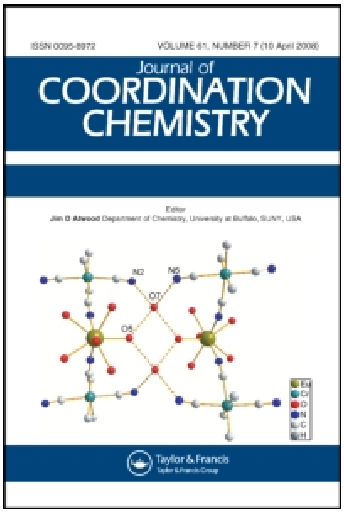

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Structural and spectroscopic characterization of Cu(salen) complexes bearing long alkoxy chains

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Structural and spectroscopic characterization of Cu(salen) complexes bearing long alkoxy chains

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Cu(II) salen (salen = *N*,*N*′-ethylene-bis(salicylideneimine)) complexes bearing alkoxy chains of C_{12} (**1**) and C_{10} (**2**) in the salicylidene moieties were synthesized and subsequently characterized by several independent methods: single crystal X-ray diffraction, infrared spectroscopy, mass spectrometry, and UV-Vis spectroscopy. The solid state structures show that the spatial orientation and packing of the complexes are not affected by the alkyl chain length but by a coordinated solvent molecule, as demonstrated by the structure of **1** having methanol in an axial position.

Keywords: Copper; Salen; Solid state structure; Spectroscopy

1. Introduction

Even though Schiff-base metal complexes have been known for a long time [1], they still evoke much current interest and are used in a variety of applications. This is partly due to the fact that they are relatively easy to synthesize and to tune electronically and sterically [2–9]. Schiff-base metal complexes on graphite have become important as they provide a platform for precise metal patterned surfaces, e.g. for functional nanodevices and for data storage applications [10]. Typically, compounds aimed for self-assembly have long alkyl chains to provide stable 2-D structures on graphite. For instance, alkyl chain functionalized bis-salicylaldehydato and bis-salicylaldiminato Cu(II) and Pd(II) complexes [11, 12] as well as Co(II), Cu(II), and Ni(II) salophen (salophen = *N*,*N*′-*o*-phenylene-bis(salicylideneimine)) complexes [13] have been self-assembled on the liquid–graphite interface and it has been shown that the highly-ordered 2-D patterns formed could be controlled very precisely [11–13].

Besides for 2-D assemblies, metal Schiff-base, particularly salen (salen = *N*,*N*′-ethylene-bis(salicylideneimine)), complexes with long alkyl chains have been widely studied as non-conventional liquid crystal compounds [6, 7, 14–25]. Thus, solid state

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structures of bridged Schiff-base complexes bearing long (C_4–C_{16}) alkyl chains in the salicylidene moieties [6, 7, 14, 17, 22–27] as well as of analogous *N*-salicylideneimine complexes [15, 28–30] are of interest. In this study, three solid state structures and 3-D packings of Cu(II) salen complexes **1** (crystallized with and without a coordinated methanol molecule) and **2** (figure 1) are presented. The effect of axially coordinated solvent on the spatial orientation and packing of otherwise similar Cu(II) salen-type complexes is described. The structure of **1** has been previously determined at 153 K [23]; here the discussion is limited to structures determined at the same temperature (173 K).

2. Experimental

2.1. *General methods*

The ^{1}H-NMR spectra were recorded with a Varian Gemini 200 apparatus and the infrared (IR) spectra (from powders) with a Perkin Elmer Spectrum One. EI and HRMS (ESI-TOF) mass spectra were recorded with JEOL JMS-SX 102 (ionizing

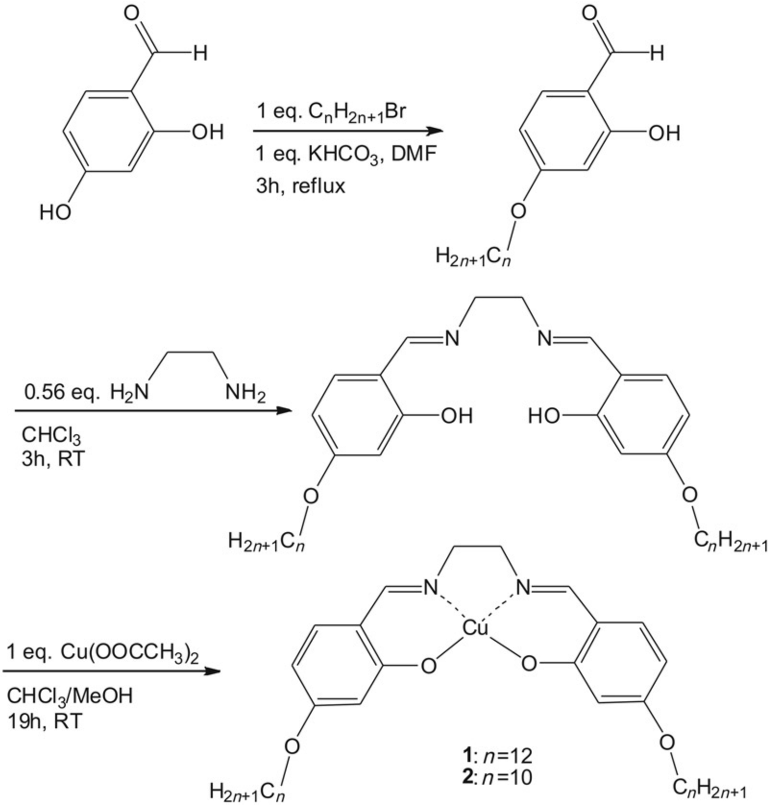

Figure 1. Synthetic scheme for Cu(II) salen complexes **1**–**2**. For details of the first reaction step, see [31].

voltage 70 eV) and Bruker micrOTOF mass spectrometers, respectively. Elemental analyses were performed with an EA 1110 CHNS-O CE instrument. All chemicals were purchased from Aldrich and used as received. The 4-alkyloxy-2-hydroxy-benzaldehydes were prepared according to a literature procedure [31].

2.2. *Ligand synthesis*

In a typical preparation of salen preligands, ethylenediamine (0.15 mL, 2.2 mmol) was added to $CHCl_3$ (5 mL) solution of 4-dodecyloxy-2-hydroxy-benzaldehyde (1.19 g, 3.9 mmol). The immediately formed yellow solution was stirred at room temperature for 3 h. The solvent was removed by a rotary evaporator and *N,N′*-ethylene-bis(4-dodecyloxysalicylideneimine) (**A**) was obtained as a yellow powder, which was purified by washing with *n*-hexane. Isolated yield 0.64 g, 26%. Anal. for $C_{40}H_{64}N_2O_4$: ^{1}H-NMR (200 MHz, $CDCl_3$, TMS): δ 0.88 (*t*, $^3J_{HH} = 6.8$ Hz, 6H, CH_3), 1.26 (s, 36H, CH_2), 1.70–1.84 (m, 4H, CH_2), 3.84 (s, 4H, bridge CH_2), 3.94 (*t*, $^3J_{HH} = 6.5$ Hz, 4H, OCH_2), 6.35 (d, $^3J_{HH} = 2.0$ Hz, 2H, H–Ar), 6.39 (s, 2H, H–Ar), 7.07 (d, $^3J_{HH} = 8.0$ Hz, 2H, H–Ar), and 8.19 (s, 2H, CH=N) ppm. IR (cm^{-1}): $\nu = 1628$ (C=N), $\nu = 1574$ (C=C), $\nu = 1409$ (C–N), and $\nu = 1285$ (C–O). UV-Vis (nm): λ_{max} 389. HRMS (ESI-TOF) *m*/*z* (%): $[M + H]^+$ 637 (100, calcd 637.4939. Found 637.4920, error 2.96 ppm).

N,N′-ethylene-bis(4-decyloxysalicylideneimine) (**B**) was obtained as a yellow powder. Isolated yield 26%. Anal. for $C_{36}H_{56}N_2O_4$: ^{1}H-NMR (200 MHz, $CDCl_3$, TMS): δ 0.88 (*t*, $^3J_{HH} = 6.8$ Hz, 6H, CH_3), 1.27 (s, 28H, CH_2), 1.69–1.83 (m, 4H, CH_2), 3.84 (s, 4H, bridge CH_2), 3.94 (*t*, $^3J_{HH} = 6.6$ Hz, 4H, OCH_2), 6.35 (d, $^3J_{HH} = 2.0$ Hz, 2H, H–Ar), 6.39 (s, 2H, H–Ar), 7.07 (d, $^3J_{HH} = 8.0$ Hz, 2H, H–Ar), and 8.19 (s, 2H, CH=N) ppm. IR (cm^{-1}): $\nu = 1623$ (C=N), $\nu = 1572$ (C=C), $\nu = 1410$ (C–N), and $\nu = 1284$ (C–O). UV-Vis (nm): λ_{max} 388. HRMS (ESI-TOF) *m*/*z* (%): $[M + H]^+$ 581 (100, calcd 581.4312. Found 581.4313, error 2.1 ppm).

2.3. *Complex synthesis*

In a typical Cu(II) complex synthesis, ligand precursor **A** (0.50 g, 0.8 mmol) in $CHCl_3$ (15 mL) was added into a MeOH solution (35 mL) of $Cu(OOCCH_3)_2$ (0.14 g, 0.8 mmol). After 19 h of stirring at room temperature, the formed suspension was filtered and the obtained green powder was washed with MeOH and *n*-hexane. Green crystals of *N,N′*-ethylene-bis(4-dodecyloxysalicylideneiminato)Cu(II) (**1**) were obtained after recrystallization from $CHCl_3$. Isolated yield 0.42 g, 76%. Anal. Calcd for $C_{40}H_{62}N_2O_4Cu$ (%): C 68.78, H 8.95, and N 4.01. Found: C 68.98, H 9.35, and N 3.71. IR (cm^{-1}): $\nu = 1605$ (C=N), $\nu = 1581$ (C=C), $\nu = 1386$ (C–N), and $\nu = 1302$ (C–O). UV-Vis (nm): λ_{max} 350. EIMS *m*/*z* (%): 306(10); 318(10); 637(15); and M^+ 697(100).

N,N′-ethylene-bis(4-decyloxysalicylideneiminato)Cu(II) (**2**) was synthesized similar to complex **1** from compound **B** and $Cu(OOCCH_3)_2$. Isolated yield 78%. Anal. Calcd for $C_{36}H_{54}N_2O_4CuH_2O$ (%): C 65.47, H 8.55, and N 4.24. Found: C 65.45, H 8.34, N 4.14. IR (cm^{-1}): $\nu = 1608$ (C=N), $\nu = 1584$ (C=C), $\nu = 1389$ (C–N), $\nu = 1308$ (C–O). UV-Vis (nm): λ_{max} 350. EIMS *m*/*z* (%): 148(17); 290(17); 580(23); M^+ 642(100).

Table 1. Crystallographic data and structure refinement for **1**, **2**, and **1** · MeOH.

Empirical Formula	$C_{40}H_{62}N_2O_4Cu$ (**1**)	$C_{36}H_{54}N_2O_4Cu$ (**2**)	$C_{41}H_{66}N_2O_5Cu$ (**1** · MeOH)
Formula weight	698.46	642.35	730.50
Temperature (K)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*Cc*
Unit cell dimensions (Å, °)			
a	53.185(1)	49.298(1)	55.228(3)
b	7.398(1)	7.161(1)	7.649(1)
c	9.903(1)	9.655(1)	9.072(1)
β	91.10(1)	93.51(1)	94.70(1)
Volume ($Å^3$), Z	3895.7(7), 4	3402.0(6), 4	3819.5(7), 4
Calculated density ($Mg\,m^{-3}$)	1.191	1.254	1.270
Absorption coefficient (mm^{-1})	0.600	0.682	0.617
Crystal size (mm^3)	0.30 × 0.15 × 0.10	0.33 × 0.22 × 0.06	0.25 × 0.15 × 0.15
R(int)	0.1331	0.1264	0.0340
Data/parameters	24,258/214	19,683/196	14,006/440
Number of data refined	4471	3892	7698
Goodness-of-fit on F^2	1.036	1.044	1.026
Final R indices, R^a, $wR_2{}^b$ $[I > 2\sigma(I)]$	$R_1 = 0.0749$, $wR_2 = 0.2148$	$R_1 = 0.0701$, $wR_2 = 0.1927$	$R_1 = 0.0556$, $wR_2 = 0.1533$
Residual density ($e\,Å^{-3}$)	1.892 (1.02 Å from Cu)	1.670 (0.93 Å from Cu)	0.735

[a] $R = \Sigma\,||F_o| - |F_c|| / \Sigma\,|F_o|$.

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

2.4. *Crystal structure determination*

Single crystals of the complexes were selected for X-ray measurements and mounted on a glass fiber [32]. The data were collected at 173 K using a Nonius Kappa charge-coupled device diffractometer. The intensity data were corrected for Lorentz and polarization effects as well as for absorption by the multi-scan method [33]. The metal complex structures were solved with the SIR2002 program [34]. The refinements and graphics were made using the SHELXL97 [35] and SHELXTL [36] program packages, respectively. All non-hydrogen atoms were refined anisotropically. Hydrogens were introduced in their calculated positions and refined with fixed geometry with respect to their carrier atoms. In **1** · MeOH, the ethylene-bridge and the methyl-group of the coordinated methanol are disordered. The hydrogen of the OH could not be localized from the residual electron density map. Hydrogens of the disordered ethylene-bridge and the methanol (also H(O) is disordered) are included using calculated positions. The cell parameters and specific data collection parameters are presented in table 1 and selected bond lengths and angles in table 2.

3. Results and discussion

3.1. *Solid state structures of 1 and 2*

Salen precursors were prepared by Schiff-base condensation between the appropriate 1,2-diamine and 4-alkyloxy-2-hydroxy-benzaldehyde. Cu(II) salen complexes **1** and **2** were synthesized in good yields from Cu(II) acetate and corresponding ligand precursors; the obtained green powders were purified by recrystallization from

Table 2. Selected bond lengths (Å), angles (°), and torsion angles (°) for **1**, **2**, and **1**·MeOH. The values for **1** determined in [23] are given in the brackets.

	$C_{40}H_{62}N_2O_4Cu$ (**1**)	$C_{36}H_{54}N_2O_4Cu$ (**2**)	$C_{41}H_{66}N_2O_5Cu$ (**1**·MeOH)
Cu–O	1.928(2)	1.910(2)	1.937(3)
	[1.905(3)]		1.939(3)
Cu–N	1.958(3)	1.940(3)	1.960(4)
	[1.934(3)]		1.960(4)
C=N	1.313(5)	1.295(4)	1.302(6)
			1.301(6)
O–Cu–O	92.89(14)	93.73(13)	90.61(12)
	[92.1(2)]		
O–Cu–N	94.12(11)	94.02(10)	92.16(15)
	[94.6(1)]	159.87(11)	92.33(15)
	161.57(12)		168.1(2)
	[161.7(1)]		168.2(2)
N–Cu–N	84.44(17)	84.90(15)	82.72(19)
O–Cu–N–C_{imine}	−102.7(4)	103.5(4)	91.4(9)
			−93.1(9)
			11.2(5)
			−11.9(5)
N–Cu–O–C_{Ar}	0.8(3)	−0.4(3)	−12.8(4)
	−83.9(4)	85.8(4)	13.2(4)
			−50.8(10)
			52.3(9)
O–C_{Ar}–C_{Ar}–C_{imine}	10.6(6)	−12.4(5)	2.5(9)
			−1.4(8)
Angle (°)			
NO{Cu}/{Cu}NO	24.6	26.9	16.1
Alkoxy chain 1/alkoxy chain 2	65	65	5
Mean sigma (Å) from NO{Cu}NO plane	0.27	0.29	0.22

$CHCl_3$. Crystals of **2** suitable for solid state structure determination by X-ray crystallography were obtained by slow evaporation of $CHCl_3$. Depending on the solvent, either structure **1** (from $CHCl_3$) or **1**·MeOH (from MeOH/CH_2Cl_2) was obtained for **1** when the same method was employed (table 1).

The LS fits of structures **1** and **2** are similar as the average deviations are only *ca* 0.02 Å [36]. The fittings were done using the Cu1, O1, N1A, C7A, C1–C6 of **1** and the Cu1, O1A, N1, C7, C1A–C6A of **2**. A clear correlation between the alkyl chain length and the length of the *a*-axis can be noted, as in **1** (C_{12}) the *a*-axis is 53.185 Å and in **2** (C_{10}) it is 49.298 Å. Complexes **1** and **2** possess crystallographic C_2-symmetry and Cu(II) has a distorted square-planar geometry typical of Cu(II) salen complexes (figure 2) [7, 23, 37, 38]. In both structures, salen has *gauche*-conformation where the carbons of the ethylene-bridge are on the opposite sides of the CuN_2O_2-plane.

Regardless of the length of the alkoxy substituents, the molecular packings of **1** (C_{12}) and **2** (C_{10}) are similar (figure 3), in accord with the previous study [23]. In both structures, the alternating layered structure typical of complexes with long alkyl chains is visible: layers consisting of alkyl chains alternate with layers of salen moieties. Some of the metal–metal distances increase with increasing alkyl chain length as expected. For example, the distance between the metal-ions positioned upon each other in the different layers is 26.84 Å in **1** and 24.90 Å in **2**. Analogously, the distances between the intersecting Cu ions from the different layers and planes are elongated when the alkyl chain length increases: **2**, 25.02–27.40 Å; **1**, 27.17–29.03 Å (figure 3).

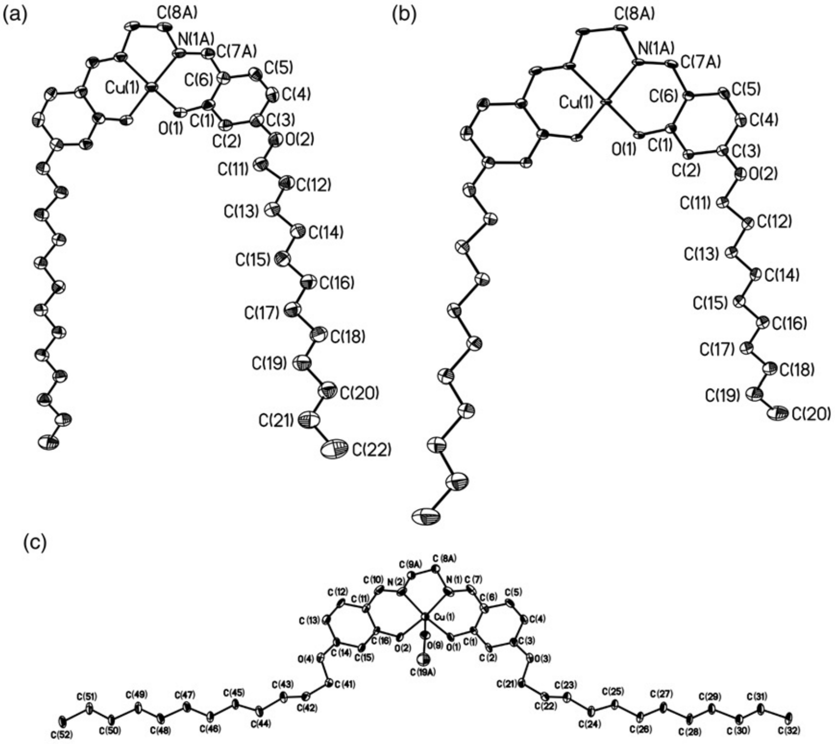

Figure 2. Molecular structures of complexes (a) **1**, (b) **2**, and (c) **1** · MeOH. Displacement ellipsoids appear at the 50% probability level. Disorders in the ethylene-bridge and in the MeOH unit of **1** · MeOH as well as hydrogens are not shown for the sake of clarity.

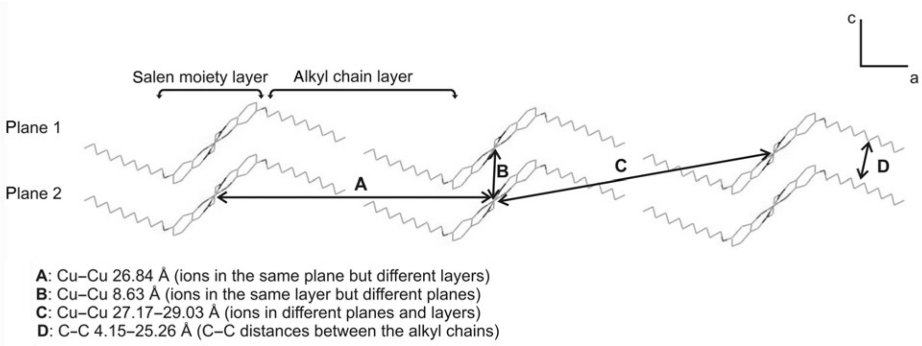

Figure 3. Crystal packing of **1** viewed along the angle showing the alternating structure of the alkyl chains and the salen moieties, and Cu–Cu distances between the intersecting Cu ions from the different layers and planes. Complex **2** is packed similar to **1**. The corresponding Cu–Cu and C–C distances A–D as marked in the figure are 24.90, 8.24, 25.02–27.40, and 4.71–20.96 Å.

In **1** and **2**, one of the two alkyl chains points upwards from the CuN_2O_2-plane and the other chain points downwards from this plane. The angle between the two planes defined by the alkoxy chains is 65° in both structures (figure 4). The corresponding torsion angles (table 2) are virtually the same in **1** and **2**, differing only by a couple of

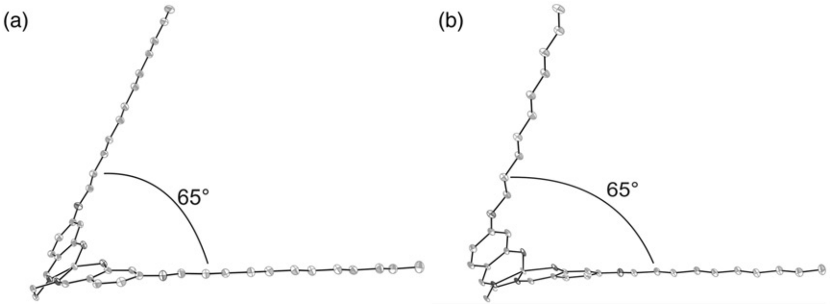

Figure 4. Molecular structures of (a) **1** and (b) **2** showing the similarity in orientations of the alkyl chains. Hydrogens have been omitted for the sake of clarity.

degrees at maximum. The shortest Cu–Cu distances are 4.85–4.96 Å and the C–C distances between the alkyl chains are of the same order of magnitude in their packing diagrams (figure 3).

1 · MeOH has nearly C_s-symmetry if the disorder in the ethylene-bridge is neglected. Also, in this structure, the salen ligand has *gauche*-conformation. An additional axially coordinated methanol results in square pyramidal geometry with N_2O_3 donors (figure 2). The angle between the line connecting Cu and O9 of MeOH and the plane defined by N1, N2, O1, and O2 is *ca* 180°. The solvent is hydrogen-bonded to the salen moiety (O9···O1 2.789 Å, O9···O2 2.784 Å, symmetry operator x, $2-y$, $0.5+z$). In addition to the axial coordination of MeOH, a very weak Cu···H contact exists, either Cu1···H8A1–C8A 3.17 Å or Cu1···H9B2–C9B 3.18 Å (due to the disorder in the structure) with a symmetry operator x, $1-y$, $-0.5+z$.

As the Cu–O and Cu–N bond lengths in **1**, **2,** and **1** · MeOH (table 2) are within the range typical for Cu(salen) complexes [7, 23, 38], MeOH in the axial position has virtually no effect on the bond lengths around the Cu ion. Also, the C=N bond lengths are within a similar, characteristic range for all complexes (table 2) [39]. The distance of 2.314(3) Å between the Cu(II) and the axial O in **1** · MeOH is typical of Cu complexes [23, 40–42]. Due to the MeOH guest, the crystal packing of **1** · MeOH (figure 5) differs from that of **1** and **2** even though it shows the layered structure of alternating alkyl chains and salen moieties. In **1** · MeOH, the shortest Cu–Cu distances (5.52 Å) are significantly longer and the C–C distances between the alkyl chains considerably shorter than for those in **1** and **2** (figures 3 and 5). In contrast to **1** and **2**, both alkoxy chains in **1** · MeOH are virtually coplanar. They deviate from each other only by 5° but point in opposite directions (figure 2c). Coordinated MeOH alters the bond and torsion angles. The differences in the equivalent bond angles around Cu(II) and in the torsion angles between the structures of **1** · MeOH and **1** and **2** are *ca* 2–8° (table 2) and even 8–34°, respectively.

3.2. *Spectroscopic characterization of 1 and 2*

Infrared spectra of preligands **A** and **B** recorded at 4000–650 cm^{-1} clearly confirm the formation of the compounds as a strong band at 1617–1628 cm^{-1} corresponding to (C=N) of the imine group is visible. In the spectra of complexes **1** and **2**, the band is shifted to 1605–1608 cm^{-1} indicating coordination of Cu to nitrogen [43, 44]. Strong

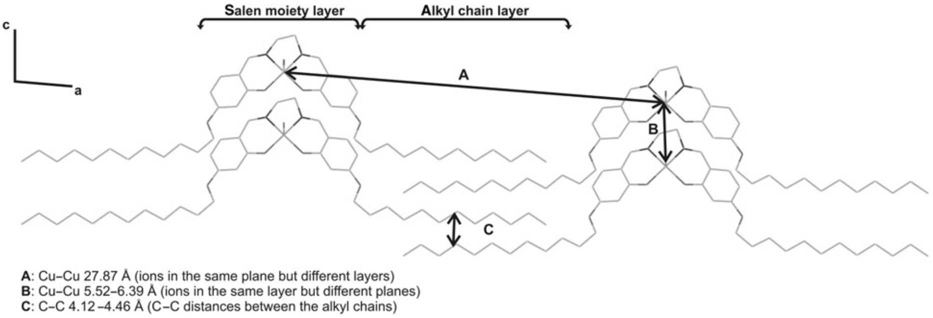

Figure 5. Crystal packing of **1** · MeOH. Hydrogens and the disorders in the ethylene-bridge and MeOH are not shown for the sake of clarity.

bands in the 793–850 cm^{-1} region in spectra of **A**, **B**, **1**, and **2** can be assigned to the out-of-plane deformation of the aromatic rings. In the spectra of preligands, a phenolic C–O, vibration is observed at 1284–1285 cm^{-1}, whereas in the spectra of the complexes the band shifts to 1302–1308 cm^{-1} and is weaker [45]. The C–N vibration shows a characteristic 10–20 cm^{-1} shift to lower wavenumber upon complex formation (1409–1410 cm^{-1} for ligands and 1386–1389 cm^{-1} for complexes) [43].

The electronic properties of **A**, **B**, **1**, and **2** were studied by UV-Vis spectroscopy at room temperature in $CHCl_3$ in which they are readily soluble. The electronic spectra of **A** and **B** exhibit an absorption at 388 nm (25,773 cm^{-1}) or 389 nm (25,707 cm^{-1}) which can be attributed to a charge transfer $n \rightarrow \pi^*$ band [43, 46]. Upon complexation in **1** and **2**, the absorption is shifted to lower wavelength (350 nm = 28571 cm^{-1}, a shoulder around 377 nm = 26525 cm^{-1}). The band at 561 nm noted in the spectra of the complexes is assignable to d–d transitions [43].

4. Conclusion

Cu(II) Schiff-base complexes with alkyl side chains are used in various applications. Significance of the alkyl chains and possible solvent molecules becomes evident especially in the field of supramolecular chemistry, studied both on surfaces and in molecular crystals. The alkyl chains and coordinated solvent molecules can have drastic effects on 2-D surface structure formation as well as on molecular structure and packing, as shown by several studies. Furthermore, even the slightest changes, such as moderately differing chain length or coordinated solvent, can alter the effects. Studies addressing these topics have the potential to provide the needed information for crystal engineering as the design and prediction of 3-D crystals and 2-D surface structures are far from trivial.

In this context, Cu(II) salen complexes **1** and **2**, bearing long alkyl chains (C_{12} and C_{10}, respectively) in the salicylidene moieties, have been synthesized and characterized by several other independent methods (IR, MS and UV-Vis). Of the determined solid state structures, two are new (**1** · MeOH and **2**) and the structure of **1** has been determined at a temperature different from the one in a previous study. The structures of **1** and **2**, differing only by the alkyl chain length, show that the chain length has no effect on the 3-D structures confirming the finding reported previously. An important finding of this study is that an axially coordinated solvent can notably change the spatial orientation and packing of the complex. This was shown by comparing the structures of **1** and **1** · MeOH where the coordinated MeOH of the latter is the only difference between their chemical structures. Moreover, when this result is put in context with previous studies, it is evident that different coordinated solvent molecules can alter the coordination sphere around Cu(II) in a different manner. Complexes **1** and **2** show crystallographic C_2-symmetry and have a distorted square-planar coordination around Cu(II), whereas in **1** · MeOH (with nearly C_s-symmetry) an axially coordinated solvent molecule results in square pyramidal coordination. In all the structures, the alkyl chains and aromatic parts alternate, typical of compounds with long alkyl chains.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre with supplementary publication CCDC nos 611867 (**2**), 611869 (**1** · MeOH), and 611870 (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(0)-1223-336033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgments

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