

Bis[2,6-bis[1-(4-fluorophenylimino)-ethyl]pyridine]-1κ³N,N',N'';3κ³N,-N',N''-di-μ-chlorido-1:2κ²Cl:Cl;-2:3κ²Cl:Cl-trichlorido-1κCl,2κCl,3κCl-2-copper(I)-1,3-dicopper(II)

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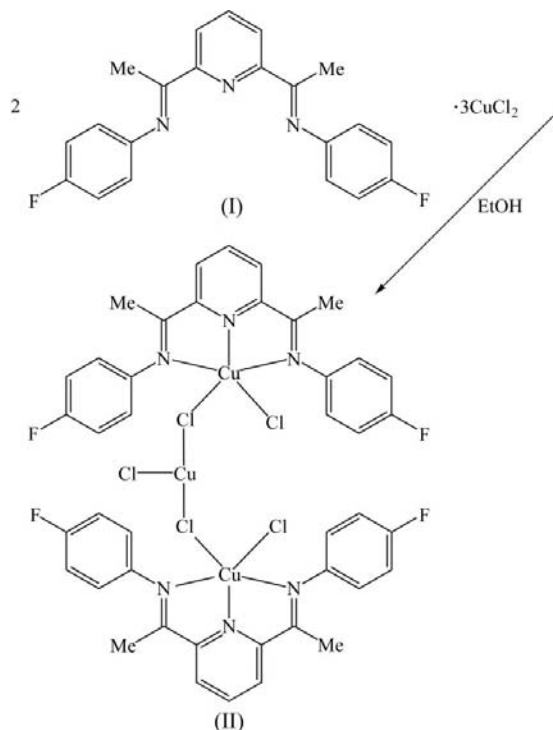
The title complex, [Cu₃Cl₅(C₂₁H₁₇N₃F₂)₂], is the first reported copper trimer including both Cu^I and Cu^{II} ions. The two Cu^{II} ions are five-coordinate in a significantly distorted square-pyramidal arrangement, with the bridging Cl atom located in the apical position, and the pyridine (py) N atom, the two imine N atoms and the other Cl atom located in the basal plane. The Cu^I ion is in a trigonal planar configuration surrounded by three Cl atoms. The structure is stabilized by intra- and intermolecular C—H···Cl and C—H···π(py) hydrogen bonds.

Comment

Multidentate ligands play an important role in transition metal chemistry, enhancing the stability of complexes and allowing the manipulation of steric and electronic parameters that control reactivity at the metal center (Togni & Venanzi, 1994). An attractive multidentate ligand is the neutral N,N',N''-tridentate pyridine-2,6-diimine (pydim) ligand, in which the central pyridine-based ring donor contains keto-imine substituents in the *ortho* positions. Upon coordination to transition metals, the bis-chelate framework may confer on such complexes interesting stoichiometries and catalytic activities (Gibson & Spitzmesser, 2003; Çetinkaya *et al.*, 1999; Dayan & Çetinkaya, 2007).

While their catalytic properties have been examined extensively, reports of the structural properties of these compounds are rare in the literature. We have therefore prepared pyridine-diimine complexes of various transition metals (Özdemir *et al.*, 2006a,b). We were attempting to obtain a monomeric complex between (I) and CuCl₂. However, CHN analyses showed that the desired product did not form, but

rather a new trimer, (II), comprising pydim and CuCl₂ in a 2:3 ratio, was obtained. Understanding the shape of the coordination polyhedra in the case of five-coordination is one of the current problems in coordination chemistry. This study of (II) establishes the structural parameters and the coordination geometries about the metal atoms.



The molecular structure of complex (II), together with the atom-labeling scheme, is shown in Fig. 1. Selected geometric parameters are listed in Table 1. The title trimer is composed of two Cu^{II} metal centers – each bound to one (*Z,E*)-2,6-bis[1-(4-fluorophenylimino)ethyl]pyridine ligand, (I), and one Cl atom – and a trichloridocopper(I) unit which links the two Cu^{II} metal centers. The ligand (I), with its two imine groups in *ortho* positions with respect to the pyridine N atom, behaves as a symmetrical N,N',N''-tridentate chelate. The two Cu^{II} ions are therefore five-coordinated by two imine N atoms, one pyridine N atom and two Cl atoms, while the Cu^I ion is coordinated by three Cl atoms (Fig. 1) in a trigonal planar configuration. The Cu1/N1/C1/C14/N3, Cu1/N1/C5/C6/N2, Cu3/N4/C22/C35/N6 and Cu3/N4/C26/C27/N5 chelate rings are approximately planar, with maximum deviations of 0.024 (3), 0.020 (2), 0.031 (2) and 0.010 (2) Å for atoms C14, N1, N6 and N5, respectively. The Cu1- and Cu3-containing pairs of chelate rings make dihedral angles of, respectively, 3.00 (12) and 1.74 (12)° with one another, indicating that they are nearly coplanar.

Five-coordinate copper(II) complexes have geometries ranging from trigonal bipyramidal to square pyramidal. Energetically, these limiting forms are often almost equally favorable, with a low activation barrier to interconversion. Further information can be obtained by determining the structural index, τ , which represents the relative amount of trigonality [for a square pyramid, $\tau = 0$, and for a trigonal

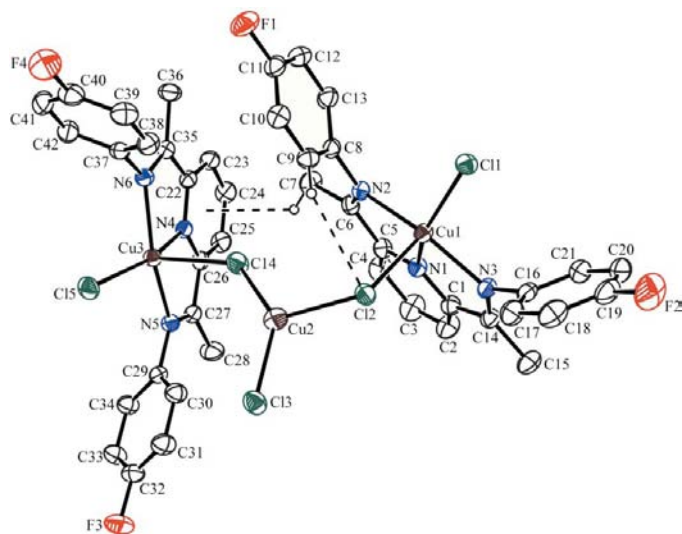


Figure 1

A view of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme. For clarity, only H atoms involved in hydrogen bonding (dashed lines) have been included.

bipyramid, $\tau = 1$; $\tau = (\beta - \alpha)/60^\circ$, α and β being the two largest angles around the central atom (Addison *et al.*, 1984)]. The values of τ for atoms Cu1 and Cu3 in (II) are 0.23 and 0.03, respectively, indicating that the coordination geometry of the Cu^{II} ions is closer to a regular square pyramid than to a regular trigonal bipyramid. For both Cu^{II} ions, the axial positions are occupied by the Cl atoms coordinated to a Cu^{I} ion, while the four basal positions are occupied by the other chloride ligand

and the three N-atom donors of the tridentate ligand (I). Atoms Cu1 and Cu3 lie 0.4210 (4) and 0.2659 (3) Å, respectively, out of the least-squares planes of the pyramid bases. As can be seen in Table 1, the bond lengths and angles at the Cu^{II} ions show that the coordination geometries are distorted significantly (from equal lengths and 90° angles). Axial Cu—Cl distances are longer than equatorial Cu—Cl distances, confirming the weaker interactions between the bridging Cl atoms and the Cu atoms. When the Cu—Cl distances in polymeric Cu^{I} —Cl or Cu^{II} —Cl compounds are surveyed, it is observed that elongation of the bridging Cu—Cl distances in the axial position is common for these types of complexes (Schuitema *et al.*, 2003; Johansson *et al.*, 2004; Rybak-Akimova *et al.*, 1997; Vasilevsky *et al.*, 1989).

A comparison of the appropriate bond distances and angles in (II) indicates that the two Cu^{II} ions possess approximate noncrystallographic C_s symmetry about a plane bisecting the central pyridine ring and containing the metal atom and the two halogen atoms. The planes of the benzene rings substituted on the bis(imino)pyridine ligand backbone make dihedral angles of 52.94 (16), 71.88 (15), 56.48 (15) and 81.95 (16) $^\circ$ with the plane of the central pyridine ring for the C8—C13, C16—C21, C29—C34 and C37—C42 rings, respectively. The dihedral angle between the C8—C13 and C16—C21 rings is 86.38 (15) $^\circ$, while the dihedral angle between the C29—C34 and C37—C42 rings is 84.05 (15) $^\circ$. The geometries at the imine N-atom centers are all trigonal planar, the sums of the three bond angles around these centers being 359.9 (2), 360.0 (2), 359.9 (2) and 359.8 (2) $^\circ$, and none lies more than *ca* 0.03 Å out of its associated Cu_2 plane.

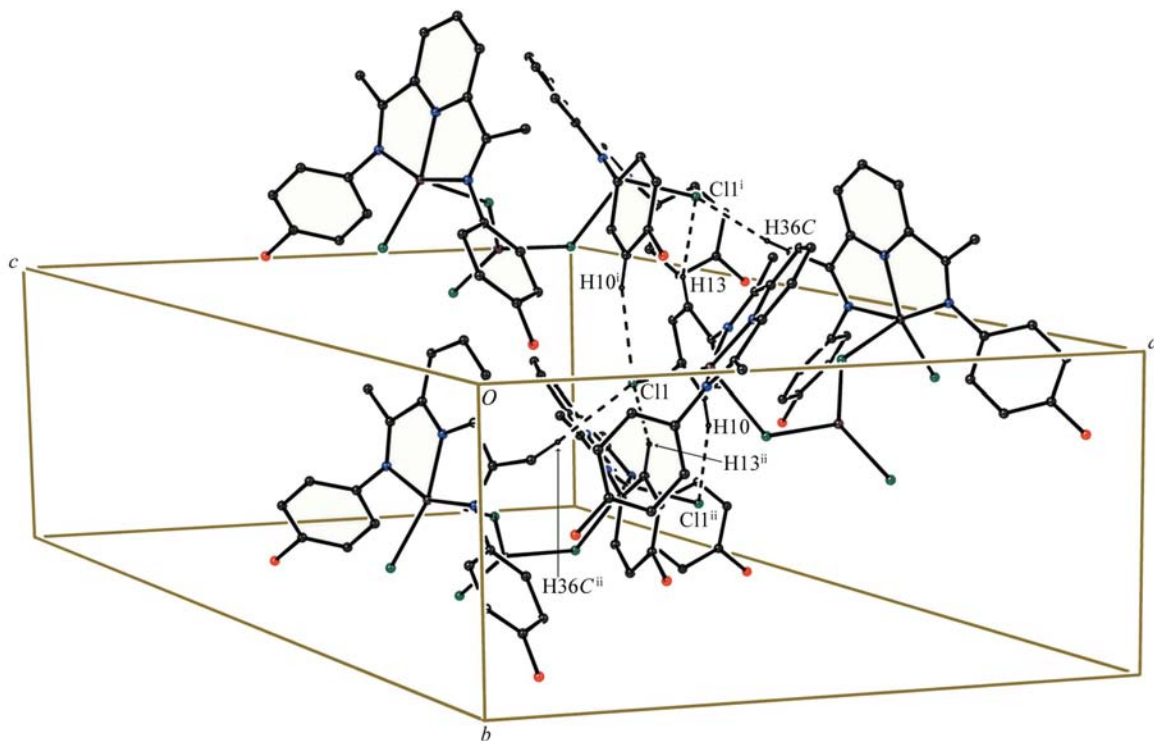


Figure 2

A partial cell packing diagram for complex (II), showing the C—H...Cl interactions (dashed lines). For clarity, only H atoms involved in hydrogen bonding have been included. [Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$]

There are several reported structures containing various transition metal complexes of pydim-based ligands (Britovsek *et al.*, 1999; Dias *et al.*, 2000; Nakayama *et al.*, 2005; Humphries *et al.*, 2005). The *M*–N bond distances in (II) and in these examples indicate that the two *M*–N_{imino} bonds are *ca* 0.1–0.2 Å longer than the corresponding *M*–N_{py} bond within each metal–tridentate-chelate unit. Furthermore, it is observed that the N_{imino}–*M*–N_{py} angle for the five-membered chelate rings of pydim complexes is inversely related to the magnitude of the *M*–N_{py} bond; as the *M*–N_{py} distance increases, the corresponding inner ‘bite’ angle decreases, as shown in Table 3.

The intra- and intermolecular interactions in (II) are given in Table 2. An intramolecular C9–H9···Cl2 interaction leads to the formation of a six-membered ring. In addition, there is also an intramolecular C–H···π contact between atom H7B and the centroid of the N4/C22–C26 ring (entry 2 in Table 2, and Fig. 1). Molecules of the title compound are packed in columns running along the *b* axis, and three C–H···Cl intermolecular interactions are observed (Fig. 2); these types of interaction have been observed previously (Vasilevsky *et al.*, 1989; Özdemir *et al.*, 2006a,b).

Experimental

The ligand (I) was prepared by a modification of the method of Çetinkaya *et al.* (1999). A solution of CuCl₂·2H₂O (510 mg, 3 mmol) in ethanol (10 ml) was added dropwise to a solution of (I) (350 mg, 1 mmol) in ethanol (10 ml). The resulting brown solution was refluxed for 4 h and concentrated (5 ml). Water was added dropwise, with stirring, to a final volume of 10 ml, causing a brown powder to precipitate. The brown precipitate was filtered off, washed successively with cold EtOH and Et₂O, and dried. X-ray quality crystals were grown from CH₂Cl₂–Et₂O (30 ml, 1:2 *v/v*) (yield 420 mg, 39%; m.p. 460–462 K). Analysis calculated for C₄₂H₃₄Cl₅Cu₃F₄N₆: C 47.29, H 3.21, N 7.88%; found: C 47.98, H 3.12, N 7.31%.

Crystal data

[Cu ₃ Cl ₅ (C ₂₁ H ₁₇ N ₃ F ₂) ₂]	<i>V</i> = 4349.9 (4) Å ³
<i>M_r</i> = 1066.62	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 18.4646 (9) Å	<i>μ</i> = 1.82 mm ⁻¹
<i>b</i> = 9.0930 (3) Å	<i>T</i> = 296 K
<i>c</i> = 28.0986 (14) Å	0.62 × 0.31 × 0.10 mm
<i>β</i> = 112.774 (4)°	

Data collection

Stoe IPDS-II diffractometer	39069 measured reflections
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	8530 independent reflections
<i>T</i> _{min} = 0.595, <i>T</i> _{max} = 0.883	6353 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.057

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.032	545 parameters
<i>wR</i> (<i>F</i> ²) = 0.072	H-atom parameters constrained
<i>S</i> = 1.01	Δρ _{max} = 0.31 e Å ⁻³
8530 reflections	Δρ _{min} = -0.60 e Å ⁻³

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96 and 0.93 Å for CH₃ and aromatic CH groups, respectively. The displacement parameters of the H atoms were constrained [*U*_{iso}(H) = 1.2*U*_{eq}(C) for nonmethyl and *U*_{iso}(H) = 1.5*U*_{eq}(C) for methyl H atoms]. Riding methyl H atoms

Table 1

Selected geometric parameters (Å, °).

Cu1–N1	1.942 (2)	Cu3–N5	2.065 (2)
Cu1–N2	2.060 (2)	Cu3–N6	2.092 (2)
Cu1–N3	2.063 (2)	Cu3–Cl5	2.1903 (8)
Cu1–Cl1	2.2320 (7)	Cu3–Cl4	2.6082 (8)
Cu1–Cl2	2.4884 (8)	N2–C6	1.289 (3)
Cu2–Cl3	2.2111 (8)	N3–Cl4	1.281 (3)
Cu2–Cl4	2.2221 (8)	N5–C27	1.287 (3)
Cu2–Cl2	2.3594 (8)	N6–C35	1.283 (3)
Cu3–N4	1.937 (2)		
N1–Cu1–N2	79.16 (9)	N4–Cu3–N5	78.77 (9)
N1–Cu1–N3	78.25 (9)	N4–Cu3–N6	77.93 (9)
N2–Cu1–N3	157.24 (8)	N5–Cu3–N6	156.49 (9)
N1–Cu1–Cl1	143.28 (7)	N4–Cu3–Cl5	158.17 (7)
N2–Cu1–Cl1	99.40 (6)	N5–Cu3–Cl5	100.56 (6)
N3–Cu1–Cl1	97.00 (6)	N6–Cu3–Cl5	99.90 (6)
N1–Cu1–Cl2	102.11 (7)	N4–Cu3–Cl4	98.36 (6)
N2–Cu1–Cl2	96.52 (6)	N5–Cu3–Cl4	94.16 (6)
N3–Cu1–Cl2	90.90 (7)	N6–Cu3–Cl4	92.24 (6)
Cl1–Cu1–Cl2	114.43 (3)	Cl5–Cu3–Cl4	103.44 (3)
Cl3–Cu2–Cl4	134.91 (3)	Cu2–Cl2–Cu1	121.71 (3)
Cl3–Cu2–Cl2	108.13 (3)	Cu2–Cl4–Cu3	138.68 (4)
Cl4–Cu2–Cl2	116.69 (3)		

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the N4/C22–C26 ring.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C9–H9···Cl2	0.93	2.74	3.572 (3)	149
C7–H7B···Cg1	0.96	2.81	3.518 (3)	131
C36–H36C···Cl1 ⁱ	0.96	2.72	3.666 (3)	169
C10–H10···Cl1 ⁱⁱ	0.93	2.73	3.626 (3)	162
C13–H13···Cl1 ⁱ	0.93	2.81	3.428 (3)	125

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

Table 3

M–N_{py} bond lengths (Å) and N_{imino}–*M*–N_{py} angles (°) in (II) and some pydim complexes.

	<i>M</i> –N _{py}	N _{imino} – <i>M</i> –N _{py} (average)
[CoMe(pydim)] ^a	1.833 (3)	81.17
[RhMe(pydim)](OTf) ₂ ^b	1.911 (3)	79.8
(II) ^c	1.940 (2) (average)	78.53
[CrCl ₃ (pydim)] ^d	2.001 (3)	76.6
[FeCl ₂ (pydim)] ^e	2.110 (6)	72.8

Notes: (a) Humphries *et al.* (2005) (Ar = 2,6-*i*-Pr₂C₆H₃); (b) Dias *et al.* (2000) (Ar = 2,6-*i*-Pr₂C₆H₃ and OTf is triflate); (c) this work; (d) Nakayama *et al.* (2005) (Ar = C₆F₅); (e) Britovsek *et al.* (1999) (Ar = 2,4,6-Me₃C₆H₂).

were allowed to rotate freely during refinement using the AFIX 137 command of *SHELXL97* (Sheldrick, 2008).

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3087). Services for accessing these data are described at the back of the journal.

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