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Synthesis and X-ray structural characterization of sterically hindered bis(3,5-di-*tert*-butylsalicylaldiminato)Cu(II) complexes

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ABSTRACT

Bis(3,5-di-*tert*-butylsalicylaldiminato)Cu(II) complexes were prepared in high yields from a sterically hindered 3,5-di-*tert*-butylsalicylaldehyde and a variety of amines using three synthetic approaches. They were all thoroughly characterized by various spectroscopic methods (UV–Vis, IR, EPR and EI-MS). Crystal structures of seven complexes determined by X-ray crystallography show the Cu ion in a N_2O_2 coordination environment and a tetrahedrally distorted square–planar geometry. The UV–Vis and EPR results indicated that the complexes have the same geometry also in solution. In two solid state structures of the complexes the ligands have obtained an unusual *cis*-orientation whereas the rest of the complexes are *trans*-isomers. Computational studies carried out by the density functional theory method verified that in the case of complex with *N*-alkyl fragment the preferred isomer is *trans*, while the opposite behavior is observed for the complex with *N*-phenyl substituent.

1. Introduction

Schiff base metal complexes are constantly used in numerous fields of applications varying from catalysis to pharmaceuticals. For instance, transition metal Schiff base complexes catalyze cyclopropanation, aziridination, oxidation, epoxidation, polymerization and hetero-Diels–Alder reactions. Cu complexes of Schiff base derivatives are also an important class of bioactive compounds as they exhibit good antibacterial and antimalarial activities [1].

Salicylaldimine ligands have been reported to enhance metal ion chelation and provide additional stability to the metal center [2]. Introduction of bulky *tert*-butyl substituents to the ligands may cause significant changes in the chemical properties of the resulting complexes [3]. Due to their many potential applications, crystallographic data of Cu(II) complexes with salicylaldimine ligands having two bulky substituents are of importance. So far, there are several structural studies of Cu(II) complexes with differently substituted bi-, tri- and tetra-dentate salicylaldimine ligands [4]. However, structures of complexes having two bidentate ligands specifically with two *tert*-butyl substituents in the salicylaldimine moieties are still rare [5]. Recently, we have studied such Cu(II) complexes as catalysts in the aerobic oxidation of benzylic alcohols and the corresponding ligand structures in solution and solid state [6]. In continuation to our ongoing research with Cu(II) Schiff base complexes [6a,c,7], we report herein the synthesis and characterization of sterically hindered bis(3,5-di-*tert*-butylsalicylaldiminato)Cu(II) complexes. Seven of these complexes were structurally characterized by X-ray crystallography.

2. Experimental

2.1. General

All chemicals were obtained from commercial suppliers and used without further purification. Melting points were determined in an electrothermal melting point apparatus and EI-mass spectra were run with a JEOL JMS–SX 102 mass spectrometer (ionization voltage 70 eV) from solid samples. IR spectra were collected with Perkin Elmer Spectrum GX spectrometer and elemental analyses were made by an EA 1110 CHNS-OCE instrument. UV–Vis spectra were recorded with a Hewlett Packard 8453 spectrophotometer from toluene solution.

The yields of **2**, **3** and **5**–**9** prepared from bis(3,5-di-*tert*-butylsalicylaldehydato)Cu(II) (**1**) [8] intermediate were not optimized. Their purities were verified by elemental analysis and melting point measurements. The complex formations were also confirmed by IR spectroscopy. The C=O band (1615–1640 cm^{-1}) observed in the spectra of the complex precursor **1** disappeared upon the bis(3,5-di-*tert*-butylsalicylaldiminato)Cu(II) complex formation and the characteristic C=N band at 1614–1629 cm^{-1} appeared.

Detailed synthesis and analysis of the ligands and complexes **2**, **5** and **8** can be found in elsewhere [6]. The yields of the complexes

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varied (**2**: 83% or 80%. **5**: 86%, 91%, 90% or 96%. **8**: 85%, 85%, or 93%) depending on the used synthetic procedure.

2.2. Synthesis of bis(salicylaldiminato)Cu(II) complexes

A methanol (60 mL) solution of $Cu(CH_3COO)_2$ (1.26 mmol) was slowly added in a solution of ligand (2.5 mmol in 15 mL MeOH) and stirred for 1 h at room temperature. The brown solid was separated with suction filtration and recrystallized from a mixture of MeOH and CH_2Cl_2. This preparation method was applicable for synthesis of **2**–**8**.

Alternatively, complex precursor **1** (265 mg, 0.5 mmol) was suspended in EtOH (10 mL) and the corresponding amine (1 mmol) was added. The resulting mixture was refluxed for 6 h and the solid product formed was separated with suction filtration and recrystallized from a mixture of MeOH and CH_2Cl_2. Complexes **2**, **3** and **5**–**9** could be synthesized with this procedure.

In one-pot synthesis of the complexes, a methanol (30 mL) solution of $Cu(CH_3COO)_2$ (181.1 mg, 1 mmol) was added dropwise to a stirred MeOH (5 mL) solution of 3,5-di-*tert*-butylsalicylaldehyde (468 mg, 2 mmol) and Et_3N (2 equiv.). The greenish-brown solid was formed at room temperature. The corresponding amine (2 mmol) was then added and the resulting mixture was heated to reflux for 6 h. During the course of the reaction, the solid was dissolved and the color of the solution changed from green to brown, which indicates the *in situ* formation of the copper Schiff base complex. The product formed was separated with suction filtration and recrystallized from a mixture of MeOH and CH_2Cl_2. This synthetic procedure was applicable for the preparation of **2**, **3** and **5**–**9**.

2.2.1. Bis[(N-p-methyphenyl-3,5-di-tert-butylsalicylaldiminato)]Cu(II) (*3*)

Synthesis and detailed analyses of **3** can be found in the literature [9]. Brown crystals of **3** suitable for X-ray structure determination were grown in a refrigerator by a slow evaporation of a saturated toluene solution (mp 269–273 °C, literature mp > 260 °C). Yield 86%, 82% or 90% depending on the synthetic procedure. *Anal.* Calc. for $C_{44}H_{56}CuN_2O_2$ (708.5 g/mol): C, 74.59; H, 7.97; N, 3.95. Found: C, 75.34; H, 7.86; N, 4.13%. IR (cm^{-1}): 2956–2867 (ν_{C-H} from *tert*-butyl groups), 1615 ($\nu_{C=N}$), 1427 (ν_{C-O}). UV–Vis λ_{max} (nm): 296, 368, 421, 597, 628. MS (EI): *m/z* = 707–711 with appropriate isotopic ratio for $[C_{44}H_{56}CuN_2O_2]^+$.

2.2.2. Bis[(N-p-nitrophenyl-3,5-di-tert-butylsalicylaldiminato)]Cu(II) (*4*)

Brown crystals of **4** suitable for X-ray structure determination were grown by a slow evaporation of a saturated CH_2Cl_2 solution in DMSO (mp 260–262 °C). Yield: 78%. *Anal.* Calc. for $C_{42}H_{50}CuN_4O_6$ (770.4 g/mol): C, 65.48; H, 6.54; N, 7.27. Found: C, 65.57; H, 6.69; N 6.91%. IR (cm^{-1}): 2952–2868 (ν_{C-H} from *tert*-butyl groups), 1521 ($\nu_{C=N}$), 1421 (ν_{C-O}). UV–Vis λ_{max} (nm): 287, 317, 437, 583, 628. MS (EI): *m/z* = 770–773 with appropriate isotopic ratio for $[C_{42}H_{50}CuN_4O_6]^+$.

2.2.3. Bis[(N-cyclohexyl-3,5-di-tert-butylsalicylaldiminato)]Cu(II) (*6*)

Synthesis and detailed analyses of **6** can be found in the literature [10]. Brown needles of **6** suitable for X-ray structure determination were grown at room temperature by slow layer diffusion of MeOH into a CH_2Cl_2 solution of **6**. (mp 250–252 °C; literature mp 151 °C). Yield: 91%, 89% or 93% depending on the synthetic procedure. *Anal.* Calc. for $C_{42}H_{64}CuN_2O_2$ (692.5 g/mol): C, 72.84; H, 9.32; N, 4.05. Found: C, 71.60; H, 8.54; N, 3.95%. IR (cm^{-1}): 2931–2855 (ν_{C-H} from *tert*-butyl groups), 1615 ($\nu_{C=N}$), 1436 (ν_{C-O}). UV–Vis λ_{max} (nm): 284, 328, 379, 487, 657. MS (EI): *m/z* = 693–696 with appropriate isotopic ratio for $[C_{42}H_{64}CuN_2O_2]^+$.

2.2.4. Bis[(N-benzyl-3,5-di-tert-butylsalicylaldiminato)]Cu(II) (*7*)

Brown plate-like crystals of **7** suitable for X-ray structure determination were formed in a reaction mixture after a few days storage at room temperature. Single crystals with toluene solvent molecule were grown in a refrigerator by a slow evaporation of a saturated toluene solution. (mp 128–130 °C). Yield 91%, 87% or 92% depending on the synthetic procedure. *Anal.* Calc. for $C_{44}H_{56}CuN_2O_2$ (708.5 g/mol): C, 74.59; H, 7.97; N, 3.95. Found: C, 74.18; H, 8.15; N, 3.80%. IR (cm^{-1}): 2952–2867 (ν_{C-H} from *tert*-butyl groups), 1617 ($\nu_{C=N}$), 1433 (ν_{C-O}).UV–Vis λ_{max} (nm): 284, 328, 385, 486, 657. MS (EI): *m/z* = 707–710 with appropriate isotopic ratio for $[C_{44}H_{56}CuN_2O_2]^+$.

2.2.5. Bis[(N-n-hexyl-3,5-di-tert-butylsalicylaldiminato)]Cu(II) (*9*)

Synthesis and detailed analyses of **9** can be found in the literature [10]. Brown crystals of **9** suitable for X-ray structure determination were obtained by a slow layer diffusion of DMSO into a CH_2Cl_2 solution of **9** at room temperature (mp 155–158 °C, literature mp 193 °C). Yield: 86% or 95% depending on the synthetic procedure. *Anal.* Calc. for $C_{42}H_{68}CuN_2O_2$ (696.5 g/mol): C, 72.42; H, 9.84; N, 4.02. Found: C, 72.48; H, 9.63; N, 4.03%. IR (cm^{-1}): 2956–2854 (ν_{C-H} from *tert*-butyl groups), 1619 ($\nu_{C=N}$), 1433 (ν_{C-O}). UV–Vis λ_{max} (nm): 284, 327, 380, 486, 657. MS (EI): *m/z* = 696–699 with appropriate isotopic ratio for $[C_{42}H_{68}CuN_2O_2]^+$.

2.3. EPR spectroscopy

X-band EPR spectra of Cu(II) complexes **2**, **5** and **6** were measured using 10 μM toluene solutions of the complexes. Experiments were carried out on a Bruker ESP 300E spectrophotometer equipped with the Bruker NMR gaussmeter ER035M and the Hewlett–Packard microwave frequency counter with 100 kHz field modulation and microwave power of 20 mW at room temperature (quartz capillary tubes) and at 77 K (quartz tube, internal diameter ca. 1.7 mm, liquid N_2). Simulations of the EPR spectra were performed using Bruker WinEPR Simfonia software in order to calculate the *A* and *g* values.

2.4. X-ray crystallography studies

Single-crystal X-ray diffraction studies of **3–4**, **6**–**7**, **7T** (molecule crystallized with toluene solvent) and **9** were carried out on a Bruker–Nonius Kappa-CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Direct methods (SHELXS-97) were used for structure solution and refinement (SHELXL-97), full-matrix least-squares on F^2 [11]. Semi-empirical absorption corrections were applied, and H atoms were localized by difference electron density determination and refined using a riding model. Details of the data collection and structure refinement are given in Table 1 and in footnotes.[1,2] The data obtained for **4** are not of very high quality but allows the discus-

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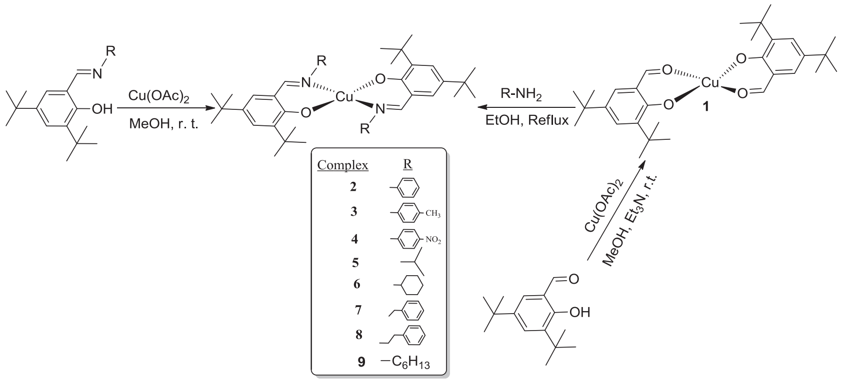
[1] **7**: $C_{44}H_{56}CuN_2O_2$, $M = 708.45$, data collected at 123(2) K, crystal size 0.50 × 0.35 × 0.25, monoclinic, space group $P2_1/n$ (No. 14): $a = 20.605(2)$ Å, $b = 23.360(2)$ Å, $c = 26.541(2)$ Å, $\beta = 95.56(1)°$, $V = 12714.9(19)$ Å^3, $Z = 12$, $\rho_{Calc} = 1.110$ mg m^{-3}, $F(000) = 4548$, $\mu = 0.550$ mm^{-1}, 74066 reflections ($2\theta_{max} = 50°$), 22177 unique [$R_{int} = 0.098$], 1324 parameters, 0 restraints, R_1 ($I > 2\sigma(I)$) = 0.070, wR_2 (*all data*) = 0.143, GOF = 1.01, largest difference in peak and hole 0.777/−0.657 e Å^{-3}. Use of SIMU and DELU restraints did not improve the quality of the crystal structure (they had an opposite effect). There is a slight disorder in some *tert*-butyl and phenyl groups which could not be resolved reasonably.

[2] **4**: $C_{42}H_{50}CuN_4O_6$, $M = 770.40$, data collected at 123(2) K, crystal size 0.08 × 0.30 × 0.40, orthorhombic, space group *Pccn* (No. 56): $a = 24.641(29)$ Å, $b = 30.417(3)$ Å, $c = 12.039(1)$ Å, $V = 9023.3(14)$ Å^3, $Z = 8$, $\rho_{Calc} = 1.134$ mg m^{-3}, $F(000) = 3256$, $\mu = 0.529$ mm^{-1}, 43523 reflections ($2\theta_{max} = 50°$), 7892 unique [$R_{int} = 0.122$], 478 parameters, 0 restraints, R_1 ($I > 2\sigma(I)$) = 0.150, wR_2 (*all data*) = 0.394, GOF = 1.18, largest difference in peak and hole 1.657/−0.693 e Å^{-3}. Forty electrons from diffuse solvent found in voids. Use of SQUEEZE did not improve the structure significantly.

Table 1
Crystallographic data for **3**, **6**, **7T** and **9**.

	3	**6**	**7T**	**9**
Empirical formula	$C_{44}H_{56}Cu\ N_2O_2$ – 1.5 toluene	$C_{42}H_{64}CuN_2O_2$	$C_{44}H_{56}CuN_2O_2$ – toluene	$C_{42}H_{68}CuN_2O_2$
Formula weight	846.65	692.49	800.58	696.52
Temperature (K)	123(2)	173(2)	123(2)	123(2)
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	*Pbcn* (No. 60)	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
Unit cell dimension				
a (Å)	10.906(1)	29.629(6)	18.488(2)	9.356(1)
b (Å)	15.114(2)	12.913(3)	9.367(1)	10.923(1)
c (Å)	15.583(3)	21.370(4)	26.192(4)	20.045(2)
α (°)	112.20(1)	90	90	90
β (°)	90.41(1)	90	99.23(1)	94.68(1)
γ (°)	90.54(1)	90	90	90
V (Å^3)	2377.9(6)	8176(3)	4477.1(10)	2041.7(4)
Z	2	8	4	2
D_{Calc} (g cm^{-3})	1.182	1.125	1.188	1.133
Absorption coefficient (mm^{-1})	0.501	0.568	0.528	0.569
$F(000)$	908	3000	1716	758
Crystal dimensions (mm)	0.45 × 0.25 × 0.10	0.35 × 0.10 × 0.10	0.55 × 0.30 × 0.15	0.50 × 0.25 × 0.15
$2\theta_{max}$ (°)	55	50	50	55
Number of collected data	53788	44021	55400	22118
Number of unique data	10754	7314	7832	9303
$R_{int.}$	0.032	0.076	0.047	0.045
Number of parameters/restraints	537/36	421/0	484/149	424/26
$R^a[I > 2\sigma(I)]$	0.032	0.042	0.057	0.058
$wR_2{}^b$	0.084	0.102	0.140	0.130
Goodness-of-fit (GOF) on F^2	1.04	1.02	1.05	1.03
Largest difference peak and hole (e A^{-3})	0.562/−0.451	0.309/−0.308	1.254/−1.012	1.239/−0.607

[a] $R = \Sigma ||F_o|-|F_c|| / \Sigma |F_o|$.
[b] $wR_2 = [\Sigma [w(F_o^2-F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$.



Scheme 1. Synthesis of bis(3,5-di-*tert*-butylsalicylaldiminato)Cu(II) complexes (**2**–**9**).

sion about the isomeric form of the complex. In **4** there are 40 electrons localized in voids (diffuse electron density of solvent DMSO) by using SQUEEZE [12]. For **9** the absolute structure was determined by refinement of Flack's *x*-parameter (*x* = −0.005(13)).

2.5. Computational studies

Optimizations of molecular structures were carried out at the B3LYP/6-311G* level of theory. Symmetry constraints were not applied and imaginary frequencies were not found at the computed IR spectra. The program suite employed was GAUSSIAN09 [13].

Table 2
EPR parameters for **2**, **5** and **6** in toluene.

Complex	$g_{iso}{}^a$	A_{iso} [G]^a	$g_{\|\|}{}^b$	$A_{\|\|}$ [G]^b	$g_{\perp}{}^b$	$g_{\|\|}/A_{\|\|}$ [cm]
2	2.116	59	2.235	167	2.042	133.83
5	2.124	71	2.238	170	2.049	131.65
6	2.117	67	2.231	170	2.046	131.24

[a] Room temperature.
[b] 77 K.

3. Results and discussion

3.1. Synthesis of ligands and complexes

Ligands used in this study were all prepared following the literature procedures [6,14]. Sterically hindered bis(3,5-di-*tert*-butylsalicylaldiminato)Cu(II) complexes (**2**–**9**) can be synthesized in good yields using three different approaches (Scheme 1). In the method which is the most commonly used synthetic approach for these types of complexes, the firstly prepared 3,5-di-*tert*-butylsalicylaldimine is reacted with Cu(II) acetate in a 2:1 M ratio at room temperature to obtain complexes **2**–**8**. In another method the bis(3,5-di-*tert*-butylsalicylaldehydato)Cu(II) complex precursor (**1**) is prepared by mixing the aldehyde and Cu(II) acetate (2:1) in the presence of Et_3N at room temperature [8]. Then **1** is

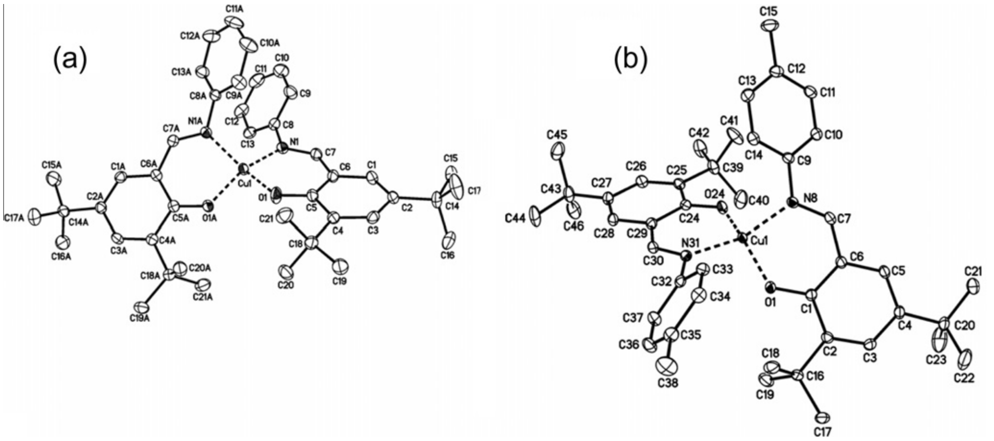


Fig. 1. Molecular structures of complexes (a) **2** [6a] and (b) **3** with the atom numbering schemes. Displacement parameters are drawn at 50% probability level. Toluene solvent molecules of **3** and hydrogen atoms are omitted for clarity.

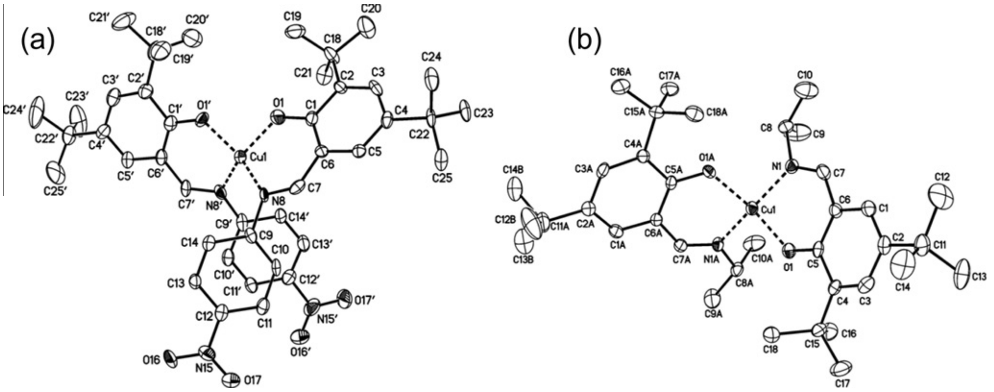


Fig. 2. Molecular structures of (a) **4** and (b) **5** [6c] with the atom numbering schemes. Displacement parameters are drawn at 50% probability level. Hydrogen atoms and the disorder in one of the *tert*-butyl groups of **5** are omitted for clarity.

converted to the bis(3,5-di-*tert*-butylsalicylaldiminato) complexes (**2**, **3** and **5**–**9**) by adding amine in refluxing condition. Alternatively, the complexes (**2**, **3** and **5**–**9**) can be obtained using the developed facile one-pot synthesis. First aldehyde, Cu(II) acetate and Et_3N are reacted in 1:2:2 M ratio at room temperature to generate *in situ* the precursor **1**. Then **1** is converted into the aimed complex simply by refluxing it with the appropriate amine (amine:1 M ratio of 1:2).

It is noteworthy that with alkyl and phenylalkyl amines the transformation of **1** into the corresponding imine complex (**2**–**9**) is more facile than with phenyl amine, and that the transformation was not successful with aryl amine having an electron withdrawing NO_2 group at *para* position. It is likely that the electron withdrawing group, which reduces the basicity of amine nitrogen, causes the slower reaction rate or even prevents the imine formation altogether. Moreover, aryl amine with an electron releasing methyl group has better reactivity than phenyl amine.

3.2. Spectroscopic characterization of complexes

The electronic spectra of the complexes in toluene show bands in the 284–370 nm and 379–437 nm regions assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electron transitions of C=C (aromatic) and C=N (imine) bonds, respectively [9,10,15]. Low-intensity bands appearing in the 486–597 nm and 628–657 nm regions are related to d–d transitions of the metal center and are characteristic for distorted square-planar Cu(II) complexes [9,10].

The infrared spectra of the free ligands show a stretching vibration band between 2949 and 2966 cm^{-1} indicating the presence of phenolic hydroxyl group [6b]. The absence of this band in the IR spectra of the Cu(II) complexes indicates deprotonation of the ligand and formation of Cu–O bond [10]. The C=N stretching vibration observed for the ligands between 1570 and 1635 cm^{-1} is shifted in the complexes to lower frequencies (1520 and 1629 cm^{-1}) [6b]. This is indicative of Cu–N coordination bond formation [15]. In the complex spectra bands are observed also in the 540–550 cm^{-1} and 500–430 cm^{-1} regions due to Cu–O and Cu–N stretching vibration modes, respectively [10].

Three complexes with different electronic and steric effects were chosen for EPR studies to compare their solid state and solution structures. The X-band EPR spectra of **2**, **5** and **6** in toluene show a typical pattern for monomeric distorted square–planar Cu(II) complexes (Table 2). The EPR spectra in toluene at room temperature exhibit four-line isotropic signals with g_{iso} 2.116–2.124 and A_{iso} 59–71 G, being in good agreement with other reports on Cu(II) complexes with salicylaldimine ligands [10]. The frozen toluene solutions of Cu(II) salicylaldimine complexes display four lines corresponding to Cu hfs, ($g_{zz} > g_{xx} = g_{yy}$, A^{Cu} = 167–170 G), spectra parameters were obtained from simulations and they are consistent with spectra observed for well-known distorted tetrahedral Cu(II) complexes [16]. The degree of distortion in complexes **2**, **5** and **6** is relatively small as $g_{||}/A_{||}$ values are 131.24–133.83 cm [17a]. In **2** bulky phenyl substituents create steric effects and the structure is most distorted. The results suggest that

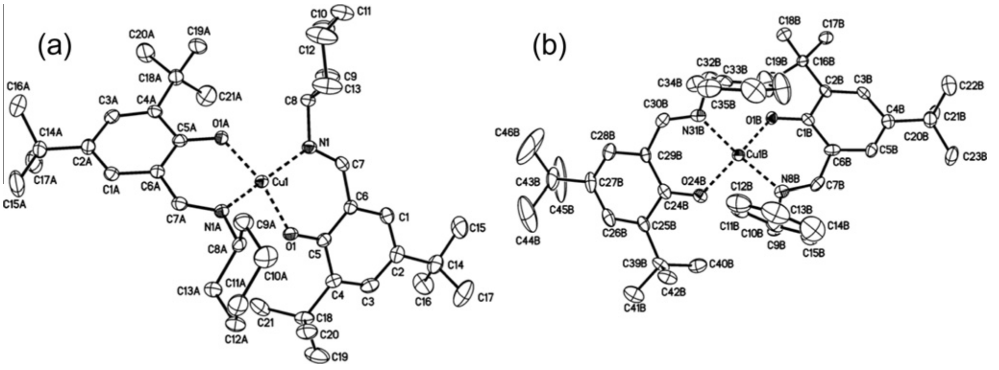


Fig. 3. Molecular structures of (a) **6** and (b) **7** with the atom numbering schemes. Displacement parameters are drawn at 50% probability level and H atoms are omitted for clarity. For **7** only one crystallographically independent molecule is shown.

complexes **2**, **5** and **6** have similar coordination spheres both in solution and in solid state (see X-ray diffraction studies below).

3.3. Crystal structures

Crystal structures of complexes **3**, **6**, **7** and **9** were determined by X-ray crystallography. For complex **7** two different structures, **7**[1] and **7T** (with toluene solvent molecule in the asymmetric unit), were obtained. The data obtained for **4** are not of very high quality[2] but allow the discussion about the isomeric form of the complex. Despite of all efforts, single crystals suitable for X-ray structure determination were not obtained for **8**. The structures of **2**, **5** and the ligand precursors used in this work have been shown in our other papers [6] but for comparison they are shortly discussed also herein.

3.3.1. Crystal structures of bis(salicylaldiminato)Cu(II) complexes

Bis(salicylaldiminato)Cu(II) complexes **2**, **3**, **5**–**7**, **7T** and **9** have a distorted square-planar geometry where the coordination sphere around the Cu(II) consists of the N_2O_2 donor atoms of the bidentate ligands (Figs. 1–4). In the structure of **3**, there is an additional interaction between the Cu(II) and H atom of toluene solvent molecule. The Cu···H distance (3.00 Å) is shorter than the sum of the corresponding van der Waals radii ($r_{\mathrm{Cu\cdots H}}$ = 3.117 Å), indicating a non-bonded interaction [17]. In two complexes, **2** [6a] and **4**, the ligands are in an unusual *cis*-configuration with respect to each other whereas rest of the complexes (**3**, **5** [6c]-**7**, **7T**, **9**) are typical *trans*-isomers. Complexes **2** and **4** have Ph and *p*-NO_2Ph substituents, respectively, at the imine nitrogens. It is likely that the driving force for the *cis* arrangement is π–π stacking of the Ph substituents which is observed in both structures.[3]

However, it is not clear why **3**, which has *p*-MePh substituted at imine nitrogens, then crystallized as a *trans*-isomer. Presumably, interaction between the Cu(II) and H atom of solvent molecule in **3** could affect the geometric arrangement of the corresponding ligand and thus the ligands adopt a *trans*-configuration. It is noteworthy that crystals of **3** suitable for X-ray structural characterization could not be obtained from other solvents besides toluene. Accordingly, the solvent could have an important role during the crystallization and to the formation of a preferred isomer [18]. Crystal structures of compounds similar to **2**–**9**, namely bis(*N*-(4-dimethylaminophenyl)-3,5-di-*tert*-butylsalicylaldiminato)Cu(II), bis(*N*-(4-diethylamino-2-methylphenyl)-3,5-di-*tert*-butylsalicylal diminato)Cu(II), bis((*R*)-*N*-(1-(cylcohexyl)ethyl)-3,5-di-*tert*-butylsalicylaldiminato)Cu(II) and bis(*N*-(2,3,4-trifluorophenyl)-3,5-di-*tert*-butylsalicylaldiminato)Cu(II), show the Cu centers in a distorted square-planar geometry with typical Cu–N (1.959(5)–1.994(4) Å) and Cu–O (1.875(4)–1.918(4) Å) bond lengths. All these complexes have the ligands in a *trans*-configuration [4a,5,19].

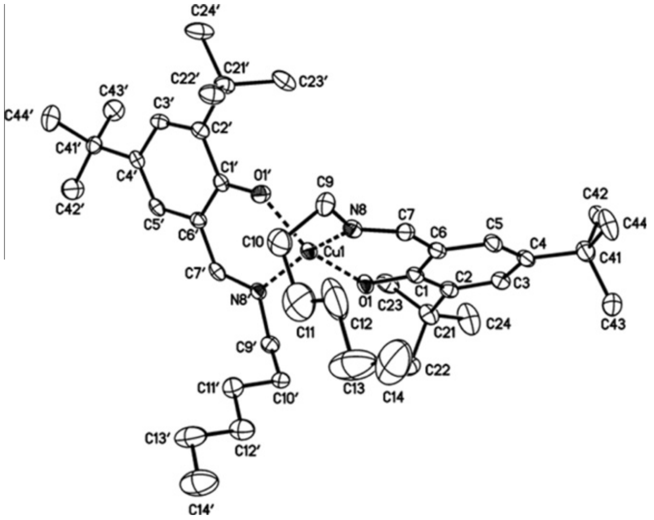


Fig. 4. Molecular structure of **9** with the atom numbering scheme. Displacement parameters are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

The closest intermolecular Cu···Cu distances (7.00–7.20 Å) between the crystallographically independent molecules of **7** are considerably longer than the Cu···Cu van der Waals distance (2.80 Å) and that of in metallic Cu (2.56 Å) [17,20]. This indicates that there is no interaction between the Cu centers. Molecular structure of **7T** does not differ significantly from that of **7**, except in **7T** one of the *tert*-butyl groups is disordered and there is one toluene solvent molecule in the asymmetric unit.

The Cu(II) complexes **2**, **3**, **5**–**7**, **7T** and **9** show a different degree of tetrahedral distortion which can be best evaluated by comparing their N8′–O1–N8–O1′ (in *trans*-isomers) and O1′–O1–N8–N8′ (in *cis*-isomers) dihedral angles (Δθ, Table 3). The distortion level can also be assessed by calculating $\Delta\mathrm{CP} = \sum(\text{observed angle} - \text{theoretical angle})^2$, where the angle is O1–Cu–N8, O1′–Cu–N8′, O1–Cu–N8′, O1′–Cu–N8, O1–Cu–O1′, and N1–Cu–N8′ (Table 3). When the structures without any solvent of crystallization (**2**, **5**–**7**, **9**) are compared, the smallest Δθ and ΔCP values are in the structure of **5** and the highest in **2**. It seems that in these structures the distortion correlates with sterical effects caused by the *N*-substituted groups. The distortion is increasing with the increasing bulkiness of the *N*-substituted group as follows: **2** > **6**, **7**, **9** > **5**. However, also

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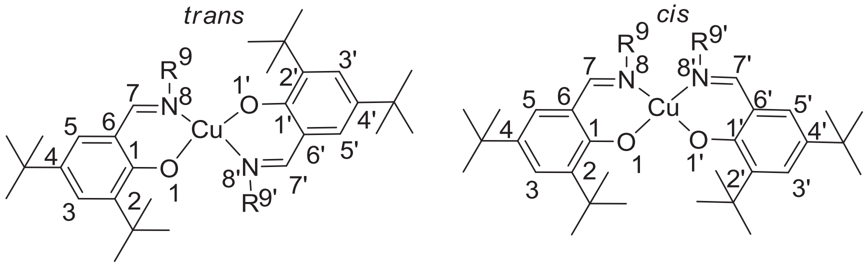
[3] In complex **2**, the distances between the centers of two N–Ph planes are 3.41 and 3.25 Å. Similarly, they are 3.36 and 3.23 Å in complex **4**.

Table 3
Selected geometrical parameters (in Å and °) of metallocyclic part for **2**–**3**, **5**–**7**, **7T** and **9**. Structures of **2** and **5** have been previously published [6] but they are included here for comparison reasons.



	2	3	5	6	7[a]			7T	9
Cu–O1	1.9011(12)	1.8923(10)	1.918(2)	1.8976(17)	1.917(3)	1.910(3)	1.914(3)	1.905(2)	1.902(2)
Cu–O1′	1.9123(10)	1.8876(10)	1.907(2)	1.9106(17)	1.911(3)	1.915(3)	1.922(3)	1.904(2)	1.900(3)
Cu–N8	1.9838(13)	1.9544(11)	1.963(3)	1.981(2)	1.952(3)	1.956(3)	1.951(4)	1.952(3)	1.957(3)
Cu–N8′	1.9772(13)	1.9576(11)	1.966(3)	1.981(2)	1.953(4)	1.954(3)	1.944(4)	1.945(3)	1.968(3)
O1–Cu–N8	93.24(5)	93.65(5)	92.79(11)	92.97(8)	93.13(13)	93.32(13)	90.65(15)	92.16(10)	93.52(12)
O1′–Cu–N8′	92.31(5)	93.75(5)	91.96(11)	92.00(8)	91.38(14)	91.27(14)	93.27(15)	92.48(11)	92.97(11)
O1–Cu–N8′	150.45(5)	94.96(4)	91.49(11)	91.09(8)	91.97(14)	91.66(13)	93.60(15)	91.22(11)	92.19(11)
O1′–Cu–N8	152.82(5)	93.54(5)	90.99(11)	92.96(8)	92.99(14)	93.32(14)	92.69(15)	91.86(10)	91.40(12)
O1–Cu–O1′	87.90(5)	147.43(5)	156.83(10)	155.68(8)	156.49(12)	155.38(12)	155.33(12)	156.33(10)	153.92(12)
N1–Cu–N8′	99.69(5)	151.38(5)	161.91(11)	158.44(9)	156.57(14)	157.34(14)	155.88(14)	161.10(12)	157.53(12)
ΔCP [b]	1726	1944	879	1079	1126	1146	1222	933	1213
Δ*θ*: N8′–O1–N8–O1′ (*trans*) O1′–O1–N8–N8′ (*cis*)	37	40	28	31	32	32	32	29	32

[a] Three crystallographically independent molecules.
[b] ΔCP = $\sum$(observed angle − theoretical angle)^2, where the angle is O1–Cu–N8, O1′–Cu–N8′, O1–Cu–N8′, O1′–Cu–N8, O1–Cu–O1′, and N1–Cu–N8′.

Table 4
Comparison of selected bond distances (Å) and angles (°) in Cu(II) complexes (**2**, **3**, **5**–**7**, **7T** and **9)** The corresponding values found in the structures of free ligands are given in the parenthesis when available. Structures of the ligands and the complexes **2** and **5** can be found in Ref. [6].

	2	3[a]	5[b]	6	7[c]			7T	9
O1–C1	1.307(2) 1.3110(18) [1.3575(16)]	1.3049(16) 1.3022(16) [1.352(3)] [1.355(3)]	1.325(4) 1.326(4) [1.362(2)] [1.365(2)] [1.363(2)]	1.317(3) 1.312(3) [1.365(5)]	1.311(5) 1.320(5) [1.358(3)]	1.297(5) 1.319(5) [1.358(3)]	1.311(5) 1.308(5) [1.358(3)]	1.308(4) 1.308(4) [1.358(3)]	1.316(4) 1.305(4)
N8–C7	1.318(2) 1.3084(19) [1.2885(18)]	1.2939(18) 1.2944(18) [1.287(3)] [1.288(3)]	1.296(4) 1.288(4) [1.283(3)] [1.286(3)] [1.285(3)]	1.296(3) 1.292(3) [1.277(5)]	1.280(5) 1.280(5) [1.282(3)]	1.288(5) 1.275(5) [1.282(3)]	1.285(6) 1.288(6) [1.282(3)]	1.279(4) 1.281(4) [1.282(3)]	1.293(5) 1.279(5)
N8–C9	1.4357(19) 1.4404(18) [1.4234(17)]	1.4228(17) 1.4241(17) [1.421(3)] [1.423(3)]	1.499(4) 1.494(4) [1.477(3)] [1.474(3)] [1.475(3)]	1.491(3) 1.494(3) [1.464(5)]	1.467(5) 1.471(5) [1.461(3)]	1.487(5) 1.470(5) [1.461(3)]	1.477(5) 1.473(6) [1.461(3)]	1.460(4) 1.461(4) [1.461(3)]	1.469(5) 1.468(4)
O1…N8	2.824 2.806 [2.566]	2.806 2.807 [2.585] [2.563]	2.810 2.785 [2.572] [2.579] [2.550]	2.814 2.800 [2.620]	2.810 2.765 [2.579]	2.812 2.766 [2.579]	2.749 2.811 [2.579]	2.778 2.780 [2.579]	2.811 2.805
C7–N8–C9	116.81(13) 117.64(13) [123.25(12)]	118.78(11) 117.70(11) [120.1(2)] [121.5(2)]	120.1(3) 120.4(3) [119.10(18)] [119.24(18)] [120.59(19)]	118.4(2) 117.7(2) [118.5(4)]	114.9(3) 117.0(4) [118.7(2)]	116.2(4) 117.9(3) [118.7(2)]	117.3(4) 114.8(4) [118.7(2)]	116.6(3) 116.8(3) [118.7(2)]	118.3(3) 118.2(3)
C6–C7–N8	127.93(14) 127.92(14) [121.14(12)]	127.36(12) 127.81(12) [122.2(2)] [121.3(2)]	127.0(3) 125.9(3) [122.3(2)] [122.57(19)] [122.27(19)]	128.4(2) 127.4(2) [123.3(4)]	128.7(4) 127.9(4) [122.5(2)]	128.5(4) 127.0(4) [122.5(2)]	126.1(4) 128.7(5) [122.5(2)]	128.0(3) 127.9(3) [122.5(2)]	127.8(4) 127.9(3)
O1–C1–C6	122.85(14) 122.27(12) [120.14(11)]	122.59(12) 122.47(12) [120.0(2)] [120.3(2)]	121.1(3) 121.6(3) [119.49(18)] [119.65(18)] [119.47(18)]	122.1(2) 122.4(2) [119.9(3)]	121.5(4) 122.2(4) [119.9(2)]	122.2(4) 122.2(4) [119.9(2)]	122.2(4) 121.6(4) [119.9(2)]	122.1(3) 121.9(3) [119.9(2)]	121.5(3) 122.1(3)

[a] Two crystallographically independent molecules in the asymmetric unit of the ligand structure.
[b] Three crystallographically independent molecules in the asymmetric unit of the ligand structure.
[c] Three crystallographically independent molecules in the asymmetric unit of the complex.

Table 5
Comparison of the total energies for optimized structures of the selected complexes.

Complex	Energy in Ha	E_{diff} in kcal/mol
trans-Isomer of **2**	−3532.71318197	0
cis-Isomer of **2**	−3532.71382517	0.40
trans-Isomer of **5**	−3306.45065811	4.99
cis-Isomer of **5**	−3306.44270085	0

the electronic effects into the geometry must be taken into account, especially in the structures of **3** and **7T** where there are additional Cu···H interactions between the Cu ion and toluene solvent molecules.

As expected, in all structures the Cu–N coordination bonds (1.944(4)–1.9838(13) Å) are significantly longer than the covalent Cu–O bonds (1.8876(10)–1.922(3) Å). They are all within the expected range for Cu(II) Schiff base complexes [8,21]. The C=N bond lengths (1.275(5)–1.318(2) Å) indicate that the double bond character is maintained upon the complex formation as the C_{sp2}=N is 1.279(8) Å [22]. The bond distances within the metallocyclic part of the molecule indicate a strong π-electron density delocalization through the six-membered rings surrounding the Cu ion. As a result of this, some bond distances and angles of the free ligands are affected by the Cu coordination (Table 4). For example, the C–O, C=N and C–N distances are slightly elongated upon the Cu complex formation. The O···N distance, on the other hand, is considerably longer (0.17–0.26 Å) in the complexes than in the corresponding free ligands. The longest O···N distance is found in **2** (2.824 Å) which might be caused by the π–π stacking of two phenyl groups in the structure. Similar long distance (2.814 Å) has been found in bis(*N*-3,5-di-*tert*-butyl-phenylsalicylaldiminato)Cu(II) where the ligands are in a *cis*-arrangement [3]. In the complexes the C6–C7–N8 (3.6–6.8°) and O1–C1–C6 (1.6–2.7°) angles are expanded when compared to the corresponding free ligands. This is probably related to the lack of the intramolecular N···H–O hydrogen bond in the complex structures.

3.4. Computational studies

Structures of two complexes, namely bis[(*N*-phenyl-3,5-di-*tert*-butylsalicylaldiminato)]Cu(II) (**2**) and bis[(*N*-isopropyl-3,5-di-*tert*-butylsalicylaldiminato)]Cu(II) (**5**), were optimized to see whether *trans* or *cis* isomer is preferred in terms of energy (Table 5). In the case of complex **5** with *N*-isopropyl fragment the preferred isomer is *trans*, while the opposite behavior is observed with **2** having *N*-phenyl substituent. The energy differences are comparable with the values found normally for hydrogen bonding energies. It seems obvious that the choice of solvent could have an important role during the crystallization and the formation of a preferred isomer as found previously [18].

4. Conclusions

A series of Cu(II) complexes with sterically hindered 3,5-di-*tert*-butylsalicylaldimine ligands were prepared in high yields. The simplest way to prepare the complexes was a one-pot synthesis where 3,5-di-*tert*-butylsalicylaldehyde and the corresponding amine were condensed in the presence of Et_3N and the Cu(II) salt. The reactivity of different amines toward transformation into imine compound with the salicylaldehyde was noticed to decrease in the following order: alkyl or phenylalkyl amine > aryl amine with a methyl group (electron releasing group) > phenyl amine > aryl amine with a nitro group (electron withdrawing group). In fact, with the latter amine imine could not be formed altogether under the used reaction conditions. Electron withdrawing group decreases basicity of amine nitrogen which can further retard the reaction rate or even prevent the imine formation.

All bis(3,5-di-*tert*-butylsalicylaldiminato)Cu(II) complexes were characterized by spectroscopic methods and their crystal structures, except that of **8**, were determined. The structural studies show the Cu ions in a N_2O_2 coordination environment with a distorted square–planar geometry. In two complexes the ligands have adopted a *cis*-orientation whereas the rest of the complexes are *trans*-isomers. Computational studies revealed that in the case of complex with *N*-alkyl substituent the preferred isomer is *trans*, while the opposite behavior is observed for the *N*-phenyl containing complex. The X-band EPR spectra of the complexes in toluene show a typical pattern for monomeric distorted square–planar Cu(II) complexes. Thus, it can be concluded that the complexes have a similar coordination sphere both in solution and in solid state.

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Appendix A. Supplementary data

CCDC 826272, 826274, 826275, 826276 and 826277 contain the supplementary crystallographic data for complexes **3**, **6**, **7**, **7T** and **9**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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