Inorganica Chimica Acta 384 (2012) 275–280

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

A facile synthesis of mixed ligand Cu(II) complexes with salicylaldehyde and salicylaldimine ligands and their X-ray structural characterization

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ARTICLE INFO

Article history:
Received 3 November 2011
Received in revised form 8 December 2011
Accepted 8 December 2011
Available online 16 December 2011

Keywords:
Schiff base
Cu(II) complex
Salicylaldimine
Crystal structure
Mixed ligand complex

ABSTRACT

High yield synthetic routes to the preparation of new mixed ligand Cu(II) complexes (**1**–**7**) derived from a sterically hindered salicylaldimine and the corresponding salicylaldehyde have been developed. The complexes could be obtained either forming a salicylaldimine preligand or two optional Cu(II) complex precursors. One-pot synthesis could also be used. The complexes have been fully characterized by means of elemental analysis, UV–Vis and IR spectroscopy. Crystal structures obtained for four [(3,5-di-*tert*-butylsalicylaldehydato)(*N*-R-3,5-di-*tert*-butylsalicylaldiminato)]Cu(II) (where R = phenyl (**1**), isopropyl (**3**), benzyl (**5**) and 2-phenylethyl (**6**)) complexes show that three of them are *cis*-isomers and one is a *trans*-isomer with respect to the phenolic O-atoms. Complexes **1**, **5** and **6** form preferably loose dimers while **3** favors to exist in a loose polymeric structure in a crystal. In all these polynuclear forms the geometry around the Cu(II) ions is a distorted octahedron.

1. Introduction

Mixed ligand metal complexes are well-known to play a significant role in various biological systems such as galactose oxidase (GO), vitamin B12, chlorophyll, laccases and hemoglobin [1]. These naturally occurring mixed ligand Cu, Co, Fe and Mg complexes have at least two different ligand moieties or in a case the ligand is a single macromolecule, it consists of two or more different kinds of donor sets of atoms. Synthetic mixed ligand Cu, Ni, Co, Mn and Cd complexes have been widely studied as well. Such complexes have traditionally bioactive compounds, e.g. purine, aminoacid, bipyridine, phenanthroline or imidazole as ligands and some of them have very promising antimicrobial activities [2]. Mixed ligand complexes are biologically more active than their constituting ligands or the corresponding homoligated bis-complexes [2g–h] which is another important motivation for the studies.

Cu(II) salicylaldimine complexes are a common class of compounds actively used in various fields of catalysis. They are efficient catalysts for instance in oxidation reactions [3]. As an example, Cu(II) complexes based on 3,5-di-*tert*-butylsalicylaldimines are highly efficient catalytic systems for the aerobic oxidation of primary benzylic, allylic and heterocyclic alcohols under mild reaction conditions [3e].

Structures of metal complex catalysts are constantly modified in different ways to achieve a better understanding over the functioning of the catalyst systems and for development of more active catalyst species. Geometry of the complexes can be tuned by the choice of ligands and specifically by adjusting steric bulkiness of the ligand backbone. In nonbridged Cu(II) Schiff base complexes the metal ion is typically found in a distorted square-planar geometry and the salicylaldimine ligands have adopted a *trans*-orientation with respect to each other. Such complexes with *cis*-coordinated ligands are rare [3e,4]. In contrast to extensive research done with bis(salicylaldiminato)Cu complexes, mixed ligand Cu complexes with salicylaldimine and salicylaldehyde ligands are scarce [5,6] and only in one case the structure has been determined by X-ray diffraction method [6].

Herein, we report the synthesis, characterization and X-ray structures of a series of mixed ligand Cu(II) complexes derived from 3,5-di-*tert*-butylsalicylaldehyde and various 3,5-di-*tert*-butylsalicylaldimines.

2. Experimental

2.1. General

All chemicals were obtained from commercial suppliers and were used without a further purification. Melting points were determined in an electrothermal melting point apparatus. EI-mass spectra were run with a JEOL JMS-SX 102 mass spectrometer (ionization voltage 70 eV) from solid samples. IR and UV–Vis spectra

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doi:10.1016/j.ica.2011.12.009

were collected with a Perkin Elmer Spectrum GX spectrometer and a Hewlett Packard 8453 spectrophotometer, respectively. Elemental analyses were made by an EA 1110 CHNS-OCE instrument.

2.2. Synthesis of bis(3,5-di-tert-butylsalicylaldiminato)Cu(II) (**A**) and ligands

A detailed description of the synthesis of bis(3,5-di-*tert*-butylsalicylaldiminato)Cu(II) complexes (**A**) and the corresponding 3,5-di-*tert*-butylsalicylaldimine (**D**) ligands can be found elsewhere [3e,7,11b].

2.3. Synthesis of bis(3,5-di-tert-butylsalicylaldehydato)Cu(II) complex precursor (**B**)

Slight modifications were made to the literature procedure [8] to synthesize bis(3,5-di-*tert*-butylsalicylaldehydato)Cu(II) (**B**). To a stirred mixture of 3,5-di-*tert*-butylsalicylaldehyde (**C**) (468 mg, 2 mmol) and Et_3N (2 equivalents) in MeOH (5 mL) was added dropwise a MeOH (30 mL) solution of $Cu(OAc)_2$ (181.1 mg, 1 mmol). After 1 h, the formed brown microcrystals were isolated by filtration and recrystallized from a CH_2Cl_2–DMSO mixture (1:1, v/v) to obtain brown plate-like crystals of **1** (466 mg, 0.88 mmol, 88% yield, mp 260–263 °C). Crystals suitable for X-ray diffraction studies were grown by slow layer diffusion of CH_2Cl_2 into a DMSO solution of **B**. The structure is a monoclinic polymorph[1] of the published orthorhombic structure [8]. *Anal.* Calc. for $C_{30}H_{42}CuO_4$ (530.2 g/mol) C, 67.96; H, 7.98. Found: C, 67.81; H, 7.96%. IR (cm^{-1}): 2950–2869 (ν_{C-H} from *tert*-butyl groups), 1613 ($\nu_{C=O}$), 1422 (ν_{C-O}). UV–Vis λ_{max} (nm): 284, 347, 365 (sh), 627, 657. EI MS: *m/z* 530–532 with appropriate isotopic ratio for $[C_{30}H_{42}CuO_4]^+$.

2.4. Synthesis of mixed ligand complexes

2.4.1. Method proceeding through imine preligand formation (*I*)

Typically, a MeOH (20 mL) solution of $Cu(CH_3COO)_2$ (0.5 mmol) was added slowly to a 1:1 mixture of preligand **D** (0.5 mmol) and **C** (0.5 mmol) in MeOH (10 mL). The resulting mixture was then stirred for 1 h at room temperature and in case of complexes **1**–**4** it was further refluxed for 2 h. A green solid formed in the reaction mixture and was separated with a suction filtration. Pure product was obtained after recrystallization from CH_2Cl_2–DMSO–MeOH. Complexes **1**–**6** were obtained in 60–85% yields.

2.4.2. Method proceeding through bis(salicylaldehydato)Cu(II) complex (*II*)

Complex precursor **A** (265 mg, 0.5 mmol) was suspended in EtOH (10 mL) and the corresponding amine (0.5 mmol) was added. The resulting mixture was stirred for 1 h at room temperature and then refluxed for 2 h. Complexes **1**–**7** were obtained in 50–93% yields.

2.4.3. One-pot synthesis (*III*)

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 **C** (468 mg, 2 mmol) and Et_3N (2 equivalents). After stirring at room temperature for 15 min a brown solid was formed and the corresponding amine (1 mmol) was then added dropwise. In the case of most complexes, at this stage the brown solid converted into a green suspension but in any case the reaction mixture was refluxed for 1 h. Complexes **1**–**7** were obtained in 60–90% yields.

2.4.4. Method proceeding through bis(salicylaldiminato)Cu(II) complex (*IV*)

Equimolar amounts of complex precursors **A** (53 mg, 0.1 mmol) and **B** were added in 3 mL of toluene [5]. The resulting solution was refluxed for 2 h followed by solvent removal with rotary evaporator. The green solid obtained was dissolved in CH_2Cl_2 and DMSO was introduced on the top of the solution. After several days, green or yellowish green crystals separated providing the pure product. Complexes **1**–**7** were obtained in 71–90% yields.

*2.4.4.1. [(3,5-Di-tert-butylsalicylaldehydato)(N-phenyl-3,5-di-tert butylsalicylaldiminato)]Cu(II) (**1**).* Respective yields with methods **I**-**IV** were 61%, 67%, 63% and 72%. Brown crystals of **1** suitable for X-ray structure determination were grown in refrigerator by slow evaporation of *n*-hexane. mp 230–232 °C. *Anal.* Calc. for $C_{36}H_{47}CuNO_3$ (605.3 g/mol): C, 71.43; H, 7.83; N, 2.31. Found: C, 70.90; H, 7.74; N, 2.36%. IR (cm^{-1}): 2951–2865 (ν_{C-H} from *tert*-butyl groups), 1614 ($\nu_{C=O}$), 1595 ($\nu_{C=N}$), 1429 (ν_{C-O}). UV–Vis λ_{max} (nm): 297, 365, 415, 488, 627.

*2.4.4.2. [(3,5-Di-tert-butylsalicylaldehydato)(N-(p-methylphenyl)-3,5-di-tert-butylsalicylaldiminato)]Cu(II) (**2**).* Respective yields with methods **I**–**IV** were 85%, 88%, 83% and 78%. mp 223–225 °C. *Anal.* Calc. for $C_{38}H_{49}CuNO_3$ (619.3 g/mol): C, 71.75; H, 7.97; N, 2.26. Found: C, 72.06; H, 7.82; N, 1.96%. IR (cm^{-1}): 2950–2868 (ν_{C-H} from *tert*-butyl groups), 1605 ($\nu_{C=O}$), 1589 ($\nu_{C=N}$), 1429 (ν_{C-O}). UV–Vis λ_{max} (nm): 296, 365, 407, 488, 627.

*2.4.4.3. [(3,5-Di-tert-butylsalicylaldehydato)(N-isopropyl-3,5-di-tert-butylsalicylaldiminato)]Cu(II) (**3**).* Respective yields with methods **I**–**IV** were 81%, 93%, 90% and 79%. mp 207–210 °C. *Anal.* Calc. for $C_{33}H_{49}CuNO_3$ (571.3 g/mol): C, 69.38; H, 8.65; N, 2.45. Found: C, 69.42; H, 8.49; N, 2.62%. IR (cm^{-1}): 2957–2867 (ν_{C-H} from *tert*-butyl groups), 1621 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$), 1412 (ν_{C-O}). UV–Vis λ_{max} (nm): 284, 332, 395 (sh), 630.

*2.4.4.4. [(3,5-Di-tert-butylsalicylaldehydato)(N-cyclohexyl-3,5-di-tert-butylsalicylaldiminato)]Cu(II) (**4**).* Respective yields with methods **I**–**IV** were 60%, 53%, 60% and 71%. mp 215–218 °C. *Anal.* Calc. for $C_{36}H_{53}CuNO_3$ (611.4 g/mol): C, 70.73; H, 8.74; N, 2.29. Found: C, 70.48; H, 8.49; N, 2.24%. IR (cm^{-1}): 2951–2869 (ν_{C-H} from *tert*-butyl groups), 1614 ($\nu_{C=O}$), 1590 ($\nu_{C=N}$), 1422 (ν_{C-O}). UV–Vis λ_{max} (nm): 284, 337, 390 (sh), 486, 624.

*2.4.4.5. [(3,5-Di-tert-butylsalicylaldehydato)(N-benzyl-3,5-di-tert-butylsalicylaldiminato)]Cu(II) (**5**).* Respective yields with methods **I**–**IV** were 84%, 88%, 79% and 82%. mp 199–200 °C. *Anal.* Calc. for $C_{38}H_{49}CuNO_3$ (619.3 g/mol): C, 71.75; H, 7.97; N, 2.26. Found: C, 71.92; H, 8.01; N, 2.55%. IR (cm^{-1}): 2949–2866 (ν_{C-H} from *tert*-butyl groups), 1622 ($\nu_{C=O}$), 1599 ($\nu_{C=N}$), 1413 (ν_{C-O}). UV–Vis λ_{max} (nm): 285, 327, 390, 630.

*2.4.4.6. [(3,5-Di-tert-butylsalicylaldehydato)(N-(2-phenylethyl)-3,5-di-tert-butylsalicylaldiminato)]Cu(II) **(6)**.* Respective yields with methods **I**–**IV** were 73%, 79%, 90% and 83%. mp 226 °C. *Anal.* Calc. for $C_{38}H_{51}CuNO_3$ (633.4 g/mol): C, 72.06; H, 8.12; N, 2.21. Found: C, 71.73; H, 8.13; N, 2.09%. IR (cm^{-1}): 2955–2868 (ν_{C-H} from *tert*-butyl groups), 1620 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$), 1464 (ν_{C-O}). UV–Vis λ_{max} (nm): 285, 326, 390, 632.

*2.4.4.7. [(3,5-Di-tert-butylsalicylaldehydato)(N-(n-hexyl)-3,5-di-tert-butylsalicylaldiminato)]Cu(II) (**7**).* Respective yields with methods **II**–**IV** were 84%, 75% and 80%. mp 170–173 °C. *Anal.* Calc. for

[1] Orange crystals, $C_{30}H_{42}CuO_4$, $M = 530.18$, crystal size $0.20 \times 0.15 \times 0.10$ mm, monoclinic, space group $P2_1/n$ (No. 14): $a = 11.603(1)$ Å, $b = 8.066(1)$ Å, $c = 15.399(1)$ Å, $\beta = 106.53(1)°$, $V = 1393.5(2)$ Å^3, $Z = 2$, ρ(calcd) = 1.264 Mg m^{-3}, $F(000) = 566$, $\mu = 0.815$ mm^{-1}, 6574 reflections ($2\theta_{max} = 50°$), 2450 unique [$R_{int} = 0.038$], 160 parameters, R_1 ($I > 2\sigma(I)$) = 0.053, wR_2 (all data) = 0.133, GOOF = 1.12, largest diff. peak and hole 1.352 and −0.364e Å^{-3}.

$C_{36}H_{55}CuNO_3$ (613.4 g/mol): C, 70.49; H, 9.04; N, 2.28. Found: C, 70.43; H, 9.22; N, 2.50%. IR (cm^{-1}): 2998–2864 (ν_{C-H} from *tert*-butyl groups), 1621 ($\nu_{C=O}$), 1602 ($\nu_{C=N}$), 1464 (ν_{C-O}). UV–Vis λ_{max} (nm): 284, 330, 366, 374 (sh), 487, 627.

2.5. X-ray crystallography studies

Single-crystal X-ray diffraction studies of **1**, **3**, **5**, and **6** 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) [9]. 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. The structures of **3**, **5**, and **6** are disordered allowing only the discussion about the conformation of the complexes and the crystal packing.

3. Results and discussion

3.1. Synthesis of ligands and complexes

Salicylaldimines (**D**) used as preligands for synthesis of mixed ligand Cu(II) complexes (**1**–**7**) are prepared in a typical condensation reaction between appropriate amine and 3,5-di-*tert*-butylsalicylaldehyde (**C**) [7,11b]. The complexes **1**–**7** with **C** and **D** ligands can be obtained via four different routes (marked as **I**–**IV** in Scheme 1). The most facile approach for their synthesis is one-pot synthesis (**III**) but on the other hand method **II**, which proceeds via a formation of bis(salicylaldehydato)Cu(II) complex (**B**), provides a convenient means for production of libraries of mixed ligand complexes. The complexes are prepared in good 41–89% yields, depending on the complex and the used method (see Section 2 for the details).

In the method **I**, the complexes **1**–**7** are synthesized by reacting the preformed ligand **D**, **C** and Cu(II) acetate in 1:1:1 molar ratio at room temperature. In the method **II**, complex precursor **B** is first obtained by reacting **C** and Cu(II) acetate in 2:1 molar ratio at room temperature. Complex **B** is then converted to the mixed ligand complex simply by reacting it with the appropriate amine. In the one-pot synthesis (**III**) which is done under refluxing conditions, **C** is allowed to react with Cu(II) acetate in the presence of Et_3N followed by the addition of appropriate amine. Interestingly, method **IV** produces the mixed ligand complexes readily when a 1:1 mixture of complex precursors **A** and **B** is refluxed in toluene [5]. The complexes **1**–**7** were carefully analyzed by IR and UV–Vis measurements and purities of the complexes were verified by elemental analysis and melting point measurements. These types of complexes can be successfully used as a complex precursor for synthesis of novel heteroligated bis(phenoxyimino)Cu complexes which are active catalysts toward oxidation of variety of alcohols [10]. Significantly, the catalysts worked efficiently also for secondary alcohols unlike other reported Cu/TEMPO (2,2,6,6-tetramethylpiperidinyloxyl) systems.

3.2. Spectroscopic characterization of mixed ligand complexes **1**–**7**

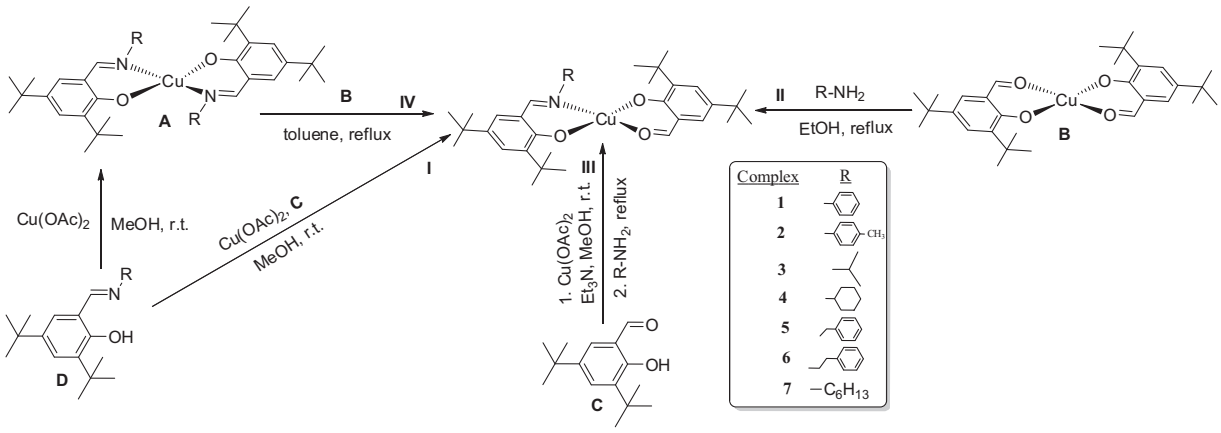
UV–Vis spectra of the mixed ligand complexes **1**–**7** in toluene have $\pi \rightarrow \pi^*$ transitions of the aromatic rings in the range of 284–365 nm. A band at 390–415 nm can be assigned to $n \rightarrow \pi^*$ electron transition of C=N (imine) [11]. It appears as a shoulder in case of N-alkyl compounds (**3**, **4**, **7**) whereas *N*-phenyl and *N*-alkylphenyl compounds (**1**, **2**, **5**, **6**, **8**) show it as a strong absorption band. Bands appearing with low intensities in the 486–488 and 624–632 nm regions are related to d-d transitions of the metal center and are characteristic for distorted square-planar Cu(II) complexes [11].

The IR spectra of the studied complexes exhibit the characteristic C=N stretching vibration in the 1589–1601 cm^{-1} region which is shifted to lower frequencies by 25–33 cm^{-1} when compared to spectra of the corresponding free salicylaldimine ligands (1614–1634 cm^{-1}) [7]. This is indicative of Cu–N coordination bond formation [12]. The band appearing in the 1605–1623 cm^{-1} region is assignable to the $\nu_{C=O}$. It is shifted to lower frequencies by 27–45 cm^{-1} when compared to spectra of the free aldehyde ligand (1650 cm^{-1}). In the spectrum of complex precursor **B** $\nu_{C=O}$ is

Table 1
Crystallographic data for mixed ligand Cu(II) complexes **1**, **3**, **5** and **6**.

	1	**3**	**5**	**6**
Empirical formula	$C_{36}H_{47}CuNO_3$	$C_{33}H_{49}CuNO_3$	$C_{37}H_{49}CuNO_3$	$C_{38}H_{51}CuNO_3$
Formula weight	605.29	571.27	619.31	633.34
T (K)	123(2)	123(2)	123(2)	123(2)
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	Pbcn (No. 60)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a (Å)	12.745(1)	26.510(2)	12.722(1)	24.669(5)
b (Å)	15.119(1)	10.996(1)	16.106(1)	15.758(3)
c (Å)	17.806(1)	10.816(1)	16.403(1)	9.631(2)
β (°)	102.60(1)		101.80(1)	107.98(2)
V (Å^3)	3348.4(4)	3152.9(5)	3290.0(4)	3561.1(12)
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.201	1.203	1.250	1.181
Absorption coefficient (mm^{-1})	0.686	0.724	0.699	0.648
F(000)	1292	1228	1324	1356
Crystal dimensions (mm)	0.40 × 0.20 × 0.04	0.50 × 0.20 × 0.10	0.32 × 0.16 × 0.08	0.40 × 0.12 × 0.06
$2\theta_{max}$ (°)	55	50	55	50
Number of collected data	33138	27876	69524	16756
Number of unique data	7668	2777	7531	3142
R_{int}	0.053	0.036	0.043	0.053
Number of parameters/restraints	370/0	167/3	342/34	177/0
R^a [$I > 2\sigma(I)$]	0.043	0.073	0.039	0.043
wR_2[b]	0.105	0.169	0.093	0.091
GOF	1.05	1.10	1.05	1.07
Largest difference peak and hole (e A^{-3})	0.493/−0.712	1.047/−1.502	0.741/−0.436	0.626/−0.443

[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. Different synthetic routes to preparation of mixed ligand Cu(II) complexes **1**–**7**. Methods **I** and **II** proceed through salicylaldimine preligand and bis(salicylaldehydato)Cu(II) complex, respectively. Method **III** is a one-pot synthesis whereas in method **IV** the mixed ligand complex is obtained via successive formations of imine preligand and bis(salicylaldiminato)Cu(II) complex and by final addition of bis(salicylaldehydato)Cu(II).

observed at 1613 cm^{-1}. The disappearance of ν_{OH} vibration in the spectra of the complexes is indicative of Cu–O coordination bond formation [11b].

3.3. Crystal structures

The crystal structures of the salicylaldimine preligands used in this work have been published in our previous paper [7]. Structures of mixed ligand Cu(II) complexes **1**, **3**, **5** and **6** were determined by X-ray diffraction method (Figs. 1–4). In case of **3**, **5**, and **6** only the conformation of the complexes and the crystal packing are discussed due to disorder. In **3** and **6** the ligands are disordered about a twofold axis in a 1:1 ratio, while in **5** the ligands are disordered about a mirror plane approximately in a 3:1 (77:23) ratio.

Complexes **3**, **5** and **6** crystallized as *cis*-isomers and **1** as a *trans*-isomer with respect to phenolic O-atoms. In the structures

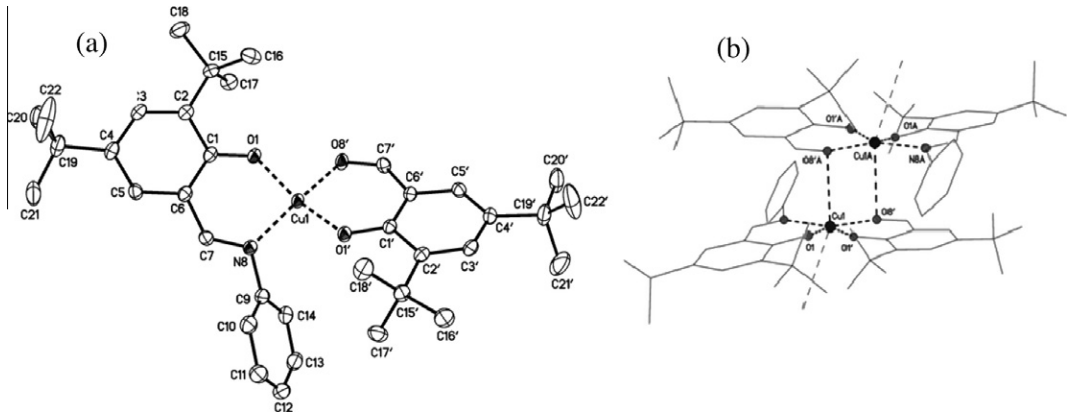


Fig. 1. (a) Molecular structure of the monomeric unit of **1** with the atom numbering scheme (displacement parameters are drawn at 50% probability level). Hydrogen atoms are omitted for clarity. (b) Dimeric structure of **1** showing the intermolecular Cu···O and Cu···H contacts with dashed lines. Selected bond lengths (Å) and angles (°): Cu1–O1 1.8868(15); Cu1–O1′ 1.8963(15); Cu1–O8′ 1.9556(16); Cu1–N8 1.9637(19); O1–C1 1.310(3); C7′–O8′ 1.255(3); C7–N8 1.301(3); N8–C9 1.448(3); Cu1–H (symmetry operator: $-x+1, y-½, -z+½$) 3.12; Cu1–O8′ (symmetry operator: $-x+1, -y+1, -z+1$) 2.8181(16); O1–Cu1–O1′ 159.29(7); O1–Cu1–O8′ 86.99(7); O1′–Cu1–O8′ 92.70(6); O1–Cu1–N8 92.79(7); O1′–Cu1–N8 92.84(7); O8′–Cu1–N8 164.75(7).

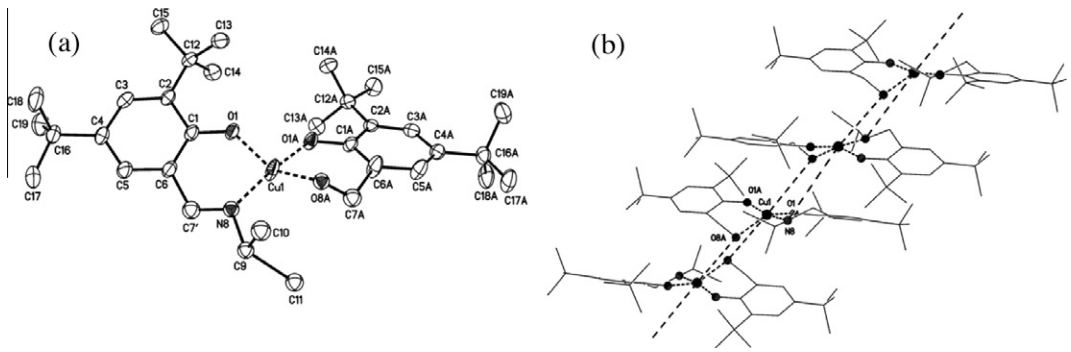


Fig. 2. (a) Molecular structure of the monomeric unit of **3** with the atom numbering scheme (displacement parameters are drawn at 50% probability level). Hydrogen atoms and the disorder about the twofold axis of **3** are omitted for clarity. (b) Polymeric structure of **3** showing the Cu···O, Cu···N and Cu···O···Cu···N contacts with dashed lines.

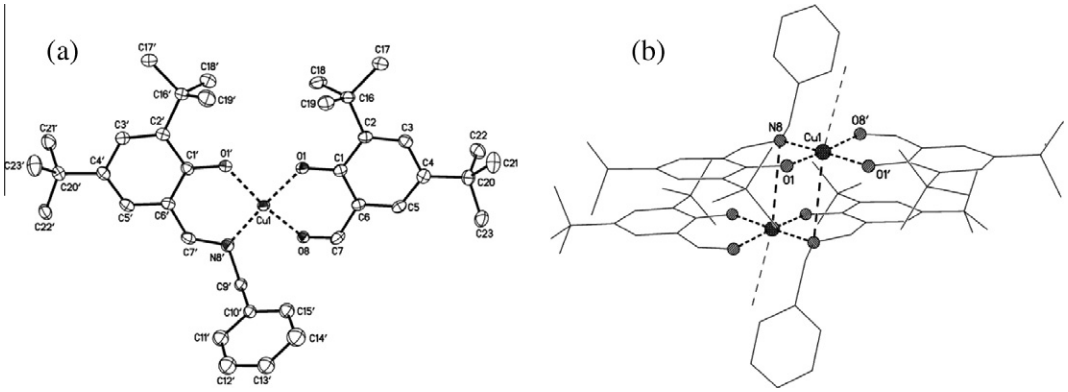


Fig. 3. (a) Molecular structure of the monomeric unit of **5** with the atom numbering scheme (displacement parameters are drawn at 50% probability level). Hydrogen atoms and the minor disordered part of **5** are omitted for clarity. (b) Dimeric structure of **5** with dashed lines indicating the intermolecular Cu···N and Cu···H contacts.

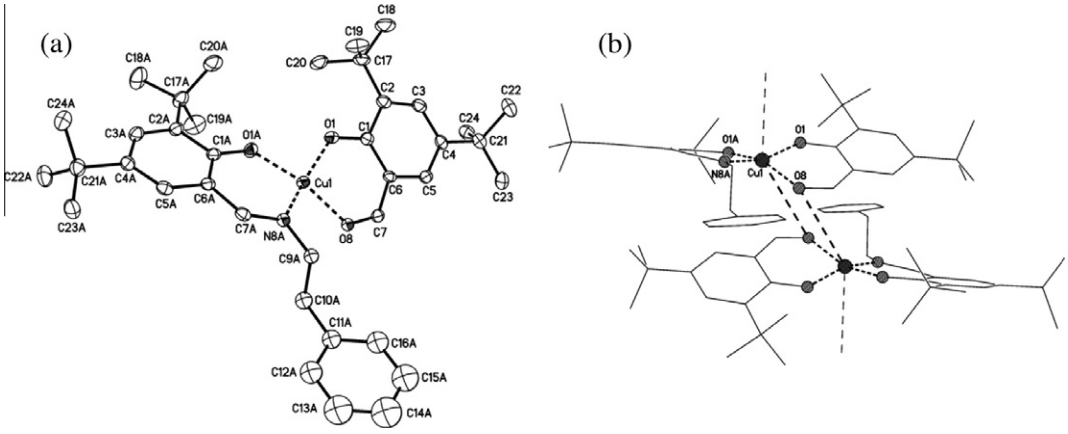


Fig. 4. (a) Molecular structure of the monomeric unit of **6** with the atom numbering scheme (displacement parameters are drawn at 50% probability level). Hydrogen atoms and the disorder about the twofold axis of **6** are omitted for clarity. (b) Dimeric structure of **6** where the dashed lines indicate the intermolecular Cu···O and Cu···H contacts.

two monoanionic, bidentate ligands are coordinated to the Cu(II) which has adopted an octahedral geometry in their dimeric or polymeric form. 3,5-Di-*tert*-butylsalicylaldehydato coordinates to the metal center through its *O*,*O*-donor atoms and salicylaldiminato through its *N*,*O*-donor set. In most crystal structures reported for nonbridged Cu(II) Schiff bases the salicylaldimine ligands have adopted *trans*-orientation and a geometry around the metal center is a distorted square-plane [13]. Complexes having *cis*-oriented ligands are sparce [3e,4].

In **1** the Cu(II) centers of two closest molecules are bridged by their aldehydato O atoms with the intermolecular Cu···O distances of 2.8181(16) Å (Fig. 1b). The distorted octahedral coordination sphere around Cu(II) is completed with *tert*-butyl H atom of aldehydato moiety (from the neighboring dimer) the Cu···H distances being 3.12 Å. The Cu–N_{imine} and Cu–$O_{phenolic}$ bond distances of **1** are in the ranges observed for similar structures [13]. The Cu–$O_{carbonyl}$ bonds are significantly longer than the Cu–$O_{phenolic}$ bonds as observed also in analogous bis(salicylaldehydato)Cu(II) complexes [14].[1]

Complex **3** forms a polymeric structure where intermolecular Cu···O (3.811(3) Å), Cu···N (4.615(7) Å) as well as Cu–O···Cu–N contacts can be found (Fig. 2b). In **5** and **6** the apical positions of the octahedral geometry are occupied by H atoms (Cu···H 2.95 Å in **5** and 3.10 Å in **6**) (Fig. 3b). The complex **5** forms dimers mainly via Cu–N···Cu–N coordination bonds but due to the disorder also a Cu–O···Cu–O dimer and a mixed Cu–O···Cu–N dimer exist in 9:6:1 ratio. The same dimeric pattern can be observed in **6** in 1:2:1 ratio (Fig. 4b). The Cu···O distances in **5** and **6** are 2.826(8) and 3.683(2) Å whereas the Cu···N distances are 3.295(3) and 3.852(9) Å, respectively.

4. Conclusions

A series of novel mixed ligand Cu(II) complexes with 3,5-di-*tert*-butylsalicylaldimine and the corresponding aldehyde ligands have been synthesized in good to excellent yields using the developed synthetic methods. The simplest way to prepare the complexes is a one-pot synthesis. Two other procedures are based on the formation of a complex precursor, either bis(salicylaldehydato)Cu(II) or bis(salicylaldiminato)Cu(II). The fourth used method proceeds through salicylaldimine preligand. The crystal structures of four complexes, determined by X-ray diffraction studies, show that three of the complexes are *cis*-isomers and one is a *trans*-isomer with respect to the phenolic O-atoms. In all structures the Cu(II) center has adopted a distorted octahedral geometry in their dimeric or polymeric form. In three structures the Cu(II) complexes from loose dimers in a crystal while with the fourth studied complex loose polymers are observed. These types of mixed ligand complexes can provide convenient synthetic routes to heteroligated bis(phenoxyimino)Cu complexes.

Acknowledgments

We gratefully acknowledge financial support from the Graduate School of Inorganic Materials Chemistry (J.U.A.). M.N. thanks the Academy of Finland (Project No. 128800).

Appendix A. Supplementary material

CCDC 794404, 848926, 848927, 848928 and 799405 contain the supplementary crystallographic data for complexes **B**, **1**, **3**, **5** and **6**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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