117. Synthesis, Crystal Structure, and Thermal Behaviour of Some New Copper Complexes with Tridentate β-Iminoketone Ligands

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The reaction of $Cu(AcO)_2 \cdot H_2O$ and tridentate β-iminoketone ligands yielded four new copper complexes: acetato{4-{[2-(dimethylamino)ethyl]amino}pent-3-en-2-onato}copper(II) (**1**), triacetato{4-{[3-(dimethylamino)-propyl]amino}pent-3-en-2-onato}dicopper(II) (**2**), {4-{[2-(dimethylamino)ethyl]amino}-1,1,1-trifluoropent-3-en-2-onato}(trifluoroacetato)copper(II) (**3**), and pentaacetato{4-{[3-(dimethylamino)propyl]amino}-1,1,1-trifluoro-pent-3-en-2-onato}tricopper(II) (**4**). All compounds were coloured and air-stable solids. The crystal structures of **1** and the dioxane adduct of **3**, μ-(1,4-dioxane)bis{{4-{[2-(dimethylamino)ethyl]amino}-1,1,1-trifluoropent-3-en-2-onato}(trifluoroacetato)copper(II)} (**3a**), were determined. Complex **1** consists of dimeric units $[\{Cu(AcO)L\}_2]$ in the solid state (L = β-iminoketonato ligand). In **3a**, two $[Cu(CF_3COO)L]$ are linked *via* the O-atoms of the coordinated solvent 1,4-dioxane. Compound **1** crystallized in the monoclinic space group $P2_1/n$ with a formula unit in a cell having the dimensions $a = 11.152(6)$ Å, $b = 10.104(3)$ Å, $c = 11.805(7)$ Å, and $\beta = 99.02(4)$ Å, and compound **3a** crystallized in the triclinic space group $P\bar{1}$ with a formula unit in a cell having the dimensions $a = 8.709(3)$ Å, $b = 9.439(4)$ Å, $c = 12.395(3)$ Å, $\alpha = 67.57(3)°$, $\beta = 77.01(2)°$, and $\gamma = 84.17(3)°$. Mass spectra (MS), thermal analysis (DTA/TG), and evaporation-rate measurements are reported for all compounds. The influence of fluorination on the structure and volatility will be discussed.

Introduction. – Metal-organic chemical vapor deposition (MOCVD) is an established technology for the preparation of thin metallic films [1] using volatile metal-containing compounds. Especially, the deposition of metallic Cu is of increasing interest for microelectronic applications [2] [3]. The preparation of Cu films using hydrogen reduction of copper(II) acetylacetonates at elevated temperatures was described for the first time in 1965 by *van Hemert et al.* [4]. Most of the Cu^{II} complexes used today are fluorinated β-diketonates [5]. The replacement of some of the strong Cu–O bond in the β-diketonates by a weak Cu–N bond is a possible way to change the deposition parameters. Therefore, investigations of β-iminoketonates as possible precursors are of current interest. We have studied film-growth kinetics using (β-diketonato)- and (β-iminoketonato)coppers [6]. The ligands of the (β-iminoketonato)coppers were tridentate β-iminoketones, and the synthetic part of this work will be presented here.

In the literature, only a few examples of Cu^{II} complexes with tridentate β-iminoketone ligands are described. Their structures can be abbreviated as [CuLX] where L is a singly deprotonated 4-[(2-aminoethyl)amino]pent-3-en-2-one or a 4-[(aminomethyl)amino]-pent-3-en-2-one and X is acetate, Br or Cl [7–10]. In the solid state, these complexes consist of dimeric units $[(CuLX)_2]$ and the Cu-atoms are in the center of a five-coordinated distorted square pyramid.

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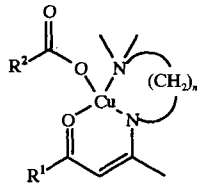
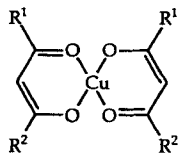
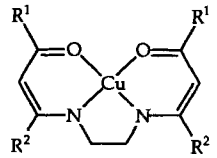
We used tridentate β-iminoketones with a terminal Me_2N group, and in two cases Me(1) was replaced by CF_3(1) to investigate the influence of fluorination on the coordination, and we hoped that the synthesis of coordinative saturated octahedron $[CuL_2]$ complexes are possible. The four new Cu^{II} complexes **1**–**4** were obtained by the reaction of $Cu(AcO)_2 \cdot H_2O$ and the tridentate β-iminoketones 4-{[2-(dimethylamino)ethyl]amino}-pent-3-en-2-one (HL^1), 4-{[3-(dimethylamino)propyl]amino}pent-3-en-2-one (HL^2), 4-{[2-(dimethylamino)ethyl]amino}-1,1,1-trifluoropent-3-en-2-one (HL^3), and 4-{[3-(dimethylamino)propyl]amino}-1,1,1-trifluoropent-3-en-2-one (HL^4). The complexes **1**–**4** were characterized by mass spectrometry (MS) and thermal analysis (TG = thermogravimetry and DTA = differential thermal analysis), and the crystal structures of **1** and **3a** were determined by X-ray diffraction. Evaporation-rate measurements were carried out in a horizontal MOCVD apparatus [11]. We compared the thermal behaviour and volatility of **1**–**4** with that of the known (see below) (β-diketonato)- and (β-iminoketonato)coppers bis(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II) ([Cu(tmhd)$_2$]; **5**), bis(1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionato)copper(II) ([Cu(fhd)$_2$]; **6**), [*N,N'*-ethylenebis(4-aminopent-3-en-2-onato)]copper(II) (**7**), and [*N,N'*-ethylenebis(4-amino-1,1,1-trifluoro-pent-3-en-2-onato)]copper(II) (**8**).







1 [Cu(AcO)L^1] $R^1 = R^2 = Me$, $n = 2$
2 [Cu$_2$(AcO)$_3$L^2] $R^1 = R^2 = Me$, $n = 3$
3 [Cu(CF$_3$COO)L^3] $R^1 = R^2 = CF_3$, $n = 2$
4 [Cu$_3$(AcO)$_3$L^4] $R^1 = CF_3$, $R^2 = Me$, $n = 3$

5 [Cu(tmhd)] $R^1 = R^2 = t$-Bu
6 [Cu(fhd)] $R^1 = CF_3$, $R^2 = t$-Bu

7 $R^1 = R^2 = Me$
8 $R^1 = CF_3$, $R^2 = Me$

Results and Discussion. – *Synthesis.* The Cu^{II} complexes **1**–**4** were obtained by adding the liquid ligand to a solution of $Cu(AcO)_2 \cdot H_2O$ in an organic solvent. Heating was necessary to obtain clear coloured solutions. These complexes were isolated and purified by standard methods. They could be stored in air and did not decompose within weeks.

With the help of X-ray data, molecular-weight determination, and microanalysis, the degree of oligomerisation of the compounds **1**–**4** could be inferred: oligomerization depends strongly on the length of the $(CH_2)_n$ chain between the N-atoms of the two amino groups of the ligand. While for the short CH_2CH_2 chain, the mononuclear species **1** and **3a** were isolated, for the $(CH_2)_3$ chain, oligomers **2** and **4** were obtained. The nonfluorinated **2** has a dinuclear and the fluorinated **4** a trinuclear structure.

Obviously, the trifluoroacetato coligand in **3** originates from excess and hydrolyzed ligand. All attempts to reduce the high ratio ligand/copper acetate to < 2 resulted in oils which did not solidify. Complex **3** crystallized in dioxane as the dimer solvent complex **3a**. The dioxane could be removed by sublimation or recrystallization in CH_2Cl_2.

Structural Studies. The geometry at each Cu-atom in **1** and **3a** is best described as a distorted (4 + 1) square-based pyramid. The basal plane consists of atoms O(1), N(1), N(2), and O(21) (*Figs. 1* and *2*). The apical site of the pyramid is occupied by either one

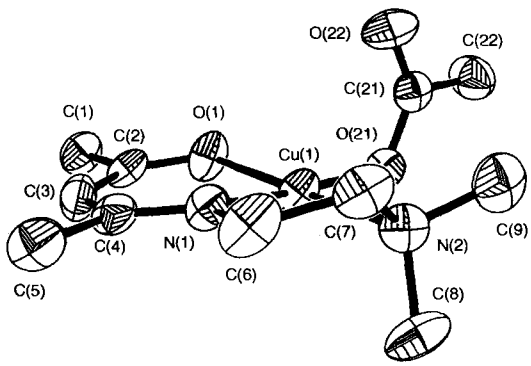


Fig. 1. *Molecular structure of acetato-{4-{[2-(dimethylamino)ethyl]amino}pent-3-en-2-onato}-copper(II)* (**1**). Arbitrary numbering.

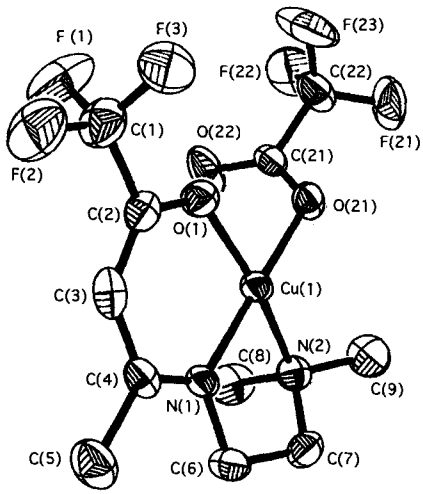
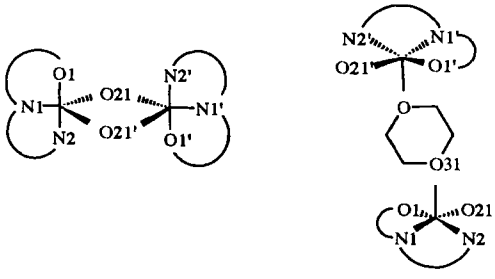


Fig. 2. *Molecular structure of μ-(1,4-dioxane)bis{{4-{[2-(dimethylamino)ethyl]amino}-1,1,1-trifluoropent-3-en-2-onato}(trifluoroacetato)copper(II)}* (**3a**). Arbitrary numbering.

O-atom of another acetate anion that is basal to the second Cu-atom in a dimer (see **1**) or an O-atom of dioxane (see **3a**). A view of the dimeric units are given in *Fig. 3*.

Complex **1** consists of $[\{CuL(\mu\text{-}X)\}_2]$ units, and Cu–O–Cu bridges *via* one of the O-atoms of the acetato coligand are formed. This mode of bridging is unusual compared to that in $Cu(AcO)_2$ where the Cu-atoms are linked *via* the two O-atoms (Cu–O–C–O–Cu) of the acetato group [12] [13]. In **3a** the Cu-atom is bridged *via* the two O-atoms of the dioxane molecule. The bond lengths Cu–O(21′) in **1** and Cu–O(31) in **3a** are in the same range, *i.e.* 2.57(1) and 2.52(1) Å, respectively, indicating rather weak interactions between the Cu-center and the bridging O-atom. For comparison, the Cu–O(21) bond lengths in the basal plane are 1.968(4) Å in **1** and 1.924(6) Å in **3a**; these values are typical for Cu–O bonds. The Cu–N bond lengths are also within the range of values normally found for such bonds: Cu–N(1) and Cu–N(2) distances are 1.942(5) and 2.084(5) Å in **1** and 1.933(8) and 2.028(6) Å in **3a**. The coordination polyhedron of **1** and **3a** is best described as a five-coordinated square pyramid. These results are very similar to the literature data for the [CuLX]-type complex (L = singly deprotonated 4-[(2-aminoethyl)amino]pent-3-en-2-one or 4-[(aminomethyl)amino]pent-3-en-2-one and X = AcO, Br, or Cl [7] [8] [10]).



3a

Fig. 3. *Schematic representation of acetato{4-{[2-(dimethylamino)ethyl]amino}pent-3-en-2-onato}-copper(II)* (**1**) *and μ-(1,4-dioxane)bis{{4-{[2-(dimethylamino)ethyl]amino}-1,1,1-trifluoropent-3-en-2-onato}(trifluoroacetato)copper(II)}* (**3a**)

The crystal structure of compound **4** is still under investigation because the *R* values are > 10%, and only preliminary results will be presented here. The structure consists of [CuL(μ-AcO)] and [$Cu_2(AcO)_4$] units (1:1). The units are linked together *via* the two O-atoms of the acetato ligand in [CuL(μ-AcO)], and bridging occurs in the Cu–O–C–O–Cu mode. The coordination sphere around the Cu-atom is tetrahedrally distorted as shown in *Fig. 4*, and the metal center is not involved in the bridging.

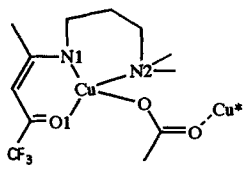


Fig. 4. *Schematic representation of the molecular structure of pentaacetato{4-{[3-(dimethylamino)propyl]-amino}-1,1,1-trifluoropent-3-en-2-onato}tricopper(II)* (**4**). Cu* represents one Cu-atom of $[Cu(OAc)_2]_2$.

The main differences between the structures investigated here and the ones described in the literature [7–10] are: *a*) the NH_2 is replaced by a Me_2N group in the tridentate β-iminoketonato ligand, and *b*) Me(1) is replaced by CF_3(1) in ligand HL^3 and HL^4. These replacements are not sufficient to avoid dimeric units in the crystal structure of **1** and **3a**, which may be responsible for their low volatility. In addition, the coordination sphere of these compounds is still a five-coordinated distorted square pyramid as usually found for this type of complex. However, the Cu-atom in **4** is in the center of a four-coordinated distorted tetrahedron. This type of coordination polyhedron in Cu compounds is rarely observed, further examples being β-diimine complexes [14] [15] and bis{4-[(2,2,2-trifluoroethyl)imino]-1,1,1,5,5,5-hexafluoropentan-2-onato}copper(II) [16]. For the latter one, a high volatility was observed. Unfortunately, **4** is non-volatile due to its trinuclear nature.

Mass Spectrometry. Ions containing Cu-atoms were identified by the two isotopes ^{63}Cu and ^{65}Cu showing a ratio of 100:44.7. The results are listed in *Tables 1* and *2*. Mass

Table 1. *Mass Spectra*[a]) *of the Nonfluorinated Complexes Acetato{4-{[2-(dimethylamino)ethyl]amino}pent-3-en-2-onato}copper(II)* (**1**) *and Triacetato{4-{[3-(dimethylamino)propyl]amino}pent-3-en-2-onato}dicopper(II)* (**2**)

Fragments[b])	[Cu(AcO)L^1] (**1**) *m/z* [%]	[$Cu_2(AcO)_3L^2$] (**2**) *m/z* [%]
$[Cu_2(AcO)L_2]^+$	523(3)	551(< 1)
$[Cu_2(AcO)(L-58)]^+$	465(< 1)	–
$[CuL_2]^+$	401(< 1)	429(1)
$[Cu_2(AcO)L]^+$	354(2)	368(2)
$[Cu(AcO)L]^+$	291(6)	305(71)
$[CuL]^+$	232(35)	246(71)
$[CuL-Me]^+$	217(3)	231(5)
$[CuL-CH_2NMe_2]^+$	174(6)	188(9)
$[CuL^*]^+$	174(6)	174(58)
$[CuL^*-CH_2NH]^+$	145(1)	145(6)
$[CuL^*-CuH]^+$	110(3)	110(13)
$[CH_2NMe_2]^+$	58(100)	58(100)

[a]) All masses are nominal masses and given in *m/z*; rel. intensities in % in parentheses.
[b]) Fragments are listed for ^{63}Cu; $L^* = L-(CH_2)_{n-1}NMe_2$.

Table 2. *Mass Spectra*[a]) *of the Fluorinated Complexes {4-{[2-(Dimethylamino)ethyl]amino}-1,1,1-trifluoropent-3-en-2-onato}(trifluoroacetato)copper(II)* (**3**) *and Pentaacetato{4-{[3-(dimethylamino)propyl]amino}-1,1,1-trifluoropent-3-en-2-onato}tricopper(II)* (**4**)

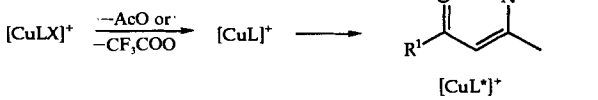
Fragments[b])	$[Cu(CF_3COO)L^3]$ (**3**) *m/z* [%]	$[Cu_3(AcO)_5L^4]$ (**4**) *m/z* [%]
$[Cu_2(AcO)L_2]^+$	–	659(< 1)
$[Cu_2L_2 - 2]^+$	–	598(< 1)
$[Cu_2(AcO)L]^+$	–	422(3)
$[Cu(CF_3COO)L]^+$	399(< 1)	–
$[Cu(AcO)L]^+$	–	359(51)
$[CuXL - F]^+$	380(< 1)	340(< 1)
$[CuL]^+$	286(7)	300(100)
$[CuL - CH_2NH]^+$	257(< 1)	271(10)
$[CuL^*]^+$	228(< 1)	228(2)
$[CuL - CuH]^+$	222(< 1)	236(7)
$[CH_2NMe_2]^+$	58(100)	58(59)

[a]) All masses are nominal masses and given in *m/z*; rel. intensities in % in parentheses.
[b]) Fragments are listed for ^{63}Cu; $L^* = L - (CH_2)_{n-1}NMe_2$; X = CF_3COO, AcO.

spectra of **1–4** show small intensities for signals of masses above the fragment $[CuLX]^+$ (L = β-iminoketonato L^1–L^4 (see **1–4**), X = AcO in **1**, **2**, and **4**, and CF_3COO in **3**). The origin of small signals of oligonuclear species with *m/z* > $[CuLX]^+$ remains unclear, because these ions can either result from species created in a thermal reaction during heating in the sample holder of the mass spectrometer [17] or from oligonuclear species which already existed in the solid state (*e.g.* in **2** and **4**). The crystal structure showed compound **4** to be trinuclear, $[Cu_3(AcO)_5L^4]$, and the vapor-pressure osmometry showed **2** to be dinuclear, $[Cu_2(AcO)_3L^2]$. While for **2** and **4** no signals from the dinuclear and trinuclear species are found in the mass spectra, the mononuclear species **1** and **3** can be identified, with rather low intensities. The base peak (100% intensity) is the fragment $[CH_2NMe_2]^+$ in the spectra of **1–3** and $[CuL]^+$ in the one of **4**.

The main fragmentation pattern of all copper complexes **1–4** is demonstrated in the *Scheme* and can be discussed as follows: Starting from $[CuXL]^+$, the loss of X = AcO or CF_3COO followed by the loss of parts from the iminoketonato ligand L in the species $[CuL]^+$ leading to ions $[CuL^*]^+$ with *m/z* 174 for the nonfluorinated and *m/z* 228 for the fluorinated ligand, L* representing $L - (CH_2)_{n-1}NMe_2$. The loss of Cu^IH or CH_2NH from $[CuL^*]^+$ in the spectra of the nonfluorinated complexes **1** and **2** or from $[CuL]^+$ in the spectra of the fluorinated complexes **3** and **4** is also observed: it is well known that decomposition processes like rearrangements involving elimination of even-electron species (CH_2NH, Cu^IH) is predominant for Cu^I, whereas the elimination of radicals ($CF_3\cdot$,

Scheme. *MS Fragmentation Pattern of Copper Complexes* **1–4**



$[CuL^*]^+$

$F\cdot$) are processes of the decomposition of Cu^{II} [18] [19]. Elimination of $CF_3\cdot$ and $F\cdot$ from $[CuL^*]^+$ or $[CuL]^+$ is not observed in the present case and, therefore, the fragmentation to Cu^IH is only understandable, assuming an intramolecular reduction from Cu^{II} to Cu^I in $[Cu^{II}L^*]^+$ or $[Cu^{II}L]^+$ in the preceding step.

Volatility Studies. The thermal behaviour of all Cu^{II} complexes **1–8** was investigated. Results of the thermal analysis of $[Cu(tmhd)_2]$ (**5**), $[Cu(fhd)_2]$ (**6**), **7**, and **8** were similar to literature data [20–22], although experimental conditions were sometimes different from those used in our experiments. The results of the thermal analysis are summarized in *Table 3*, and a schematic thermogravimetric diagram is given in *Fig. 5*. $[Cu(tmhd)_2]$ (**5**)

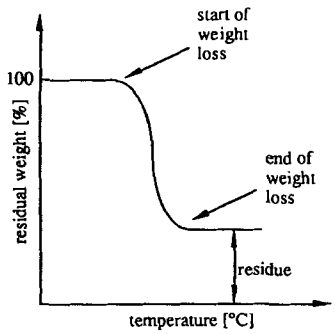


Fig. 5. *Schematic representation of the results of the thermogravimetric analysis*

and $[Cu(fhd)_2]$ (**6**) showed the transition from solid state to gas phase without any decomposition, and no residues were left in the vessel after the heating process in the DTA/TG. Different results were obtained for complexes **1–4**, **7**, and **8** where residues in the range of 10 to 37% were observed. Therefore, decomposition of the material during heating was the major process in the latter cases, and mainly decomposition products were evaporated. The calculated residue for a 100% conversion of the precursors to the copper oxides are also given in *Table 3*. The observed residues are more important than

Table 3. *DTA/TG Measurements of the Cu^{II} Compounds in Ar Using a Heating Rate of 10 K min^{-1}*

Complex	M.p. [°C] (DTA)	Start of weight loss [°C]	Obs. residue [%] (at temp. [°C])	Theor. residue of CuO/Cu_2O [%]
1	165	170	38(260)	
			33(550)	27/25
2	178	140	49(225)	
			38(550)	16/15
3a	214	85[a]), 217	30(500)	20/18
4	120	85	28(500)	10/9
5	198	165	1(340)	–
6·H_2O	110	98	1(225)	–
7	145	155	26(315)	–
			22(500)	
8	217	220	10(500)	–

[a]) Weight loss due to evaporation of coordinated solvent dioxane.

the theoretical amount of copper oxide that could be formed. Therefore, the observed residues have to consist of a mixture of stable Cu-species containing C, N, O, or F. This behaviour can be explained by the weaker Cu–N bond in the β-iminoketonates as compared to the stronger Cu–O bond in the β-diketones.

Compounds **1**, **3**, and **5**–**8** could be sublimed between 80 and 190° in a pressure range of 0.1 mbar (see *Exper. Part*). Although, successful sublimation is a good indication of volatility, no quantitative information was obtained, however. Sublimation rates were determined by weight-loss experiments in our MOCVD apparatus. Small samples (20 mg range) of the complexes were filled in a ceramic boat and placed in the sublimation zone of the apparatus. Sublimation rates in a He gas flow (66 ml/min) under reduced pressure (21 mbar) were measured at different temperatures and plotted in an *Arrhenius* plot (*Fig. 6*). From this plot, the ΔH of the phase transitions was obtained (*Table 4*). The values of ΔH are in the range of 90–150 kJ/mol which are similar to those obtained from the literature [31] [32].

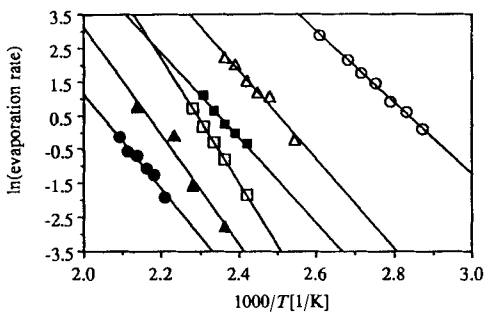


Fig. 6. *Evaporation rates of the copper complexes.* Gas flow 66 ml/min, total gas pressure 21 mbar; **1** □, **3** ●, **5** △, **6** ○, **7** ■, and **8** ▲.

Table 4. *Some Physical Properties of the Cu^{II} Complexes*

	M.p. [°C]	T[a]) [°C]	ΔH [kJ/mol]
1	155 (dec.)	140–165	150 ± 2
3	200–202	180–205	116 ± 4
5	197–198	120–150	109 ± 4
6·H_2O	100–110 (melting + dehydration)	75–110	88 ± 2
7	144	140–160	104 ± 3
8	200 (dec.)	150–195	133 ± 6

[a]) Temperature range of the weight-loss measurements.

It should be noted here that compounds **1**, **3**, **5**, **6**, and **8** really sublime and **7** evaporates, because for **7**, the temperature range of the weight-loss measurements is above the melting point (see *Table 4*).

The following order of decreasing volatility was obtained from the *Arrhenius* plot (*Fig. 6*): **6** > **5** > **7** > **1** > **8** > **3**. By considering the values of the start of weight loss in *Table 3* (thermogravimetry), similar results were obtained: **6** > **5** ≈ **7** ≈ **1** > **8** ≈ **3**. The

influence of fluorination in **6** when compared with **5** is quite clear from this result: the CF_3 group of **6** increases the volatility due to the reduction of intermolecular interactions. But although **3** and **8** contain CF_3, their volatility is rather low and even lower than that of their nonfluorinated counterparts. Indeed, the fluorination in ligands of metal complexes leads to an increased *Lewis* acidity of the metal center [23], and solvates or adducts can be formed easily. Complex **3a** is an excellent example for this: dioxane is coordinated to the Cu-atom, and the two O-atoms of dioxane form a bridge between two adjacent Cu complexes. Similar interactions might also exist in the solid state of non-solvated **3** which can be responsible for the low volatility. In **7** and **8**, the two iminoketone units are connected *via* an ethylene bridge forming a quadridentate ligand and a planar complex [24] [25]. The structure of fluorinated **8** consists of nearly parallel molecular planes, thus allowing a stacked arrangement, and resulting in the formation of infinite copper chains (Cu–Cu distance 4.625 Å). Although, the molecules in **7** are also stacked in pairs, the Cu-atom is surrounded only by C-atoms, and no metal-metal association is observed. Obviously, the Cu–Cu association is responsible for the low volatility of fluorinated **8**.

It can be summarized, that fluorination in the ligands may lead to an increase in volatility; however, intermolecular interactions due to increased *Lewis* acidity and association in the solid phase may produce the opposite. Steric hindrance using *tert*-butyl groups is an important tool to reduce intermolecular interactions, *e.g.* $[Cu(acac)_2]$ (acac = pentane-2,4-dionato) is less volatile than $[Cu(tmhd)_2]$ (**5**) [20]. Combination of *tert*-butyl and imino groups in the acetylacetone framework is an opportunity for future precursor ligand design. Very recently, *Marks* [26] published the synthesis of new ligands of this type.

Conclusion. In conclusion, it was not possible to synthesize coordinative saturated octahedron $[CuL_2]$ complexes with tridentate ligands. Dimeric units in the crystal structure of **1** and **3a** were observed, and the coordination sphere of these compounds is a five-coordinated distorted square pyramid as usually found for this type of complex. The most interesting structure is **4** with its distorted tetrahedral geometry. In the solid state, bridging does not involve the metal center and, therefore, bridging may be avoided using coligands other than acetate.

The volatility of compounds **1**–**4** is low compared to other β-iminoketonates and, therefore, their ability as MOCVD precursor is rather limited to the low-pressure range. Fluorination of the ligands may lead to an increase in volatility; however, intermolecular interactions due to increased *Lewis* acidity and association in the solid phase may have the opposite effect.

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Experimental Part

General. The chemicals and solvents were purchased from *Fluka* in the highest purity available. The ligands 4-{[2-(dimethylamino)ethyl]amino}pent-3-en-2-one (HL^1), 4-{[3-(dimethylamino)propyl]amino}pent-3-en-2-one, (HL^2), 4-{[2-(dimethylamino)ethyl]amino-1,1,1-trifluoropent-3-en-2-one (HL^3), and (4-{[3-(dimethylamino)propyl]amino}-1,1,1-trifluoropent-3-en-2-one) (HL^4) were synthesized according to [27]. The syntheses 2,2,6,6-tetramethylheptane-3,5-dione H(tmhd) and 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione H(fhd) are described in [11]. Bis(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II) ([Cu(tmhd)$_2$]; **5**) and bis(1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionato)copper(II) ([Cu(fhd)$_2$]; **6**) were synthesized according to [28] and *N,N*-ethylene(4-iminopentane-2-onato)copper(II) (**7**) and *N,N'*-ethylenebis(1,1,1-trifluoropentane-2,4-diiminato)copper(II) (**8**) according to [29].

Thermoanalyses: Mettler TA-2000C thermoanalyzer; heating rate 10 K/min; sample under Ar at atmospheric pressure. Dynamic evaporation experiments were carried out in a horizontal CVD system described in [11]. M.p.: open capillary tubes; *Büchi-510* instrument. Electron-impact mass spectra (EI-MS): *VG Tritech Tribrid* mass spectrometer; mass resolution ($A/\Delta m$) = 1000; ionizing energy 70 eV, ion source potential + 4 kV, ion source temp. 150–250°, source pressure 10^{-5} mbar, and analyzer pressure 10^{-7} mbar.

Acetato{4-{[2-(dimethylamino)ethyl]amino}pent-3-en-2-onato}copper(II) ([Cu(AcO)L^1]; **1**). $Cu(AcO)_2 \cdot H_2O$ (15 mmol, 2.93 g) was stirred in acetone (100 ml), and HL^1 (15 mmol, 2.55 g) was added slowly. A dark soln. was obtained refluxing the mixture for 5 min. After cooling to r.t. and stirring overnight, the solvent was evaporated and the crude product dried *in vacuo* and sublimed at 140°/0.1 mbar: dark blue product (2.73 g, 60%). Crystals suitable for X-ray diffraction were obtained from acetone soln. M.p. 155° (dec.). Vapor-pressure osmometry: calc. $M_{rel.}$: 291.84 g/mol, found 296.39 g/mol (± 1.99%). Anal. calc. for $C_{11}H_{20}CuN_2O_3$ (291.84): C 45.27, H 6.91, N 9.60; found: C 45.71, H 6.74, N 9.61.

Trisacetato{4-{[3-(dimethylamino)propyl]amino}pent-3-en-2-onato}dicopper(II) ([$Cu_2(AcO)_3L^2$]; **2**). $Cu(AcO)_2 \cdot H_2O$ (27.1 mmol, 5.41 g) and HL^2 (27.1 mmol, 5.00 g) were refluxed in AcOEt (50 ml) for 90 min and cooled to r.t. The soln. was filtered through a frit (medium porosity) to remove unreacted educt. The filtrate was evaporated and the green oil crystallized after the addition of a few ml of toluene/AcOEt 1:1 and cooling in the refrigerator. The green crystals (5.20 g, 78%) were filtered and dried *in vacuo*. Sublimation (150°/0.1 mbar) was not possible without decomposition. M.p. 170° (dec.). Vapor-pressure osmometry: calc. $M_{rel.}$: 487.5 g/mol, found 506.23 g/mol (± 1.85%). Anal. calc. for $C_{16}H_{28}Cu_2N_2O_7$ (487.50): C 39.42, H 5.79, N 5.75; found: C 39,48, H 6.00, N 5.75.

μ-(1,4-Dioxane)bis{{4-{[2-(dimethylamino)ethyl]amino}-1,1,1-trifluoropent-3-en-2-onato}(trifluoroacetato)copper(II)} ([{Cu(CF_3COO)L^3}$_2$ {μ-(1,4-dioxane)}]; **3a**). To a soln. of $Cu(AcO)_2 \cdot H_2O$ (1.00 mmol, 0.20 g) in 20 ml of 1,4-dioxane, HL^3 (2.00 mmol, 0.50 g) was added. The soln. was refluxed for 20 min. After cooling to r.t. and stirring overnight, the soln. was evaporated to near dryness. Within two days, blue crystals grew from the soln. They were filtered off and dried: 0.33 g (74%) of **3a** which was submitted to X-ray diffraction analysis. M.p. 200–202°. Anal. calc. for $C_{13}H_{18}CuF_6N_2O_4$ (443.83): C 35.18, H 4.09, N 6.31; found: C 35.39, H 4.02, N 6.35.

{4-{[2-(Dimethylamino)ethyl]amino}-1,1,1-trifluoropent-3-en-2-onato}(trifluoroacetato)copper(II) ([Cu(CF_3COO)L^3]; **3**). Sublimation of **3a**, starting at *ca.* 170°/0.1 mbar, yielded first a mixture which could not be analyzed exactly. The material obtained above 190° was **3** (yield 56%). Recrystallization of **3a** in CH_2Cl_2 resulted also in **3**. M.p. 200–202°. Anal. calc. for $C_{11}H_{14}CuF_6N_2O_3$ (399.78): C 33.05, H 3.53, N 7.01; found: C 33.28, H 3.33, N 7.00.

Pentaacetato{4-{[3-(dimethylamino)propyl]amino}-1,1,1-trifluoropent-3-en-2-onato}tricopper(II) ([$Cu_3(AcO)_5L^4$]; **4**). $Cu(AcO)_2 \cdot H_2O$ (4.5 mmol, 0.90 g) and HL^4 (9 mmol, 2.14 g) were refluxed in 50 ml of EtOH for 10 min and cooled to r.t. The solvent was evaporated and CH_2Cl_2 added. The soln. was filtered through a frit (medium porosity) to remove unreacted $Cu(AcO)_2 \cdot H_2O$. The solvent was evaporated, and the green oil crystallized after the addition of a few ml of EtOH: 0.38 g (30%) of **4**·EtOH as green crystals after drying *in vacuo*. M.p. 170° (dec.). Anal. calc. for $C_{22}H_{37}F_3Cu_3N_2O_{12}$ (769.18): C 34.35, H 4.85, N 3.64; found: C 34.01, H 4.86, N 3.86.

X-Ray Diffraction Studies. Crystal-structure determinations were performed on a *Nicolet P21* four-circle diffractometer (MoK_α radiation, γ = 0.7173 Å, graphite-monochromatized). The structures were solved by direct methods and difference *Fourier* calculations of the program *Siemens* SHELXTL PLUS (VSM) [30]. Crystallographic data are listed in *Table 5* and selected bond lengths and bond angles in *Table 6*. Atom coordinates, an entire list of bond distances and bond angles, temperature factors, and structure factors are available from the *K.-H. Dahmen* upon request and are deposited with the *Cambridge Crystallographic Data Center.*

Table 5. *Crystallographic Data of Acetato{4-{[2-(dimethylamino)ethyl]amino}pent-3-en-2-onato}copper(II)* (**1**) and *μ-(1,4-Dioxane)bis{{4-{[2-(dimethylamino)ethyl]amino}-1,1,1-trifluoropent-3-en-2-onato}(trifluoroacetato)copper(II)}* (**3a**)

	1	**3a**
Crystal dimensions [mm]	0.1 × 0.2 × 0.2	0.12 × 0.25 × 0.3
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	11.152(6)	8.709(3)
b [Å]	10.104(3)	9.439(4)
c [Å]	11.805(7)	12.395(3)
α [°]		67.57(3)
β [°]	99.02(4)	77.01(2)
γ [°]		84.17(3)
V [Å^3]	1313.8(11)	917.6(5)
Z	4	2
Maximum value $(\sin\theta)/\lambda$	0.538	0.481
Measured reflections	1957	1864
Unique reflections	172	61713
Observed reflections	1151[a])	1264[a])
No. of parameter	154	235
R[b]) [%]	4.17	4.38
R_w[c]) [%]	4.86[d])	4.38[e])
Min. residual electron density	0.36 eÅ^{-3}	0.45 eÅ^{-3}
Min. residual electron density	−0.35 eÅ^{-3}	−0.38 eÅ^{-3}

[a]) $I > 4\sigma(I)$. [b]) $R = \Sigma(\|F_0\| - \|F_c\|)/\Sigma F_0$. [c]) $R_w = (\Sigma w = (\|F_0\| - \|F_c\|)^2/\Sigma w|F_0|^2)^{1/2}$. [d]) $w^{-1} = \sigma^2(F) + 0.0005\ F^2$. [e]) $w^{-1} = \sigma^2(F) + 0.0002\ F^2$.

Table 6. *Selected Bond Distances* [Å] *and Bond Angles* [°] *of* **1** *and* **3a**. For numbering, see *Figs. 1* and *2*.

	1	**3a**		**1**	**3a**
Cu(1)–O(1)	1.939(4)	1.901(5)	C(4)–N(1)	1.317(9)	1.274(13)
Cu(1)–N(1)	1.942(5)	1.933(8)	C(6)–N(1)	1.475(8)	1.476(10)
Cu(1)–N(2)	2.084(5)	2.028(6)	C(6)–C(7)	1.500(11)	1.495(15)
Cu(1)–O(21)	1.9684(4)	1.924(6)	C(7)–N(2)	1.469(9)	1.485(11)
Cu(1)–O(31)	–	2.52(1)	C(21)–C(22)	1.502(10)	1.511(16)
Cu(1)–O(21′)	2.57(1)	–	C(21)–O(21)	1.270(8)	1.254(12)
C(1)–C(2)	1.516(9)	1.508(15)	C(21)–O(22)	1.235(9)	1.196(15)
C(2)–O(1)	1.272(9)	1.257(12)	O(1)–Cu(1)–N(1)	92.3(2)	93.5(3)
C(2)–C(3)	1.381(10)	1.366(15)	N(1)–Cu(1)–N(2)	83.0(2)	85.8(3)
C(3)–C(4)	1.401(10)	1.429(14)	O(1)–Cu(1)–N(2)	174.6(2)	170.1(3)
C(4)–C(5)	1.507(9)	1.506(14)	N(1)–Cu(1)–O(21)	175.2(2)	178.5(3)

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