Dichloro[(1*E*,1′*E*)-1,1′-(pyridine-2,6-diyl)diethanone bis(*O*-methyloxime)-$\kappa^3 N^1, N^2, N^6$]copper(II)

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In the title compound, [CuCl$_2$(C$_{11}$H$_{15}$N$_3$O$_2$)], the Cu^{II} ion is five-coordinated in a strongly distorted trigonal–bipyramidal arrangement, with the two methyloxime N atoms located in the apical positions, and the pyridine N and the Cl atoms located in the basal plane. The two axial Cu—N distances are almost equal (mean 2.098 Å) and are substantially longer than the equatorial Cu—N bond [1.9757 (15) Å]. It is observed that the N(oxime)—*M*—N(pyridine) bond angle for five-membered chelate rings of 2,6-diacetylpyridine dioxime complexes is inversely related to the magnitude of the *M*—N(pyridine) bond. The structure is stabilized by intra- and intermolecular C—H···Cl hydrogen bonds which involve the methyl H atoms, except for one of the two acetylmethyl groups.

Comment

Remarkable advances in homogeneous catalyst technology have recently been achieved with systems comprising late transition metals and 2,6-diiminopyridyl ligands (Small & Brookhart, 1998, 1999; Britovsek *et al.*, 1999). Upon coordination to a transition metal, the bis(chelate) framework may confer on such complexes interesting stoichiometric and catalytic reactivities (Çetinkaya *et al.*, 1999; Dayan & Çetinkaya; 2005; Gibson & Spitzmesser, 2003). This family of catalysts has attracted great interest, both in academia and in industry (Gibson & Was, 1999; Bennett, 1999). Although a number of 2,6-diacetylpyridine dioxime-based Cu^{II} complexes have been reported (Glynn & Turnbull, 2002; Baugh *et al.*, 2003; Chandra & Gupta, 2001, 2002; Singh *et al.*, 1997; Abboud *et al.*, 1994; Nicholson *et al.*, 1980, 1982), the chemistry of the related 2,6-diacetylpyridine bis(*O*-methyloxime) complexes has been rarely studied. In addition, copper is an oligo-element with an essential role in a number of enzymes (Price, 1987). It has been demonstrated that copper chelates are good anticonvulsant agents for the treatment of epileptic seizures.

Moreover, many classes of copper chelates, including amino acids, salicylates and Schiff bases, as well as copper chelates of well known anti-epileptic drugs, are more effective anticonvulsants than the parent ligand (Viossat *et al.*, 2003).

In the present study, the title five-coordinate compound, (II), was synthesized in good yield (81%) by the reaction sequence depicted in the scheme below. The composition of this complex has been confirmed by CHN analyses and IR spectroscopy. Understanding the shape of coordination polyhedra in the case of five-coordination is one of the current problems in coordination chemistry. In order to establish the coordination geometry about the metal atom and to examine the structural parameters in this case, we present here the synthesis and crystal structure of this mononuclear copper 2,6-diacetylpyridine bis(*O*-methyloxime) compound with two chloride ligands.
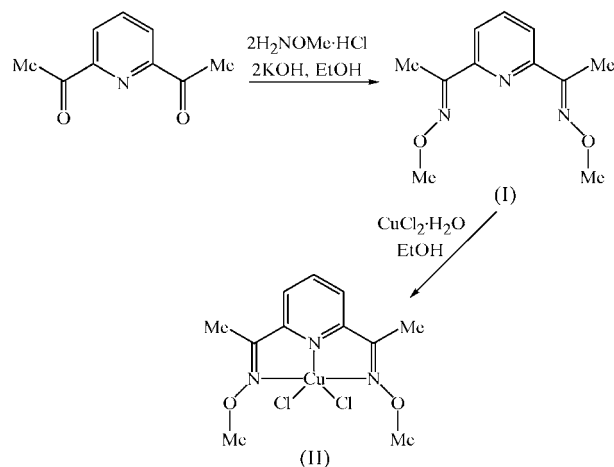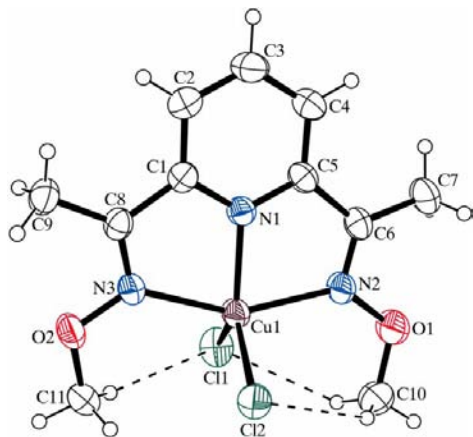

The molecular structure of complex (II), together with the atom-labelling scheme and the intramolecular hydrogen bonding, are shown in Fig. 1. Selected geometric parameters are listed in Table 1. The structure of (II) is composed of a 2,6-diacetylpyridine bis(*O*-methyloxime) ligand with a Cu^{II} metal centre and two Cl ligands. As expected, complex (II) does not crystallize with solvent molecules and the ligand, (I), with its two imino groups in *ortho* positions with respect to the pyridine N atom, behaves as a symmetrical *N,N′,N*-tridentate chelate. The Cu^{II} ion is pentacoordinated by two methyloxime N atoms, one pyridine N atom and two Cl atoms (Fig. 1). The five-membered chelate rings formed by atoms Cu1/N1/C1/C8/N3 and Cu1/N1/C5/C6/N2 are essentially planar and the maximum deviations from their planes are 0.0221 (9) and −0.0368 (11) Å, respectively, for atoms N1 and N2. These two chelate rings make a small dihedral angle of 2.37 (10)° 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 favourable, with a low activation barrier to interconversion. The question arises as to whether the coordination polyhedron around the Cu^{II} ion in complex (II) can be best described as a distorted square pyramid or a distorted trigonal bipyramid. 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 bipyramid $\tau = 1$; $\tau = (\beta - \alpha)/60°$, α and β being the two largest angles around the central atom (Addison *et al.*, 1984)]. The value of τ for the Cu^{II} ion in (II) is 0.53, indicating that the coordination geometry lies almost midway between a regular square pyramid (SQP) and a regular trigonal bipyramid (TBP), but can be accepted as a strongly distorted trigonal bipyramid, since the value of τ is a little closer to TBP than SQP, as can also be seen from the distances and angles around the metal atom (Table 1). Atoms Cl1, Cl2 and N1 act as the basal plane of the trigonal bipyramid, while the apical positions are occupied by atoms N2 and N3. In the axial direction, the N2—Cu1—N3 angle of the bipyramid deviates greatly from linearity. However, the bond angles within the basal plane have nearly the ideal value of 120° for a perfect TBP, and the apical N atoms are symmetrically disposed above and below the plane. This ligand disposition in (II) is consistent with approximate C_{2v} point group symmetry for the molecule. Atoms N1, Cl1 and Cl2 are coplanar, and the Cu^{II} ion is located in the middle of the base of the TBP, 0.0148 (5) Å out of the mean plane (toward N2) formed by the equatorial ligand atoms. The axial–equatorial (ax–eq) angles fall into two groups, with N_{ax}—Cu—N_{eq} values in the range 76.66 (6)–76.85 (6)° and N_{ax}—Cu—Cl_{eq} in the range 93.72 (5)–99.73 (4)°, which also reflects the fact that the Cu atom is displaced out of the plane of the three equatorial atoms. In the molecular structure, the bond lengths of C6=N2 and C8=N3 conform to the value for a double bond, while those of N2—O1 and N3—O2 conform to the value for a single bond.
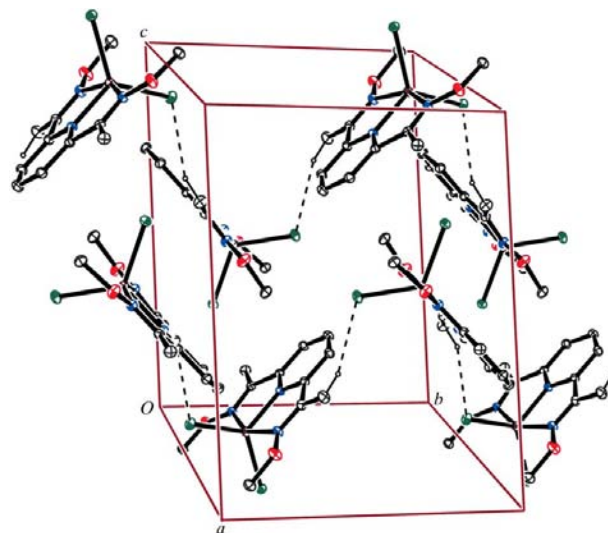
The Cu1—N2 and Cu1—N3 bond distances in the axial direction are longer than the Cu1—N1 bond in the equatorial plane. In addition, the basal Cu1—Cl2 distance is 0.02 Å longer than the other basal Cu1—Cl1 distance. Since the electronic ground state in this Cu^{II} complex is not likely to be degenerate, the observed variations in these bond distances are probably due to a second-order Jahn–Teller effect of the d^9 metal atom. Pearson (1969) has examined this problem of molecular distortions with the aid of second-order perturbation theory and group theory. His analysis has shown that, for molecules with a non-degenerate ground state and low-lying excited states (within about 4 eV), only totally symmetric motions will occur until the energy of the molecule is minimized. Thus, the bond lengths and angles change to produce the lowest energy configuration that still retains the original point-group symmetry of the molecule. The Jahn–Teller effect is also observed in the UV spectrum, in which complex (II) exhibits a weak transition at 565 nm corresponding to $^2B_{1g} \rightarrow {}^2B_{2g}$, which indicates the presence of fivefold coordination around copper (Lever, 1984). A less intense band at 364 nm is due to the Jahn–Teller effect in the complex. The absorption band below 330 nm results from the overlap of a low-energy π–π* transition mainly localized within the imine chromophore and the ligand-to-metal charge-transfer bands (LCMT).

There are several structures reported in the literature containing various metal complexes of 2,6-diacetylpyridine dioxime ligands (Sproul & Stucky, 1973; Nicholson *et al.*, 1982; Abboud *et al.*, 1994; Glynn & Turnbull, 2002). An examination of the M—N bond distances in (II) and in these examples indicates that the two M—N(oxime) bonds are *ca* 0.1–0.2 Å longer than the corresponding M—N(pyridine) bond within each metal–tridentate chelate unit. This structural feature contrasts with that observed for α-amine oxime (Liss & Schlemper, 1975; Gavel & Schlemper, 1979; Curtis *et al.*, 2004) and trinuclear Cu^{II}–oxime complexes (Ross *et al.*, 1974). In these particular systems, the trend is reversed, with the Cu—N(oxime) distances consistently 0.03–0.07 Å shorter than the interior Cu—N(amine) distances. Finally, it is observed that the N(oxime)—M—N(pyridine) bond angle for the five-membered chelate rings of 2,6-diacetylpyridine dioxime complexes is inversely related to the magnitude of the M—N(pyridine) bond. As the M—N(pyridine) distance increases

Figure 1
A view of the molecule of (II), showing 40% probability displacement ellipsoids and the atom-numbering scheme. Intramolecular C—H···Cl contacts are represented by dashed lines.

Figure 2
The molecular packing of (II), viewed along the *a* axis. Dashed lines show the C—H···Cl interactions. For clarity, only H atoms involved in hydrogen bonding have been included.

from 1.837 (4) Å for Ni(DAPD)$_2$ (DAPD is 2,6-diacetyl-pyridine dioximate; Sproul & Stucky, 1973) to 1.9757 (15) Å for (II) to 2.063 (2) Å for Zn(DAPDH$_2$)Cl$_2$ (DAPDH$_2$ is 2,6-diacetylpyridine dioxime; Nicholson *et al.*, 1982) to 2.180 (5) Å (average) for [Mn(DAPDH$_2$)$_2$](ClO$_4$)$_2$ (Glynn & Turnbull, 2002), the corresponding inner 'bite' angle decreases continually from 82.4 (average) to 76.76 (average) to 73.7 (average) to 70.65° (average), respectively.

In the molecular structure of (II), three intramolecular interactions are observed between the methyl H and the Cl atoms, forming six-membered rings. In the construction of the intermolecular connections, 2$_1$ screw symmetry-related molecules, which form pairs of neighbouring molecules translated linearly along the *b* axis of the unit cell, play an active bridging role. Atom C7 acts as a hydrogen-bond donor, *via* atom H7*B*, to atom Cl1 at $(1 - x, -\frac{1}{2} + y, -\frac{1}{2} - z)$. Extension of this hydrogen-bonding interaction along *b* in a zigzag arrangement results in the formation of molecular chains along the [010] direction (Fig. 2). There are no intermolecular interactions in the *a* or *c* directions. The full geometry of the intra- and intermolecular interactions is given in Table 2.

Experimental

Melting points were determined in open capillary tubes on a digital Electrothermal 9100 melting point apparatus. IR spectra (KBr pellets) were recorded in the range 400–4000 cm^{-1} on an ATI UNICAM 2000 spectrophotometer. Elemental analyses were carried out by the analytical service of TÜBİTAK (the Scientific and Technical Research Council of Turkey) using a Carlo Erba 1106 apparatus. CuCl$_2$·2H$_2$O (Merck), diacetylpyridine (Fluka) and methoxylamine hydrochloride (Acros) were used as received. Compound (I) was prepared by a modification of the method of Çetinkaya (Çetinkaya *et al.*, 1999; Dayan & Çetinkaya, 2005; Gibson & Spitzmesser, 2003). Solvents were of analytical grade and were distilled after drying. A solution of CuCl$_2$·2H$_2$O (77 mg, 0.45 mmol) in ethanol (10 ml) was added dropwise to a solution of (I) (100 mg, 0.45 mmol) in ethanol (10 ml). The resulting brown solution was refluxed for 4 h and then concentrated (5 ml). Et$_2$O was added dropwise with stirring to a final volume of 20 ml, causing a brown powder to precipitate. The brown precipitate was filtered off, washed with Et$_2$O and dried. X-ray quality crystals of (II) were grown from a solution in CH$_2$Cl$_2$–Et$_2$O (30 ml, 1:2 *v/v*) (yield 130 mg, 81%; m.p. 483–485 K). Analysis calculated for C$_{11}$H$_{15}$Cl$_2$CuN$_3$O$_2$: C 37.14, H 4.25, N 11.81%; found: C 36.92, H 4.1, N 11.56%. IR (KBr): 1621 ($\nu_{C=N}$) cm^{-1}.

Crystal data

[CuCl$_2$(C$_{11}$H$_{15}$N$_3$O$_2$)]	$Z = 4$
$M_r = 355.70$	$D_x = 1.639$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.1308$ (6) Å	$\mu = 1.89$ mm^{-1}
$b = 10.4656$ (5) Å	$T = 296$ K
$c = 13.6747$ (7) Å	Prism, brown
$\beta = 115.152$ (4)°	$0.54 \times 0.51 \times 0.48$ mm
$V = 1441.93$ (13) Å^3	

Data collection

Stoe IPDS-2 diffractometer	19881 measured reflections
ω scans	3441 independent reflections
Absorption correction: integration	3005 reflections with $I > 2\sigma(I)$
(*X-RED32*; Stoe & Cie, 2002)	$R_{int} = 0.070$
$T_{min} = 0.309$, $T_{max} = 0.574$	$\theta_{max} = 28.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$+ 0.2674P]$
$wR(F^2) = 0.087$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
3441 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
177 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	(Sheldrick, 1997)
	Extinction coefficient: 0.0389 (19)

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.9757 (15)	O1—N2	1.380 (2)
Cu1—N3	2.0805 (18)	O2—N3	1.374 (2)
Cu1—N2	2.1151 (16)	N2—C6	1.281 (3)
Cu1—Cl1	2.2802 (6)	N3—C8	1.291 (2)
Cu1—Cl2	2.3057 (5)		
N1—Cu1—N3	76.85 (6)	N1—Cu1—Cl2	119.42 (5)
N1—Cu1—N2	76.66 (6)	N3—Cu1—Cl2	95.08 (5)
N3—Cu1—N2	153.50 (6)	N2—Cu1—Cl2	98.31 (5)
N1—Cu1—Cl1	121.79 (5)	Cl1—Cu1—Cl2	118.77 (2)
N3—Cu1—Cl1	99.73 (4)	N3—C8—C1	113.33 (16)
N2—Cu1—Cl1	93.72 (5)		

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C11—H11$A\cdots$Cl1	0.96	2.60	3.457 (2)	148
C10—H10$C\cdots$Cl1	0.96	2.68	3.467 (3)	139
C10—H10$A\cdots$Cl2	0.96	2.82	3.563 (3)	135
C7—H7$B\cdots$Cl1^i	0.96	2.81	3.700 (3)	155

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

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96 and 0.93 Å for methyl and aromatic H atoms, respectively. The displacement parameters of the H atoms were constrained as $U_{iso}(H) = 1.2U_{eq}$ (1.5U_{eq} for methyl) of the parent atom.

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, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); 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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