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Synthesis of Volatile Copper(II) β-Diketonates, β-Ketiminates, and β-Diiminates. The Problem of Synthesis of Copper(II) Bis(2,2,6,6-tetramethyl-3-methylaminoheptane-5-onate)

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Abstract—The methods of synthesis of the copper(II) β-diketonates, β-ketiminates, and β-diiminates containing in the composition CH_3, CF_3, $C(CH_3)_3$, and Ph substituents were summarized. At the formation of metallocycles with 2,2,6,6-tetramethyl-3-methylaminoheptane-5-one ligand the intraligand repulsion of *tret*-butyl group and the methyl group at the nitrogen atom is noted, impeding the complexation.

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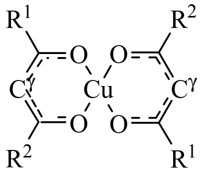
This paper considers the volatile copper(II) β-diketonates, β-ketiminates, and β-diiminates of the general structure **I–III**, respectively. The description of the structure and the nomenclature of these complexes are published in reviews [1–5]. The six-membered metallocycles formed at the complexation allow both a complete symmetrization at the delocalization of π-interaction and a covalent σ-binding of the metal to the ligand [1–5]. Stability of these complexes originates mainly from the σ-bonding of the metal to the ligand [6].



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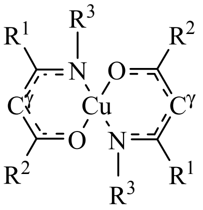

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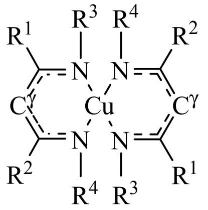

III

R^1, R^2 = CH_3, CF_3, $C(CH_3)_3$, Ph; R^3, R^4 = H, Me, Et, Ph etc.

Some of the metal β-diketonates are catalysts of the alcohols oxidation to aldehydes and ketones [7], certain of them can be used as effective antioxidants for motor oils and greases [7]. β-Diketonates can also be used for the synthesis of carbon nanotubes [8], for preserving epoxy resin [9], for metals purification by zone melting [6], and in other processes. But the most important property of the β-diketonates, β-ketiminates, and β-diiminates is their ability to reversibly go over to the gas phase at low heating. The volatility of these complexes is used for their purification by the fractional sublimation [6, 10], for gas chromatographic analysis [10, 1], but the most important their application consists in producing metallic and oxide coatings by their thermolysis on overheated substrates (MO CVD, Metal Organic Chemical Vapor Deposition) [12, 13]). The volatility of these complexes mainly depends on the structure of the substituents (R^1 and R^2) in the ligand, on the valence state of the metal and to a lesser extent on the presence of other functional groups in the β-Diketonates $R^1C(O)CH_2C(O)R^2$, β-enaminoketones $R^1C(O)CH{=}C(NHR^3)R^2$, and β-enaminoimines $R^1C(NR^3)CH{=}C(NHR^4)R^2$ used in the study

Comp. no.	Notation	R^1	R^2	R^3	R^4	Название
I	L^1	CH_3	CH_3			Pentane-2,4-dione (acetylacetone)
II	L^2	CH_3	CF_3			1,1,1-Trifluoropentane-2,4-dione (trifluoroacetylacetone)
III	L^3	CH_3	$C(CH_3)_3$			2,2-Dimethylhexane-3,5-dione (pivaloylacetone)
IV	L^4	CH_3	Ph			1-Phenylbutane-1,3-dione (benzoylacetone)
V	L^5	CF_3	CF_3			1,1,1,5,5,5-Hexafluoropentane-2,4-dione (hexafluoroacetylacetone)
VI	L^6	CF_3	$C(CH_3)_3$			1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dione (pivaloyltrifluoroacetone)
VII	L^7	CF_3	Ph			4,4,4-Trifluoro-1-phenylbutane-1,3-dione (benzoyltrifluoroacetone)
VIII	L^8	$C(CH_3)_3$	$C(CH_3)_3$			2,2,6,6-Tetramethylheptane-3,5-dione (dipivaloylmethane)
IX	L^9	$C(CH_3)_3$	Ph			4,4-Dimethyl-1-phenylpentane-1,3-dione (benzoylpivaloylmethane)
X	L^{10}	Ph	Ph			1,3-Diphenylpropane-1,3-dione (dibenzoylmethane)
XI	L^{11}	CH_3	CH_3	H		4-Amino-3-penten-2-one
XII	L^{12}	CH_3	CH_3	CH_3		4-Methylamino-3-penten-2-one
XIII	L^{13}	CH_3	CH_3	Ph		4-Phenylamino-3-penten-2-one
XIV	L^{14}	$C(CH_3)_3$	$C(CH_3)_3$	H		5-Amino-2,2,6,6-tetramethyl-4-hepten-3-one
XV	L^{15}	$C(CH_3)_3$	$C(CH_3)_3$	CH_3		5-Methylamino-2,2,6,6-tetramethyl-4-hepten-3-one
XVI	L^{16}	CH_3	CH_3	H	H	2-Imino-4-amino-3-pentene
XVII	L^{17}	CH_3	CH_3	CH_3	CH_3	2-Methylimino-4-methylamino-3-pentene

molecule [6]. Therefore, the volatility of a metal β-diketonates, β-ketiminates, and β-diiminates with the same terminal substituents is similar.

At the coating with a metal it is important that the precursor contains less oxygen atoms, which can oxidize the growing film. In the chelate nodes of the metal β-ketiminates its content is twice less than in β-diketonates, and in the metal β-diiminates the oxygen is totally absent. Therefore, nitrogen-containing metal β-ketiminates, especially metal β-diiminates, have an advantage in producing metallic coatings by MO CVD method [14]. Despite the obvious benefits of nitrogen-containing chelates in obtaining metal films, most of successful applications of the MO CVD methods utilize β-diketonates and, to a lesser extent, β-ketiminates. β-Diiminates of metals are to a much lesser extent studied and used. This is due to the difficulties in the synthesis of nitrogen-substituted metallocomplexes.

In this paper we consider the complexes of copper(II) with the ligands having four terminal substituents: R^1, R^2 = CH_3, CF_3, $C(CH_3)_3$, and Ph. Combining these substituents in pairs, it is theoretically possible to construct ten β-diketones (see the table). The choice of just these ligands is due to the fact that the metal complexes with these ligands cover the area of the volatility characteristic of the entire class of β-diketonates [6]. The table shows some β-ketimines, which in the free state usually are in the tautomer form of β-enaminoketones [4, 15, 16] and some β-diimines that in the free state exist in the tautomer font of β-enaminoimines.

A number of reviews considers the methods of synthesis of the metal β-diketonates [17–20], β-ketiminates [4, 16, 20] and β-diiminates [20, 21], but the methods for the synthesis of these class complexes have not been compared.

For the successful synthesis of any compound it is necessary to know its stability in some area defined by the boundary values of *P* and *T*, the concentration range of reactants and reaction products, the range of pH of the environment, and the permitted concentrations of additional substances and occasional impurities. For each ligand, these areas are considerably different. The published data on the stability estimation of the compounds in question are scarce. For instance, the synthesis of these complexes can be carried out at temperatures below 350°C, because at higher temperatures the ligands and complexes are thermally unstable [6]. More detailed information on the thermal stability can be obtained by analyzing the vapor pressure of the complexes. Usually such experiments are ended at the noticeable vapor pressure of the products of thermal degradation. Thus the vapor pressure of $Cu(L^1)_2$ has been measured at the temperature up to 195°C [22], for $Cu(L^{11})_2$ up to 180°C [23], for $Cu(L^{16})_2$, to 125°C and for $Cu(L^{17})_2$, to 105°C [24]. Thermal lability of $Cu(L^{12})_2$ has become an obstacle for determining the vapor pressure by the flow method (our unpublished experiments), but we have estimated the upper limit of thermal stability of the complex at ~120°C.

It was found that the stability of the copper(II) β-diketonate increases with decreasing acidity of β-diketone [10]. When comparing the properties of copper(II) β-diketonates, β-ketiminates, and β-diiminates it turns out that the region of existence of β-diketonate complexes is wider by many parameters than that of their nitrogen analogs [4]. Most copper(II) β-diketonates can be obtained in aqueous solution by reacting copper(II) acetate with the ligand [17]. The resulting acetic acid does not prevent the chelation. The ketiminates synthesis under these conditions is impossible, as these ligands are readily hydrolyzed in weakly acidic aqueous solutions [4]. Diimine ligands are still more prone to hydrolysis, so the synthesis is performed in non-aqueous solvents [25–27]. It is evident that the region of stability of the considered copper(II) chelates is the greater, the less number of nitrogenous groups is contained in the metallocycle.

Methods of synthesis of copper(II) β-diketonates. The synthesis of copper(II) β-diketonates by reacting the ligand with the metal salt is usually carried out in aqueous solution [10, 17, 18, 28]. All copper(II) β-diketonates are known to be destroyed in the presence of strong mineral acids. This is often used to purify the β-diketones after their synthesis with 10–15% solution of H_2SO_4 [10]. At the same time, in the extraction-spectroscopic methods of analysis the extraction of copper(II) chelates with benzene in the presence of β-diketone is performed at pH 3.6 [10]. Then the excess of the ligand is washed out by 0.005 M solution of NaOH. These methods are possible because the copper(II) β-diketonates are stable over a wide pH range, from 3 to 9. However, usually the synthesis is carried out at pH 6–7. To create the optimal synthesis conditions the alkaline buffer solutions of sodium acetate or sodium carbonate are used [18, 19, 29]. Usually, the starting compounds are inorganic water-soluble copper(II) salts and the corresponding ligands. Some ligands (L^6, L^8, L^{10} etc.) are poorly soluble in water, then the synthesis is carried out in an aqueous-alcoholic media. All copper(II) β-diketonates are insoluble in water and soluble in organic solvents. The complexes are usually isolated by filtering them off from aqueous suspensions. The extraction with an organic solvent immiscible with water (chloroform, toluene, and heptane) is also possible. For the synthesis the water-insoluble compounds of copper(II), for example, precipitated hydroxide [17, 30] or copper(II) hydroxycarbonate can also be used [17, 31]. Synthesis of copper(II) β-diketonates based on inorganic copper salts can be carried out successfully in non-aqueous media, but such methods are used mainly for the synthesis of copper(II) β-ketiminates and β-diiminates, so they will be discussed later.

For the synthesis of β-diketonates methods are also developed of a direct interaction between β-diketone and the metal in the vapor phase. The synthesis is performed in a vacuum system [32]. The evaporation of the metal is carried by electron bombardment, heating by laser beam, microwave radiation or resistive heating. The direct interaction of a metal vapor with a β-diketone is carried out at the temperatures of 80–250°C. The resulting complex can be simply separated from the initial reagents and most impurities in a vacuum. This method is particularly suitable for commercial production of volatile chelates of high purity. In addition, it is the most environmentally friendly method that completely eliminates a release of chemicals into the environment [32]. Electrochemical methods are also direct methods of interaction of metals with ligands. The synthesis is performed in different solvents, but more commonly acetonitrile, alcohols, THF, and pyridine are used [20, 32]. To improve the electrical conductivity of electrolytes additives of $LiClO_4$, NH_4ClO_4, $NaBF_4$, R_4NClO_4, etc are used. The advantages of electrochemical methods over conventional chemical methods is the possibility of the process control, mild conditions and high yields of the complexes. However, the method requires a special electronic equipment, and the resulting chelate should be purified to remove solvents and conductive additives. The method of synthesis of $Cu(L^1)_2$ in an oxidizing system has been described in [33] and of $Cu(L^4)_2$ by copper dissolution in molten HL^4 [32]. However, examples of the synthesis of copper(II) β-diketonates in an oxidizing environment, in the melt or at boundary friction are scarce [32].

The methods based on replacing metal or ligands in coordination compounds may also be applied to the synthesis of copper(II) β-diketonates. The drawback of such methods is the use for the replacement of a large excess of the ligand or copper salt [4]. Moreover, a thorough purification the complex obtained from the reactants and reaction products should be carried out. We used this method to get a mixed-ligand complex $Cu(L^1)(L^5)$ by the reaction of $Cu(L^1)_2$ with HL^5 excess (our unpublished data). It was established later than a more efficient method for the synthesis of mixed-ligand complexes is disproportionation of two homoligand chelates in solutions [34], which can also be regarded as the method of replacement.

The mixed-ligand copper(II) β-diketonates were first described in 1968 [31]. More recently it was found that in solutions of two homoligand complexes all possible forms of the molecules existed, but from the oxygen containing solvents (alcohols, ketones, esters) only the crystals of the parent homoligand chelates precipitated [35]. The most convenient method of obtaining a mixed-ligand copper(II) crystal is the dissolution of the two homoligand chelates in hydrocarbons or halogenated hydrocarbons, followed by evaporation. Of the 45 mixed-ligand complexes, with the substituents in the ligands R^1, $R^2 = CH_3$, CF_3, $C(CH_3)_3$, Ph, the crystals of only twelve mixed-ligand chelates could be obtained successfully, which were identified by different methods of analysis [35]. The crystals of five complexes were grown, and their structures were identified: $Cu(L^1)(L^5)$, $Cu(L^4)(L^5)$, $Cu(L^5)(L^9)$, $Cu(L^3)(L^5)$, and $Cu(L^4)(L^6)$ [2]. Instead of the expected mixed-ligand complex $Cu(L^5)(L^{10})$ at the evaporation of solvents formed a mixture of crystals consisting of $2Cu(L^5)(L^{10})\cdot Cu(L^5)_2$ and $Cu(L^{10})_2$ [2]. The reasons of this have not yet been elucidated.

In addition, the synthesis was performed and the structure was determined of the complex $Cu(L^8)(L^1Cl)$, where L^1Cl, is 3-chloropentane-2,4-dione [36]. At the attempt to obtain a mixed-ligand complex from $Cu(L^{10})_2$ and its decafluoro-substituted analog a crystal has grown containing both homoligand complexes [37].

The mixed-ligand copper(II) β-diketonates remain still a poorly studied area. It follows from [2, 35] that the the crystals of mixed-ligand complexes grow from a solution only when one of the ligands (R^1 or R^2) bears at least one CF_3 group, and the other ligand has only aliphatic substituents. If both ligands are fluorinated or nonfluorinated, then in the solutions are formed only homoligand complexes.

An interesting class of β-diketonate copper(II) complexes comprises the ionic coordination compounds formed due to the possibility of copper(II) to coordinate up to three β-diketonate ligands to form $[Cu(\beta\text{-dik})_3]^-$. In the ionic packing of $[Cu(Phen)_2]^+\cdot[Cu(L^5)_3]^-$ [38] copper ions with charges +1 and +2 are present simultaneously. Also the structure is known of a ionic complex of the composition $[Cu(L^1)(Phen)(H_2O)]^+\cdot[L^5]^-\cdot H_2O$ [39]. But up till now only the structures were identified of ionic coordination compounds with hexafluoroacetylacetone. Nothing is known about their volatility. We believe that some of these ionic coordination compounds may be volatile. For instance, the ionic crystals $[NiL_2(i\text{-}Bu_2PS_2)]^+[i\text{-}Bu_2PS_2]^-$, where L = 2,2'-Bipy or Phen, and $i\text{-}Bu_2PS_2$ = diisobutyldithiophosphinate [40] are volatile. In a vacuum $P = {\sim}10^{-1}$ Torr at 200°C they are sublimated with the retention of the composition. However, mass spectrometric studies of these compounds performed at $P = {\sim}10^{-4}$ Torr [40] showed that upon heating the complex molecules lost initialy a Bipy or Phen molecule, namely, decomposed, and to the gas phase were released the $Ni(i\text{-}Bu_2PS_2)_2$ molecules. Obviously, at 150°C in the condensation zone the ionic coordination compound is formed again.

So far not many crystals of ionic chelate coordination compounds were obtained and studied. We hope that in the future, the properties of this interesting class of metal complexes will be studied in detail, and it may be that these compounds will find practical application, for example, at the electrochemical metal coating from solutions.

Methods of synthesis of copper(II) β-ketiminates. Some of copper(II) β-ketiminates can be obtained like copper(II) β-diketonates in a water-alcohol solution, but it is necessary to take into account the possibility of destruction (hydrolysis) of the ligand in the acidic medium in the presence of water molecules [4]. Therefore, the synthesis must be arranged to maintan pH of the medium no less than 6. Usually first an aqueous solution is prepared of ketimine and alkali or ammonium hydroxide, and then to it slowly a solution of a copper(II) salt is poured, but not vice versa. This method is suitable for the synthesis of $Cu(L^{11})_2$ [23], unsuitable for the synthesis of methyl-, ethyl-, propyl-, phenyl- and other N-substituted ketimine analogs. This is due to the fact that the N-substituted ketimines in most cases cannot compete with the hydroxyl anions for a place in the coordination sphere of the copper(II) cation. So the interaction of methylketimine and inorganic copper(II) salt in aqueous alkali results not in the complexation, but in copper(II) hydroxide formation (our unpublished data):

$$NaL_{O,N-R} + CuCl_2 + 2H_2O = 2NaCl + Cu(OH)_2\downarrow + HL_{O,N-R}$$

To obtain N-substituted copper(II) ketiminates an improved well-known method of interaction of the ligand with copper(II) hydroxide was used [17, 30]. Its peculiarity consists in that the N-substituted ketimines can displace the hydroxyl group from the coordination sphere of copper(II) after evaporation of solvent, virtually in the solid phase [41, 42].

The difference in the coordination strength of NH-, NR-substituted ketimines can be attributed to the different structure of their chelates [43]. So the copper(II) ketiminate $Cu(L^{11})_2$ has a structure with both ligands arranged in the same plane (Fig. 1a) [1], while the related N-substituted copper(II) ketiminates $Cu(L^{12})_2$ [41], $Cu(L^{13})_2$ [42], and other are not flat. The metallocycles are turned with respect to each other due to the presence of bulky substituents R^3. Such turn is up to 44.0° in $Cu(L^{13})_2$ [41] and 47.2° in $Cu(L^{12})_2$ [41] (Fig. 1b). This feature reduces the stability of the complexes with N-substituted ketimines and complicates their synthesis.

To prevent hydrolysis of N-substituted copper(II) ketiminates the synthesis can be carried out in non-aqueous solvents like methanol, ethanol, dioxane, etc. [4]. For example, the synthesis of $Cu(L^{12})_2$ can be carried out in an anhydrous alcohol solution of HL^{12}, by pouring to it an alcoholic solution of ammonia and copper(II) nitrate or acetate. The product was isolated by cooling, or precipitated by dilution with water. In the latter case, the complex precipitates rapidly and the time is insufficient for hydrolyzis [4].

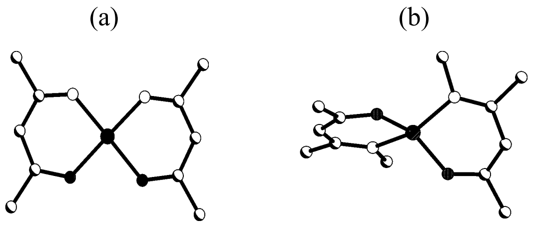

Fig. 1. Structure of molecule (a) $Cu(L^{11})_2$ and (b) $Cu(L^{12})_2$ complexes.

The methods for the direct interaction of copper vapor with β-ketimines are not described. It is noted [32] that the gas-phase synthesis of metal chelates mainly corresponds to the class of transition metal β-diketonates, because of the high stability of β-diketones and β-diketonates in the gas-phase. Electric dissolution of metals in non-aqueous solvents [32] can be used for the synthesis of azomethine complexes of copper(II), including β-ketiminates. Recently, for the activation of metal electric dissolution was used ultrasound [44].

Some of copper(II) ketiminates can be obtained by connecting components. Thus, in [4] was noted that copper(II) bis-acetylethylenediiminate can be obtained from acetylacetone, ethylenediamine and copper ion. However, attempts of condensation of hexafluoroacetylatsetona and ethylenediamine in the presence of copper acetate were unsuccessful.

The copper(II) β-ketiminates can also be obtained in non-aqueous solvents by displacement of a chelating agent HL' from the complex by other chelating agent HL''. In this case, the hydrolysis is excluded, but a copper(II) chelate is required, and an excess of β-ketimine [4]. The experimental method consists in heating the mixture and the metal chelate ligand in a suitable solvent. A drawback of this method consists in the slow process of ligand exchange and the formation of mixed-ligand complexes CuL'L'' [4].

Methods of obtaining ketiminates include the metal exchange between two compounds, one of which is β-diketonate [4]. The disadvantage of this method is the difficulty of removal of the original complex and the compounds of the first metal.

The copper(II) β-ketiminates can also be obtained by the amine exchange, when a primary amine H_2NR' replaces NR'' group in the metallocycle. [4]. The another primary amine formed must be removed, for example, by distillation. This method is applicable to

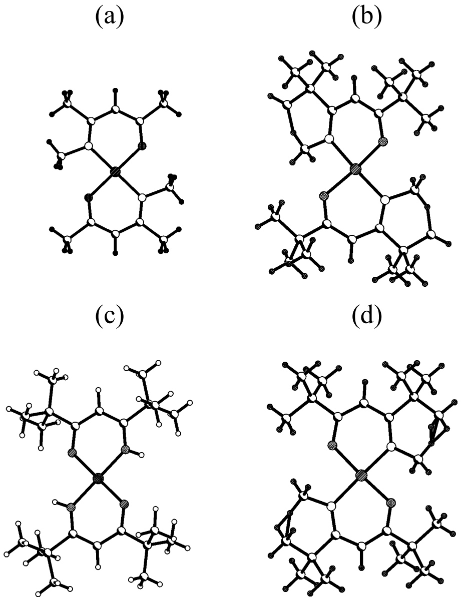

Fig. 2. The structure of the $Cu(L^{12})_2$ molecule according to XRD data (a) and the structure of $Cu(L^{15})_2$ obtained by the geometry simulation (b). The structure of the $Cu(L^{14})_2$ molecule according to XRD data (c) and the structure of $Cu(L^{15})_2$ obtained by the geometry simulation (d).

insert an amine boiling at a higher temperature than the amine released at the exchange [4]. Potentially, this method can be applied for the conversion of copper(II) β-diketonates in β-ketiminates. However, our attempts of amination of copper(II) hexafluoroacetylacetonate with ammonia and primary amines were unsuccessful. Nevertheless, it is known that heating a mixture of copper(II) acetylacetonate and ethylenediamine leads to formation of copper(II) bis(acetylacetoneethylenediiminate) [4].

There are also some other methods for the synthesis of copper(II) ketiminates [4]. However, we met problems at the synthesis of $Cu(L^{15})_2$. We tried repeatedly to get the complex by electrochemical method in nonaqueous solvents by the interaction of the ligand with freshly prepared $Cu(OH)_2$ precipitate followed by drying the mixture, and used some other methods, but failed. In addition, we found that L^{15} does not react with sodium metal in dioxane, in contrast to HL^8 and HL^{14}. Solution of HL^{15} in dioxane was heated to boiling (~101°C), but no interaction was observed, the sodium weight after heating for hours remained unchanged. In this regard, the reduced ability of the ligand to form complexes should be explained. To do this, we decided to simulate the structure of a hypothetical $Cu(L^{15})_2$ complex using the SHELXTL program [45], based on data on the structure of molecules $Cu(L^{12})_2$ [44] (Fig. 2a) and $Cu(L^{14})_2$ [46] (Fig. 2c). The modeling consisted of converting the terminal CH_3 groups into $C(CH_3)_3$ group in the $Cu(L^{14})_2$ molecule and NH groups into NCH_3 groups in the molecule of $Cu(L^{12})_2$. In the $Cu(L^{14})_2$ molecule all hydrogens of terminal methyl groups were replaced geometrically by three carbon atoms at a distance of 1.54 Å with the geometrically attached hydrogen atoms at a distance of 1.0 Å. In the molecule of $Cu(L^{15})_2$ the two N-hydrogen atoms were similarly replaced geometrically by C atoms at a distance of 1.45 Å with the hydrogen atoms at a distance of 1.0 Å. The resulting structure of a hypothetical molecule $Cu(L^{15})_2$ based on the molecules of two different complexes is shown in Figs. 2b, 2d.

The simulation showed that upon formation of $Cu(L^{15})_2$ intraligand overlap of the atoms of methyl group at the nitrogen atom and one of the methyl groups in the *tert*-butyl substituent can occur. Therefore, the chelation of copper by the HL^{15} ligand is difficult. This may explain our unsuccessful attempts to synthesize this chelate ligand. Additionally, the search in the Cambrige database of the molecules containing metallocycle $[M(CH_3)_3CC(NC)CHC(O)C)]$ was carried out where M is any metal, with a carbon-containing substituent at the nitrogen (N–C bond) at the side of the *tert*-butyl substituent in the ligand. As a result, we have found three structures: $Ti(L)_2Cl_2$ where L is 2,2-dimethyl-3-phenylimino-6,6,6-trifluorohexan-2-one (Refcode QUNJIT, QUNJOZ) [47], $Er(L)_3$ where L is 2,2,6,6-tetramethyl-3-methoxyethylamino-heptane-5-one (Refcode WUPMEZ) [48], and $Yb(L)_3$ where L is 2,2,6,6-tetramethyl-3-propylaminoheptane-5-one (Refcode EBEPUW) [49].

These three examples suggest that the copper(II) complexe with the ligand HL^{15} is possible. Therefore the development of methods for the synthesis of $Cu(L^{15})_2$ was continued. As a result, this complex was obtained by a method described in the experimental section.

Synthesis methods of copper(II) diiminates. In the case of the diimine ligands the requirements associated with the possibility of destruction (hydrolysis) in water become more significant. Besides, the β-diimines, as well as ketimines with substituents at nitrogen, are weak complexing agents, and in most cases cannot compete in aqueous solutions with hydroxyl ions for a place in the copper(II) ion coordination sphere. Therefore, the synthesis of these complexes is carried out in anhydrous media, usually in anhydrous alcohol [5, 24–26]. In particular, polyfluorinated copper(II) diiminates were synthesized by the reaction of the free ligand with $Cu(OAc)_2$ [50] or CuO in acetone [51]. Acetic acid or water formed in the synthesis do not prevent chelation at a high dilution. We believe that a $Cu(OH)_2$ suspension in acetone also can be used for the synthesis of similar complexes.

In [21] the diimine complexes were synthesized by reacting the lithium salt of the ligand with a metal chloride in anhydrous solvents. In [52, 53] the methods were described of the synthesis of mixed-diimine complexes of copper(II) $CuL_{N,N}L'$ where $L_{N,N}$ is a diimine ligand, L' is Cl, OPh, CNPh, etc. In [54] the methods of the synthesis of dual-core mixed-ligand copper complexes $[CuL_{N,N}Hlg]_2$ where $L_{N,N}$ is a diimine ligand were described. Most of the methods of synthesis of copper(II) diiminates are very time-consuming, and require the use of water-free solvents. As a precursor of copper(II) compound $\{N[C(CH_3)_3]_4\}_2\cdot[CuBr_4]$ [55] readily soluble in anhydrous alcohol and toluene can be used. As a ligand precursor a salt of the diimine ligand with an alkali metal prepared by dissolving the metal in an alcohol solution of the ligand is commonly used. Pouring together the solutions of these precursors gives the diimine complex [5, 24–26]. Methods of the direct synthesis (gas-phase, electrochemical, tribochemical etc.) of the copper(II) diimine complexes have not been described.

So far the methods of synthesis of copper(II) diimine complexes were developed for the derivatives of acetylacetone [14, 24–26, 56], heptafluoroacetylacetone [50, 51], benzoylacetone [25, 26], dibenzoylmethane [57] and benzoylpivaloylmethane [25].

EXPERIMENTAL

A universal method of synthesis of β-diketonates and some copper(II) β-ketiminates. A simple method of synthesis of the copper(II) β-diketonates and β-ketiminates is as follws. Copper(II) hydroxide is obtained in a water-acetone (1:1) medium at the interaction of solutions of a copper(II) inorganic salt with alkali. The resulting $Cu(OH)_2$ precipitate is filtered off, washed with acetone and water (1:1) and then with acetone. The moiste sludge is placed in a flusk, a free ligand is added, and the mixture is stirred. For more efficient use of the ligand $Cu(OH)_2$ should be taken in excess. The mixture is left till evaporation of all the solvents. After 6–12 h, the dry residue is washed with a suitable organic solvent (chloroform, acetone, benzene, etc.) on a paper filter. The resulting solution of the complex is concentrated and then purified. Use of copper(II) hydroxide for the synthesis of complexes was described in [17, 30, 58], but just the evaporation to dryness of the solvents mixture allows the preparation of copper(II) β-ketiminates. This method is applicable to the synthesis of copper(II) β-diketonates and β-ketiminates [except $Cu(L^{15})_2$]. Perhaps this method can be applicable to the synthesis of polyfluorinated copper(II) diiminates.

Synthesis of copper(II) bis(2,2,6,6-tetramethyl-3-methylamino-5-heptanonate) $Cu(L^{15})_2$. The ligand was obtained as previously described [46]. The synthesis of the complex was performed in two stages. First, to 20 mL of methanol 0.120 g (~0.005 mol) of Na was added. After the dissolution of Na 1 g (~0.005 mol) of H L^{15} was added. Separately a solution was prepared of 0.340 g (0.0025 mol) of anhydrous $CuCl_2$ (MERCK) in 20 mL in methanol, and it was poured to the mixture of sodium alcoholate and the ligand. The reaction flask was flushed with nitrogen The mixture was evaporated to dryness during the night. Then 30 mL of toluene was added and the mixture was heated to ~100°C and evaporated to dryness in the nitrogen flow. The solid residue was ground in a mortar and sublimated in a vacuum gradient furnace (P ~10^{-2} Torr, $T_{\max}$ ~250°C). A green crystalline powder was obtained, yield 50%, mp 152–153°C. The substance is readily soluble in organic solvents. In the solid state Cu $(L^{15})_2$ is stable, but at the evaporation of the solution in air the complex hydrolyzed. Found, %: C 63.0, H 9.9, N 6.1. $C_{24}H_{44}CuN_2O_2$. Calculated, %: C 63.2, H 9.7, N 6.2.

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