COPPER(II) COMPLEXES WITH SCHIFF BASES: STRUCTURES AND THERMAL BEHAVIOR

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Ligands with Schiff bases are obtained in the condensation of propylenediamine (pda) or 2,2dimethylpropylenediamine (dmpda) with acetylacetone (Hacac) in the 1:2 molar ratio. The ligands are characterized by the elemental analysis methods, $T_{melt} = 90-92$ °C for pda(Hacac)₂ (pda(acac)₂ is N,N'propylene-bis(acetylacetoniminato) (2-)), $T_{melt} = 84-86$ °C for dmpda(Hacac)₂ (dmpda(acac)₂ is N,N'-2,2dimethylpropylene-bis(acetylacetoniminato) (2-)). The tautomerism of the ligands is established by the single crystal X-ray diffraction (XRD) analysis, IR spectroscopy, and ¹H, ¹³C NMR spectrometry. The synthesized complexes [Cu(pda(acac)₂)] (1), $T_{melt} = 121-122$ °C and [Cu(dmpda(acac)₂)] (2), $T_{melt} = 156-$ 158 °C are studied by the XRD method. In both complexes, copper atoms have a planar square geometry, and the chelate bond lengths and angles are: Cu–O ≈ Cu–N 1.903(2)-1.942(3) Å, ∠O–Cu–N = 94.44(12)-94.99(12)° for 1 and Cu–O ≈ Cu–N 1.909(1)-1.943(2) Å, ∠O–Cu–N = 94.63(6)° for 2. By the thermogravimetric method it is found that both complexes can be passed practically quantitatively into the gas phase.

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Keywords: ligands with Schiff bases, copper(II) complexes, single crystal X-ray diffraction analysis, thermogravimetry.

INTRODUCTION

Complexes of 3*d* transition metals with Schiff bases are being extensively studied with respect to their practical application as catalysts [1-3] and oxygen carriers [4]. Some copper(II) chelates with Schiff bases exhibit luminescent properties [5]. One-electron Cu(II)/Cu(I) reduction processes of $[Cu(pda(acac)_2)\cdot H_2O]$ and $[Cu(pda(acac)_2)\cdot KClO_4]$ [6] complexes in acetonitrile solutions are investigated.

Copper(II) chelates with Schiff bases ($[Cu(en(acac)_2)]$ and $[Cu(Meen(acac)_2)]$) were synthesized for the first time by McCarthy et al. [4]. By the electronographic study of the gas phase the structure of a number of complexes is determined: $[Cu(en(acac)_2)]$ [7, 8], [Cu(salen)] [8, 9] ($en(acac)_2$ is N,N'-ethylene-bis(acetylacetoniminato) (2-), salen is N,N'-ethylene-bis(salicylaldiminato) (2-)). It is shown that the molecules have an almost planar structure of the CuN₂O₂ coordination center. In [10] it is reported that the [Cu(en(acac)_2)] complex sublimates congruently in the temperature range of 450-600 K and can be considered as a potential precursor for obtaining copper-containing films by metal organic chemical vapor deposition

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(MO CVD). The main problem hindering the wide application of copper(II) complexes with the mentioned ligands is their moderate volatility.

Variation of functional groups in the ligands makes it possible to change the volatility of the respective copper(II) complexes in wide ranges [11-13]. As a rule, the introduction of terminal CF₃ groups results in an increase in the volatility of transition metal complexes with β -diketones and their derivatives by a few orders of magnitude [11, 12]. However, in a number of works it is shown that in the case of Ni and Cu chelates with Schiff bases the introduction of CF₃ groups causes a decrease in volatility [12, 13]. By the example of [Ni(en(acac)₂)] and [Ni(Meen(acac)₂)] complexes it is shown that the variation of substituents in the ethylenediimine moiety leads to a four times increase in the vapor pressure [14, 15].

In this work we report the results of a study of the effect of ligand substituents on the crystallochemical characteristics and thermal behavior of copper(II) complexes with Schiff bases.

EXPERIMENTAL

Precursors. In the work the following reagents were used: propylenediamine and 2,2-dimethylpropylenediamine (Merck, purity >98 %), CuCl₂·2H₂O (DalKhim, purity >97 %), acetylacetone (Hacac) (DalKhim, purity >98 %). Acetone, toluene, and heptanes were used as solvents (Khimreaktiv, purity >97 %).

Synthesis of precursors. The [pda(Hacac)₂] and [dmpda(Hacac)₂] reagents were obtained by the procedure [4]. The [dmpda(Hacac)₂] precursor was first obtained by the interaction of 2,2-dimethylpropylenediamine (0.01 mol, 1.9 ml) with acetylacetone (0.02 mol, 3.7 ml). The exothermal reaction is accompanied by the water vapor release, and the obtained solution turns yellow. The solution was heated on a water bath (60 °C) for 2 h, then it was cooled using the CCl₄/N₂₍₁₎ mixture. The light yellow crystallized precipitate was twice recrystallized in heptane. The [dmpda(Hacac)₂] yield is 60 %, $T_{melt} = 84-86$ °C. Calculated for C₁₅H₂₆O₂N₂ (M = 266.4 g/mol): C 67.6, H 9.8, N 10.5. Found: C 67.5, H 9.9, N 10.7. Ligand. ¹H (500 MHz, 25 °C, ppm): 1.07 [s, (CH₃)₂C(CH₂)₂]; 1.89 [s, 2(CH₃CNH–)]; 2.06 [s, 2(CH₃CO)]; 3.15 [d, (CH₃)₂C(CH₂)₂, ³ $J_{H-H} = 6$ Hz]; 4.98 [s, 2(CH)]; 11.18 [br, s, 2(NH)]. ¹³C NMR{¹H} (125.76 MHz, 25 °C, ppm): 18.93 [s, 2(CH₃CNH–)]; 23.59 [s, (CH₃)₂C(CH₂)₂]; 28.73 [s, 2(CH₃CO)]; 35.76 [s, (CH₃)₂C(CH₂)₂]; 50.31 [s, (CH₃)₂C(CH₂)₂]; 95.68 [s, 2(CH)]; 163.65 [s, 2(CO)]; 195.09 [s, 2(CNH)]. The [pda(Hacac)₂] precursor was obtained by the interaction of propylenediamine (0.01 mol, 1.6 ml) with acetylacetone (0.02 mol, 3.7 ml) and purified by the above described procedure. The ligand yield was 65 %, $T_{melt} = 91-93$ °C. Calculated for C₁₃H₂₂O₂N₂ (M = 238.3 g/mol): C 65.5, H 9.3, N 11.8. Found: C 65.3, H 9.3, N 11.7.

Synthesis of copper(II) complexes. Complexes 1 and 2 were synthesized using the procedure [4] by the interaction of the corresponding ligand and freshly precipitated copper(II) hydroxide washed with acetone. In a day after the evaporation of solvents the dry residue was placed into a funnel with paper filter and washed with benzene. The dark green solution obtained was boiled down and recrystallized from heptane. The yields of complexes 1 and 2 were ~80 %. For chelate 1 $T_{melt} = 121-122^{\circ}C$; calculated for $C_{13}H_{20}O_2N_2Cu$ (M = 299.9 g/mol, Cu 21.2 %): C 52.1, H 6.7, N 9.3; found: C 52.0, H 6.8, N 9.3. For chelate 2 $T_{melt} = 156-158^{\circ}C$; calculated for $C_{15}H_{24}O_2N_2Cu$ (M = 327.9 g/mol, Cu 19.4 %): C 54.9, H 7.4, N 8.5; found: C 55.0, H 7.6, N 8.4.

Identification of compounds. The C, H, N elemental analysis was performed on a Carlo-Erba 1106 (Italy) analyzer. IR absorption spectra of the samples under study were measured on a Scimitar FTS 2000 spectrometer in the range 375-4000 cm⁻¹. The samples were prepared by pressing the pellets with KBr. The IR spectral bands were assigned by comparing them with the literature data [16]. ¹H and ¹³C NMR spectra of solutions in CDCl₃ were measured at room temperature on an AVANCE 500 BRUKER spectrometer. Chemical shifts were measured with respect to the chloroform signal and recalculated with respect to TMS.

Single crystals suitable for XRD were grown by slow crystallization from the acetone solution. XRD of the complexes was carried out by the standard procedure on an automated four-circle Bruker X8 Apex diffractometer equipped with a two-dimensional CCD detector at a temperature of 150 K using molybdenum radiation ($\lambda = 0.71073$ Å) and a graphite

FABLE 1. Crystallochemical	Data and Experimental	Conditions for the	Ligand and	Copper(II) Complexes
			0	

Stoichiometric formula	$C_{15}H_{26}N_2O_2$	$C_{13}H_{20}N_2O_2Cu$	$C_{15}H_{24}N_2O_2Cu$
Molecular weight	226.4	299.9	327.9
Temperature, K	123.0(2)	150(2)	150(2)
Wavelength, Å	1.5418	0.71073	0.71073
Crystal symmetry,	P21/c	Pbca	Fdd_2
space group			
<i>a</i> , <i>b</i> , <i>c</i> , Å	10.7416(4),	14.8672(12),	11.6434(4),
	6.2329(2),	10.7597(7),	27.5742(8),
	23.8430(8)	17.1581(14)	9.7641(3)
$\alpha, \beta, \gamma, \deg$	90, 96,134(3), 90	90, 90, 90	90, 90, 90
Volume, Å ³	1587.2	2744.7(4)	3134.8
Z, density d_{cal} , mg/mm ³	4, 1,115	8, 1,451	8, 1,390
Absorption coefficient, mm ⁻¹	0.585	1.587	1.396
<i>F</i> (000)	584.0	1256	1384
Crystal dimensions, mm	0.4835×0.2901×0.2198	0.45×0.38×0.15	0.20×0.12×0.12
θ range, deg	from 7.46 to 133.52	from 2.37 to 25.35	from 2.82 to 30.50
h, k, l ranges	$-9 \le h \le 12,$	$-17 \le h \le 17,$	$-16 \le h \le 6,$
	$-7 \leq k \leq 7$,	$-8 \le k \le 12,$	$-33 \le k \le 39,$
	$-28 \le l \le 23$	$-20 \le l \le 20$	$-9 \le l \le 13$
Number of meas. / indep. reflections (R_{int})	5820 / 2768 (0.0369)	15916 / 2473 (0.0409)	7267 / 2174 (0.0385)
θ data completeness, %	98.3 (2θ = 135°)	98.5 ($2\theta = 50^{\circ}$)	$100.0 \ (2\theta = 50^{\circ})$
Maximum and minimum absorption	0.8605 and 0.7470	0.7967 and 0.5352	0.8503 and 0.7676
Number of reflections / restr. / parameters	2768 / 0 / 187	2473 / 0 / 167	2174 / 1 / 95
S-factor against F^2	1.049	1.070	1.051
<i>R</i> -factor $[I > 2\sigma(I)]$	R1 = 0.0489,	R1 = 0.0434,	R1 = 0.0251,
	wR2 = 0.1284	wR2 = 0.1095	wR2 = 0.0594
<i>R</i> - factor (all data)	R1 = 0.0569,	R1 = 0.0600,	R1 = 0.0291,
	wR2 = 0.1392	wR2 = 0.1188	wR2 = 0.0609
Max. and min. residual electron densities, $e/Å^{-3}$	0,24 and -0.22	1.278 and -0.598	0.272 and -0.221

monochromator. Reflection intentities were measured by φ -scanning of narrow (0.5°) frames. Absorption correction was applied semi-empirically using the SADABS program [17]. The structures were solved by a direct method and refined by the full-matrix least squares technique in the anisotropic approximation for non-hydrogen ordered atoms using the SHELXTL program package [17]. Details of the experiments and refinement are listed in Table 1. Hydrogen atoms are refined in the rigid body approximation. CIF files containing full information on the structures studied have been deposited with CCDC under numbers 886503 (dmpda(Hacac)₂), 886504 (Cu(pda(acac)₂)), and 886505 (Cu(dmpda(acac)₂)) (www.ccdc.cam.ac.uk/data reguest/cif).

Thermal analysis was performed on a Netzsch TG 209 F1 Iris analyzer using the Proteus analysis program package. The portion weight was 10 mg. The experiment was carried out in the helium atmosphere (30.0 ml/min, open Al₂O₃ crucible, 10 °/min). Mass spectra of the complexes were measured on a high-resolution Thermo Scientific Double Focusing Sector Mass Spectrometer (DFS HRMS); an argon/xenon mixture was used as the gas; the electron energy was 70 eV, with a direct introduction at T = 240 °C, $P = 10^{-7}$ Torr. The work was carried out at the Chemical Service Center, Siberian Branch, Russian Academy of Sciences.



Fig. 1. Synthesis scheme of precursors.



Fig. 2. Possible tautomeric forms of [dmpda(Hacac)₂] in solution.

RESULTS AND DISCISSION

Characterization of pda(Hacac)₂ and dmpda(Hacac)₂ ligands. Both precursors were obtained by the reaction shown in Fig. 1, where R = H, CH_3 . In [4] the ligands were purified by recrystallization from water. The presence of water can cause the destruction of the precursor, therefore the compounds that we obtained were purified by recrystallization from heptane. This purification method provides an increase in the yield of the precursors up to 85 %.

The [dmpda(Hacac)₂] compound obtained and purified for the first time was studied by single crystal XRD, IR spectroscopy, and NMR spectrometry. It is possible to assume its existence in the solution as four tatomeric forms **1a-1d** (Fig. 2).

The IR spectrum of the precursor exhibits the stretching vibrational bands v(N-H, O-H) at 3425 cm⁻¹ and 3226 cm⁻¹, which indicates the existence of the complex in enol form **1b** or **1c**. Similar bands of the stretching vibrations v(N-H, O-H) at 3409 cm⁻¹ and 3212 cm⁻¹ are also present in the IR spectrum of [pda(Hacac)₂]. The spectra of [pda(Hacac)₂] and [dmpda(Hacac)₂] contain intense bands in the region of 1610-1560 cm⁻¹, which, according to the data of [18, 19], can be assigned to $v(C=O)_{ac}$ and $v(C=O)_{c}$ vibrations.

The NMR spectrometric analysis of $[dmpda(Hacac)_2]$ shows that tautomer **1a** is absent in the solutions studied. The splitting of $-CH_2$ - proton signals associated with the-NH- group in a doublet with ${}^{3}J_{H-H} = 6$ Hz gives evidence in favor of the ligand existence in the solution in the form of tautomer **1c**. This conclusion is confirmed by the comparison of the chemical shifts measured in the 1 H and 13 C NMR spectra and calculated using the ChemDraw Ultra 8.0 program. However, a significant shift of the -NH- proton signal to the weak field gives grounds to assume the occurrence of the intramolecular hydrogen bonds =N...H...O= and the formation of a pseudo-aromatic structure of **1d** type.



Fig. 3. Structure of the [dmpda(Hacac)₂] molecule.



Fig. 4. Molecular structure of copper(II) complexes [Cu(pda(acac)₂)] (a) and [Cu(dmpda(acac)₂)] (b).

The structure of $[\text{dmpda}(\text{Hacac})_2]$ (Fig. 3) was identified by the single crystal XRD method. Both acetoimine groups in the precursor molecule have similar geometric characteristics. The $C_{\beta}-C_{\alpha}(N)$ bond lengths ($C_{\alpha}(X)$ is the carbon atom bonded to the X atom) are somewhat shorter than the $C_{\beta}-C_{\alpha}(O)$ bond lengths. Their values are 1.3839(22) Å, 1.3816(23) Å and 1.4152(23) Å, 1.4208(24) Å respectively. The C–O bond lengths are 1.2560(19) Å and 1.2536(22) Å, whereas for C–N they are 1.3343(19) Å and 1.3351(21) Å. Both acetoimine moieties form six-membered rings due to the appearance of intramolecular hydrogen bonds N–H…O with the lengths of 2.6514(16) Å and 2.6596(18) Å. Thus, it is possible to expect that the precursor exists in form **1d**, which is consistent with the NMR data.

Characterization of [Cu(pda(acac)₂)] and [Cu(dmpda(acac)₂)] complexes. Single crystals of [Cu(pda(acac)₂)] (1) and [Cu(dmpda(acac)₂)] (2) were grown by the evaporation of the corresponding acetone solutions of the complexes. The molecules of the complexes consist of the Cu²⁺ cation and tetradentate ligand anions ([pda(acac)₂]²⁻ or [dmpda(acac)₂]²⁻) coordinated to it (Fig. 4).

The distorted planar square environment of the copper cation is formed by two nitrogen atoms of the pda or dmpda groups and two oxygen atoms of the acac groups. The geometric parameters of the coordination core are summarized in Table 2. The Cu–O chelate bond lengths are somewhat shorter in comparison with Cu–N. A distinction in the C–O and C–N bond lengths does not exceed 0.04 Å in both complexes.

The structures of both complexes contain: two six-membered conjugated rings (CuOCCCN) and one six-membered ring (CuNCCCN). In the structure of **1** one of the CuOCCCN chelate rings is almost planar (with a bend angle along the O(1)N(1) line of 5.5°), whereas the second chelate ring is bent at 12.0° (along the O(2)N(2) line). In the structure of **2** both chelate rings are practically planar (with equal bend angles of 6.3°). A comparison of the structural parameters of copper(II) chelates [Cu(pda(acac)₂)] and [Cu(dmpda(acac)₂)] with the literature data for [Cu(en(acac)₂] [7, 8] shows that the pda and dmpda substitution for the en moiety is accompanied by a distortion of the square planar geometry of the chelate rings are 0.7° for [Cu(en(acac)₂] [7, 8], 36.8° for [Cu(pda(acac)₂)], and 37.4° for [Cu(dmpda(acac)₂)].

Molecules in the crystals of copper(II) complexes with Schiff bases are packed by van der Waals contacts. Terminal CH₃ groups freely rotate in the organic ligands. The pda and dmpda substitution for en in the diimine moiety in the molecules of copper(II) complexes is accompanied by a change in the type of molecular packing in the crystals. The crystal structure of $[Cu(en(acac)_2]$ is composed of fragments containing two molecules located practically in parallel planes and shifted relative to each other (the shortest distances between the copper atoms are 4.648 Å) [7, 8].

TABLE 2. Interatomic Distances d ((Å) and Bond	Angles ω (deg.)) for Complexes	1 and 2
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1 [Cu(pda(acac) ₂)]		2 [Cu(dmpda(acac) ₂)]		
Bond	d	Bond	d	
Cu(1)-O(1)	1.903(2)	Cu(1)-O(1) $Cu(1) O(1)^{i}$	1.909(1)	
Cu(1)=O(2) Cu(1)=N(1) Cu(1)=N(2)	1.940(3) 1.942(3)	Cu(1)=O(1) Cu(1)=N(1) $Cu(1)=N(1)^{i}$	1.909(1) 1.943(2) 1.943(2)	
Angle	ω	Angle	ω	
O(1)-Cu(1)-O(2) O(1)-Cu(1)-N(1)	89.81(10) 94.99(12)	$O(1)-Cu(1)-O(1)^{i}$ O(1)-Cu(1)-N(1)	90.40(8) 94.63(6)	
O(2)-Cu(1)-N(1) O(1)-Cu(1)-N(2) O(2)-Cu(1)-N(2)	152.41(12) 153.80(12) 94.44(11)	$\begin{array}{c} O(1)^{i} - Cu(1) - N(1) \\ O(1) - Cu(1) - N(1)^{i} \\ O(1)^{i} - Cu(1) - N(1)^{i} \end{array}$	152.65(6) 152.65(6) 94.63(6)	
N(1)-Cu(1)-N(2)	93.10(12)	$N(1)^{i}$ -Cu(1)-N(1)	93.12(9)	

^{*i*} Symmetry elements (-x, 1-y, z).

The molecules of complex 1 are located in the vertices of the primitive rectangular packing. The molecules of complexes exist in the crystals in the form of two conformational isomers that are mirror-like bonded with each other (Fig. 5). The shortest distance between the copper atoms is 5.586 Å.

Molecules in complex **2** are packed by van der Waals interactions and are located above each other with a shift along the b/2 axis, forming stacks along the *b* axis (Fig. 6). The shortest distance between the copper atoms is 7.425 Å. A similar packing type is also observed for the nickel complex with Schiff bases [20].

A comparison of the IR spectra of the precursors of $(pda(Hacac)_2)$ and $(dmpda(Hacac)_2)$ copper(II) complexes 1 and 2 shows that broad bands in the region of 3430-3230 cm⁻¹, which are present in the spectra of the precursors, are not observed in the spectra of 1 and 2 [21]. Intense characteristic bands in the region of 1610-1560 cm⁻¹, which are present in the spectra of $(pda(Hacac)_2)$ and $(dmpda(Hacac)_2)$, disappear in the spectra of copper(II) complexes. The appearance of new bands corresponding to the v(=C–O) vibrations at 1237 cm⁻¹ in the case of 1 and 1232 cm⁻¹ in the case of 2 indicates the formation of C–O–Cu bonds [22, 23]. New bands observed in the IR spectra of both complexes in the regions of 510-528 cm⁻¹ and 470-490 cm⁻¹ can be assigned to the v(Cu–N) and v(Cu–O) vibrations respectively [22].



H C N O O O C U

Fig. 5. Molecular packing of $[Cu(pda(acac)_2)]$ in the crystal.

Fig. 6. Molecular packing of $[Cu(dmpda(acac)_2)]$ in the crystal.



Fig. 7. Weight loss curves of $[Cu(pda(acac)_2)]$ 1; $[Cu(dmpda(acac)_2)]$ 2; $[Cu(en(acac)_2)]$ 3.

TABLE 3. Metal-Containing Ions in the Mass Spectrum of Cu(pda(acac)₂) and Cu(dmpda(acac)₂) Compounds

Ion	m/z	Rel. concentration, %	Ion	m/z	Rel. concentration %
	Compound 1			Compound 2	
$[CuL-C_5H_9NO]^+$	200.0	65.1	$[CuL-C_5H_9NO]^+$	228.0	3.8
$[CuL-C_6H_9NO]^+$	188.0	65.0	$[CuL-C_6H_9NO]^+$	216.1	100
$[CuL-C_7H_{11}NO]^+$	174.0	72.3	$[CuL-C_9H_{15}NO]^+$	174.0	45.6
$\left[\text{CuLC}_9\text{H}_{16}\text{NO}\right]^+$	145.0	14.6	[CuL– CuHanNO] ⁺	145.0	9.7
Cu^+	63.0	10.1	Cu^+	63.0	5.7

Synthetic procedures were performed on a laboratory device for the synthesis with reaction medium volumes up to 3 l. The synthesis was supported by the Ministry of Education of the Russian Federation (Contract No. 14.604.21.0080 on June 30, 2014; unique identifier PNI RFMEFI60414X0081).

Thermal properties of copper(II) complexes with Schiff bases. The thermogravimetric data for chelates 1, 2, and also [Cu(en(acac)₂] are presented in Fig. 7.

Compounds **1** and **2** are more volatile in comparison with **3** and some β -diketonate copper(II) derivatives [24-26]. The temperature of the 50 % weight loss is 485 K for Cu(*i*-acac)₂ [25]; 490 K for Cu(Mei-acac)₂ [25]; 516 K for **2**; 520 K for Cu(acac)₂ [25]; 528 K for **1**; 540 K for Cu(*i*-tmhd)₂ [26]; 543 K for **3**; and 550 K for Cu(tmhd)₂ [26] (*i*-acac is 2-amino-penen-4-onato(-), Mei-acac is 2-methylamino-penen-4-onato(-), *i*-tmhd is 2,2,6,6-tetramethyl-3-amino-hepten-5-onato(-), tmhd is 2,2,6,6-tetramethyl-3,5-heptandionato(-)).

Under the TG experimental conditions complexes 1 and 3 quantitatively pass into the gas phase (the weight loss is 99.4 % for 1 and 99.5 % for 3), while 2 passes into the gas phase with small decomposition (the weight loss is 93.8 %).

In the mass spectra of both compounds the peaks of ions corresponding to the molecular forms $[ML_2]^+$ are observed at m/z = 299.1 (100 %) for **1** and 327.0 (62.2 %) for **2**. Under the electronic shock impact organic moieties are separated from the complexes and the following metal-containing ions form (Table 3).

In the spectra of both compounds the peaks of ions of the same organic residues are observed at m/z = 111.0, 97.1, 55.0, and 43.0; there are also peaks corresponding to metallic copper at m/z = 63.0.

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