{2,2′-[1,1′-(4-Azaheptane-1,7-diyl-dinitrilo)diethylidyne]diphenolato}-copper(II)

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The quinquedentate ligand 2,2′-[1,1′-(4-azaheptane-1,7-diyldinitrilo)diethylidyne]diphenol in the title compound, [Cu-$(C_{22}H_{27}N_3O_2)$], furnishes an N_3O_2 donor set, which results in a distorted square-pyramidal coordination; the two O and two imine N atoms lie in the basal plane, while the secondary amine N atom of the ligand occupies the axial position. The axial Cu—N bond is 0.33 Å longer than the average of the equatorial bonds, and the O atoms are *trans*. The symmetry of the molecule is lowered by the twist–boat and chair conformations adopted by the two CuNN chelate rings. The complex contains two intramolecular C—H$\cdots$O interactions, and two molecules of the complex are linked into a dimer by means of moderate N—H$\cdots$O hydrogen bonds. Spectroscopic evidence supports the presence of hydrogen bonds.

Comment

Copper (II) complexes have been studied widely, because of their flexibility and ability to stabilize unusual oxidation states (Xifra *et al.*, 2005), and for their rôle in mimicking peculiar geometries around the metal atom, leading to very interesting spectroscopic properties and varied reactivities (Adman, 1991; Kitajima, 1992; Fenton, 1999). The complexity of the stereochemistry of copper (II) complexes is well known (Gažo *et al.*, 1982; Hathaway, 1984; Murphy, 1993). The structures of such complexes are controlled by the type of donor atoms and the steric constraints in the ligands. For instance, five-coordinated copper (II) complexes, in most cases, take on many different geometries between square-pyramidal and trigonal–bipyramidal (Hathaway, 1987).

The majority of pentadentate ligands studied have been derived from the Schiff base condensation of 2 mol of an aldehyde or ketone with 1 mol of an amine containing three donor atoms. 2,2′-[1,1′-(4-Azaheptane-1,7-diyldinitrilo)diethylidyne]diphenol, (Me-sal)$_2$dpt, is a ligand which is formed by the condensation of 2-hydroxyacetophenone (2 mol) and

dipropylenetriamine (1 mol). This ligand yields metal complexes showing distorted structures intermediate between trigonal–bipyramidal and square-pyramidal. The effect of altering the metal atom, bonded to identical ligands, can also be observed in the structures of these metal complexes. It is in this context that we have reported the nickel complexes obtained from this ligand under different experimental conditions (Amirnasr, Schenk *et al.*, 2006), and we report here the synthesis and structural characterization of the title compound, [(Me-sal)$_2$dpt]Cu, (I).

(I)
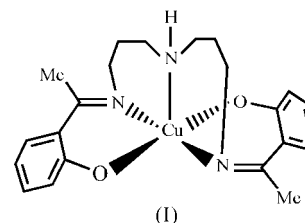
The Cu[II] atom of (I) is coordinated to three N and two O atoms, and the coordination geometry around the Cu[II] atom is distorted square-pyramidal. Two imine N atoms and two phenolate O atoms reside in the basal plane, while the secondary amine N atom occupies the axial position. Bond lengths in the coordination polyhedron are in agreement with values from analogous structures. The Cu—O [1.9533 (16) and 1.9578 (16) Å], Cu—N$_{imine}$ [1.9832 (19) and 1.9850 (19) Å] and Cu—N3 [2.309 (2) Å] bond lengths are in good agreement with the Cu—O [1.925 (5) and 1.951 (5) Å], Cu—N$_{imine}$ [1.951 (5) and 1.983 (5) Å] and Cu—N3 [2.374 (10) Å] bond lengths found in {N,N′-bis[(2-hydroxy-5-methylphenyl)-phenylmethylene]-4-azaheptane-1,7-diaminato(2−)}copper(II) (Healy *et al.*, 1975). The Cu—N3 bond in (I) is considerably longer than the corresponding Ni—N3 bond [2.0505 (12) Å] in the analogous Ni complex (Amirnasr, Schenk *et al.*, 2006) and reflects a weaker axial interaction which is typical of Jahn–Teller-sensitive copper(II) complexes. In the conformation adopted by the (Me-sal)$_2$dpt ligand, the benzene rings are bent unsymmetrically away from the axial position occupied by atom N3, owing to the difference in the conformations of the six-membered rings linking the salicylidene rings to the secondary amine atom N3. The angles between the normal to the equatorial plane defined by atoms Cu/O11/O21/N11/N21 and the normals to the C11–C16 and C21–C26 benzene rings are 50.55 (10) and 60.47 (11)°, respectively.

Within the ligand, all refined distances and angles are well within the accepted ranges. The C11–C16 benzene ring (mean deviation 0.006 Å), and indeed the whole O11/C11–C16/C17 group (mean deviation 0.014 Å), is quite flat. The C21–C26 ring is slightly twisted (mean deviation 0.022 Å) and the O21/C21–C26/C27 group (mean deviation 0.039 Å, greatest deviation 0.059 Å for atom C27) is even more warped. Atom C27 links to the twist–boat Cu/N3/C211/C210/C29/N21 ring [topological D_2 symmetry, puckering parameters (Cremer & Pople 1975): θ = 87.0 (2)° and φ = 273.61 (17)°]. As shown below, the fact that the O21/C21–C27 group is more warped than the analogous O11/C11–C17 group is a consequence of a packing impossibility. The other chelate ring is in an approx-

imate chair conformation (Fig. 1). This is in contrast with [Ni(Me-sal)$_2$dpt] (Amirnasr, Schenk *et al.*, 2006) and [Co{(Me-sal)$_2$dpt}(benzylamine)]PF$_6$ (Amirnasr, Meghdadi & Morshedi, 2006), in which a clear chair and a neat boat conformation, as well as rigorously flat O/C11–C16/C17 rings, were observed.

The shape of the title complex resembles a chubby angle-iron. On its convex side it is decorated with a Lissajous-like bulge of H atoms, within the loop of which are embedded the benzene rings. Two of these irons are held together by means of two moderate intermolecular N—H···O hydrogen bonds [Table 1, in which normalized H-atom positions are used (Jeffrey & Saenger 1991)], forming centrosymmetric dimers vaguely reminiscent of an X-shaped branding-iron. These dimers then build up the structure according to van der Waals considerations and C—H···π interactions (Fig. 2) (Hunter & Sanders, 1990). Indeed, almost the whole of the surface of this branding-iron consists of hydrogen. During the build-up of the structural edifice, the bulges of the complexes fit into the dips of neighbouring complexes in such a way that a rather compact structure is obtained (Fig. 2). This is certainly so
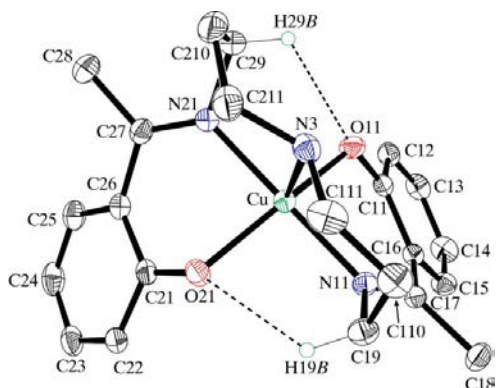

Figure 1
A view of (I), showing the atom-numbering scheme and intramolecular hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 20% probability level. Most H atoms have been omitted for clarity.
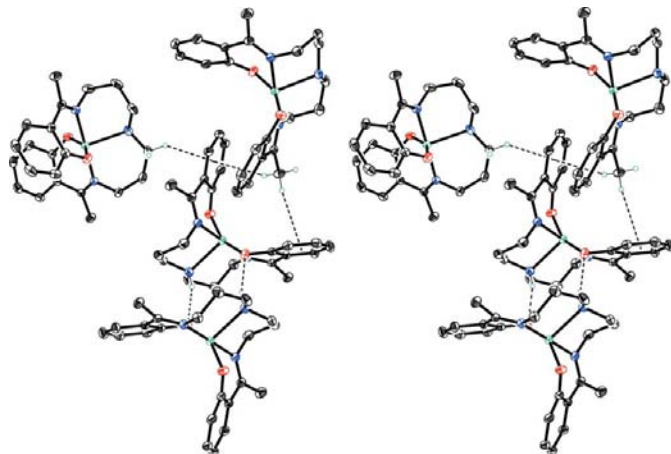

Figure 2
A stereoview, showing the N—H···O and C—H···π intermolecular interactions (dashed lines) in (I). Most H atoms have been omitted for clarity.

when viewed along the *a* and *c* axes, but there are four tiny (roughly 2 Å wide) channels per unit cell along the *b* axis. These are the places where a methylene group stands perpendicular to the C21–C26 benzene ring (shortest contacts $\simeq$ 1.8 Å). In these instances, there is obviously a steric compromise to tolerate the channels mentioned above.

It is interesting to note that the N—H···O hydrogen bond is corroborated by IR spectroscopy. Indeed, the sharp band corresponding to the amine ν(N—H) stretching vibrations of free H$_2$(Me-sal)$_2$dpt appears at 3295 cm^{-1}, but the band is shifted by about 83 cm^{-1} in (I) relative to the uncoordinated amine and becomes relatively broad, owing to intermolecular hydrogen bonding. These data thus confirm the attribution of the N—H···O hydrogen bonds. The same behaviour was also observed in [Co{(Me-sal)$_2$dpt}(benzylamine)]PF$_6$ (Amirnasr, Meghdadi & Morshedi, 2006), in which the H···O distances are even shorter. The C—H···O hydrogen bonds are corroborated by the chemical shift of the H$_c$ atoms on the C—N groups. In the free ligand, the chemical shift of the H$_c$ atom of NHCH$_2$CH$_2$CH$_2$—N=C is 3.63 (4H, *t*, H$_c$), and that of NHCH$_2$CH$_2$CH$_2$N=C is 2.15 (1H, *br*, N—H). The H$_c$ atom is even more deshielded in metal complexes. For example, the chemical shifts of H$_c$ protons in [Co{(Me-sal)$_2$dpt}(benzylamine)]PF$_6$ are in the range 3.65–5.20 p.p.m. The H$_c$ protons are therefore capable of forming intramolecular hydrogen bonds with the O atom. It is also interesting to note that the broad-band characteristic of the OH group of the free H$_2$(Me-sal)$_2$dpt ligand (3300–3400 cm^{-1}) is absent in the IR spectrum of the title complex, indicating that the equatorial ligand is coordinated in its deprotonated form.

Furthermore, there are two intramolecular C—H···O hydrogen bonds in the complex (Table 1). Again, the lengths and angles of all hydrogen bonds fall perfectly in the ranges given by Jeffrey & Saenger (1991) or Desiraju & Steiner (1999). These weakish hydrogen bonds manifest themselves in the IR spectrum as a splitting of the ν(C—H) band at 3052 cm^{-1} in the free ligand into two bands at 3046 and 3013 cm^{-1}. The same situation also occurs in the Co complex.

Experimental

H$_2$(Me-sal)$_2$dpt was prepared as reported elsewhere (Amirnasr, Schenk *et al.*, 2006). To a boiling solution of H$_2$(Me-sal)$_2$dpt (367 mg, 1 mmol) in dichloromethane (10 ml), a solution of Cu(OAc)$_2$·4H$_2$O (253.7 mg 1 mmol) in methanol (10 ml) was added slowly and the mixture stirred until the dichloromethane had evaporated. Solid KOH (112 mg, 2 mmol) was then added to the remaining solution and the mixture was stirred for an additional 5 min. A green precipitate was finally obtained. The reaction mixture was cooled to room temperature and the green precipitate was filtered off and washed with methanol. Green crystals of [Cu{(Me-sal)$_2$dpt}], (I), suitable for X-ray crystallography were grown by slow evaporation of a hot toluene solution of the complex at 351 K. Analysis calculated for C$_{22}$H$_{27}$CuN$_3$O$_2$: C 61.6, H 6.34, N 9.80%; found: C 61.3, H 6.30, N 9.70%. We have actually recorded data from two crystals of (I). The first was bounded by a {111} dipyramid, an {012} prism and an {001} pinacoid, but on the second one – from which the data of this report stem – these forms were only partially developed and were completed by appropriate fracture planes to close the polyhedron.

Crystal data

[Cu($C_{22}H_{27}N_3O_2$)]
$M_r = 429.01$
Orthorhombic, $Pbca$
$a = 18.120\ (4)$ Å
$b = 11.317\ (2)$ Å
$c = 19.777\ (4)$ Å
$V = 4055.6\ (14)$ Å^3
$Z = 8$
$D_x = 1.405$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 26946
  reflections
$\theta = 2.1–29.5°$
$\mu = 1.10$ mm^{-1}
$T = 293\ (1)$ K
Fractured dipyramid, blue–green
$0.4 \times 0.2 \times 0.12$ mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration
  (X-RED; Stoe & Cie, 2005)
  $T_{min} = 0.824$, $T_{max} = 0.903$
36949 measured reflections
5497 independent reflections

4147 reflections with $I > 2\sigma(I)$
$R_{int} = 0.080$
$\theta_{max} = 29.3°$
$h = -24 \rightarrow 24$
$k = -15 \rightarrow 15$
$l = -27 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.097$
$S = 1.09$
5497 reflections
255 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2$
  $+ 1.2681P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

Table 1
Normalized inter- and intramolecular hydrogen-bond geometry (Å, °).

C—H and N—H distances have been set at the neutron values obtained from International Tables for Crystallography (1995, Vol. C, Table 9.5.1.1).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N3—H3$\cdots$O11^i	1.01	2.16	3.143 (3)	165
C19—H19$B\cdots$O21	1.09	2.45	3.090 (3)	116
C29—H29$B\cdots$O11	1.09	2.46	3.094 (3)	116

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

All H atoms were made to ride on their carrier atoms, with C—H = 0.93–0.97 Å and N—H = 0.91 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}(C_{methyl})$. Torsional degrees of freedom were allowed for the methyl groups. The somewhat high R_{int} value might be due to the presence of some concave regions in the measured crystal. Since we measured two different crystals on two different diffractometers, a few comparative items from the other, unpublished, crystal might be of interest. The cell was: $a = 18.118\ (4)$, $b = 11.327\ (2)$ and $c = 19.826\ (4)$ Å, and $V = 4068.8\ (14)$ Å^3; the Cu—N3 bond was 2.3068 (18) Å; the N3—H3$\cdots$O11 hydrogen bond had parameters of 2.17 Å, 3.152 (2) Å and 165°; finally, the dihedral angles between the

equatorial plane and the benzene rings were 50.45 (7) and 60.53 (6)°, respectively.

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2005); program(s) used to solve structure: *DIRDIF96* (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2003) and *X-RED*.

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