, 628–636.

39 E. N. Baker, *J. Mol. Biol.*, 1988, **203**, 1071–1095.

40 D. Reardon, G. Aharonian, S. Gambarotta and G. P. A. Yap, *Organometallics*, 2002, **21**, 786–788.

41 L. A. Mendez, J. Jimenez, E. Cerrada, F. Mohr and M. Laguna, *J. Am. Chem. Soc.*, 2005, **127**, 852–853.

42 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.

43 G. M. Sheldrick, *SHELXTL Version 6.10 Reference Manual*, Bruker AXS Inc., Madison, Wisconsin, USA, 2000; G. M. Sheldrick, *International Tables for Crystallography*, Kluwer, Boston, 1995, vol. C.