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Bis{1-*n*-hexyl-3-methyl-4-[1-(phenylimino)propyl]-1*H*-pyrazol-5-olato}copper(II): a new copper(II) complex with a chelating alkylpyrazolone-based enamine

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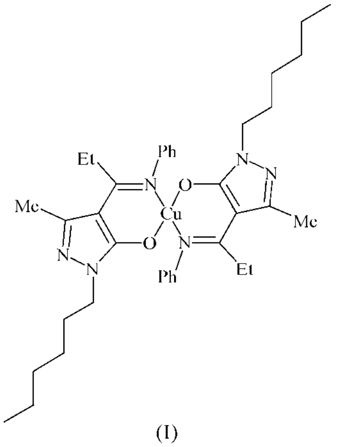
The title compound, $[Cu(C_{19}H_{26}N_3O)_2]$, is the first reported complex of the alkylpyrazolone-derived ligand 1-*n*-hexyl-3-methyl-4-[1-(phenylimino)propyl]-1*H*-pyrazol-5(4*H*)-one. The most notable feature is the imine–enol character presented by the ligand due to coordination, in spite of its enamine–ketone structure in the free state. The ligand chelates through N and O atoms, resulting in a square-planar coordination around the Cu^{II} atom, which lies on an inversion centre.

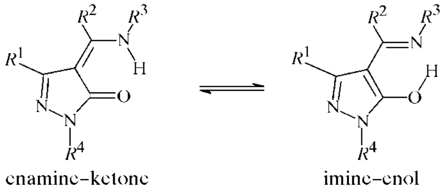
Comment

Pyrazolones constitute an important group of organic compounds (Elguero, 1996), for both theoretical and practical reasons. Their application fields include analgesic and anti-inflamatory drugs (Gürzov *et al.*, 2000), dyes (Emeleus *et al.*, 2001), extractants for several ions (Petinari *et al.*, 2000), *etc.* Pyrazolones have attracted much attention because they exhibit prototropic tautomerism (Elguero *et al.*, 1976; Uraev *et al.*, 2000; Gilchrist, 2001) and they have been extensively studied both in solution and in the crystalline phase (Chmutova *et al.*, 2001).

Pyrazolones have usually been obtained by the same synthetic procedure, *via* a condensation between an acyl acetate and a hydrazine, for more than a century (Knorr, 1884). In spite of the many advantages of 1-alkylpyrazolone derivatives (*viz.* their greater solubility), most literature reports deal with 1-phenylpyrazolones or N1-unsubstituted pyrazolones. This situation may result from the fact that the few commercially available alkylhydrazines are very expensive. Furthermore, there are no convenient syntheses for their preparation. Emeleus *et al.* (2001) described the use of some alkylpyrazolones that were obtained following a different procedure (Butler & de Wald, 1971). However, alkylhydrazines were still one of the required reagents.



(I)



prototropic tautomerism

More recently, with the aim of studying the tautomerism involved, it was shown that pyrazolone could be easily alkylated at N1 with primary alkyl halides (Bartulin *et al.*, 1992, 1994; Belmar *et al.*, 1997, 1999). This procedure finally allowed the obtention of several enamines derived from 4-acyl-1-*n*-hexyl-3-methyl-5-pyrazolones (Belmar *et al.*, 2004, 2005) and even some nitride complexes using these ligands (Pérez *et al.*, 2005). In addition to these reports, papers by Maurya *et al.* (1992) and Dey *et al.* (1999) described some complexes using 1-phenylpyrazolone-based imines. In this paper, we present the structure of the title compound $Cu(L)_2$ {*L* is the 1-*n*-hexyl-3-methyl-4-[1-(phenylimino)propyl]-1*H*-pyrazol-5-olate anion}, (I), which is the first copper complex ever reported using a chelating 1-alkylpyrazolone-based enamine ligand.

Compound (I) is monomeric and consists of a tetracoordinated Cu^{II} atom lying on an inversion centre, coordinated to two chelating (symmetry-related) bidentate *L* ligands (Fig. 1). The resulting CuO_2N_2 core is perfectly planar, due to the restraints imposed by symmetry. The coordination bond lengths do not depart significantly from average values taken from a selected subset of 80 structures with a similar coordination scheme found in the November 2004 release of the Cambridge Structural Database (CSD; Allen, 2002), *viz.* Cu—N = 2.036 (3) Å and Cu—O = 1.879 (2) Å in this work, compared with 2.001 (20) and 1.887 (21) Å, respectively, from the CSD. The ligand *L* does not twist appreciably because of chelation. Fig. 2 presents a superposition diagram of the free ligand (Belmar *et al.*, 2004) and the ligand in (I); both cores overlap almost entirely, the larger departure being found in the phenyl ring [average discrepancies are 0.08 (8) Å for non-phenyl atoms and 1.8 (11) Å for phenyl atoms]. The free

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ligand forms an intramolecular N—H···O hydrogen bond, which rocks the conformation.

The pyrazine ring and its two substituents at C1 and C2 define a planar group [mean deviation 0.01 (1) Å], which binds in a slightly slanted way through the outermost atoms (O1 and N3) to the Cu coordination plane [dihedral angle = 16.8 (1)°]. Thus, the O1/C1/C2/C5/N3/Cu1 six-membered ring presents an envelope conformation, with the Cu atom deviating by 0.38 (1) Å from the planar group defined by the remaining five atoms.

There are four lateral substituents attached to the planar main frame of (I), namely methyl at C3, ethyl at C5, *n*-hexyl at N1 and phenyl at N3. All of them, with the obvious exception of the methyl group, are almost perpendicular to the quasi-planar coordination core, the phenyl group subtending an angle of 77.4 (1)° and the two aliphatic chains deviating from the vertical by 17 (1)°. The *n*-hexyl group presents a striking unperturbed almost planar zigzag conformation, with torsion angles in the range 177.1 (1)–179.2 (1)°. A survey of the CSD showed this to be a rather infrequent conformation: in 842 cases (89% out of a total of 947 hexyl groups reported), the aliphatic chain presented greater deviations from a perfect unperturbed zigzag state, as measured by the largest torsion angle deviation from an expected 180°. It is worth noting that only one out of the 947 structures surveyed showed a symmetry-forced perfectly planar conformation.

This particular disposition of the sustituents in (I) introduces a strong steric limitation to the approach of planar groups from different molecules, and thus precludes the most noteworthy intermolecular interaction found in the structure of the free ligand (Belmar *et al.*, 2004), *viz*. the π–π contact between aromatic rings.

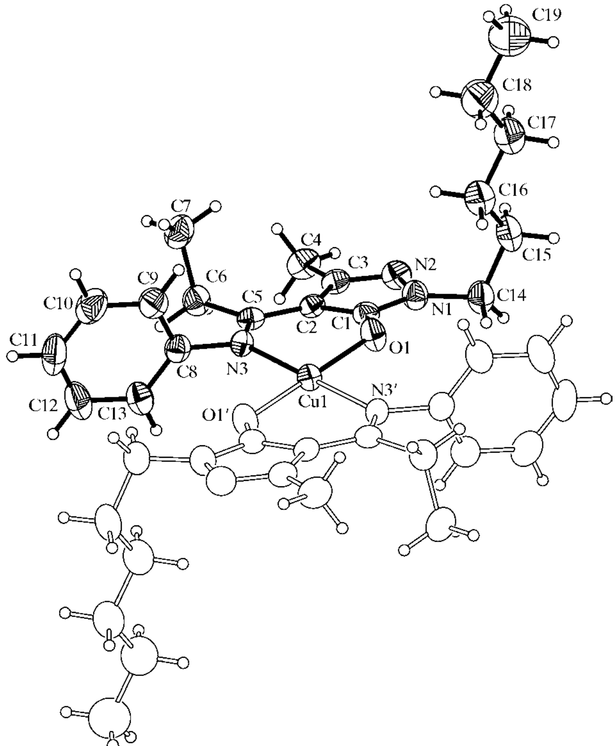

Figure 1

A molecular diagram of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of rabitrary radii. Shaded ellipsoids denote the independent part of the molecule and open ellipsoids denote the symmetry-related moiety at $(1 - x, 1 - y, 1 - z)$.

Previously reported structural work on complexes derived from related ligands strongly suggests an 'enamine-to-imine' shift of the character of the ligand upon coordination, *viz*. a nitridomanganese(V) complex with *N*,*N*′-bis[(1-*n*-hexyl-3-methyl-5-oxo-2-pyrazolin-4-yl)propyliden-1-yl]ethylenediamine (Belmar *et al.*, 2005). In those cases, however, the comparison of conformations 'before' and 'after' coordination could only be made through the use of similar (but not the same) ligands, as the present study is the first case where both structures (free ligand and a derived complex) are known from an X-ray analysis. A comparison of selected ligand bond distances for (I) and their homologues in the free moiety (taken from Belmar *et al.*, 2004) is shown in Fig. 3. Although individual differences are subtle enough to be considered not relevant, the overall trend of the bond-length changes in the N3—C5—C2—C1—O1 chain clearly points to an enamine-to-imine shift of the ligand character after complexation.

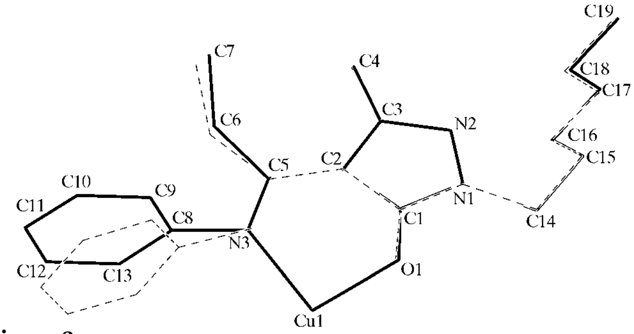

Figure 2

A superposition diagram, showing the similarities between the nuclei in (I) (solid lines) and in the free ligand (dashed lines; Belmar *et al.*, 2004).

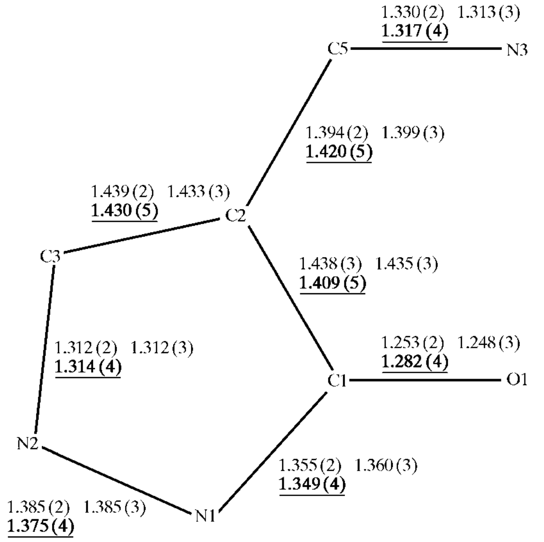

Figure 3

A comparison of selected bond distances for the coordinated ligand *L* in (I) (underlined bold type) and the uncoordinated ligand in Belmar *et al.* (2004) (regular type).

Experimental

The protonated ligand *L*H (Belmar *et al.*, 2004, 2005; 0.1 g, 0.32 mmol) and $Cu(O_2CCH_3)_2{\cdot}H_2O$ (0.032 g, 0.16 mmol) were dissolved in ethanol (10 ml) and heated under reflux for 1 h. The solution was then evaporated to a final volume of 5 ml and allowed to cool to room temperature. The solid was filtered off and crystallized by slow evaporation from a chloroform–hexane mixture (1:1 *v*/*v*) [yield 0.08 g, 73%; m.p. 396 (2) K].

Crystal data

$[Cu(C_{19}H_{26}N_3O)_2]$
$M_r = 688.40$
Triclinic, $P\overline{1}$
$a = 8.0366\ (10)$ Å
$b = 8.8767\ (11)$ Å
$c = 14.3438\ (17)$ Å
$\alpha = 94.121\ (2)^\circ$
$\beta = 95.416\ (2)^\circ$
$\gamma = 115.946\ (2)^\circ$
$V = 908.67\ (19)$ Å^3

$Z = 1$
$D_x = 1.258$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1870 reflections
$\theta = 3.6\text{–}23.5^\circ$
$\mu = 0.64$ mm^{-1}
$T = 298\ (2)$ K
Prism, brown
0.30 × 0.16 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.86$, $T_{\rm max} = 0.91$
7009 measured reflections

3530 independent reflections
2449 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\rm max} = 26.0^\circ$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.139$
$S = 1.02$
3530 reflections
217 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.49$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.879 (2)	N3—C5	1.317 (4)
Cu1—N3	2.036 (3)	N3—C8	1.446 (4)
O1—C1	1.282 (4)	C1—C2	1.409 (5)
N1—C1	1.349 (4)	C2—C5	1.420 (5)
N1—N2	1.375 (4)	C2—C3	1.430 (5)
N1—C14	1.445 (5)	C3—C4	1.486 (5)
N2—C3	1.314 (4)		
O1—Cu1—N3	92.24 (11)		

H atoms were placed in their theoretical positions, with aromatic C—H = 0.93 Å, CH_2 C—H = 0.97 Å and methyl C—H = 0.96 Å, and allowed to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ for the first two cases and $1.5U_{\rm eq}({\rm C})$ for the third. The methyl groups were also allowed to rotate around their C—C axes.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1229). Services for accessing these data are described at the back of the journal.

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