Two New Copper (II) Complexes with the Same NNO Donor Schiff Base Ligand: A Monomer and a Dimer

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Z. Naturforsch. **2012**, *67b,* 192 – 196; received December 10, 2011

Two new copper(II) complexes, $[(CuL)_2(\mu_{1,1}\text{-}N_3)_2]\cdot 2H_2O$ (**1**) and $[Cu(HL)(2,2'\text{-bipy})(CH_3COO)]\cdot ClO_4\cdot H_2O$ (**2**), have been synthesized using the tridentate NNO Schiffbase ligand 2-[(2-aminoethylimino)methyl]-6-methoxyphenol (HL). They have been characterized by elemental analysis, IR spectroscopy, thermal analysis, and single-crystal X-ray analysis. The copper environment is distorted square pyramidal in complex **1**: two nitrogen atoms and one oxygen atom from the ligands and two nitrogen atoms from two azido ligands build the coordination polyhedron around the copper atom. The Cu–N_{azide}–Cu angle in complex **1** is 85.6°. This is unusually small in comparison with the same angle in other end-on doubly azido-bridged dimers. Complex **2** is mononuclear with the Cu atom having a slightly distorted octahedral geometry. Magnetic measurements of **1** have been performed in the temperature range from 2 to 300 K. The experimental data indicate an antiferromagnetic exchange interaction between copper(II) ions bridged by the azido ligand. The best-fit parameters for complex **1** are $g = 2.18$ and $J = -1.31$ cm^{-1}.

Key words: Asymmetric Azide Bridge, Copper(II) Complex, Schiff Base, Magnetic Properties

Introduction

Schiff bases have often been used as chelating ligands in the field of coordination chemistry, and their metal complexes have been extensively investigated due to their potential applications in gas storage and catalysis [1 – 13]. It is known that reactions of NNO donor Schiff base ligands with transition metal ions have produced a series of complexes with interesting structures and magnetic properties [14 – 21]. However, $3d$-$4f$ complexes with NNO donor Schiff base ligands are still rare or lacking [22, 23]. For a better insight into the magnetic properties of these $3d$-$4f$ complexes, the synthesis of different compounds seems to be necessary. In this paper, we describe the sythesis of a "half-unit" copper complex (CuL) with an NNO Schiff base ligand by a template procedure. The reaction of CuL with rare earth ions in the presence of ancillary ligands (azido ligand and 2,2′-bipyridine) yielded green solutions from which two unexpected complexes $[(CuL)_2(\mu_{1,1}\text{-}N_3)_2]\cdot 2H_2O$ (**1**) and $[Cu(HL)(2,2'\text{-bipy})(CH_3COO)]\cdot ClO_4\cdot H_2O$ (**2**) were isolated. Herein, we describe the syntheses and crystal structures of these two complexes. The variable-temperature magnetic study of complex **1** is also reported.

Experimental Section

Materials

The precursor complex CuL [HL = 2-[(2-aminoethylimino)methyl]-6-methoxyphenol] was prepared according to an experimental process previously described for similar complexes [23]. Other chemicals were of reagent grade and obtained commercially and used without further purification.

Synthesis of $[(CuL)_2(\mu_{1,1}\text{-}N_3)_2]\cdot 2H_2O$ (1)

0.05 mmol (0.0238 g) $Dy(NO_3)_3\cdot 6H_2O$ were dissolved in 10 mL of methanol, and 10 mL of a methanol solution containing 0.1 mmol (0.0313 g) CuL was added under constant stirring. 1 mmol (0.065 g) sodium azide dissolved in 10 mL of water was then added. The resulting solution was heated for 2 h and filtered. Well-shaped dark-green single crystals suitable for X-ray diffraction analysis were obtained after one week upon slow evaporation of the solution (yield 60 %). – Anal. for $C_{20}H_{30}Cu_2N_{10}O_6$ (633.64): calcd. C 37.91, H 4.77, N 22.11; found C 37.84, H 4.58, N 22.05. – Characteristic IR absorptions (KBr): ν = 3471, 3261, 2045, 1639, 1600, 1449, 1319, 1214, 1120, 1050, 968, 744, 667, 444 cm^{-1}.

Synthesis of $[Cu(HL)(2,2'\text{-bipy})(CH_3COO)]\cdot ClO_4\cdot H_2O$ (2)

0.05 mmol (0.0285 g) $Dy(ClO_4)_3\cdot 6H_2O$ were dissolved in 10 mL of methanol, and 10 mL of a methanol solution containing 0.1 mmol (0.0313 g) CuL was added under constant stirring. 0.1 mmol (0.0156 g) 2,2′-bipyridine dissolved in 10 mL of methanol was then added. The resulting solution was filtered. After a few days of storage of the filtrate at ambient temperature, dark-green single crystals suitable for X-ray diffraction analysis were obtained (yield 72 %). – Anal. for $C_{22}H_{27}ClCuN_4O_9$ (590.48): calcd. C 44.75, H 4.61, N 9.49; found C 44.77, H 4.70, N 9.45. – Characteristic IR absorptions (KBr): ν = 3440, 3325, 3269, 1640, 1599, 1470, 1439, 1320, 1240, 1219, 1079, 1020, 968, 854, 766, 750, 623 cm^{-1}.

Physical measurements

Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer 2400II analyzer. The infrared spectra were recoded on an Avatar-360 spectrometer using KBr pellets in the range 400 – 4000 cm^{-1}. Thermogravimetric analysis was carried out with an EXSTAR6000 TG/DTA6300 SII type analyzer in a nitrogen atmosphere with a temperature increasing rate of 10 °C min^{-1}. Magnetic measurements were performed on a few manually selected single crystals with a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all atoms.

X-Ray crystallography

Single crystals of compounds **1** and **2** were selected and mounted on a Bruker Smart APEX diffractometer with a CCD detector using graphite-monochromatized MoK_α radiation (*lambda* = 0.71073 Å). Lorentz and polarization corrections were applied to the intensity data, and absorption corrections were performed using the program SADABS [24]. The crystal structures were solved by Direct Methods and refined by full matrix least-squares using the SHELXTL program suite [25]. The positions of hydrogen atoms were calculated and included in the final cycles of refinement in a riding model along with the attached carbon atoms. The crystal used for the structure determination of **2** was an inversion twin, the BASF parameter refined to 0.50(2). Crystal data and parameters pertinent to data collection and refinement are given in Table 1.

CCDC 857509 (**1**) and 857510 (**2**) contain the supplementary crystallographic data. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and numbers pertinent to data collection and refinement for complexes **1** and **2**.

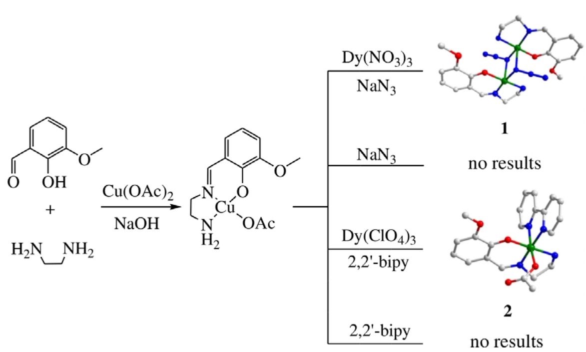
Complex	**1**	**2**
Empirical formula	$C_{20}H_{30}Cu_2N_{10}O_6$	$C_{22}H_{27}ClCuN_4O_9$
Formula weight	633.64	590.48
Crystal system	monoclinic	orthorhombic
Space group	$C2/c$	$P2_12_12_1$
a, Å	19.606(3)	13.162(2)
b, Å	10.104 (1)	13.631(2)
c, Å	13.044 (2)	14.012(2)
β, deg	92.176(2)	90
V, Å^3	2582.2(6)	2514.0(6)
Z	4	4
D_{calc}, (g cm^{-3})	1.63	1.56
μ(MoK_α), mm^{-1}	1.7	1.0
T, K	296(2)	296(2)
Index ranges hkl	$-22 \rightarrow 25$, ± 13, ± 16	± 15, ± 16, ± 16
Refl. measd. / indepd.	10194 / 2962	17013 / 4673
R_{int}	0.0221	0.0421
Ref. parameters	181	336
$R1$ / $wR2$ [$I \geq 2\sigma(I)$]^{a,b}	0.0271 / 0.0729	0.0534 / 0.1442
$R1$ / $wR2$ (all data)^{a,b}	0.0356 / 0.763	0.0356 / 0.1577
Goodness-of-fit^c	1.096	1.072
BASF	–	0.50(2)
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.26 / −0.37	0.70 / −0.48

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; ^{c} GoF $= [\Sigma w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$.

Results and Discussion

Synthesis of the complexes

The synthesis of complexes **1** and **2** was carried out as shown in Scheme 1. The intermediate complex CuL of the 1 : 1 : 1 reaction product of copper acetate monohydrate, 2-hydroxy-3-methoxybenzaldehyde and 1,2-ethylenediamine (Scheme 1) plays a very important role during the synthesis of the title complexes. In order to obtain the intermediate complex, the template reaction method was adopted for CuL. Through the reaction of the intermediate CuL with rare earth cations, we had hoped to obtain 3d-4f complexes. Notably, although the rare earth cations were added to the reactions, the products contained only Cu(II). When only Cu(II) was used under the same conditions, we could not obtain similar results. It may be assumed that on



Scheme 1 (color online). Synthesis of complexes **1** and **2**.

addition of the dysprosium salt, the pH of the system was changed leading to the formation of complexes **1** and **2** [26]. More details on the synthesis procedures can be found in the Experimental Section.

Caution! Although not encountered in our experiments, azido complexes of metal ions are potentially explosive especially in the presence of organic compounds. Only a small amount of the materials should be prepared, and it should be handled with special care.

IR spectra

There are broad bands at 3471 cm^{-1} (**1**) and 3440 cm^{-1} (**2**) observed for the complexes, due to the presence of water molecules. The sharp peaks at 3261 and 3325 cm^{-1} for complexes **1** and **2** are indicative of *nu*(N–H) stretching vibrations. The other characteristic bands are easily located at 1639 cm^{-1} (**1**) and 1640 cm^{-1} (**2**) for *nu*(C=N) vibrations. Complex **1** shows a strong absorption band at 2045 cm^{-1}. This is the characteristic stretching vibration of coordinated azido ligands. The broad band at 1079 cm^{-1} for complex **2** indicates the presence of ClO_4^- anions. The characteristic *nu*(C–H) vibration of 2,2′-bipyridine was detected at 766 cm^{-1}. In comparison with that of free 2,2′-bipyridine (755 cm^{-1}), it has been shifted resulting from the coordination to the metal centers.

Thermal properties

Thermogravimetric analyses (TGA) have shown (Fig. 1) that compound **1** loses 5.61 % of the total weight in the 64 – 128 ℃ temperature range, corresponding to the loss of two solvent water molecules (expected, 5.69 %). The further decomposition of **1** continues through one step, with a loss of 13.21 % of the total weight in the temperature range 222 – 245 ℃, which corresponds to the decomposition of the azido ligands (expected, 13.25 %). The residue remaining after the total pyrolysis of **1** at 1000 ℃ most probably corresponds to CuO and Cu_2O.

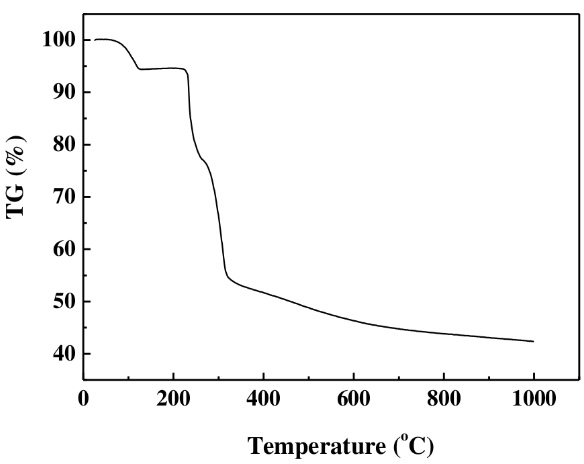


Fig. 1. Thermogravimetric analysis (TGA) for complex **1**.

Description of the molecular structures

The X-ray single-crystal structure analysis has revealed that complex **1** features an end-on doubly azido-bridged dimeric Cu(II) complex located around a crystallographic center of inversion. As illustrated in Fig. 2, it consists of a neutral binuclear molecule and two uncoordinated water molecules. The copper atoms are each placed in a distorted square-pyramidal environment. The basal plane is composed of three nitrogen and one oxygen donor atom. Among them, one nitrogen atom is from the bridging azide anion, and the other two nitrogen atoms and one phenoxo oxygen atom are from the tridentate NNO Schiffbase ligand. The Cu(1)–N(1), Cu(1)–N(2) and Cu(1)–N(3) in-plane distances are 1.947(2), 2.004(2) and 1.991(2) Å, respectively, which are consistent with the corresponding distances of related copper complexes [27 – 29]. The axial position is filled with one nitrogen atom of the symmetry-related azide group (symmetry code; $1-x$, $-y$, $-z$). The corresponding axial bond length (2.609 Å) is significantly longer than the basal distances. The square pyramidal geometry within each subunit is distorted, *i. e.*, the copper(II) ion is displaced from the basal plane towards the apical nitrogen atom by 0.0570 Å. The diagonal basal angles N(1)–Cu(1)–N(3) (168.08°) and N(2)–Cu(1)–O(1) (175.19°) and the basal-apical N(3)–Cu(1)–N(3)A angle (94.362°)

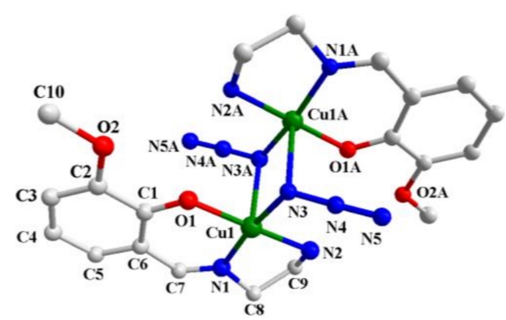


Fig. 2 (color online). Molecular structure of complex **1** in the crystal. The water molecules and all hydrogen atoms were omitted for clarity.

deviate from the ideal values. The Cu···Cu distance through the end-on azido bridges is 3.159 Å, similar to the values reported in the literature [27, 29].

The end-on double-bridge adopts a basal-apical disposition with asymmetric Cu–N distances, *i. e.*, the same nitrogen atom of the azido-bridge resides in the basal plane of one copper but on the apical position of the neighboring copper, with the apical Cu–N distance (2.609 Å) being significantly longer than the basal one (1.991 Å). This inequality in bond lengths makes the azido complex a rare example of an unsymmetric end-on ($\mu_{1,1}$) double-bridged structure [26]. Both azido ions are quasilinear with the N–N–N angles being *ca.* 178° and show unsymmetric N–N bond lengths with the bonds involving the donor atoms being relatively long. The Cu–N_{azide}–Cu angle is found to be *ca.* 85.6°. To our knowledge, this complex is possessing the smallest Cu–N_{azide}–Cu angle among the end-on doubly azido-bridged binuclear complexes.

Complex **2** crystallizes in the non-centrosymmetric space group $P2_12_12_1$ with Z = 4. It consists of one [Cu(HL)(2,2′-bipy)(CH_3COO)] cation, one perchlorate anion and one solvent water molecule. The crystal is an inversion twin, and the Flack parameter refined by the TWIN/BASF commands is 0.50(2). Thus the chiral complex **2** is present as racemate in the crystals. The structure of the complex is shown in Fig. 3, and selected bond lengths and angles are listed in Table 2.

The copper(II) atom is hexa-coordinated, adopting a distorted pseudo-octahedral geometry. The equatorial square plane around each Cu(II) center is formed

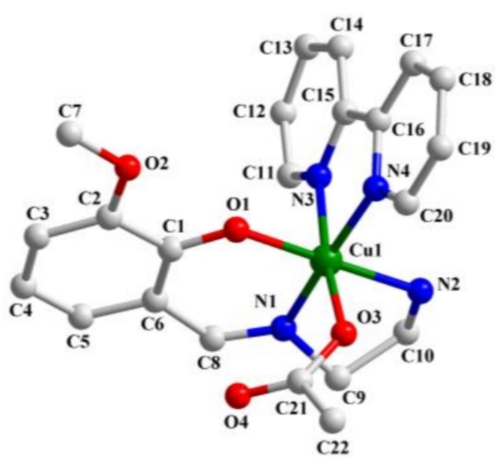


Fig. 3 (color online). Molecular structure of complex **2** in the crystal. All hydrogen atoms were omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (deg) for **1** and **2**.

Compound **1**[a]			
Cu(1)–O(1)	1.911(1)	O(1)–Cu(1)–N(1)	93.21(6)
Cu(1)–N(1)	1.947(2)	O(1)–Cu(1)–N(2)	175.19(6)
Cu(1)–N(2)	2.004(2)	N(1)–Cu(1)–N(2)	84.48(7)
Cu(1)–N(3)	1.991(2)	O(1)–Cu(1)–N(3)A	89.59(6)
Cu(1)–N(3)A	2.609(2)	N(1)–Cu(1)–N(3)A	97.46 (6)
Compound **2**			
Cu(1)–N(1)	1.867(4)	Cu(1)–O(3)	1.901(4)
Cu(1)–N(2)	1.947(4)	Cu(1)–N(4)	1.935(4)
Cu(1)–N(3)	1.957(4)	Cu(1)–O(1)	1.880(3)
O(3)–Cu(1)–N(3)	171.69(17)	N(4)–Cu(1)–N(1)	175.85(19)
N(3)–Cu(1)–N(4)	82.4(2)	N(4)–Cu(1)–N(2)	91.09(17)
N(3)–Cu(1)–N(2)	92.08(17)	Cu(1)–O(3)–C(21)	130.4(4)
N(3)–Cu(1)–N(1)	95.34(19)	N(2)–Cu(1)–O(1)	178.74(19)
N(3)–Cu(1)–O(1)	88.60(16)	O(1)–Cu(1)–N(1)	95.48(17)

[a] Symmetry transformation: A = $1-x, -y, -z$.

by the two nitrogen atoms (N1 and N2) and one oxygen atom (O1) of the tridentate Schiff base ligand, and N4 of one 2,2′-bipy ligand, whereas the axial coordination sites are occupied by the nitrogen atom N3 of a 2,2′-bipy ligand and O3 of the coordinated acetate ion. The octahedron is distorted, with the bond angles N(4)–Cu(1)–N(2) [91.09(17)°o], N(1)–Cu(1)–N(2) [85.52(18)°], N(1)–Cu(1)–O(1) [95.48(17)°], and O(1)–Cu(1)–N(4) [87.94(16)°] close to orthogonality. The Cu atom is displaced from the mean N_3O equatorial plan by 0.0116 Å towards O(3). This leads to the non-orthogonal angles O(3)–Cu(1)–N(4) = 89.57(19)°, O(1)–Cu(1)–O(3) = 93.16(17)°, N(1)–Cu(1)–O(3) = 92.58(19)° and O(3)–Cu(1)–N(2) = 86.03(17)° and results in an O(3)–Cu(1)–N(3) axis deviating with an angle of 171.69(17)°slightly from linearity.

Magnetic properties

The magnetic susceptibility of complex **1** was measured in the range of 2 – 300 K. The curves of χ_M and μ_{eff} *versus* T are shown in Fig. 4. At r. t., the μ_{eff} value of complex **1** is 2.68 μ_B, which is slightly higher than that expected for uncoupled binuclear ions (2.45 μ_B). Upon cooling, the μ_{eff} value of the complex decreases slowly up to *ca.* 25 K, then sharply to 1.85 μ_B upon cooling to 2 K, probably due to antiferromagnetic interactions in the dimer.

The magnetic analysis was carried out by using the theoretical expression of the magnetic susceptibility containing the correction term *theta* for intermolecular interactions, and N_α for the temperature-independent paramagnetism based on the Heisenberg spin operator ($\hat{H} = -2J\hat{S}_{Cu1}\hat{S}_{Cu2}$).

$$\chi_M = \frac{2Ng^2\beta^2}{K(T-\theta)}\left[\frac{1}{3+\exp(-2J/KT)}\right] + N_\alpha,$$
$$N_\alpha = 120\times10^{-6}\ \mathrm{cm^3\ mol^{-1}},$$

where J is the exchange integral between two copper ions in the binuclear moiety. The best-fit parameters are $J = -1.31$ cm^{-1}, $g = 2.18$, *theta* = -0.16 K. The agreement factor $R = \Sigma(\chi_{obsd} - \chi_{calcd})^2/\Sigma\chi_{obsd}{}^2$ is 2.17×10^{-4} is satisfactory as shown in Fig. 4. The negative J value suggest that the interactions between Cu(II) ions is weakly antiferromagnetic.

Acknowledgement

We acknowledge the generous financial support of the Natural Science Foundation of Henan Province (no. 092300410031) and of the Natural Science Foundation of Henan University (no. 2010YBZR007).

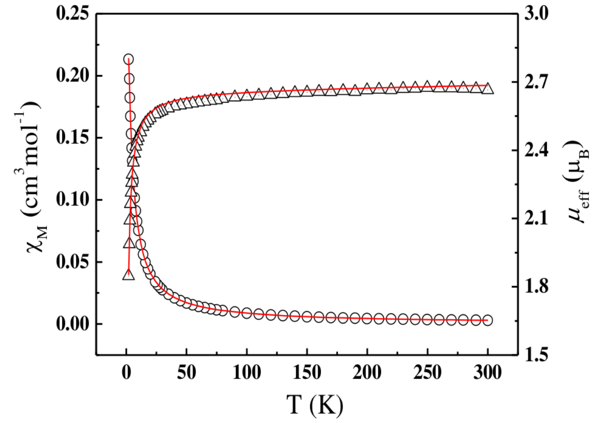


Fig. 4 (color online). χ_M and μ_{eff} *versus* T plots for complex **1**.

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