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Di-μ-chlorido-bis({2-[1-(2-pyridylethylimino)ethyl]pyrrolato-κ^3N,N',N''}copper(II))

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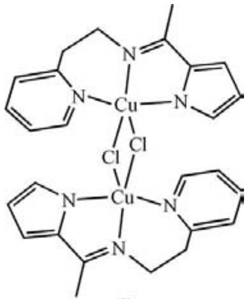
The title compound, $[Cu_2(C_{13}H_{14}N_3)_2Cl_2]$, is a neutral dimeric copper(II) complex. The two Cu^{II} atoms are asymmetrically bridged by two chloride ions. Each Cu^{II} atom is also bound to the three N atoms of a deprotonated tridentate Schiff base ligand, giving a distorted square-pyramidal N_3Cl_2 coordination environment overall. The dinuclear complex lies across an inversion centre in the space group $P\overline{1}$. This work demonstrates the effect of ligand flexibility and steric constraints on the structures of copper(II) complexes.

Comment

In recent years, much attention has been paid to the complexes of a wide range of acyclic Schiff base ligands, in particular pyridine-containing systems. However, much less is known about complexes of the pyrrole analogues of such ligands, despite their potentially interesting similarities to porphyrins. Recently, we have focused on the copper(II) chemistry of *N*,*N*′,*N*″-tridentate Schiff base ligands, in particular mixed pyrrole–imine–pyridine ligands. Ligands L_1^-, L_2^- and L_3^-, the deprotonated forms of 2-(2-pyridyl)-*N*-(1*H*-pyrrol-2-ylmethylene)ethanamine (HL_1), *N*-[1-(1*H*-pyrrol-2-yl)ethylidene](2-pyridyl)methanamine (HL_2) and 2-(2-pyridyl)-*N*-[1-(1*H*-pyrrol-2-yl)ethylidene]ethanamine (HL_3), are of this type.

These ligands are closely related to pyridine–imine–pyridine ligands, which have been well studied (Arriortua *et al.*, 1991; Cortés *et al.*, 1992, 1995; Garland *et al.*, 1996; Larramendi *et al.*, 1991, 1992; Rojo *et al.*, 1990). In our previous work using ligands L_1^- and L_2^-, monomeric, dimeric and one-dimensional chain polymeric copper(II) complexes have been synthesized (Li, Moubaraki *et al.*, 2008; Li, Zhao *et al.*, 2008), depending on the nature of the ligand and the choice of halide or pseudohalide coligand. Among these complexes, the dimeric and one-dimensional chain polymeric complexes exhibit weak antiferromagnetic exchange.

These examples, together with those obtained with the pyridine–imine–pyridine ligands mentioned above, indicate that the use of less flexible tridentate ligands tends to result in the formation of monomeric and dimeric complexes, while the use of more flexible tridentate ligands tends to give rise to dimeric or polymeric complexes. Ligand L_3^- is very closely related to L_1^- and L_2^-, with its flexibility being similar to that of L_1^- but greater than that of L_2^-. In addition, attachment of a methyl substituent to the C atom of the imino C=N bond of L_1^-, which results in L_3^-, imposes some steric constraints on L_3^-. These differences in ligand flexibility and steric constraints are expected to influence the structural properties of the complexes of this ligand. The title compound, $[Cu_2(L_3)_2(\mu\text{-}Cl)_2]$, (I), has been prepared using L_3^- as the next example within the framework of our ongoing studies. We report here the crystal structure of (I) and compare it with those of the copper(II) complexes of ligands L_1^-, L_2^- and some other previously reported closely related tridentate ligands.



(I)

The asymmetric unit of (I) (Fig. 1) contains one-half of the neutral dimeric molecule; the other half is generated by a centre of inversion. The two Cu^{II} atoms are asymmetrically bridged by two chloride ions. Each Cu atom is also bound to the three N atoms (pyrrole, pyridine and imine) of the tridentate ligand, L_3^-, giving an N_3Cl_2 coordination environment overall. The coordination geometry about each Cu^{II} ion can be described as a distorted square pyramid according to the τ value of 0.14 (Addison *et al.*, 1984). The basal coordination sites are occupied by the three N atoms of L_3^- and one bridging chloride ion, Cl1. The apical position is occupied by the second bridging chloride ion, Cl1^i [symmetry code: (i) $-x+1, -y, -z$]. The apical Cu—Cl bond is significantly longer than the basal Cu—Cl bond (Table 1), a feature which appears frequently in square-pyramidal copper(II) complexes (Urtiaga *et al.*, 1996; Rojo *et al.*, 1987). The coordination mode and geometry about the Cu^{II} ions in (I) are very similar to those observed for the Cu^{II} ions in the analogous doubly halide-bridged dimers of ligand L_1^-, *viz.* $[Cu_2(L_1)_2(\mu\text{-}X)_2]$ [$X = Cl^-$, (II); $X = Br^-$, (III)] (Li, Moubaraki *et al.*, 2008). However, the low completeness of the data set for complex (II) prevents detailed comparison of the geometric parameters between structures (I) and (II). On the other hand, the chlorido-copper(II) complex of ligand L_2^- is a monomer, $[Cu(L_2)Cl]$, (IV), and the central Cu^{II} ion is bound to the three N atoms of L_2^- and to one Cl^- ion in a square-planar N_3Cl coordination (Li, Zhao *et al.*, 2008). So the coordination mode and

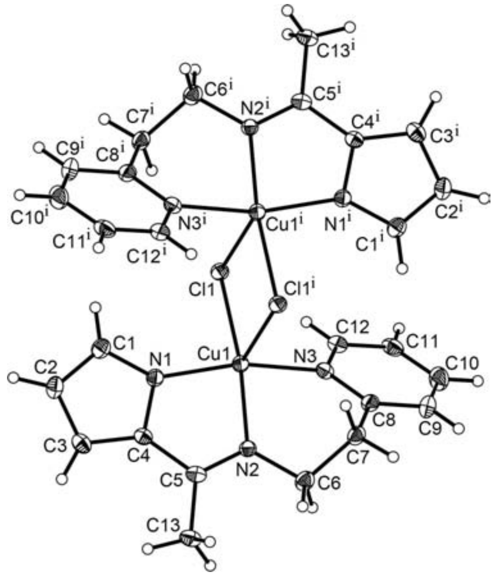


Figure 1

A view of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1$, $-y$, $-z$.]

arrangement of donor atoms around the Cu^{II} centre in (IV) are different from those observed for the copper(II) dimers of L_1^- and L_3^-, *i.e.* (I)–(III).

Of the three basal Cu—N bond lengths in (I), the shortest (Cu1—N1) occurs between the Cu atom and the deprotonated negatively charged pyrrole N atom and the longest (Cu1—N3) between the Cu atom and the pyridine N atom, which is *trans* to the pyrrole N atom. This phenomenon was also seen in (II)–(IV). In the coordination polyhedron, the average value of the Cl(apical)—Cu1—atom(basal) angles is 96.0°, while the average value of the *cis* basal angles is 89.5°. The three Cu—N basal bond distances and one *cis* basal angle (N1—Cu1—N2) in (I) are very close to those in (III) and (IV). The other three *cis* basal angles in (I) are quite different from those in (IV), although they are very similar to the corresponding angles in (III). As expected, the *cis* basal angle N2—Cu1—N3 in (I) [90.17 (11)°] is much larger than that in (IV) [80.55 (9)°], since in (I) it forms in the six-membered pyridine–imine chelate, while in (IV) it forms in the five-membered pyridine–imine chelate. On the other hand, the two *cis* N—Cu—Cl basal angles in (I) are smaller than those in (IV). These bond distances and angles also compare well with the values reported for related copper(II) complexes (Bertrand & Kirkwood, 1972; Brooker & Carter, 1995; Colacio *et al.*, 2000; Larramendi *et al.*, 1991; Matsumoto *et al.*, 1999). It is worth noting that the Cu—N3 distance lies at the high end of the literature range. This is probably because of the strong bond between the deprotonated negatively charged pyrrole N atom and the Cu^{II} atom.

The two basal planes, *viz.* N1/N2/N3/Cl1 and N1^i/N2^i/N3^i/Cl1^i, are exactly parallel to each other, by symmetry, and the average distance between them is just 2.922 Å. The four basal atoms are closely coplanar, with a maximum deviation from the mean basal plane of only 0.0773 (14) Å observed for imine atom N2. The Cu atom is located 0.2063 (13) Å out of the basal plane towards the apical ligand.

The bridging Cu_2Cl_2 core is exactly planar due to the presence of the crystallographic inversion centre in the middle of the dimer and is approximately rectangular [Cu1—Cl1—Cu1^i = 90.85 (4)° and Cl1—Cu1—Cl1^i = 89.15 (4)°]. The same type of bridging Cu_2X_2 core was also found in (II) (X = Cl$^-$) and (III) (X = Br$^-$), as well as in [Cu$_2$(apyhist)$_2$(μ-Cl)$_2$](ClO$_4$)$_2$ (apyhist = 2-{1-[2-(imidazol-4-yl)ethylimino]ethyl}pyridine), (V) (Alves *et al.*, 2003), and [Cu$_2$(terpy)$_2$(μ-Cl)$_2$](PF$_6$)$_2$ (terpy = 2,2′:6′,2″-terpyridine), (VI) (Rojo *et al.*, 1987). These angles are close to the corresponding angles in (III) [Cu—Br—Cu^i = 88.23 (5)° and Br—Cu—Br^i = 91.77 (5)°]. The Cu_2Cl_2 plane is nearly perpendicular to the basal N$_3$Cl planes, with a dihedral angle of 87.40 (5)°, which is smaller than the corresponding angle in (III) [97.75 (6)°]. The intramolecular Cu···Cu separation is 3.5573 (14) Å, which is, as expected, shorter than in (III) [3.772 (3) Å]. However, (I) has a slightly longer Cu···Cu separation compared with that in (V) [3.478 (1) Å] and (VI) [3.510 (14) Å]. This is presumably because (I) has a longer Cu—Cl(basal) bond distance and a larger Cu—Cl—Cu^i bond angle in comparison with the corresponding values in (V) [2.271 (1) Å and 87.46 (4)°] and (VI) [2.218 (19) Å and 89.9 (2)°].

Ligands L_1^-, L_2^- and L_3^- are very closely related to each other. However, their complexation with CuCl$_2$ gives two different structural types, *viz.* monomer and dimer. Examination of these ligands shows that L_1^- and L_3^- have similar flexibility but both ligands are more flexible than L_2^-. Correspondingly, copper(II) dimers (I) and (II) form with L_3^- and L_1^-, respectively, while the copper(II) monomer, (IV), is obtained with L_2^-. It is probably the reduced flexibility and greater steric constraint of L_2^- that results in the formation of such a monomer. In addition, comparison of (I) and (II) indicates that attachment of a bulky methyl substituent to the imino C atom of L_1^-, which gives L_3^- and imposes some steric constraints on it, makes (I) more distorted towards trigonal bipyramidal than (II) [τ = 0.14 for (I) and nearly zero for (II)], although the imposed steric constraints have no influence on the dimerization of the [Cu(L_3)Cl] unit to form the dimer (I), [Cu$_2$(L_3)$_2$(μ-Cl)$_2$]. However, the introduction of a bulky Br substituent at the β position on the pyrrole ring of L_1^- results in the formation of a singly bromide-bridged one-dimensional chain polymeric copper(II) complex (Li, Moubaraki *et al.*, 2008).

Experimental

HL_3 was synthesized from the condensation of 2-acetylpyrrole with 2-(2-aminoethyl)pyridine. To a solution of HL_3 (0.340 mmol) in methanol (5 ml) was added triethylamine (0.347 mmol) in methanol (5 ml). To the resulting solution was added a green solution of copper(II) chloride dihydrate (0.338 mmol) in methanol (5 ml), and a precipitate formed. The resulting mixture was stirred for 3.5 h, after which the solid was collected by filtration, washed with methanol and dried *in vacuo* [yield 0.083 g, 79% based on copper(II) chloride used].

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Single crystals of (I) suitable for X-ray determination were obtained by vapour diffusion of diethyl ether into a dichloromethane solution. Analysis found: C 50.15, H 4.65, N 13.44%; calculated for $C_{26}H_{28}Cl_2Cu_2N_6$: C 50.16, H 4.53, N 13.50%.

Crystal data

$[Cu_2(C_{13}H_{14}N_3)_2Cl_2]$
M_r = 622.54
Triclinic, $P\bar{1}$
a = 8.122 (2) Å
b = 8.412 (3) Å
c = 9.240 (3) Å
α = 91.973 (8)°
β = 93.386 (9)°
γ = 92.464 (8)°
V = 629.2 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.93 mm^{-1}
T = 213 (2) K
0.42 × 0.20 × 0.05 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.531, T_{max} = 0.908
6145 measured reflections
2286 independent reflections
1939 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.085
S = 1.13
2286 reflections
165 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—N1	1.952 (3)	Cu1—Cl1	2.3139 (10)
Cu1—N2	2.009 (3)	Cu1—Cl1^i	2.6676 (11)
Cu1—N3	2.041 (3)		

Symmetry code: (i) $-x+1, -y, -z$.

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3235). Services for accessing these data are described at the back of the journal.

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