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Counterion and Solvent Effects on the Primary Coordination Sphere of Copper(II) Bis(3,5-dimethylpyrazol-1-yl)acetic Acid Coordination Compounds

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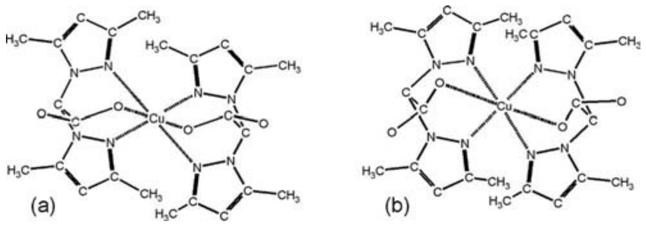
Four copper(II) coordination compounds with the neutral ligand bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza, $C_{12}H_{16}N_4O_2$) and its anionic form (bdmpza$^-$), namely [Cu(Hbdmpza)$_2$](HSO$_4$)$_2$ (**1**), [Cu(Hbdmpza)$_2$]Cl$_2$ (**2**), [Cu(bdmpza)$_2$](CH$_3$COOH)(H$_2$O) (**3**), and [Cu(bdmpza)$_2$]-[Cu$_2$(O$_2$CCH$_3$)$_4$] (**4**) have been synthesized starting from different metal salts. All the compounds have been fully characterized by physical and analytical methods. In addition, a single-crystal XRD analysis revealed the 3D structure of **1**, which exhibits tridentate, vicinal *N*,*N*,*O*-coordination of two symmetry-related Hbdmpza ligands in an elongated octahedral arrangement with four equatorial nitrogen atoms and two axial oxygen atoms. The neutral carboxylic moiety acts as a hydrogen-bond donor to a HSO_4^- counterion. The two hydrogensulfates form a unique hydrogen-bonded pair $(HSO_4^-)_2$ with very short O···O distances (2.59 Å) bridged between adjacent [Cu(HL)$_2$]$^{2+}$ coordination units. Also a short O···O contact (2.54 Å) is present between the C–OH and an O of a hydrogensulfate. A characteristic IR C=O vibration is observed at 1700 cm^{-1} for **1** and **2**, whereas the $\nu_{as}(O_2C)$ vibration is present at 1650 cm^{-1} for **3** and **4**. These IR data strongly suggest the presence of Hbdmpza ligands in **1** and **2** and the deprotonated form bdmpza$^-$ in **3** and **4**. A mononuclear coordination unit [CuL$_2$], as proven for **1** by X-ray diffraction, is also proposed for the other compounds **2**–**4**. In compound **4**, an additional dinuclear [Cu$_2$(O$_2$CCH$_3$)$_4$] neutral coordination unit is present, as deduced from the vibration bands $\nu_{as}(O_2C)$ at 1600 cm^{-1} and $\nu_s(O_2C)$ at 1420 cm^{-1}, which are typical of a carboxylate function, and from the two-species analysis of the $\chi_M T(T)$ curve of the magnetic susceptibility data ($2J = -322$ cm^{-1}). Also, the EPR spectra recorded at different temperatures agree with this structure.

Introduction

The chemistry of polypyrazolyl ligands is an extremely broad and still evolving area of research, largely focused on the design of model compounds that mimic the active site of metalloenzymes.[1–4]

The coordination sphere of a metal center may be altered significantly through the involvement of different solvent molecules or counterions, even if noncoordinated (crystal packing). Water clearly is the ideal solvent in bioinorganic chemistry as it is the solvent surrounding metalloproteins.

Taking into account the above considerations, a polypyrazolyl derivative, namely bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza), has been used to prepare copper(II) compounds under aqueous conditions. This scorpionate-type ligand exhibits coordination versatility as it may act as a tridentate (*N*,*N*,*O*) donor or as a bidentate (*N*,*N*) ligand (Scheme 1).[5–11]



Scheme 1. Solvent-induced change of the coordination chromophore from CuN$_2$O$_2$N$_2$ in [Cu(bdmpza)$_2$] obtained in CH$_3$CN to CuN$_4$O$_2$ in [Cu(bdmpza)$_2$](H$_2$O)$_2$ prepared in water.[10]

Following on from our earlier studies with this ligand, herein we describe four new coordination compounds bearing the mononuclear copper(II) building block [CuL$_2$] with two tridentate centrosymmetric *N*,*N*,*O* ligands (Hbdmpza/

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bdmpza$^-$). Despite the obvious similarities, several differences are found between the respective coordination spheres that clearly originate from the presence of noncoordinated moieties.

Results and Discussion

Single-crystal X-ray studies revealed that the molecular structure of **1** is composed of the complex cation $[Cu(Hbdmpza)_2]^{2+}$ and two HSO_4^- anions. Two symmetry-related neutral Hbdmpza ligands are coordinated in a tridentate, vicinal *N*,*N*,*O* fashion generating an octahedral-based geometry. The square plane of the octahedron contains four pyrazole nitrogen atoms with two carboxylic oxygen atoms occupying the elongated Jahn–Teller axis (Figure 1). To the best of our knowledge, such a coordination mode for the protonated ligand Hbdmpza represents only the second example of a (pyrazolecarboxylic *N*,*N*,*O* scorpionate)-based complex that exhibits this ligand arrangement around the metal center, the first case being illustrated by the compound $[Cu_2Cl_4(Hbdmpza)_2]$.[11] The Cu–N12 and Cu–N22 coordination distances are 2.036(2) and 1.987(2) Å, respectively, and the Cu–O20 bond length is 2.540(2) Å. Selected bond lengths and angles are listed in Table 1. All the parameters are within the expected ranges for elongated octahedral copper(II) species and are comparable to those found for the related compounds[10] $[Cu(bdmpza)_2]$ (**5**) and $[Cu(bdmpza)_2](H_2O)_2$ (**6**). The complex cations are interconnected by hydrogen bonds between the carboxylic hydrogen atoms and the oxygen atoms of the HSO_4^- anions [O19(H)···O4 2.535(4) Å, 174(5)°; Figure 1]. In addition, the HSO_4^- anions are associated through strong, double "head-to-tail" hydrogen bonds, forming pairs of anions [O6(H)···O3 2.594(4) Å, 172(6)°; Figure 1]. These strong hydrogen-bonding interactions also appear to be involved in the arrangement of molecules in the crystal lattice. The importance of this hydrogen-bonding network is corroborated by the fact that the material is highly hygroscopic and loses its crystallinity when it is removed from the mother liquor, which suggests that another hydrogen-bonding network is formed with molecules of water from the atmosphere.

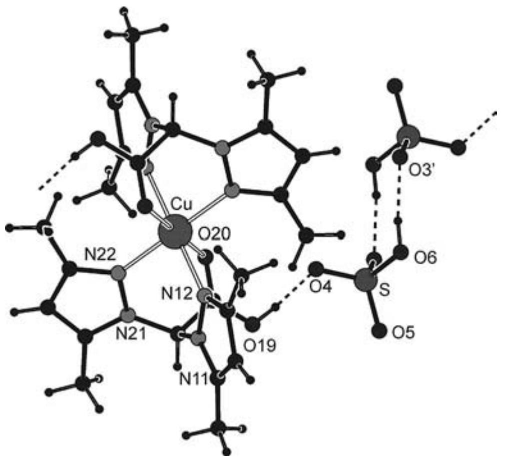


Figure 1. Representation of the single-crystal X-ray structure of $[Cu(Hbdmpza)_2](HSO_4)_2$ (**1**). The hydrogen-bonding network generates a zig-zag arrangement of ions, resulting in a chain of molecules.

Table 1. Selected bond lengths and angles for **1**.

Bond lengths [Å]			
Cu–N12	2.036(2)	Cu–N22	1.987(3)
Cu–O20	2.540(2)		
C18–O20	1.206(4)	C18-O19	1.298(4)
S–O3	1.462(3)	S–O4	1.440(3)
S–O5	1.429(3)	S–O6	1.541(3)
Bond angles [°]			
O20–Cu–N22^i	99.18(9)	O20–Cu–N22	80.82(9)
O20–Cu–N12^i	91.90(9)	O20–Cu–N12	88.10(9)
N12–Cu–N22	85.81(10)	N12–Cu1–N22^i	94.09(10)
O3–S–O4	109.72(19)	O4–S–O5	114.6(2)
O3–S–O5	112.56(19)	O4–S–O6	107.22(18)
O3–S–O6	106.37(18)	O5–S–O6	105.70(18)
O6–H61···O3^{ii}	2.594(4), 172(6)	O19–H191···O4^{iii}	2.535(4), 174(5)

i: 1 – *x*, –*y*, 1 – *z*; ii: –*x*, 1 – *y*, –*z*; iii: *x*, *y* – 1, *z* – 1

The hydrogen-bonding pattern in **1** differs significantly from that observed in the related compound $[Cu(bdmpza)_2](H_2O)_2$ (**6**),[10] in which two parallel water bridges, which are not hydrogen-bonded, connect two neutral $[CuL_2]$ units. In **6**, the $[CuL_2]$···(H)O hydrogen bonds are much weaker, as reflected by the corresponding distances of 2.813(4) and 2.868(4) Å. This difference may explain the significantly longer Cu···O Jahn–Teller axis observed in **1** [2.540(2) Å] compared with **6** [2.293(2) Å]. Note that when the $[CuL_2]$ units are not hydrogen-bonded, as in compound **5**, the Cu···O coordination distance is even shorter [1.983(2) Å], such that the Jahn–Teller axis N···Cu···N involves two nitrogen atoms instead of two oxygen atoms.

Spectroscopy and Magnetism

Although the $[Cu(HL)_2]$ (compound **1**) and $[CuL_2]$ (compounds **5** and **6**) units exhibit comparable coordination geometries, the presence or absence of the carboxylic hydrogen atom of the tridentate *N*,*N*,*O* scorpionate ligand (Hbdmpza vs. bdmpza$^-$) appears to be of paramount importance. Furthermore, whether or not coordination of the carboxylic group of the neutral ligand (Hbdmpza) occurs may also be significant. Interestingly, for the only other example of a copper(II) compound with neutral Hbdmpza ligands, that is, $[Cu_2Cl_4(Hbdmpza)_2]$ (**7**),[11] the carboxylic moieties are not coordinated, in contrast to **1**. Thus, the distinct environments provided by the carboxylato/carboxylic groups of the coordinated bdmpza$^-$/Hbdmpza are reflected by the different hydrogen-bonding networks as well as by the distinct Cu···O coordination bond lengths. The variations in Cu···O distances observed in compounds **1**, **5**, **6**, and **7** may justify the redshift of the electronic d–d band (Figure 2). The differences are likely related to different lengths of the Jahn–Teller axis. Indeed, the increasing absorbance values, namely 570 nm for **1**, 655 nm for **6** and 720 nm for **5** correlate to the corresponding Cu···O bond lengths, the longest one being observed for **1** and the shortest for **5**. The diffuse reflectance ligand-field spectra for the related [CuL$_2$] compounds with the ligands Hbdmpza or bdmpza$^-$ are depicted in Figure 2. The line crossing the absorption peaks suggests a relationship between the positions of the d–d bands. Thus, the Cu···O coordination distances for compounds **2**–**4**, the molecular structures of which could not be determined, may be estimated by comparison of their ligand-field spectra with those of compounds **1**, **5**, and **6** (Figure 2). The IR spectra of the [Cu(H)bdmpza$_2$] compounds **1**–**7** (Figure 3) show a band at 1560 cm^{-1} typical of the pyrazole ring. The compounds may be compared in the 1550–1750 cm^{-1} range through the observation of carboxylate and/or carboxylic acid vibration bands. For compounds **5** and **6**, which were reported earlier,[10] the $\nu_{as}(O_2C)$ vibration is observed as one signal at 1645 cm^{-1} for **5** and as two signals at 1669 and 1634 cm^{-1} for **6**. Comparable vibration bands are also found for compounds **3** and **4**, which suggests the presence of carboxylato bdmpza$^-$ ligands in a neutral [CuL$_2$] core. Hence, both the IR and UV/Vis data for **3** and **4** (see Figures 2 and 3) characterize a $CuN_2O_2N_2$ chromophore, like that of **5**, in which no hydrogen bonds occur. When the ligand is neutral, that is, the ligand Hbdmpza in [CuHL$_2$]Cl$_2$ (**2**), both the $\nu_{as}(O_2C)$ and the d–d signals are found at different positions compared with **1** and **3**–**5**. In fact, the ν(C=O) values for compound **2** (1697, 1665 cm^{-1}) are in the same region as those of compound **1** (1702 cm^{-1}), which suggests the occurrence of strong hydrogen-bonding interactions between the [Cu(Hbdmpza)$_2$]$^{2+}$ cations and Cl$^-$ anions associated with an elongation of the Cu···O$_{\text{axial}}$ distance. This carboxylic group in **1** (Cu···O20 = C–O19–H···O4) is coordinated by the oxygen atom O20 [C–O 1.206(4) Å], whereas the oxygen atom O19 [C–O 1.298(4) Å] acts as a hydrogen donor group. Therefore the stretching of the C=O20 bond requires less energy (1702 cm^{-1}) than the ν(C=O) vibration of the Hbdmpza ligand in the free form (1746 cm^{-1}) or in [Cu$_2$Cl$_4$(Hbdmpza)$_2$] (**7**; 1732 cm^{-1}).[11] However, a higher energy is needed than for the $\nu_{as}(O_2C)$ vibration of compounds **5** and **6**. As a result of a dominant band at 1642 cm^{-1} in the IR spectrum of [Cu(bdmpza)$_2$](CH$_3$COOH)(H$_2$O) (**3**), attributed to the $\nu_{as}(O_2C)$ vibration, the absorption peak observed at 1715 cm^{-1} is assigned to the ν(C=O) vibration of lattice acetic acid molecules. For compound **4**, in addition to the bands at 1648 and 1555 cm^{-1}, strong signals are observed at 1602 and 1414 cm^{-1}, which are ascribed to the $\nu_{as}(O_2C)$ and $\nu_s(O_2C)$ vibrations of the bridging acetato ligands that generate the dinuclear paddle-wheel moiety.[12]

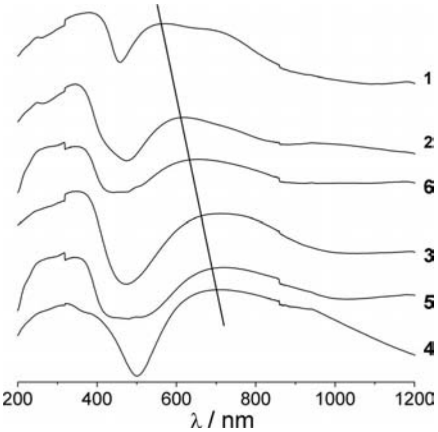


Figure 2. Ligand-field spectra of compounds **1**–**6**, revealing a redshift of the d–d transition bands. The longest Cu···O bond length is found for **1** and the shortest for **5**.

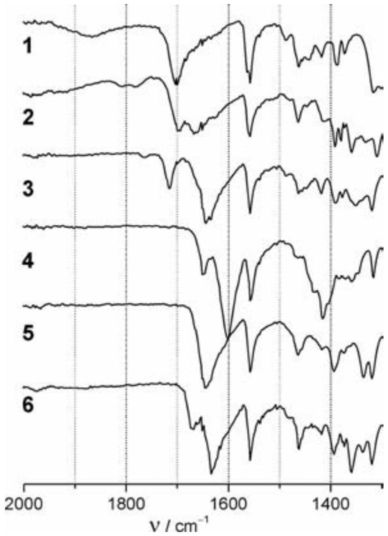


Figure 3. IR spectra of the copper(II) coordination compounds **1**–**6** with the ligands (H)bdmpza.

The progressive redshift of the d–d bands is most clearly observed for compounds **1**–**3**, and **6** (Figure 2), all isolated from aqueous solutions of different acids and/or counterions/molecules. In compounds **4** and **5**, isolated from acetonitrile, no such versatility was observed. In addition, in methanol, Hbdmpza esterifies, yielding Mebdmpza as a ligand.[13]

The supposed presence of non-mononuclear species in **4** prompted us to study the magnetic susceptibility at different temperatures. Indeed, the $\chi_M T$ versus T curve for compound **4** (Figure 4) can be divided into two sections. The high-temperature region shows a steady decrease in the value of $\chi_M T$ from 350 to 80 K. This behavior is in agreement with antiferromagnetic (AFM) interactions between two copper(II) centers and an $S = 0$ ground state below 80 K for the dinuclear units. Below this temperature, the observed constant value of $\chi_M T$ of 0.43 cm^3 mol^{-1} characterizes the paramagnetic (mononuclear) Cu^{II} species. To estimate the magnitude of the AFM coupling, the magnetic susceptibility data were fitted to the Bleaney–Bowers equation [Equation (1)] for two interacting copper(II) ions with the interaction Hamiltonian $H_{\text{int}} = -2JS_1S_2$.[14] The second term accounts for mononuclear units. The fitting procedure

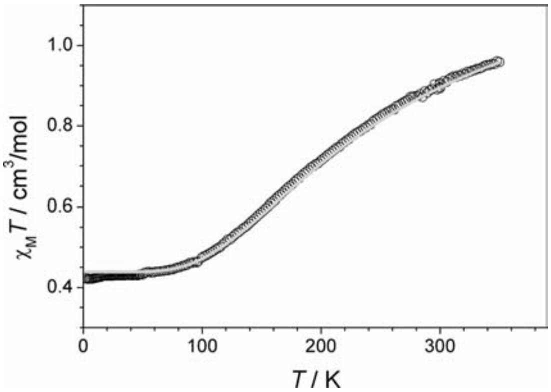


Figure 4. $\chi_M T$ vs. T curve for compound **4** exhibiting two sections, from 350 to 80 K and from 80 to 2 K. The high-temperature region shows a decrease of $\chi_M T$ with temperature, whereas the low-temperature region shows a constant $\chi_M T$ value.

gives $g = 2.16$ and $2J = -322\ \text{cm}^{-1}$. The value of J is in agreement with the presence of $[Cu_2(O_2CCH_3)_4]$ building blocks.[15,16]

$$\chi_M = \frac{2N_A g^2 \mu_B^2}{kT(3 + e^{-2J/kT})} + \frac{N_A g^2 \mu_B^2}{4kT} \tag{1}$$

The EPR spectra of **1**–**3** show the characteristic signals expected for a spin $S = ½$ of an elongated octahedral species, as observed for compounds **5** and **6**.[10] The corresponding $g_\parallel$ values are 2.26 (**1**), 2.29 (**2**), and 2.28 (**3**) and the $g_\perp$ values are 2.06 (**1**), 2.07 (**2**), and 2.09 (**3**). The hyperfine splitting values $A_\parallel$ of 16.4 (**1**), 16.1 (**2**), and 14.7 mT (**3**) are typical of an isolated tetragonal Cu^{II} center. For **4**, a dominant signal is found at 300 mT in the spectra recorded at 295 and 96 K spectra (Figure 5). In addition, in the 295 K spectrum, additional lower-intensity signals are observed at 50–250 and 423 mT. The intensity of these signals decrease with temperature; at 96 K only the signal at 480 mT is observed. In contrast to the 295 K spectrum, in the 96 K spectrum, a well-resolved signal at 300 mT is found with $g_\parallel = 2.30$, $g_\perp = 2.07$ and $A_\parallel = 15.3$ mT. The other signals are assigned to the dinuclear Cu^{II} paddle-wheels and have a D value of 0.3 cm^{-1}, typical of such species.

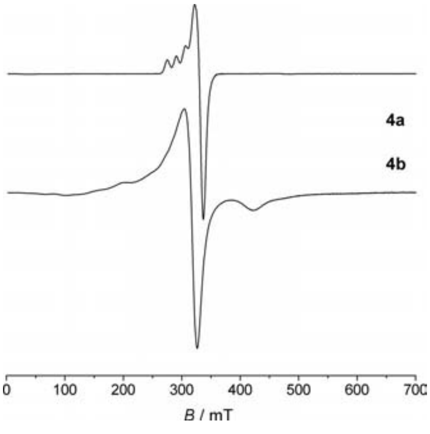
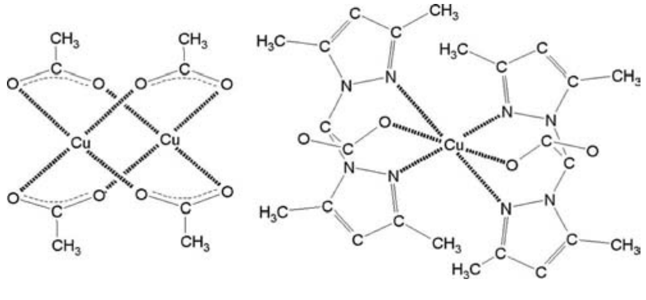


Figure 5. EPR spectra of **4** measured at a) 96 K and b) 295 K.

Two types of co-crystallized coordination species appear to be present in $[Cu(bdmpza)_2][Cu_2(O_2CCH_3)_4]$ (**4**; Scheme 2), and both the susceptibility and EPR data are consistent with the specific properties of these copper(II) species. The two different coordination units are probably connected through weak semi-coordination bonds (e.g., the semi-coordination of the carboxylate oxygen atom belonging to the mononuclear unit to the axial position of the dinuclear paddle-wheel moiety), as seen in other co-crystallized mononuclear–dinuclear species.[16] The variable-temperature susceptibility studies (Figure 4) reveal the occurrence of antiferromagnetic (AFM) interactions between the copper(II) ions of the dinuclear unit and an underlying paramagnetic species, namely the mononuclear entity. The non-observation of any additional interactions, for example, between the di- and mononuclear species in **4**, may be explained by the overwhelmingly strong intradimer AFM above 100 K. Below 100 K, the fully diamagnetic dinuclear species does not point to the presence of additional intermolecular interactions.



Scheme 2. Schematic representation of the co-crystallized compound $[Cu(bdmpza)_2][Cu_2(O_2CCH_3)_4]$ (**4**), including mononuclear $[Cu(bdmpza)_2]$ species together with dinuclear (*paddle-wheel*) moieties.

Conclusions

A series of copper(II) coordination compounds with the neutral ligand bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza, $C_{12}H_{16}N_4O_2$) and its anionic form bdmpza$^-$ have been synthesized. The structures and properties of these four new compounds, namely $[Cu(Hbdmpza)_2](HSO_4)_2$ (**1**), $[Cu(Hbdmpza)_2]Cl_2$ (**2**), $[Cu(bdmpza)_2](CH_3COOH)(H_2O)$ (**3**), and $[Cu(bdmpza)_2][Cu_2(O_2CCH_3)_4]$ (**4**), have been compared with the earlier reported related complexes $[Cu(bdmpza)_2]$ (**5**), $[Cu(bdmpza)_2](H_2O)_2$ (**6**), and $[Cu_2Cl_4(Hbdmpza)_2]$ (**7**). The molecular structures of compounds **1**, **5**, **6**, and **7**, determined by single-crystal X-ray diffraction, are available.

Although several $[ML_2]$ species with the *N*,*N*,*O*-tridentate scorpionate ligand Hbdmpza (and related ligands) have already been described in the literature, the compound $[Cu(Hbdmpza)_2](HSO_4)_2$ (**1**) represents the first example with the neutral form of the ligand. This ligand neutrality most likely arises from the strongly acidic conditions used to synthesize **1** and the presence of lattice HSO_4^- ions. As a result of the fully closed coordination shell of such [ML_2] species, further chemistry often cannot be carried out with this type of compound. However, a change in the *N*,*N*,*O* scorpionate coordination mode at the metal center may be a possible route to complex activation. Hence, the change in the Jahn–Teller axis caused by different counterions/molecules in compounds **1**–**4** in water or acetonitrile may play an important role in this activation process. The modification of the O–C–O coordination (Jahn–Teller) bond length associated with the presence of distinct lattice molecules, which is long in **1** (HSO_4^-), intermediate in **6** (H_2O), and short in **5** (no lattice molecules), is clearly revealed by spectroscopic studies.

Experimental Section

Physical Measurements: CHN analyses were carried out at the Micro Analysis Department of Leiden University. Infrared spectra were recorded with a Perkin–Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate Diamond ATR as sample support. Ligand-field spectra of the solid compounds were recorded in the 300–2000 nm range with a Perkin–Elmer Lambda 900 UV/Vis/NIR spectrometer in the diffuse reflectance mode with MgO as a reference. The magnetic susceptibility data for **4** were obtained with a Quantum Design SQUID MPMS-XL-5 magnetometer equipped with a 5 T magnet. These data were recorded in the temperature range 2–350 K in a magnetic field of H = 1000 Oe and were corrected for the experimentally determined contribution of the sample holder. Corrections for temperature-independent paramagnetism and the diamagnetic response of the compounds due to closed atomic shells, as estimated from Pascal's constants, were applied.[14] X-band powder EPR spectra were obtained at various temperatures with a Bruker ELEXSYS E-500 electron spin resonance spectrometer.

Single-crystal XRD data for **1** were collected with an Enraf–Nonius CAD4 diffractometer. Mo-K_α radiation (λ = 0.71073 Å) was applied with a graphite monochromator. The structure was solved by automated Patterson techniques using DIRDIF/PATTY[17] and refined on F^2 by using full-matrix least-squares techniques with SHELXL-97.[18] The positions of the non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms, except for the hydrogen atoms of the carboxylic groups and the HSO_4^- ions, were placed at calculated positions and were refined riding on the parent atoms. The hydrogen atoms of the carboxylic groups and the HSO_4^- ions were taken from a difference Fourier map and were freely refined. Geometric calculations and molecular graphics were performed with PLATON.[19] Crystal data for **1**: $C_{24}H_{34}CuN_8O_{12}S_2$, M_r = 754.3, triclinic, $P\bar{1}$, a = 8.4739(10), b = 9.4476(14), c = 10.7275(14) Å, α = 71.293(12), β = 77.158(15), γ = 75.423(10)°, V = 777.83(18) Å^3, violet block, T = 293(2) K, Z = 1, D_{calcd} = 1.61 g cm^{-3}, μ(Mo-K_α) = 9.11 cm^{-1}, F(000) = 391, $\theta_{min/max}$ 3.0/26.3, $h/k/l$ –10,10/–11,0/–13,12. Total/observed reflections [$F_o > 4.0\sigma(F_o)$]: 3150/2485, 226 refined parameters, final R_1, wR_2: 0.041, 0.104, min./max. residual density = –0.38/0.43 e Å^{-3}.

CCDC-820416 contains 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: All commercial starting compounds and solvents were of analytical grade quality and used as received. Hbdmpza and the copper(II) coordination compounds [Cu(bdmpza)$_2$] (**5**), [Cu(bdmpza)$_2$](H_2O)$_2$ (**6**), and [Cu_2Cl_4(Hbdmpza)$_2$] (**7**) were prepared following reported procedures.[7,10,11]

[Cu(Hbdmpza)$_2$](HSO_4)$_2$ (1): Hbdmpza (50 mg, 0.20 mmol) was dissolved in aq. H_2SO_4 (10 mL, 24%). $CuSO_4\cdot5H_2O$ (50 mg, 0.20 mmol) was subsequently added to the ligand solution. The closed reaction mixture was left unperturbed at room temperature. After 3 days, violet crystals of **1** were isolated by filtration. The solid product obtained was dried in a desiccator for 3 d. Note that **1** is hygroscopic. Single crystals, suitable for the XRD analysis were isolated; yield 40% (30 mg, 0.040 mmol). $C_{24}H_{34}CuN_8O_{12}S_2$ (754.2): calcd. C 38.2, H 4.54, N 14.9; found C 37.3, H 4.31, N 14.6. IR: $\tilde{\nu}$ = 3400, 2990, 1702, 1560, 1485, 1461, 1440, 1418, 1387, 1373 1315 cm^{-1}. UV/Vis: λ_{max} = 380, 570, 680 (sh) nm. EPR (295 K): $B_\parallel$ = 295.7, $A_\parallel$ = 16.4, $B_\perp$ = 324.1 mT; $g_\parallel$ = 2.26, $g_\perp$ = 2.06.

[Cu(Hbdmpza)$_2$]Cl_2 (2): Hbdmpza (100 mg, 0.40 mmol) was dissolved in aq. HCl (10 mL, 10%). $CuCl_2\cdot2H_2O$ (68 mg, 0.40 mmol) was subsequently added to the ligand solution. The resulting reaction mixture was left unperturbed in a closed flask at room temperature. After 2 d, blue crystals of **2** were isolated by filtration; yield 60% (75 mg, 0.12 mmol). $C_{24}H_{32}Cl_2CuN_8O_4$ (631.0): calcd. C 45.7, H 5.11, N 17.8; found C 45.8, H 4.99, N 17.8. IR: $\tilde{\nu}$ = 2983, 1697, 1665, 1559, 1463, 1391, 1359, 1309 cm^{-1}. UV/Vis: λ_{max} = 345, 618 nm. EPR (295 K): $B_\parallel$ = 291.4, $A_\parallel$ = 16.1, $B_\perp$ = 322.7 mT; $g_\parallel$ = 2.29, $g_\perp$ = 2.07.

[Cu(bdmpza)$_2$](CH_3COOH)(H_2O) (3): Hbdmpza (100 mg, 0.40 mmol) was dissolved to aq. acetic acid (10 mL, 25%). Next, [$Cu_2(CH_3COO)_4(H_2O)_2$] (80 mg, 0.20 mmol) was added and the solution obtained was left unperturbed in a closed flask at room temperature. After 2 d, compound **3** was isolated as a blue solid product by filtration; yield 60% (75 mg, 0.12 mmol). $C_{26}H_{36}CuN_8O_7$ (636.2): calcd. C 49.1, H 5.70, N 17.6; found C 48.9, H 5.39, N 17.5. IR: $\tilde{\nu}$ = 3380, 2920, 1715, 1642, 1558, 1460, 1419, 1390, 1351, 1319, 1249 cm^{-1}. UV/Vis: λ_{max} = 345, 715 nm. EPR (295 K): $B_\parallel$ = 293.3, $A_\parallel$ = 16.1, $B_\perp$ = 319.2 mT; $g_\parallel$ = 2.28, $B_\perp$ = 2.09.

[Cu(bdmpza)$_2$][$Cu_2(O_2CCH_3)_4$] (4): An acetonitrile/acetic acid mixture (10 mL, v/v = 1:1) was added to a mixture of [$Cu_2(CH_3COO)_4(H_2O)_2$] (40 mg, 0.10 mmol) and Hbdmpza (25 mg, 0.10 mmol). The resulting solution was left unperturbed in a closed flask at room temperature. After 4 d, compound **4** was obtained as a green solid, which was removed by filtration; yield 68% (31 mg, 0.034 mmol). $C_{32}H_{42}Cu_3N_8O_{12}$ (921.4): calcd. C 41.7, H 4.59, N 12.2; found C 41.6, H 4.47, N 12.2. IR: $\tilde{\nu}$ = 1648, 1602, 1555, 1414, 1316 cm^{-1}. UV/Vis: λ_{max} = 320, 380 (sh), 710 nm. EPR (295 K): B = 317.7, 422.7 mT. EPR (96 K): $B_\parallel$ = 298.5, $A_\parallel$ = 15.3, $B_\perp$ = 331.3, B = 480 mT; $g_\parallel$ = 2.30, $g_\perp$ = 2.07.

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