Unsaturated Hetero Chains, IX[+]

1:1- and 2:1-Copper(II) Complexes From Primary *N*-Acylamidines

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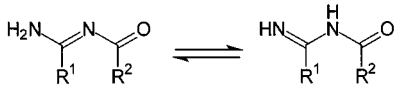
Four different types of six-membered chelate Cu^{II} complexes **2**–**5** have been synthesized from copper(II) salts and primary *N*-acylamidines ($H_2N–CR^1=N–CR^2=O$) **1**. The twofold positively charged complexes **2**–**4** contain two neutral ligands around the Cu^{II} ion. In the 1:1 compound **2** the copper(II) ion is four coordinate, leading to a distorted square coordination. The 2:1 compounds **3** and **4** show similar structural properties; the approximate square plane of the complexes is complemented by one or two loose apical contacts to the triflate counter ions. In the centrosymmetric, neutral 2:1 complex **5**, two anionic ligands interact with the central Cu^{II} ion, leading to an approximate square-planar coordination of the Cu^{II} ion. The structural versatility of these *N*-acylamidine complexes is discussed in terms of counter ion and solubility influences. All complexes have been completely characterized, including X-ray diffraction analysis.

Introduction

In order to investigate the fundamental properties of oligonitriles we initiated a thorough research program concentrating on the complex-forming ability of these new oligomers.[1] In a recent paper we reported the synthesis and structural properties of two palladium(II) complexes of differently substituted tetrameric *N*-acylated and *N*-thioacylated oligonitriles.[2] The formation of six-membered chelate rings involving either two nitrogen atoms or one nitrogen and one sulfur atom were characteristic features of these complexes. We are now focussing on the copper(II) complexes of small donor substituted model oligonitriles, the *N*-acylamidines **1**. They also offer coordination sites for the formation of six-membered chelates, namely the oxygen atom of the acyl functionality and the nitrogen atom of the amino group. In case of *N*-acylamidines **1** containing a $-NH_2$ (primary *N*-acylamidines) or a -NHR group (secondary *N*-acylamidines) tautomerism involving 1,3 proton shifts may be expected (isomers **A** and **B**).



A **B**

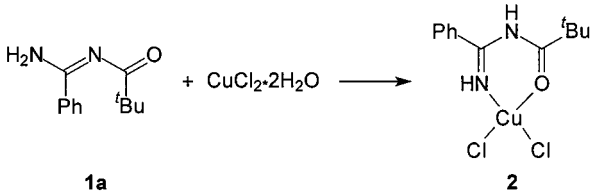
However, spectroscopic studies[3] as well as X-ray diffraction determinations[4] indicate the predominance of the *N*-acylamidine structures **A** in solution and in the solid phase. The second tautomer **B**, with the two protons on different nitrogen atoms, plays only a minor role in the equilibrium.

In this paper we present four different copper(II) complexes representing three different types of primary *N*-acylamidine complexes. To the best of our knowledge, there is only one report of a metal complex with a simple primary *N*-acylamidine in the literature; in 1978, the preparation and X-ray structure determination of a 2:1 nickel complex involving an anionic *N*-acylamidine ligand was reported by an Italian group.[5] *N*-Acylamidines may be considered to be aza analogues of enaminones (3-aminopropenones); several metal complexes of these ligands are known.[6]

Results

Depending on the reaction conditions, we were able to synthesize and characterize spectroscopically and by X-ray diffraction three different types of *N*-acylamidine copper(II) complexes.

If *N*-pivaloyl benzamidine (**1a**) and $Cu^{II}Cl_2 \cdot 2\,H_2O$ are dissolved in an equimolar ratio in acetonitrile, dark green crystals **2** are obtained in 67.5% yield after careful precipitation using diethyl ether.



1a **2**

The new compound **2** was studied by X-ray analysis. Crystalline **2** forms a mononuclear 1:1 complex, including 1.5 molecules of acetonitrile, with a *cis*-$CuCl_2$ unit. Complexation at the oxygen atom and nitrogen atom N(5) (crystallographic numbering) of neutral **1a** by the copper ion leads to the six-membered chelate ring of metal complex **2**

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[++] X-ray diffraction analyses.

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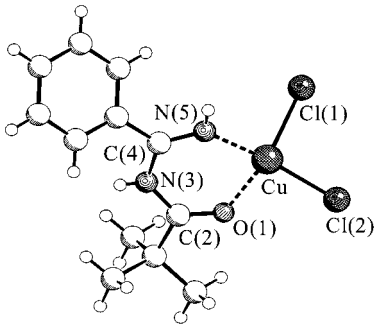


Figure 1. Molecular structure of **2**; selected bond parameters: bond lengths [Å]: Cu−Cl(1) 2.2786(7), Cu−Cl(2) 2.2167(7), Cu−O(1) 2.0245(15), Cu−N(5) 1.932(2), O(1)−C(2) 1.225(3), C(2)−N(3) 1.355(3), N(3)−C(4) 1.385(3), C(4)−N(5) 1.271(3); bond angles [°]: Cl(1)−Cu−Cl(2) 96.41(3), N(5)−Cu−O(1) 85.35(7), N(5)−Cu−Cl(1) 90.77(6), O(1)−Cu−Cl(2) 91.76(5), O(1)−C(2)−N(3) 122.3(2), C(2)−N(3)−C(4) 127.2(2), N(5)−C(4)−N(3) 120.6(2); torsional angles [°]: N(5)−Cu−O(1)−C(2) 12.22 (0.24), Cl(2)−Cu−O(1)−C(2) −176.89 (0.24), Cl(1)−Cu−O(1)−C(2) −71.69 (0.27), Cu−O(1)−C(2)−N(3) −10.17 (0.40), O(1)−C(2)−N(3)−C(4) −2.82 (0.43), C(2)−N(3)−C(4)−N(5) 9.31 (0.41), N(3)−C(4)−N(5)−Cu −2.43 (0.40), O(1)−Cu−N(5)−C(4) −5.61 (0.26)

(Figure 1). The organic section of the chelate ring is rather flat, with the copper atom well in the plane of the ligand. One of chlorides is also located in the plane; the other chloride, however, is positioned far below the plane (see Figure 1), resulting in a strongly tetrahedrally deformed square planar coordination geometry around copper(II) (sum of angles: 364.29°). Coordination bond lengths are 1.932(2) to N, 2.205(2) to O and 2.217(1) and 2.279(1) Å to chlorine. The N−Cu−O bond angle amounts to 85.35°.

Due to complexation, the amino group of the ligand is transformed into an imine moiety by a formal 1,3-shift of one of the amino hydrogen atoms to nitrogen atom N(3). The lone pair of the sp^2 hybridized imine-type nitrogen atom N(5) acts as the coordination site; thus, a conjugated 6π/5z ligand is present in the complex, carrying a central planar sp^2 amino group. This ligand may also be understood as a combination of a ketiminato and a ketono donor connected by an amino group, as can be seen from the rather similar C=N and C=O bond lengths [1.271(3) versus 1.225(3) Å]. The same applies to the C−N bonds [1.355(3) and 1.385(3) Å]. The phenyl ring is twisted out of the plane of the complex by around 40°, possibly due to packing effects rather than intramolecular steric strain. The IR spectra (KBr) show two broad absorptions at 3400 and 3200 cm^{-1}, which are assigned to the =NH and −NH stretching vibrations (isomer **B**); in contrast, the free ligand shows bands at 3320 and 3160 cm^{-1}, which are attributed to the unsymmetrical and symmetrical NH_2 stretching vibrations (isomer **A**). UV absorptions of low intensity are observed at 464 and 391 nm due to d→d transitions at the metal ion, causing the green-yellow color of solutions of **2**.

The reaction of two equivalents of either *N*-(4-methylbenzoyl) benzamidine (**1b**) or *N*-pivaloyl benzamidine (**1a**) with one equivalent of $Cu(CF_3SO_3)_2$ in acetonitrile leads to the formation of the respective copper(II) complexes **3** (Figure 2) and **4** (Figure 3). Crystallization was achieved by

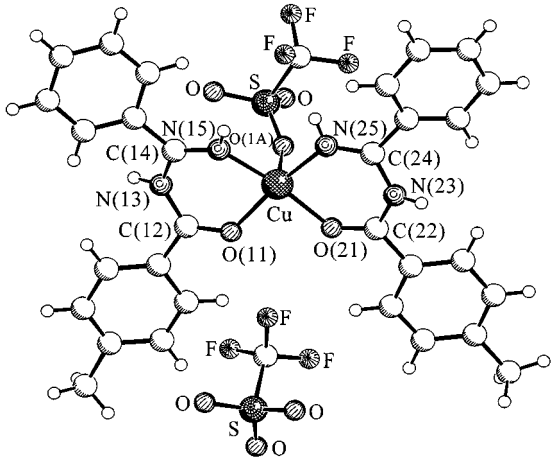
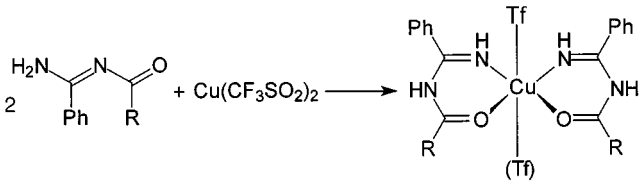


Figure 2. Molecular structure of **3**; selected bond parameters: bond lengths [Å]: Cu−O(1A) 2.282(4), Cu−O(11) 1.944(4), Cu−O(21) 1.956(4), Cu−N(15) 1.936(5), Cu−N(25) 1.930(5), O(11)−C(12) 1.243(7), C(12)−N(13) 1.375(8), N(13)−C(14) 1.383(8), C(14)−N(15) 1.295(7), O(21)−C(22) 1.247(7), C(22)−N(23) 1.363(8), N(23)−C(24) 1.373(8), C(24)−N(25) 1.267(8); bond angles [°]: N(25)−Cu−N(15) 95.5(2), N(15)−Cu−O(11) 88.00(19), N(25)−Cu−O(21) 88.3(2), O(11)−Cu−O(21) 86.90(17), N(25)−Cu−O(1A) 96.2(2), N(15)−Cu−O(1A) 95.19(19), C(12)−O(11)−Cu 127.5(4), O(11)−C(12)−N(13) 122.2(5), C(12)−N(13)−C(14) 126.3(5), N(15)−C(14)−N(13) 120.1(5), C(14)−N(15)−Cu 127.1(4), C(22)−O(21)−Cu 129.4(4), O(21)−C(22)−N(23) 121.9(6), C(22)−N(23)−C(24) 127.5(5), N(25)−C(24)−N(23) 121.1(6), C(24)−N(25)−Cu 130.0(5); torsional angles [°]: O(1A)−Cu−O(11)−C(12) −69.69 (0.49), N(15)−Cu−O(11)−C(12) 25.40 (0.49), Cu−O(11)−C(12)−N(13) −9.00 (0.81), O(11)−C(12)−N(13)−C(14) −18.51 (0.91), C(12)−N(13)−C(14)−N(15) 16.49 (0.88), N(13)−C(14)−N(15)−Cu 12.44 (0.79), O(11)−Cu−N(15)−C(14) −26.95 (0.50), O(1A)−Cu−N(15)−C(14) 66.00 (0.51), N(25)−Cu−O(21)−C(22) 9.41 (0.50), Cu−O(21)−C(22)−N(23) −3.20 (0.84), O(21)−C(22)−N(23)−C(24) −10.72 (0.98), C(22)−N(23)−C(24)−N(25) 13.73 (0.98), N(23)−C(24)−N(25)−Cu −2.65 (0.86), O(21)−Cu−N(25)−C(24) −6.34 (0.53)

adding surplus of diethyl ether, yielding metal complexes **3** (83.5% yield, from **1b**) and **4** (91.2% yield, from **1a**).



1a, 1b

	R
1a, 4	^{t}Bu
1b, 3	4-Tolyl

3, 4

Both compounds **3** and **4** were analyzed by X-ray diffraction. Both complexes consist of two neutral *N*-acylamidines in their C=NH tautomeric form **B** (analogously to **2**) complexing a central copper(II) ion (mononuclear 2:1 complexes); the two counter ions are in close vicinity to the doubly positively charged complex (see below). As in **2**, conjugated six-membered chelate rings are formed by coordination of the oxygen atoms and terminal nitrogen atoms of the *N*-acylamidines (isomer **B**) to copper (II). In both complexes *cis* O−Cu−O and *cis* N−Cu−N coordination is observed. A fifth (and in **4**, a sixth as well) coordination

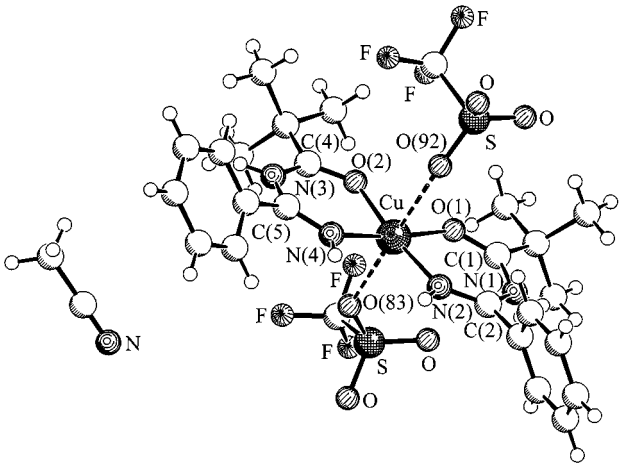


Figure 3. Molecular structure of **4**; selected bond parameters: bond lengths [Å]: Cu−N(2) 1.923(2), Cu−O(2) 1.9447(16), Cu−O(1) 1.9479(18), Cu−N(4) 1.951(2), Cu−O(83) 2.4028(19), C(1)−O(1) 1.226(3), C(1)−N(1) 1.372(3), C(2)−N(2) 1.270(3), C(2)−N(1) 1.388(3), C(4)−O(2) 1.226(3), C(4)−N(3) 1.363(3), C(5)−N(4) 1.279(3), C(5)−N(3) 1.393(3); bond angles [°]: N(2)−Cu−O(1) 88.20(8), O(2)−Cu−O(1) 86.09(7), N(2)−Cu−N(4) 97.26(9), O(2)−Cu−N(4) 88.15(8), N(2)−Cu−O(83) 96.14(9), O(2)−Cu−O(83) 88.04(8), O(1)−C(1)−N(1) 122.0(2), N(2)−C(2)−N(1) 121.9(2), O(2)−C(4)−N(3) 122.5(2), N(4)−C(5)−N(3) 121.1(2), C(1)−O(1)−Cu 131.00(17), C(5)−N(4)−Cu 129.13(18), C(1)−N(1)−C(2) 126.3(2), C(2)−N(2)−Cu 129.71(19), C(4)−N(3)−C(5) 126.8(2), C(4)−O(2)−Cu 130.73(17); torsion angles [°]: N(1)−C(1)−O(1)−Cu −7.45 (0.36), N(2)−Cu−O(1)−C(1) 8.29 (0.22), O(2)−Cu−O(1)−C(1) −175.87 (0.22), N(4)−Cu−O(1)−C(1) 151.03 (0.60), N(3)−C(5)−N(4)−Cu 6.76 (0.35), N(2)−Cu−N(4)−C(5) 178.13 (0.22), O(2)−Cu−N(4)−C(5) 2.69 (0.22), O(1)−C(1)−N(1)−C(2) −2.64 (0.39), N(2)−C(2)−N(1)−C(1) 9.47 (0.40), N(1)−C(2)−N(2)−Cu −6.03 (0.38), O(2)−Cu−N(2)−C(2) −37.27 (0.81), O(1)−Cu−N(2)−C(2) −1.21 (0.24), O(2)−C(4)−N(3)−C(5) 5.05 (0.39), N(4)−C(5)−N(3)−C(4) −12.82 (0.38), N(3)−C(4)−O(2)−Cu 8.66 (0.36), N(2)−Cu−O(2)−C(4) −150.95 (0.63), N(4)−Cu−O(2)−C(4) −10.83 (0.22), O(83)−Cu−O(2)−C(4) 82.55 (0.22)

site of copper is loosely occupied by an oxygen atom of a $CF_3SO_3^-$ anion, although the corresponding Cu−O distances are substantially longer (see below). In compound **3**, the copper atom is five-coordinate, having an approximately flat square-pyramidal geometry, in compound **4** the central ion is six-coordinate, forming an elongated octahedral or square-bipyramidal geometry, as is known for other copper(II) complexes. Coordination bond lengths in **3** are: Cu−N: 1.930(5),1.936(5); Cu−O: 1.944(4), 1.956(4), 2.282 (4) Å (to $CF_3SO_3^-$). Coordination bond lengths in **4** are: Cu−N: 1.923(2), 1.951(2); Cu−O: 1.945(2), 1.948(2), 2.403(2), 2.560(2) Å (both to $CF_3SO_3^-$).

The IR absorptions in the NH_2 region are similar to those of **2** (3400 and 3220 cm^{-1}). Low intensity d→d transitions at 627 nm (**3**) and 626 nm (**4**) cause the blue color of the complexes.

A third type of a *N*-acylamidine copper(II) complex is obtained by treating $Cu(SO_4) \cdot 5\,H_2O$ with *N*-pivaloylpivalamidine (**1c**). $Cu(SO_4) \cdot 5\,H_2O$ and **1c** are mixed in aqueous ethanol, the solution is extracted with cyclohexane. The solvent is removed and the solid is recrystallized from acetonitrile. Metal complex **5** is obtained in 41.9% yield (calculated for **1c**) as violet needles (Figure 4).

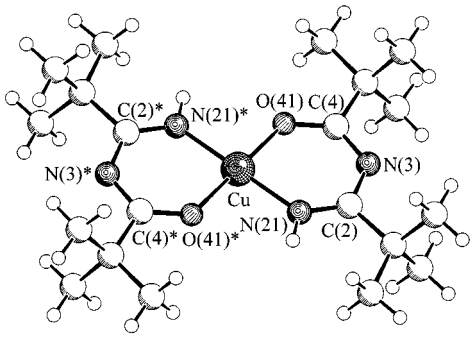
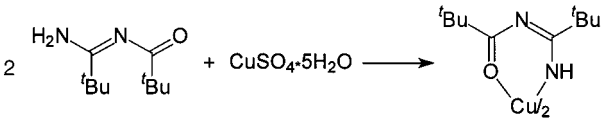


Figure 4. Molecular structure of **5**; selected bond parameters: bond lengths [Å]: Cu−N(21) 1.905(2), Cu−N(21)* 1.905(2), Cu−O(41)* 1.917(2), Cu−O(41) 1.917(2), C(2)−N(21) 1.287(4), C(2)−N(3) 1.348(4), N(3)−C(4) 1.329(4), C(4)−O(41) 1.275(4); bond angles [°]: N(21)−Cu−N(21)* 180.0(2), N(21)−Cu−O(41)* 90.5(1), N(21)*−Cu−O(41)* 89.5(1), N(21)−Cu−O(41) 89.5(1), N(21)*−Cu−O(41) 90.5(1), N(21)−C(2)−N(3) 125.1(3), C(2)−N(21)−Cu 128.2(2), C(4)−N(3)−C(2) 122.8(3), O(41)−C(4)−N(3) 127.3(3), C(4)−O(41)−Cu 126.8(2); torsion angles [°]: N(3)−C(2)−N(21)−Cu 2.30 (0.47), O(41)−Cu−N(21)−C(2) 1.53 (0.28), N(21)−C(2)−N(3)−C(4) −3.81 (0.49), C(2)−N(3)−C(4)−O(41) −0.27 (0.50), N(3)−C(4)−O(41)−Cu 5.39 (0.47), N(21)−Cu−O(41)−C(4) −5.12 (0.26)



1c **5**

In this type of 2:1 mononuclear complex two anionic *N*-acylamidines **1c** are bound to Cu^{II}, forming a neutral six-membered bis-chelate. Interestingly, the O−Cu−O and N−Cu−N units are now in a *trans* arrangement, forming the planar copper(II) complex with centric symmetry. The Cu−N [1.905(2)] and Cu−O bonds [1.917(2) Å] are rather similar in length; compared to the complexes **2**−**4** with neutral *N*-acylamidines as ligands, these bonds are shorter by about 0.05 Å as a consequence of the formally anionic ligands. As in **2**−**4** effective cyclic conjugation is indicated by the bond lengths of the ligands. However, compared to **2**−**4**, the C=O/C=N bonds in **5** are longer and the N−C−N bonds around carbon atom C(3) are shorter, resulting in a much less pronounced bond alternation.

As expected, there is only one IR signal in the NH region at 3330 cm^{-1}, occurring as a very strong, sharp absorption from the N−H stretching vibration (compare ref.[7]). The UV spectra of **5** are in sharp contrast to those of **3** and **4**; the low intensity d→d transition at 561 nm causes the purple color of the solutions and indicate stronger interactions between the ligand and the copper(II) ion than in **3** and **4**.

Discussion

As exemplified by these three types of copper(II) complexes, primary *N*-acylamidines (**1**) are rather versatile ligands for metal complexation. This is mainly due to the NH_2 groups which allow on the one hand the use of primary *N*-acylamidines as neutral ligands (isomer **B** in com-

pounds **2**−**4**), and on the other as anionic (compound **5**; see also ref.[5]) or even dianionic ligands.[8] Tautomerism between isomers **A** and **B** is important in view of the thermodynamics of the complex formation since migration of one proton to the central nitrogen atom allows the formation of a favorable cyclic conjugated six-membered chelate. Correspondingly, tertiary *N*-acylamidines carrying dialkylamino groups, which lack this possibility, are much weaker ligands compared to the primary compounds **1**.[1]

The formation of the different types of complexes obviously depends on the counter ion of the copper(II) salts employed. Independent of the stoichiometry used, ligand **1a** forms a 1:1 (**2**) and a 2:1 (**4**) complex from an acetonitrile solution if one uses copper(II) chloride and copper(II) triflate respectively. Both complexes are obtained by precipitation using diethyl ether. The solubility of the salts and complexes seems to play the important role in controlling the products. Under the conditions mentioned above, no deprotonation takes place and one obtains complexes of the neutral ligands. In contrast, reaction of the aliphatically substituted ligand **1c** in aqueous ethanol yields the neutral complex **5** containing the anionic ligand after repeated extraction with cyclohexane as nonpolar solvent. Most likely, the extraction of the highly hydrophobic complex shifts the complexation equilibrium towards the observed uncharged product, even in the absence of an additional base.

Finally, this series of closely related Cu^{II} complexes is a good demonstration of the versatility of this d^9 ion, giving *N*-acylamidine complexes with coordination numbers four, five and six, including regular square planar (**5**), tetrahedrally distorted planar (**2**), square pyramidal (**3**) and elongated octahedral (**4**) coordination; in all cases four short N−Cu/O−Cu bonds are formed. In the latter two cases, one or two long apical O−Cu contacts to the counter ions are also observed.

Experimental Section

Materials and Methods: Compounds **1a, 1b**, and **1c** were prepared as previously described.[9] Commercially available solvents (p. a. quality) were used without further purification. − CHN analyses were performed with a DiaCHN 240 (Perkin−Elmer). − IR spectra were recorded on a Perkin−Elmer PE 298 spectrophotometer as KBr pellets. − UV/Vis-spectra were recorded using a Cary 1 Bio spectrophotometer (Varian). − ^{1}H- and ^{13}C-NMR spectra were obtained using a Bruker WM 300 and a Bruker AMX 400 spectrometer. The MS (ESI) spectra were recorded using a Quattro LC-Z mass spectrometer (Micromass).

$CuCl_2$-Complex of *N*-Pivaloylbenzamidine (2): Compound **1a** (20 mg, 0.100 mmol) is treated at room temperature with $CuCl_2 \cdot 2\,H_2O$ (17 mg, 0.100 mmol) in acetonitrile (2 mL). After stirring for 5 min a clear, green solution is formed. After some time, diethyl ether (12 mL) is carefully added to form an upper layer. After five days green crystals of **2** are collected (27 mg, 0.067 mmol, 67% yield). − IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (br, NH), 3200 (br, NH), 3050 (m, $CH_{arom.}$), 2960 (s, $CH_{aliph.}$), 2850 (w, $CH_{aliph.}$), 1650 (vs, C=O), 1570 (s, $C{=}C_{arom.}$), 1480 (s), 1390 (w), 1370 (m), 1360 (m), 1280 (w), 1220 (m), 1180 (s), 1100 (w), 1060 (m), 1020 (w), 990 (w), 960 (w), 870 (m), 840 (m), 810 (m), 780 (m), 750 (s), 700 (s). − UV/Vis (acetonitrile): λ_{max} [nm] (ε) = 464 (212), 391 (136), 273 sh (10082), 245 (13274), 197 (25444). − ^{1}H NMR (400.13 MHz, CD_3CN): δ = 2.08 (s), 3.97 (br), 6.38 (br), 6.81 (br), 9.71 (br). − MS (ESI, acetonitrile): *m/z* (%) = 506.0 (3) [$C_{24}H_{32}N_4O_2CuCl^+$], 470.1 (20) [$C_{24}H_{31}N_4O_2Cu^+$], 328.0 (2) [$C_{12}H_{15}N_2OCu^+$], 235.5 [$C_{24}H_{32}N_4O_2Cu^{2+}$], 205.0 (100) [$C_{12}H_{17}N_2O^+$]. − $C_{12}H_{16}Cl_2CuN_2O \cdot 1.5$ MeCN (400.29).

X-ray Diffraction Analysis of $2 \cdot 1.5$ MeCN: ($C_{12}H_{16}Cl_2CuN_2O \cdot 1.5$ MeCN),[10] the green single crystal was analyzed using a Nonius KappaCCD diffractometer with Mo-K_α radiation (λ=0.71073 Å) using a graphite monochromator at 293(2) K. Crystal system: monoclinic, space group *C*2/c (No. 15) with cell parameters a = 15.371(1) Å, b = 12.046(1) Å, c = 21.670(1) Å, β = 106.70(1)°, V = 3843.2(4) Å^3, $\rho_{calcd.}$ = 1.384 Mg/m^3, Z = 8. Crystal size: 0.20 × 0.10 × 0.10 mm. 18292 reflections were collected leading to 5718 independent and 4061 observed [$I > 2\sigma(I)$] reflections. Absorption coefficient μ = 1.420 mm^{-1}, absorption correction via SORTAN (0.764 ≤ T ≤ 0.871). 217 refined parameters. Non-hydrogen atoms were refined anisotropically. H-Atoms were geometrically positioned (riding model). $R(F)$ = 0.0451, $wR(F^2)$ = 0.1080; residual electron density: 0.519 and −0.517 eÅ^{-3}.[11]

$Cu(CF_3SO_2)_2$ Complex of *N*-(4-Methylbenzoyl)benzamidine (3): Compound **1b** (24 mg, 0.100 mmol) is treated at room temperature with of $Cu(CF_3SO_2)_2$ (18 mg, 0.050 mmol) in acetonitrile (1.5 mL). After stirring for 2 min a clear, blue solution is formed. After some time, diethyl ether (12 mL) is carefully added to form an upper layer. After three days blue crystals of **3** are collected (35 mg, 0.042 mmol, 83.5% yield). − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (br, NH), 3220 (s, NH), 3030 (m, $CH_{arom.}$), 2900 (sh, $CH_{aliph.}$), 1640 (vs, C=O), 1600 (s, $C{=}C_{arom.}$), 1560 (m), 1500 (sh), 1480 (s), 1440 (w), 1380 (m), 1270 (vs), 1220 (vs), 1180 (m), 1160 (s), 1120 (m), 1020 (s), 940 (w), 880 (w), 830 (w), 780 (w), 740 (s), 700 (m). − UV/Vis (acetonitrile): λ_{max} [nm] (ε) = 627 (102), 465 (42), 267 (24430), 216 sh (14974), 195 (42734). − ^{1}H NMR (300.13 MHz, CD_3CN): δ = 2.32 (br), 7.19 (s), 7.62 (br), 9.62 (br). − MS (ESI, acetonitrile): *m/z* (%) = 538.1 (20) [$C_{30}H_{27}N_4O_2Cu^+$], 269.5 (12) [$C_{30}H_{28}N_4O_2Cu^{2+}$], 239.0 (100) [$C_{15}H_{15}N_2O^+$]. − $C_{32}H_{28}CuF_6N_4O_8S_2$ (838.26): calcd. C 45.85 H 3.37 N 6.68; found C 45.34 H 3.49 N 6.42.

X-ray Diffraction Analysis of 3: ($C_{32}H_{28}CuF_6N_4O_8S_2$),[10] the blue single crystal was analyzed using a Nonius KappaCCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) using a graphite monochromator at 198(2) K. Crystal system: monoclinic, space group $P2_1$ (No. 4) with cell parameters a = 10.329(1) Å, b = 16.902(1) Å, c = 10.676(1) Å, β = 109.96(1)°, V = 1751.9(3) Å^3, $\rho_{calcd.}$ = 1.589 Mg/m^3, Z = 2. Crystal size: 0.20 × 0.20 × 0.10 mm. 14055 reflections were collected leading to 5497 independent and 4390 observed [$I > 2\sigma(I)$] reflections. Absorption coefficient μ = 0.831 mm^{-1}, absorption correction via SORTAN (0.852 ≤ T ≤ 0.922). 486 refined parameters. Non-hydrogen atoms were refined anisotropically. H-Atoms were geometrically positioned (riding model). $R(F)$ = 0.0566, $wR(F^2)$ = 0.1301; Flack parameter 0.007(17); residual electron density: 0.905 and −0.717 eÅ^{-3}.[11]

$Cu(CF_3SO_2)_2$ Complex of *N*-Pivaloylbenzamidine (4): Compound **1a** (20 mg, 0.100 mmol) is treated at room temperature with $Cu(CF_3SO_2)_2$ (18 mg, 0.050 mmol) in acetonitrile (1.5 mL). After stirring for 2 min a clear, blue solution is formed. After some time, diethyl ether (12 mL) is carefully added to form an upper layer. After five days blue crystals of **4** are collected (37 mg, 0.046 mmol, 91.2% yield). − IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (br, NH), 3240 (s, NH), 3090 (w, $CH_{arom.}$), 2960 (s, $CH_{aliph.}$), 2860 (sh, $CH_{aliph.}$), 1660 (vs,

C=O), 1570 (w), 1490 (s, C=$C_{arom.}$), 1400 (w), 1380 (m), 1280 (s), 1240 (vs), 1220 (s), 1180 (m), 1160 (s), 1020 (s), 850 (w), 780 (w), 750 (m). − UV/Vis (acetonitrile): λ_{max} [nm] (ε) = 626 (67), 249 (24350), 200 (39544). − ^{1}H NMR (300.13 MHz, CD_3CN): δ = 2.35 (br), 4.58 (br), 7.20 (s), 7.49 (br), 9.60 (br). − MS (ESI, acetonitrile): *m/z* (%) = 620.1 (10) [$C_{24}H_{32}N_4O_2CuCF_3SO_3^+$], 470.1 (70) [$C_{24}H_{31}N_4O_2Cu^+$], 235.5 (62) [$C_{24}H_{32}N_4O_2Cu^{2+}$], 205.0 (100) [$C_{12}H_{17}N_2O^+$]. − $C_{28}H_{35}CuF_6N_5O_8S_2$ (811.27): calcd. C 41.45 H 4.35 N 8.63; found C 40.99 H 3.92 N 7.83

X-ray Diffraction Analysis of 4 · MeCN: ($C_{28}H_{35}CuF_6N_5O_8S_2$),[10] the blue single crystal was analyzed using a Nonius KappaCCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) using a graphite monochromator at 223(2) K. Crystal system: orthorhombic, space group *Pbca* (No. 61) with cell parameters *a* = 14.032(1) Å, *b* = 21.886(1) Å, *c* = 23.673(1) Å, *V* = 7270.1(7) Å^3, $\rho_{calcd.}$ = 1.482 Mg/m^3, *Z* = 8. Crystal size: 0.20 × 0.20 × 0.15 mm. 62323 reflections were collected leading to 8343 independent and 5919 observed [$I > 2\sigma(I)$] reflections. Absorption coefficient μ = 0.798 mm^{-1}, absorption correction via SORTAN (0.857 ≤ *T* ≤ 0.890). 464 refined parameters. Non-hydrogen atoms were refined anisotropically. H-Atoms were geometrically positioned (riding model). $R(F)$ = 0.0453, $wR(F^2)$ = 0.1069; residual electron density: 0.620 and −0.522 eÅ^{-3}.[11]

Cu^{II} Complex of *N*-Pivaloylpivalamidine (5): An excess of $Cu(SO_4) \cdot 5\,H_2O$ is suspended in 50% aqueous ethanol at room temperature. The saturated solution (2.0 mL) is mixed with a solution of **1c** (92 mg, 0.500 mmol) dissolved in ethanol (2.0 mL). About 1 g of $Cu(SO_4) \cdot 5\,H_2O$ is added. After stirring for 10 min, the mixture is filtered and the mother-liquor is extracted with cyclohexane (3 × 2 mL). The solvent is removed in vacuo. The precipitate is recrystallized from acetonitrile and affords **5** [45 mg, 0.105 mmol, 41.9% yield (calcd. for **1c**)] as violet needles. − IR (KBr): $\tilde{\nu}$ = 3330 (vs, NH), 2920 (vs, $CH_{aliph.}$), 2900 (s, $CH_{aliph.}$), 2820 (m, $CH_{aliph.}$), 1550 (vs, C=O), 1470 (vs.), 1450 (s), 1420 (s), 1380 (m), 1300 (s), 1330 (m), 1230 (sh), 1220 (s), 1200 (sh), 1020 (w), 930 (m), 870 (s), 800 (m), 760 (s), 740 (sh). − UV/Vis (acetonitrile): λ_{max} [nm] (ε) = 561 (12), 300 sh (3018), 252 (11162), 209 (10508), 192 (13290). − ^{1}H NMR (300.13 MHz, [D_8]toluene): δ = 1.25 (s), 1.67 (s), 4.96 (br), 5.80 (br). − MS (ESI, acetonitrile, cations): *m/z* (%) = 431.2 (85) [$C_{20}H_{39}CuN_4O_2^+$], 215.5 (5) [$C_{20}H_{40}CuN_4O_2^{2+}$], 185.0 (100) [$C_{10}H_{21}N_2O^+$]. − MS (ESI, acetonitrile, anions): *m/z* (%) = 464.2 (100) [$C_{20}H_{38}N_4O_2CuCl^-$], 219.0 (18) [$C_{10}H_{20}N_2OCl^-$]. − $C_{20}H_{38}CuN_4O_2$ (430.10): calcd. C 55.85 H 8.91 N 13.03; found C 56.39 H 9.13 N 13.34. −

X-ray Diffraction Analysis of 5: ($C_{20}H_{38}CuN_4O_2$),[10] the violet single crystal was analyzed using a Nonius KappaCCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) using a graphite monochromator at 198(2) K. Crystal system: monoclinic, space group $P2_1/n$ (No. 14) with cell parameters *a* = 5.952(1) Å, *b* = 18.286(3) Å, *c* = 11.469(1) Å, β = 96.55(1)°, *V* = 1240.1(3) Å^3, $\rho_{calcd.}$ = 1.152 Mg/m^3, *Z* = 2. Crystal size: 0.30 × 0.10 × 0.10 mm. 7240 reflections were collected leading to 2782 independent and 1900 observed [$I > 2\sigma(I)$] reflections. Absorption coefficient μ = 0.899 mm^{-1}, absorption correction via SORTAN (0.774 ≤ *T* ≤ 0.915). 130 refined parameters. Non-hydrogen atoms were refined anisotropically. H-Atoms were geometrically positioned (riding model). $R(F)$ = 0.0534, $wR(F^2)$ = 0.1222; residual electron density: 0.549 and −0.364 eÅ^{-3}.[11]

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