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Copper Complexes with the Ligand Methyl Bis(3,5-dimethylpyrazol-1-yl)-acetate (Mebdmpza), Generated by In Situ Methanolic Esterification of Bis(3,5-dimethylpyrazol-1-yl)acetic Acid

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Two novel complexes, $[CuCl_2(Mebdmpza)]$ (**1**) and $[Cu_2(\mu\text{-}O_4C_2)Cl_2(Mebdmpza)_2]$ (**2**) [Mebdmpza = methyl bis(3,5-dimethylpyrazol-1-yl)acetate], were synthesized by reaction of $CuCl_2$ with the precursor ligand bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) in methanol. The X-ray crystal structures of **1** and **2** revealed that the initial Hbdmpza ligand had reacted with methanol during the crystallization process to yield the esterified ligand Mebdmpza. A reverse Mebdmpza to bdmpza reaction is observed by dissolving $[CuCl_2(Mebdmpza)]$ (**1**) in water to yield $[Cu(bdmpza)_2]\cdot 2H_2O$. After drying, the latter gives water-free $[Cu(bdmpza)_2]$. The copper ion in the orange mononuclear complex **1** is tetrahedrally coordinated by two nitrogen atoms (from one ligand) and two chloride ions. The light-green dinuclear complex **2** exhibits a square-pyramidal geometry, defined by two ligand nitrogen atoms, two oxalato oxygen atoms, and one apical chloride anion. The EPR spectrum of **1** shows significant changes upon variation of the temperature, from a broad pseudo-isotropic symmetry signal at 298 K ($g_{av.} = 2.16$) to a signal characterized by an axially distorted Cu^{II} below 200 K ($g_{\parallel} = 2.34$; no $A_{\parallel}$ resolved; $g_{\perp} = 2.11$). The green, dinuclear, oxalato-bridged compound **2** is strongly antiferromagnetically coupled with $2J = -342\ cm^{-1}$. Its EPR spectrum shows only a broad line ($g_{av.} = 2.12$), which is ascribed to mononuclear impurities, as it does not disappear even at very low temperatures. No signal for a triplet of dinuclear Cu^{II} is observed at any temperature.

Introduction

The design and preparation of model complexes for metalloenzymes is a topical area of coordination chemistry. In this context, polydentate polypyrazolyl donor ligands are interesting candidates to synthesize complexes biomimicking enzyme active sites.[1] (Poly)pyrazole derivatives bearing a carboxylic acid function and with [N,N,O]-donor sets are valuable ligands for modeling certain zinc and iron enzymes.[2] Among them, bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) represents an important member of the family of tridentate scorpionates exhibiting the facial coordination mode. So far, several mononuclear metal complexes with Hbdmpza have been reported, as well as some di-, tetra-, and hexanuclear compounds.[3,4] Coordination compounds with more than one metal nucleus are often of great interest for applications in enzyme biomimetics, catalysis, or magnetism. Anionic bdmpza, by loss of H^+ from Hbdmpza, may act as a tridentate ligand (scorpionate), but other coordination modes have also been reported.[3] Almost all examples described in the literature exhibit deprotonated bdmpza ligands, and only one complex with neutral Hbdmpza ligands has been recently reported: $[Cu_4Cl_8(Hbdmpza)_2]$.[5] Usually, the starting ligands are stable under the reaction conditions, and only deprotonation of the carboxylic acid, followed by the coordination to the metal ion, occurs. Nevertheless, a number of examples are known where related starting ligands have experienced a chemical transformation.[6] In such cases, the observed alterations of the initial ligands are suggested to be metal-assisted.[7]

Herein, the preparation and structural characterization of two new coordination compounds obtained from the parent ligand Hbdmpza, namely $[CuCl_2(Mebdmpza)]$ (**1**) and $[Cu_2(C_2O_4)Cl_2(Mebdmpza)_2]$ (**2**) [Mebdmpza = methyl bis(3,5-dimethylpyrazol-1-yl)acetate], are described. The coordination reactions have been carried out in methanol, which reacts with the starting Hbdmpza ligand in the presence of the copper salt, to generate the new esterified ligand Mebdmpza. In addition, the ligand transformation was found to be reversible by using water as solvent, which illustrates the crucial role of the copper ions coordinated to the ligand.

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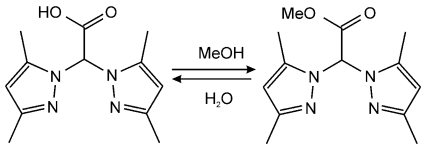
Results and Discussion

Crystal Structure Analyses of [$CuCl_2$(Mebdmpza)] (1) and [$Cu_2(\mu\text{-}O_4C_2)Cl_2$(Mebdmpza)$_2$] (2)

The crystal structures of the title compounds, [$CuCl_2$(Mebdmpza)] (**1**) and [$Cu_2(\mu\text{-}O_4C_2)Cl_2$(Mebdmpza)$_2$] (**2**), reveal the presence of the pyrazole-based ligand Mebdmpza, which results from the esterification of the precursor ligand Hbdmpza with the solvent methanol during the coordination process (Scheme 1). The involvement of copper(II) ions is strongly suggested, because in their absence no esterification is noticed [IR: ν(C=O) = 1760 for Mebdmpza, 1740 cm^{-1} for Hbdmpza]. Copper-catalyzed esterifications of organic acids with a variety of alcohols have been reported, the copper(II) species acting as a Lewis acid catalyst.[7] The dissolution of orange [$CuCl_2$(Mebdmpza)] (**1**) in water results in a blue solution and rapidly produces a blue precipitate. IR spectroscopic and powder XRD data provide evidence that this blue precipitate is actually [Cu(bdmpza)$_2$]·$2H_2O$. Even the water-free complex [Cu(bdmpza)$_2$] can be obtained after drying the isolated solid.[8] This solvent-induced change reveals a reversibility of the Mebdmpza/bdmpza(Hbdmpza) ligand transformation at very mild conditions. Preliminary experiments with other metal chlorides show that this reversible reaction occurs also in the presence of Zn^{2+} and Co^{2+} but not Fe^{2+} chlorides.



Scheme 1. Lewis acid ($CuCl_2$)-catalyzed esterification of Hbdmpza with methanol, producing the new ligand Mebdmpza. The reversed ligand transformation is taking place in water.

[$CuCl_2$(Mebdmpza)] (**1**) crystallizes in the monoclinic space group $P2_1/c$. The detailed structure solution and refinement data are summarized in Table 2. A schematic representation of **1** is depicted in Figure 1, and selected bond lengths and angles are given in Table 1. Compound **1** is constituted of a tetracoordinate copper(II) ion exhibiting a distorted tetrahedral environment, with a τ_4 value of 0.74.[9] The metal center is coordinated by two nitrogen atoms from one Mebdmpza molecule [Cu–N 1.976(2), 1.998(2) Å]. Contrary to the parent tridentate Hbdmpza ligand, Mebdmpza acts as a bidentate ligand as a result of the esterification of the carboxylic acid pendant group. The coordination sphere of the copper(II) ion is completed by two chloride anions [Cu–Cl 2.190(1), 2.240(1) Å] (Figure 1). Similar CuN_2Cl_2 chromophores have been reported for related complexes with the bidentate *N*,*N* ligands 1,3-bis(3,5-dimethylpyrazol-1-yl)propane (bdpp) and bis(2-benzimidazolyl)propane (tbz).[10,11] These two complexes and **1** exhibit an orange color, which is rarely encountered in Cu^{II} species. The electronic spectrum of complex **1** exhibits two electronic d–d bands at 1060 and 910 nm, which are in agreement with the tetrahedrally based coordination geometry of **1** [12] as well as with the spectra of related $CuCl_2N_2$ chromophore complexes.[10,11] In the visible region of the electronic spectrum of **1**, a strong charge-transfer (CT) band at 21500 cm^{-1} is noticed. The presence of a strong CT signal in the visible region and the shift of the d–d band in the near-infrared (NIR) results in this relatively unusual orange color of Cu^{II} species **1**. A comparison of the spectrum with the light-green Cu^{II} complex **2** reveals clear differences in the Vis/NIR region. First, a d–d band is noticed at 12300 cm^{-1}, which is characteristic for square-pyramidal

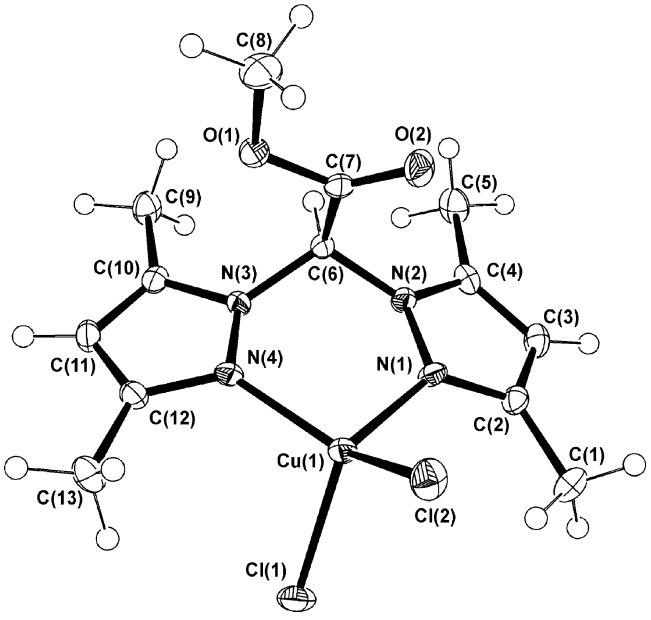


Figure 1. The distorted tetrahedral coordination environment of the central copper atom in the mononuclear complex [$CuCl_2$(Mebdmpza)] (**1**).

Table 1. Selected bond lengths [Å] and angles [°].

1			
Cu–N(3)	1.9756(18)	Cu–N(1)	1.9982(17)
Cu–Cl(2)	2.2416(6)	Cu–Cl(3)	2.1951(6)
O(2)–C(1)	1.197(3)	O(1)–C(1)	1.326(3)
O(1)–C(13)	1.461(3)		
N(3)–Cu–N(1)	94.19(7)	N(3)–Cu–Cl(3)	136.24(5)
N(1)–Cu–Cl(3)	103.67(5)	Cl(3)–Cu–Cl(2)	104.50(2)
N(3)–Cu–Cl(2)	100.17(5)	Cl(3)–Cu–Cl(2)	104.50(2)
N(1)–Cu–Cl(2)	120.00(5)		
2			
Cu(1)–N(1)	1.9996(16)	Cu(1)–N(4)	2.0106(16)
Cu(1)–O(3)	2.0112(15)	Cu(1)–O(4)	2.0051(15)
Cu(1)–Cl(2)	2.4284(7)	O(1)–C(2)	1.186(3)
O(2)–C(2)	1.319(3)	O(3)–C(1)	1.248(2)
O(4)–C(1)	1.251(2)	O(2)–C(14)	1.449(3)
N(1)–Cu–O(3)	88.71(6)	N(1)–Cu–O(4)	157.85(7)
N(1)–Cu–N(4)	90.50(7)	O(4)–Cu–O(3)	82.37(6)
O(4)–Cu–N(4)	89.66(6)	N(1)–Cu–Cl(2)	101.85(5)
N(4)–Cu–Cl(2)	100.97(5)	N(4)–Cu–O(3)	156.25(7)
O(4)–Cu–Cl(2)	99.85(6)	O(3)–Cu–Cl(2)	102.42(6)

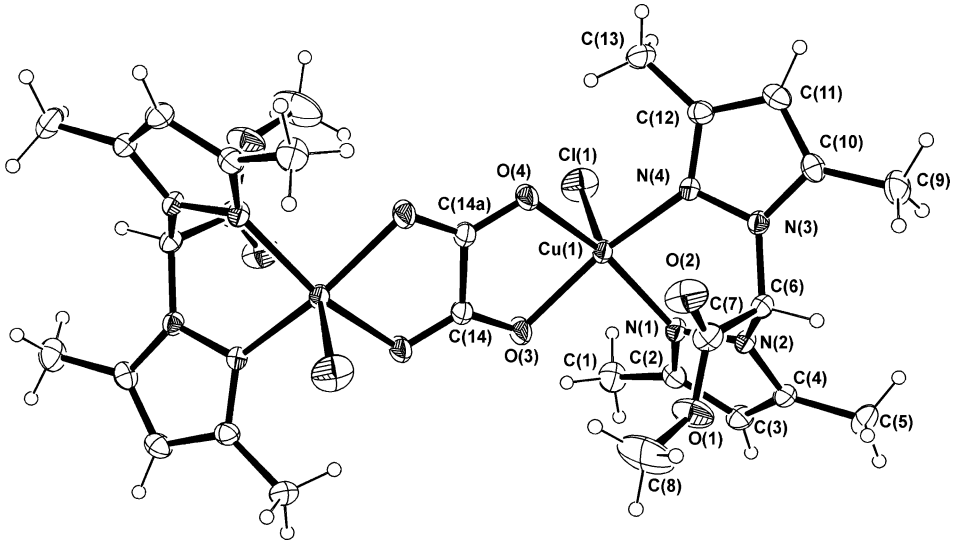


Figure 2. The dinuclear complex $[Cu_2(\mu\text{-}O_4C_2)Cl_2(Mebdmpza)_2]$ (**2**) with a bridging oxalato ligand and terminal Mebdmpza ligands. The ester oxygen atom O(1) is considered as not coordinated [Cu(1)···O(1) 3.641(2) Å].

chromophores. The CT band centered at 21500 cm^{-1} is also present for **2**, albeit much weaker than the one observed for **1**.

$[Cu_2(\mu\text{-}O_4C_2)Cl_2(Mebdmpza)_2]$ (**2**) crystallizes in the monoclinic space group $P2_1/n$. The important bond parameters and crystallographic data for the structural analysis are listed in Tables 1 and 2, respectively. A schematic representation of **2** is depicted in Figure 2. Compound **2** is composed of two crystallographically equivalent copper(II) centers bridged by an oxalate dianion. The geometry around the Cu atom is almost perfectly square-pyramidal (τ_5 = 0.03)[13] with an N_2O_2Cl donor set. The basal plane is formed by two nitrogen atoms from a terminal bidentate Mebdmpza ligand [Cu(1)–N(1) 2.000(2), Cu(1)–N(4) 2.011(2) Å] and two oxygen atoms belonging to one bridging tetradentate oxalato ligand [Cu(1)–O(3) 2.011(2), Cu(1)–O(4) 2.005(2) Å]. Actually, this bridging O_4 ligand lies on a center of symmetry (Figure 2). The apical position is filled by a chloride ion at a typically longer distance [Cu(1)–Cl(1) 2.428(1) Å]. A number of related oxalato-bridged dinuclear copper(II) complexes with CuO_2N_2Cl chromophores are known;[14,15] however, only a few of them exhibit chelating *N,N*-donor ligand rings separated by only one carbon atom,[14] resulting in important steric effects. No hydrogen-bonding interactions are observed in the crystal packings of **1** and **2**.

IR Spectroscopy

The strong IR band at 1760 cm^{-1} found in the spectra of **1** and **2** is assigned to the C=O stretching vibration of the ester group. This absorption band is shifted from 1742 cm^{-1} in the IR spectrum of complex $[Cu_4Cl_8(Hbdmpza)_2]$, which contains coordinated Hbdmpza ligands.[5] For the starting free carboxylic acid ligand Hbdmpza, this vibration is observed at even lower energy, i.e. at 1733 cm^{-1}. The ionized bdmpza ligand coordinated to copper ions gives a $\nu_{as}(CO_2)$ signal in the lower energy region, between 1630 and 1650 cm^{-1}.[8] A very strong band is detected at 1654 cm^{-1} in the IR spectrum of **2** , but not in that of **1**, thus this band is assigned to the $\nu_{as}(CO_2)$ vibration of the oxalato ligand.

EPR and Magnetic Susceptibility

Interestingly, the EPR spectrum of mononuclear complex **1** exhibits significant changes upon variation of the temperature. At room temperature, it has a very broad, almost isotropic symmetry signal, with a deviation at 320 mT ($g_{av.}$ = 2.16) (Figure 3). Below 200 K, a signal characterized by an axially distorted Cu^{II} is observed ($g_{\|}$ = 2.34; no $A_{\|}$ resolved; $g_{\perp}$ = 2.11). Apparently, the tetrahedrally based Cu^{II} relaxes too fast at room temperature, as known, for example, for the related tetrahedral complex $[Cu(bdpp)Cl_2]$.[10]

The green dinuclear oxalato-bridged compound **2** is strongly antiferromagnetic with $2J$ = –342 cm^{-1}. Its EPR spectrum shows only a broad line ($g_{av.}$ = 2.12) which is ascribed to mononuclear impurities, as it does not disappear to very low temperatures. No signal for triplet Cu^{II} is observed at any temperature, which suggests a very large zero-field splitting. Therefore, magnetic susceptibility data were recorded.

The magnetic behavior of **2** is shown in Figure 4 as a plot of $\chi_M T$ vs. T. At room temperature, the signal is below the value expected for two isolated copper(II) ions, namely 0.8 $cm^3 mol^{-1} K$, indicating a negative $2J$ value. By lowering the temperature, the $\chi_M T$ value rapidly decreases, and below 50 K the signal vanishes, suggesting an antiferromagnetic S = 0 ground state (Figure 4). To estimate the magnitude of the antiferromagnetic coupling, the magnetic susceptibility data were fitted to the Bleaney–Bowers equation [Equation (1)] for two interacting copper(II) ions with the Hamilto-

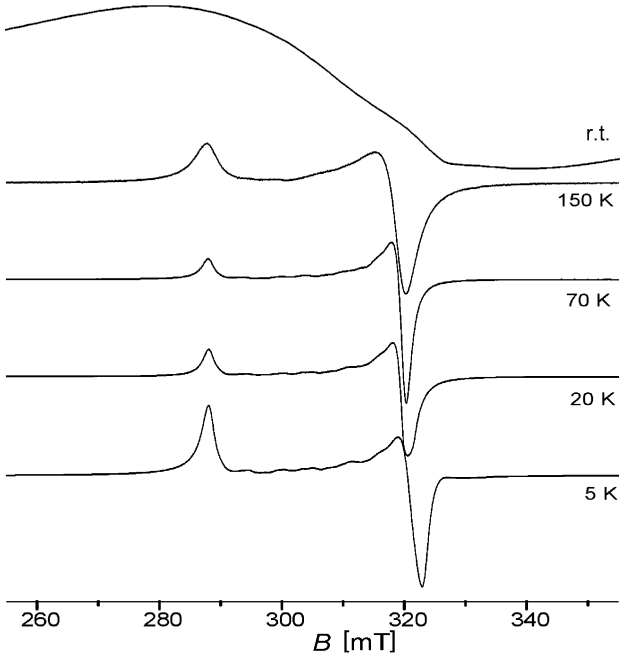


Figure 3. Temperature dependence of the EPR data for the orange compound **1** in the solid state.

nian in the form $H = -2J\, S_1 \cdot S_2$.[16] The least-squares fitting of the data to Equation (1) leads to $2J = -342(1)$ cm^{-1}, $g = 2.046(3)$, and $R = 4.85 \times 10^{-6}$ where $R = \Sigma_i(\chi_{calcd.} - \chi_{obs})^2/\Sigma_i(\chi_{obs})^2$, with a negligible residual paramagnetic contribution (ρ) of 3.4×10^{-7} Equation (1). The theoretical curve derived with the above parameters is shown as a solid line.

$$\chi_M = (1-\rho)\frac{2N_A g^2 \mu_B{}^2}{k_B T(3+e^{-2J/k_B T})} + \rho\frac{N_A g^2 \mu_B{}^2}{2k_B T} \quad (1)$$

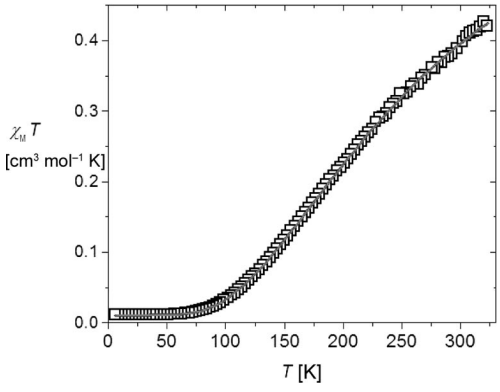


Figure 4. Experimental (□) and fitted (solid line) $\chi_M T$ vs. T curves for dinuclear complex **2**. Parameters are: $2J = -342(1)$ cm^{-1}, $g = 2.046(3)$.

The magnetic susceptibility data clearly reflect strong antiferromagnetic interactions; however, the EPR data appear not to support these magnetic studies; we were unable to check the $S = 0$ ground state by low-temperature NMR spectroscopy because of the insolubility of compound **2**. Similar EPR and susceptibility data were obtained for structurally related dinuclear oxalato complexes.[14] The absence of $S = 1$ signals in the EPR spectrum in these cases may be due to a large zero-field splitting parameter, D. This feature is most likely related to the fact that the copper(II) ion is out of the basal plane [formed by the atoms N(1), N(4), O(3), O(4)] by a distance of 0.392(1) Å towards the apical Cl(1) atom. In the related square-pyramidal $[Cu_4Cl_8(Hbdmpza)_2]$ ($CuCl_2N_2Cl$ coordination environment)[5] and $[Cu_2(\mu\text{-}ox)(H_2O)_2(tmen)_2]^{2+}$ (CuO_2N_2O coordination environment)[17] species, this (out-of-plane) distance amounts to 0.392(1) and 0.147(1) Å, respectively. From these three examples, it thus appears that the apical Cl atom attracts the Cu atom away from the basal plane more efficiently than the O atom. Consequently, the purely axial position of the chlorido ligand is lessened, resulting in an equalization of the x, y, and z coordination axes.

Conclusions

Two new Cu complexes, namely $[CuCl_2(Mebdmpza)]$ (**1**) and $[Cu_2(\mu\text{-}O_4C_2)Cl_2(Mebdmpza)_2]$ (**2**), have been synthesized in situ starting from Cu^{II} chloride and the precursor ligand Hbdmpza. Their crystal structures reveal that the original ligand Hbdmpza has been esterified to the ligand Mebdmpza in the presence of copper(II) (Lewis acid catalysis) while reacting with the crystallization solvent methanol. A reversible ligand transformation from Mebdmpza in $[CuCl_2(Mebdmpza)]$ (**1**) to bdmpza in $[Cu(bdmpza)_2]\cdot 2H_2O$ and/or $[Cu(bdmpza)_2]$ takes place when **1** is dissolved in water. The tetrahedral coordination compound **1** exhibits temperature-dependent EPR data, with a broad pseudo-isotropic symmetry signal at room temperature and axial elongated symmetry signals below 200 K. Dinuclear complex **2** is formed by two crystallographically related square-pyramidal copper centers bridged by an oxalate dianion. Complex **2** shows strong antiferromagnetism, and no $S = 1$ signals are observed in its EPR spectra, which is explained by a very large zero-field splitting. The relative ease with which the nature of the ligand changes under very ordinary conditions (methanol/water, room temperature, pressure) resembles real biological processes, where, at first sight, a small influence of the metal ions plays a crucial role in the ordinary biochemical processes.

Experimental Section

Physical Measurements

The magnetic susceptibility data of powdered polycrystalline samples of the compounds were measured with a Quantum Design SQUID magnetometer. The molar magnetic susceptibility, χ_M, was investigated in the temperature interval between 325 and 6 K. The data were corrected for the experimentally determined contribution of the sample holder. Corrections for the diamagnetic response of the compounds, due to closed atomic shells as estimated from the Pascal constants, were applied.[16] Elemental analysis was performed with a Perkin–Elmer 2400 CHN Elemental Analyzer. Infrared spectra were recorded with a Perkin–Elmer Spectrum 100 FT-IR spectrometer, equipped with a Specac Golden Gate Diamond

ATR as a solid sample support. The solution IR spectra were obtained by using a cell with CaF_2 windows separated by a teflon spacer. Electronic spectra were recorded as nujol mulls with a Perkin–Elmer Lambda 19 UV/Vis/NIR spectrometer. X-band powder EPR spectra were obtained at various temperatures with a Bruker-EMX*plus* electron spin resonance spectrometer [Field calibrated with diphenylpicrylhydrazyl (DPPH) (g = 2.0036)].

Single-crystal X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). A Cryostream Cooler (Oxford Cryosystems) was used for cooling the sample of **1**. The data were processed by using DENZO.[18] The structures were solved by direct methods implemented in SHELXS-97[19] and refined by a full-matrix least-squares procedure based on F^2 with SHELXL-98.[20] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included in the model at geometrically calculated positions and refined by using a riding model. Powder XRD data were obtained with a PANalytical X′Pert PRO MPD diffractometer with Cu-K_α radiation. Selected bond lengths and angles are presented in Table 1. Details of the crystal data, data collection, and refinement parameters are listed in Table 2. The figures of the structures were drawn with ORTEP.[21]

Table 2. Summary of relevant crystal data and data collection parameters.

Formula	$C_{13}H_{18}Cl_2CuN_4O_2$ (**1**)	$C_{28}H_{36}Cl_2Cu_2N_8O_8$ (**2**)
Formula weight	396.8	810.6
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	8.4500(1)	13.1427(2)
b [Å]	15.9645(3)	9.2826(1)
c [Å]	12.6434(2)	15.0527(3)
β [°]	103.2093(7)	107.1653(6)
V [Å^3]	1660.47(5)	1754.61(5)
Z	4	2
D_x [g cm^{-3}]	1.587	1.534
μ [mm^{-1}]	1.648	1.422
T [K]	150	293
Crystal color	orange	light-green
Crystal shape	block	block
Crystal size [mm]	0.15 × 0.10 × 0.05	0.20 × 0.15 × 0.08
θ max [°]	25.03	27.49
R_{int}	0.0157	0.0153
Refined parameters	216	190
Total data	5511	7216
Independent data	2913	3980
Observed data [$F^2 > 2\sigma(F^2)$]	2604	3430
R[a] (observed)	0.0252	0.0315
wR_2[b] (all data)	0.0639	0.0829
$\Delta\rho_{min,max}$ [e Å^{-3}]	–0.364, 0.362	–0.447, 0.504

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

CCDC-676349 and -676350 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis: The ligand Hbdmpza was prepared as first described by Burzlaff et al.[22] The other chemicals were readily available from commercial sources and were used as received without further purification. For the synthesis of the ligand Mebdmpza, the in situ methanolic esterification of Hbdmpza was applied (see below), though another procedure with the application of sulfuric acid was described recently.[23]

[$CuCl_2$(Mebdmpza)] (1): Acetonitrile (5.0 mL) and methanol (2.0 mL) were added to a solid mixture of $CuCl_2{\cdot}2H_2O$ (68 mg, 0.40 mmol) and Hbdmpza (60 mg, 0.24 mmol). The flask containing the reaction mixture was closed. After one day, a small amount of precipitate appeared, which was filtered off. The filtrate was left in air for 15 min, and the flask was then closed. This step seems to be necessary for an efficient subsequent precipitation of compound **1**, possibly because of an evaporation (cooling) of the solvent and/or a short contact with oxygen and/or moisture. The orange crystals of **1** produced after 2 d were isolated by filtration and washed with acetonitrile. Yield: 20%. The esterification reaction was followed by an IR spectroscopic investigation of the solution. The absorption bands at 1750 cm^{-1} corresponding to ν(C=O) of Hbdmpza and at 1650 cm^{-1} ascribed to $\nu_{as}(CO_2)$ of bdmpza are present in the spectrum of the green solution obtained almost immediately after mixing the reactants with the solvent. A shoulder (≈ 1765 cm^{-1}) to the 1750 cm^{-1} band, which is not found for a solution of the pure Hbdmpza ligand, is additionally noticed. Within a few hours, the original 1750 cm^{-1} band is completely replaced by a band at 1765 cm^{-1}, characterizing the ν(C=O) vibration of the esterified Mebdmpza ligand, while the band at 1650 cm^{-1} remains in the spectrum. These characteristic bands for Mebdmpza and bdmpza are observed in the spectrum of the solution also after the precipitation of **1**. $C_{13}H_{18}Cl_2CuN_4O_2$ (396.8): calcd. C 39.4, H 4.57, N 14.1; found C 39.6, H 4.66, N 14.1. IR: $\tilde{\nu}$ = 1760 (s) ν(C=O), 1560 (s) ν(C–C, C–N), 1459 (s), 1440, 1424, 1389 (s), 1316 (s) cm^{-1}. UV/Vis/NIR: $\tilde{\nu}$ (at λ_{max}) = 43500, 33300, 27000 (sh), 21500, 10600, 9100 cm^{-1}. EPR (70 K): g_{12} = 2.11, g_3 = 2.34.

[$Cu_2(\mu\text{-}O_4C_2)Cl_2$(Mebdmpza)$_2$] (2): Methanol (5.0 mL) was added to a solid mixture of $CuCl_2{\cdot}2H_2O$ (68 mg, 0.40 mmol), Hbdmpza (60 mg, 0.24 mmol), and $H_2C_2O_4{\cdot}2H_2O$ (15.0 mg, 0.12 mmol). The flask containing the reaction mixture was subsequently closed. After 2 d, light-green crystals of **2** grew from the solution, which were filtered off and washed with methanol. Yield: 30%. $C_{28}H_{36}Cl_2Cu_2N_8O_8$ (810.6): calcd. C 41.5, H 4.48, N 13.8; found C 41.1, H 4.70, N 13.2. IR: $\tilde{\nu}$ = 1759 (s) ν(C=O), 1654 (s) $\nu_{as}(CO_2)$, 1566 ν(C–C, C–N), 1467, 1420, 1393 $\nu_s(CO_2)$, 1353, 1317 (s) cm^{-1}. UV/Vis/NIR: $\tilde{\nu}$ (at λ_{max}) = 41700, 29400 (sh), 23800 (sh), 12300 cm^{-1}. EPR (5–300 K): $g_{av.}$ = 2.12, (mononuclear impurity).

Single crystals of compounds **1** and **2**, suitable for X-ray analysis, were obtained following the experimental procedures described above, but with lower concentrations of the reactants. Compounds **1** and **2** are stable in air.

[Cu(bdmpza)$_2$]·2H$_2$O and [Cu(bdmpza)$_2$]: These two compounds can be obtained by applying a procedure described earlier,[8] namely from a copper(II) salt and Hbdmpza in aqueous or acetonitrile solution, respectively. The same two compounds were now also isolated by the following procedure, from [$CuCl_2$(Mebdmpza)] (**1**) without an addition of Hbdmpza or bdmpza. Water (2 mL) was added to [$CuCl_2$(Mebdmpza)] (**1**) (56 mg, 0.10 mmol). A blue precipitate rapidly formed in the reaction solution. Depending on the drying time, [Cu(bdmpza)$_2$]·2H$_2$O or [Cu(bdmpza)$_2$] (10 mg, 0.10 mmol) could be isolated. This was confirmed by IR spectroscopic investigations and X-ray powder diffraction data analysis.[24]

Supporting Information (see footnote on the first page of this article): Powder diffraction data.

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