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[*N*,*N*′-Bis(salicylidene)-1,2-diimino-2-methylpropane]copper(II)†

Jem-Mau Lo,[a] Hsueh-Hua Yao,[a] Fen-Ling Liao,[b]
Sue-Lein Wang[b] and Tian-Huey Lu[c]

[a]*Department of Nuclear Science, National Tsing Hua University, Hsinchu, Taiwan 300,* [b]*Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, and* [c]*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300. E-mail: jmlo@ins.nthu.edu.tw*

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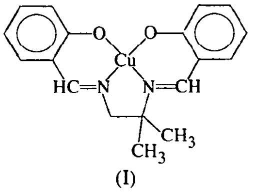
Abstract

In the title compound, $[Cu(C_{18}H_{18}N_2O_2)]$, the coordination geometry about the Cu atom is a 6–5–6 chelate ring structure, with a tetrahedrally distorted square plane composed of two imine N atoms and two phenol O atoms. The angle between the two planes, which each contain the donor atoms of a salicylaldiminato residue, and the central Cu atom is 15.8 (2)°.

Comment

Copper(II) complexes with tetradentate imine–phenols have been extensively investigated for their colour isomerism (Llewellyn & Waters, 1960; Hall & Waters, 1960), conformational influences (Clark, Hall & Waters, 1969; Baker, Hall & Waters, 1970*a*,*b*) and potential as radiopharmaceuticals (John, Bott & Green, 1994). We describe here the synthesis and characterization of the title complex, (I).



(I)

The Cu atom is four-coordinated by an N_2O_2 donor set from the imine–phenol ligand in a tetrahedrally distorted square-planar coordination geometry with the two phenolate O atoms being deprotonated. The donor atoms do not form a perfect plane but deviate by 0.190 (4) Å from their best plane. The ethylenediamine C15 and C16 atoms are displaced by 0.308 (4) and 0.289 (4) Å, respectively, in opposite directions from the CuN_2 plane. The Cu—N and Cu—O bond lengths are similar to those found in analogous structures (1.904–2.000 Å for Cu—N and 1.886–1.945 Å for Cu—O; Baker, Hall & Waters, 1970*a*; Cheeseman, Hall & Waters, 1966; Bhadbhade & Srinivas, 1993).

Perhaps the most interesting comparative aspect of copper(II) complexes with tetradentate imine–phenols involves the steric influence of (i) the length of the alkylene backbone, (ii) substitution in the alkylene bridge, and (iii) substitution in the aromatic rings upon the molecular structure. The title compound displays monomeric and four-coordinate geometry which is consistent with that of copper(II)–imine–phenols with a four-coordinate structure (Baker, Hall & Waters, 1970*a*; Bhadbhade & Srinivas, 1993; Cheeseman, Hall & Waters, 1966; Lu, Yao, Lo & Tung, 1997; Yao, Lo, Chen & Lu, 1997). This configuration is significantly distinct from monomeric Cu^{II}–*N*,*N*′-bis(salicylidene)-1,2-diiminopropane–H_2O (Llewellyn & Waters, 1960) and other dimeric copper(II)–imine–phenols with five-coordinate structures (see Table 2).

The distortion of the inner coordination sphere can be recognized by the dihedral angles between the planes defined by Cu1, N1, O1 and Cu1, N2, O2. It is seen that the dihedral angle for (I), 15.8 (2)°, is much larger than that of monomeric Cu^{II}–*N*,*N*′-bis(salicylidene)diiminoethane [5.3 (2)°; Baker, Hall & Waters, 1970*a*] and that of Cu^{II}–*N*,*N*′-bis(5-chlorosalicylidene)-1,2-diiminoethane [9.2 (3)°; Bhadbhade & Srinivas, 1993] with substitution of Cl atoms in the aromatic rings. The effect of dimethyl substitution in the ethylene

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† Alternative name: {2,2′-[2-methyl-1,2-propanediylbis(nitrilomethylidyne)]diphenolato-*N*,*N*′,*O*,*O*′}copper(II).

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bridge on the dihedral angle seems comparable to the effect of elongation of the alkylene backbone on the extent of distortion from square-planar geometry in the corresponding complexes (Lu, Yao, Lo & Tung, 1997; Yao, Lo, Chen & Lu, 1997).

Examination of the *gauche* conformation of the ethylene bridge, which has often been found to be unsymmetrical, can also provide some basis for comparison of the extent of distortion of these copper(II) imine phenols. In complexes (II)–(VI) with five-coordinate structures, the bridging ethylene C atoms are significantly asymmetrically buckled, while in the monomeric complexes without substitution in the ethylene backbone [complexes (VII) and (VIII)], there is only a slight deviation of the bridging C atoms from the CuN_2 plane. They contrast with the symmetrical displacement of the bridging C atoms [−0.289 (4) and 0.308 (4) Å from the plane] of (I), which suggests, with reference to other structural discrepancies previously discussed, that substitution of the dimethyl group in the ethylene backbone plays an important role in the symmetry of the displacement of the bridging C atoms, the coordination number and the dihedral angle in the series of copper(II) complexes of *N*,*N*′-bis(salicylidene)-1,2-diiminoethanes.

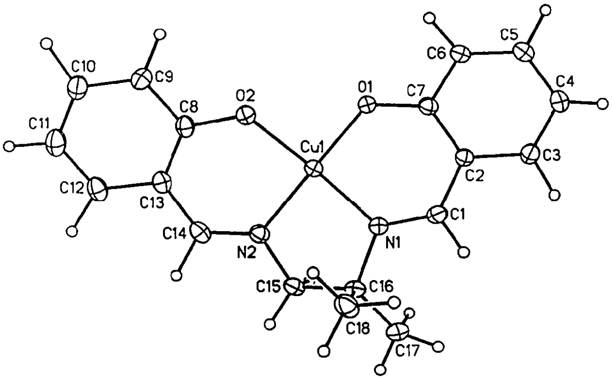

Fig. 1. A perspective view of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

N,*N*′-Bis(salicylidene)-1,2-diimino-2-methylpropane was prepared by condensation of salicylaldehyde (60 mmol) and 1,2-diamino-2-methylpropane (30 mmol) in 100 ml of ethanol. The reaction mixture was stirred for 6 h and then placed in a freezer for 24 h. The yellow precipitate was collected by filtration and then washed with cold ethanol. After recrystallization, yellow crystals were harvested and dried *in vacuo*. Copper(II) nitrate trihydrate (3 mmol) in 95% ethanol (20 ml) and *N*,*N*′-bis(salicylidene)-1,2-diimino-2-methylpropane (3 mmol) in ethanol (100 ml) were mixed and heated at 333 K for 1 h. The solution was filtered and the filtrate kept in a beaker at 277 K for crystallization. Purple crystals started appearing after 3–4 d and were then collected by filtration. Crystals suitable for X-ray diffraction were obtained by slow evaporation from a saturated ethanolic solution.

Crystal data

$[Cu(C_{18}H_{18}N_2O_2)]$
$M_r = 357.9$
Orthorhombic
Pbca
$a = 16.1059 (4)$ Å
$b = 11.5721 (2)$ Å
$c = 17.6135 (3)$ Å
$V = 3282.81 (17)$ Å^3
$Z = 8$
$D_x = 1.448$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5972 reflections
$\theta = 2.5–25.0°$
$\mu = 1.341$ mm^{-1}
$T = 296$ K
Plate
0.625 × 0.500 × 0.075 mm
Purple

Data collection

Siemens SMART–CCD diffractometer
ω rotation with narrow frame exposures
Absorption correction: empirical from equivalent data (Sheldrick, 1991)
$T_{min} = 0.547$, $T_{max} = 0.917$
14 345 measured reflections

2842 independent reflections
1960 reflections with $I > 3\sigma(I)$
$R_{int} = 0.0325$
$\theta_{max} = 25.6°$
$h = -12 \rightarrow 18$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 21$
No standard reflections

Refinement

Refinement on F
$R = 0.034$
$wR = 0.041$
$S = 0.99$
1960 reflections
209 parameters
H atoms riding with $U_{iso} = 0.08$ Å^2
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: $F_c' = F_c[1 + 0.002\chi F^2/\sin(2\theta)]^{-0.25}$
Extinction coefficient: $\chi = 0.00011 (6)$
Scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—O1	1.883 (2)	O2—C8	1.323 (4)
Cu1—O2	1.897 (2)	N1—C1	1.279 (4)
Cu1—N1	1.939 (3)	N1—C16	1.507 (4)
Cu1—N2	1.937 (3)	N2—C14	1.292 (4)
O1—C7	1.327 (4)	N2—C15	1.455 (4)
O1—Cu1—O2	88.8 (1)	Cu1—N1—C1	124.5 (2)
O1—Cu1—N1	95.0 (1)	Cu1—N1—C16	113.2 (2)
O2—Cu1—N1	166.4 (1)	C1—N1—C16	121.8 (3)
O1—Cu1—N2	170.5 (1)	Cu1—N2—C14	126.4 (2)
O2—Cu1—N2	93.5 (1)	Cu1—N2—C15	112.1 (2)
N1—Cu1—N2	84.9 (1)	C14—N2—C15	121.3 (3)
Cu1—O1—C7	126.6 (2)	N2—C15—C16	109.6 (3)
Cu1—O2—C8	127.5 (2)	N1—C16—C15	104.7 (3)

Table 2. *Comparison of copper coordination (°, Å)*

	CN	Angle†	Distances‡	
(*a*)	4	15.8 (2)	−0.289 (4)	0.308 (4)
(*b*)	5	13.6 (9)	−0.60 (2)	0.14 (2)
(*c*)	5	5.0 (5)	−0.45 (1)	0.12 (1)
(*d*)	5	11.8 (3)	−0.47 (1)	0.10 (1)
(*e*)	5	6.0 (4)	−0.47 (1)	0.09 (1)
(*f*)	5	16.3 (9)	−0.2 (1)	0.4 (1)
(*g*)	4	5.3 (5)	−0.28 (1)	0.20 (1)
(*h*)	4	9.2 (3)	−0.39 (1)	0.22 (1)

† Dihedral angle between the chelate rings defined by Cu1, O1, N1 and Cu1, O2, N2. ‡ Displacement of C atoms of the ethylene backbone from the coordination plane defined by Cu1, N1, N2.

Notes: (*a*) N,N'-bis(salicylidene)-1,2-diimino-2-methylpropanecopper(II), (I) (present work); (*b*) nitrobenzene solvate of N,N'-bis(salicylidene)-1,2-diiminoethanecopper(II), (II) (Hall & Waters, 1960); (*c*) chloroform solvate of N,N'-bis(salicylidene)-1,2-diiminoethanecopper(II), (III) (Baker, Hall & Waters, 1970*b*); (*d*) chloroform solvate of N,N'-bis(salicylidene)-1,2-diiminoethanecopper(II), (IV) (Bhadbhade & Srinivas, 1993); (*e*) N,N'-bis(5-methoxysalicylidene)-1,2-diiminoethanecopper(II), (V) (Bhadbhade & Srinivas, 1993); (*f*) N,N'-bis(salicylidene)-1,2-diiminopropanecopper(II)–H_2O, (VI) (Llewellyn & Waters, 1960); (*g*) *p*-nitrophenol solvate of N,N'-bis(salicylidene)-1,2-diiminoethanecopper(II), (VII) (Baker, Hall & Waters, 1970*a*); (*h*) N,N'-bis(5-chlorosalicylidene)-1,2-diiminoethanecopper(II), (VIII) (Bhadbhade & Srinivas, 1993).

The data collection nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.89 cm. Coverage of the unique set is over 86% complete to at least 25.6° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections; it was found to be negligible. H atoms were placed geometrically and refined with a riding model and with $U_{\rm iso}$ constrained to be 0.08 Å^2.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1145). Services for accessing these data are described at the back of the journal.

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Iodobis(pyridine-*N*)bis(η^5-trimethylsilylcyclopentadienyl)neodymium

David L. Clark,[a] John C. Gordon,[b] Brian L. Scott[b] and John G. Watkin[b]

[a]*Chemical Science & Technology Division, Mail Stop G739, Los Alamos National Laboratory, Los Alamos, NM 87545, USA, and* [b]*Chemical Science & Technology Division, Mail Stop C346, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: jwatkin@lanl.gov*

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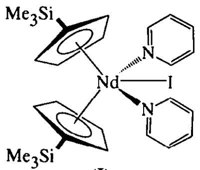
Abstract

The title complex, [$NdI(C_8H_{13}Si)_2(C_5H_5N)_2$], adopts a typical bent bis(cyclopentadienyl) geometry with one iodide and two pyridine ligands occupying the plane between the cyclopentadienyl moieties. Principal bond lengths include Nd—I 3.1483 (4), Nd—N 2.740 (3) and Nd—C 2.715 (4)–2.824 (3) Å.

Comment

We have been examining the metathesis chemistry of lanthanide triiodides with potassium salts of substituted cyclopentadienyl ligands in order to develop synthetic routes for mono- and bis(cyclopentadienyl) lanthanide complexes without the formation of intermediate salt complexes. Following the reaction of a tetrahydrofuran adduct of neodymium triiodide, [$NdI_3(thf)_3$], with two equivalents of $KC_5H_4SiMe_3$, and subsequent addition of pyridine, we have isolated the title complex, (I), in modest yield.



(I)

The molecule crystallizes in the trigonal space group $R\bar{3}c$, with the Nd and I atoms sitting on a twofold rotation axis. In the solid state, the molecule adopts

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