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A new 3s–3d heterometallic polymer containing *N*-methyliminodiacetic acid: synthesis, structure and characterization

Feng-Xian Gao, Wen Gu, Jing Qian, Yong-Sheng Yang and Shi-Ping Yan*

Department of Chemistry, Nankai University, 300071, Tianjin, People's Republic of China

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A new complex $\{[Na_2(H_2O)_3(\mu\text{-}L)_2Cu]_4\}_\infty$ (L = *N*-methyliminodiacetic acid) has been synthesized and structurally characterized. The complex crystallizes in the monoclinic, space group *C*2/*c*, with the unit cell parameters $a = 16.556(3)$ Å, $b = 8.0622(13)$ Å, $c = 12.671(2)$ Å, $\alpha = 90°$, $\beta = 95.849(2)°$, $\gamma = 90°$. The central metal Cu (II) ion is coordinated with two nitrogen atoms and four oxygen atoms belonging to two ligands. Simultaneously, the sodium is six-coordinated with oxygen atoms coming from the ligand and water molecule; the sodium atoms related are bridged by oxygen atoms, forming a sodium chain. The structure consists of CuL_2 moieties linked by sodium chain via the *exo* oxygen atoms of two ligands, forming a novel three-dimensional structure. Moreover, elemental analysis, IR, UV-vis, ESR spectroscopy and thermal stability were determined. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: copper (II); crystal structure; UV-vis; ESR; thermal stability

INTRODUCTION

In recent years, the use of suitable simple coordination compounds as building blocks for the synthesis of oligomers or polymers has been of considerable interest for designing new magnetic materials and for investigating the structure and the role of the polymetallic active sites in biological systems.[1] Indeed, many materials obtained by these self-assembly synthesis strategies exhibit novel structural topologies or profitable optical and other properties.[1,2–7] Recently, a number of complexes containing N-substituted aminopolycarboxylic acids have been investigated.[8–15] The alkyl-*N*-iminodiacetic acids are the ligands with the lowest molecule weight, and can be characterized as chelating surfactants and compounds with surface chemical properties. The alkyl-*N*-iminodiacetic acids serve as a model for larger molecules with longer and/or more alkyl chains and with EDTA-like multidentate entities for efficient and/or specific complex formation of metal ions.[16–19] With these facts in mind, in this paper, we report the structure and properties of a novel three-dimensional complex with *N*-methyliminodiacetic acid, $\{[Na_2(H_2O)_3(\mu\text{-}L)_2Cu]_4\}_\infty$.

EXPERIMENTAL

Materials and instrumentation

The ligand was purchased from Aldrich and used as received. All starting materials and solvents were of analytical purity. Elemental analyses for carbon, hydrogen and nitrogen were carried out on a model 240 Perkin-Elemer instrument. IR spectra were measured using KBr disks in a Bruker Tensor 27 FTIR spectrophotometer in the 400–4000 cm^{-1} region. The UV–vis spectra were measured on Jasci V-570 UV–vis spectrophotometer in the 200–2000 nm region. The ESR spectra were measured on an ER 200D-SRC spectrophotometer in the X bond scan.

Preparation of compound $\{[Na_2(H_2O)_3(\mu\text{-}L)_2Cu]_4\}_\infty$

A methanol–water (1 : 3) solution (20 ml) containing $CuBr_2$ (0.1119 g, 0.5mmol) and L (0.0735 g, 0.5mmol) was stirred for 5 h after heating to 70 °C, and filtered off. The dark-blue crystals (yield 0.1361g, 60%) suitable for X-ray

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*Correspondence to: Shi-Ping Yan, Department of Chemistry, Nankai University, 300071, Tianjin, People's Republic of China.
E-mail: yansp@nankai.edu.cn
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crystallographic analysis were obtained by slow evaporation of the filtrate within a couple of days. Anal. Calcd for the complex (%): C 26.39, H 4.29, N 6.10%; found: C 26.44, H4.41, N 6.17%.

X-ray crystallography

Diffraction data for the complex was collected at 293 K with a Bruker SMART 1000 CCD diffractometer using Mo–Kα radiation ($\lambda = 0.71073$ Å) with the ω–2θ scan technique. An empirical absorption correction (SADABS) was applied to raw intensities.[20] The structure was solved by direct methods (SHELX-97) and refined using full-matrix least-squares procedures on F^2 with SHELX-97.[21,22] The hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. Further details about crystal data and structure refinement for $\{[Na_2(H_2O)_3(\mu\text{-}L)_2Cu]_4\}_\infty$ are given in Table 1. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 621 954. Copies of the data can be obtained free of charge on application to CCDC (e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Data collection and processing parameters for the complex

Empirical formula	C10 H20 Cu N2 Na2 O11
Formula weight	453.80
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	$a = 16.556(3)$ Å $\alpha = 90°$ $b = 8.0622(13)$ Å $\beta = 95.849(2)°$ $c = 12.671(2)$ Å $\gamma = 90°$
Volume	1682.5(5) Å^3
Z, Calculated density	4, 1.792 mg m^3
Absorption coefficient	1.411 mm^{-1}
$F(000)$	932
Crystal size	0.22 × 0.18 × 0.16 mm
θ range for data collection	2.47–25.02°
Limiting indices	$-19 \le h \le 19, -9 \le k \le 4, -15 \le l \le 14$
Reflections collected/unique	4112/1482 [R(int) = 0.0236]
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	1.000000 and 0.638047
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1482/0/121
Goodness-of-fit on F^2	1.076
Final R indices [$I > 2\theta(I)$]	$R_1 = 0.0285$, $wR_2 = 0.0815$
R indices (all data)	$R_1 = 0.0333$, $wR_2 = 0.0847$
Largest difference peak a	0.584 and −0.639 e Å^{-3}

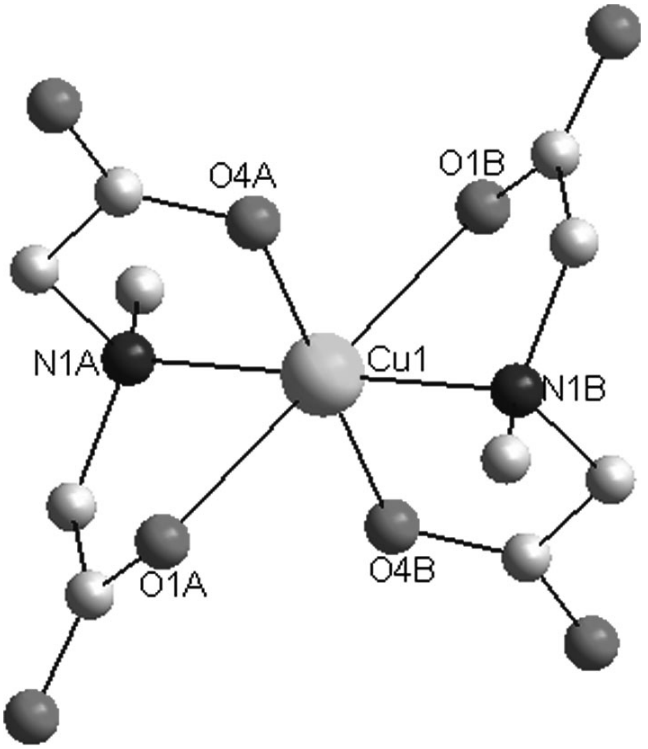

Figure 1. Diagram of the CuL_2 unit showing the coordination environment of Cu(II) ion, hydrogen and sodium ions are omitted for clarity.

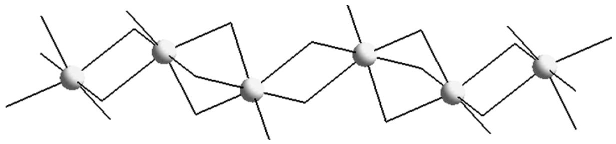

Figure 2. A one-dimensional sodium chain showing the coordination environment of Na(I) ion, all hydrogen atoms are omitted for clarity.

RESULTS AND DISCUSSION

The structures of complex are shown in Figures 1–4. The bonds lengths and angles are listed in Table 2. In Fig. 1, the Cu(II) ion displays a distorted octahedron coordination environment with N(1A), N(1B), O(4A), O(4B) forming the basal plane and O(1A), O(1B) occupying the axial position. The Cu atom locates in the basal plane absolutely, with average Cu–N_L and Cu–O_L bond lengths of 2.0132 and 1.9653 Å, respectively. The Cu–O (1A) and Cu–O (1B) bond distances (2.4522 Å) of axial position are longer than those in basal plane, thus resulting in an elongated octahedron, which

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Table 2. Selected bond lengths (Å) and angles (deg) for the complex

$Cu(1)-O(4)^a$	1.9651(18)	$O(4)^a-Cu(1)-O(4)$	180.0
$Cu(1)-O(4)$	1.9651(18)	$O(4)^a-Cu(1)-N(1)^a$	85.96(8)
$Cu(1)-N(1)^a$	2.013(2)	$O(4)-Cu(1)-N(1)^a$	94.04(8)
$Cu(1)-N(1)$	2.013(2)	$O(4)^a-Cu(1)-N(1)$	94.04(8)
$O(1)-C(1)$	1.247(3)	$O(4)-Cu(1)-N(1)$	85.96(8)
$O(1)-Na(1)$	2.362(2)	$N(1)^a-Cu(1)-N(1)$	180.00(9)
$O(2)-C(1)$	1.254(3)	$C(1)-O(1)-Na(1)$	129.67(17)
$Na(1)-O(6)$	2.378(2)	$C(4)-O(3)-Na(1)^b$	148.37(18)
$Na(1)-O(3)^d$	2.396(2)	$Na(1)^b-O(3)-Na(1)^c$	81.93(7)
$Na(1)-O(5)$	2.524(2)	$C(2)-N(1)-Cu(1)$	106.93(15)
$Na(1)-Na(1)^e$	3.160(2)	$C(5)-N(1)-Cu(1)$	111.59(17)
$Na(1)-Na(1)^c$	3.943(2)	$C(3)-N(1)-Cu(1)$	106.93(16)
$O(3)^c-Na(1)-O(5)$	81.54(6)	$O(1)-Na(1)-O(6)$	99.60(8)
$O(1)-Na(1)-O(6)^c$	92.30(8)	$O(1)-Na(1)-O(3)^d$	109.19(8)
$O(5)-Na(1)-O(6)^c$	104.62(6)	$O(6)-Na(1)-O(3)^d$	97.76(8)
$O(3)^d-Na(1)-Na(1)^e$	49.44(6)	$O(3)^d-Na(1)-O(3)^c$	84.47(8)
$Na(1)^e-Na(1)-Na(1)^c$	134.34(5)	$O(1)-Na(1)-O(5)$	80.52(7)
$Na(1)-O(6)-Na(1)^c$	104.53(8)	$O(6)-Na(1)-O(5)$	179.85(8)
$Na(1)^e-O(5)-Na(1)$	77.52(9)	$O(3)^c-Na(1)-Na(1)^c$	86.13(6)

Symmetry transformations used to generate equivalent atoms: $^a\,-y+3/2,\ -y+3/2,\ -z+1$; $^b\,y,\ -y+1,\ z+1/2$; $^c\,-y+2,\ -y+1,\ -z+1$; $^d\,y,\ -y+1,\ z-1/2$; $^e\,-y+2,\ y,\ -z+1/2$.

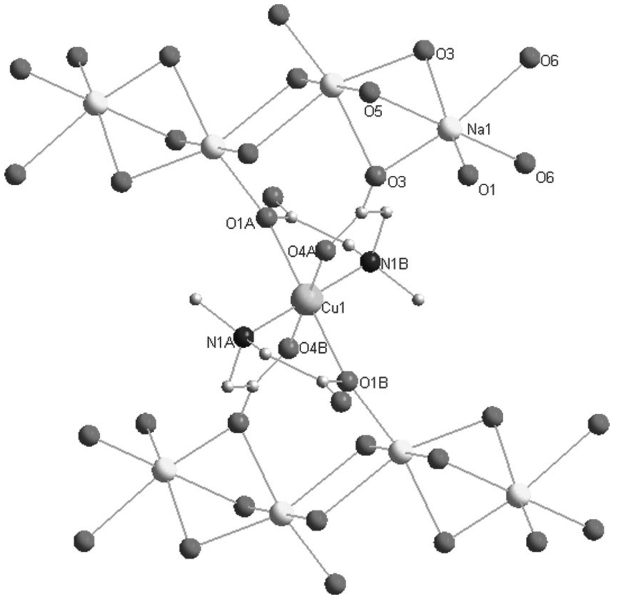

Figure 3. The aggregate of the CuL_2 unit and the sodium chains, all hydrogen atoms are omitted for clarity.

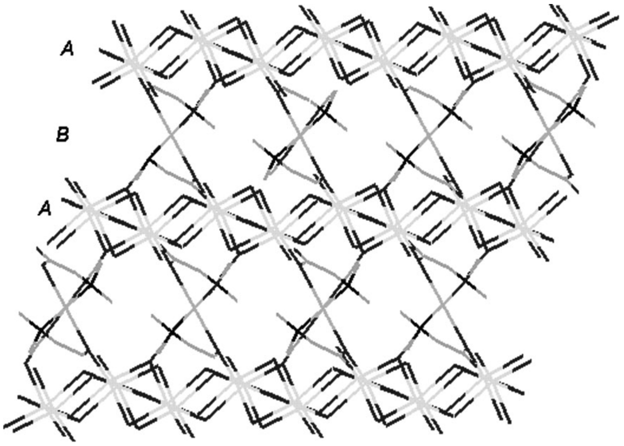

Figure 4. The three-dimensional supramolecular structure of the complex along the *b* axis (all hydrogen atoms are omitted for clarity).

may be subjected to the Jahn–Teller effect.[23,24] In the CuL_2 units, the main bond angles of N1–Cu–N1 (180°), O4–Cu–O4 (180°), O1–Cu–O1 (180°), N1–Cu–O4 (85.97°), N1–Cu–O1 (73.82°) and O4–Cu–O1 (92.67°) are quite consistent with the distorted octahedron coordination of the central metal ions. The sodium is also six-coordinated with oxygen atoms coming from the ligand and water molecule; the related sodium atoms are bridged by oxygen atoms, forming a zigzag sodium chain (Fig. 2). The two Na–Na distances are 3.1604 and 3.9435 Å, respectively. In Fig. 3, both O5 and O6 are from the water molecule. The distances Na1–O5 and Na1–O6 are 2.5239 and 3.3779 Å, respectively (Fig. 3). Thus, the sodium chain links CuL_2 moieties via the *exo* oxygen atoms of the ligands and results in a novel ABA$^{\cdots}$ layer motif (Fig. 4). The *exo* oxygen atoms of the ligands have two bridging modes: $\mu_{1,1}$ and μ_1. The formation of the three-dimensional complex may be best described as a sodium-induced self-assembly of the copper ions with help of the ligands. In other words, the

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sodium ion serves as a template in the formation of this novel complex.

IR spectrum

A strong absorption, at 1614 cm^{-1} is observed for the complex, which is vested in $\nu_{\mathrm{as(COO)}}$; the absorption band at about 1386 cm^{-1} [$\nu_{\mathrm{s(COO)}}$] also could be identified unambiguously. According to Δ (COO) $= \nu_{\mathrm{as\ (COO)}} - \nu_{\mathrm{s\ (COO)}} =$ 228 cm^{-1}, which is below 300 cm^{-1}, the COO^- coordinates to metal atoms by two modes, including monodentate and bisdentate.[25] All of these results are quite consistent with the crystal structure.

Electronic spectrum

The electronic absorption spectra of the complex were measured in distilled water solution (Fig. 5). A relatively stronger wide band centered at 705 nm was observed and can be attributed to the d–d transitions of Cu (II) in an environment that is close to octahedral.[26,27]

ESR

The X-band ESR spectra of powdered complex at room temperature have been measured. The ESR spectrum displays an asymmetric absorption (Fig. 6). The computer simulation gave the ESR parameters $g_\perp = 2.00, g_\parallel = 2.14$ for the complex. The pattern $g_\parallel > g_\perp > 2.0$ is indicative of a copper (II) d_{x2-y2} orbital ground state, which is in agreement with the distorted octahedron geometry of the complex.[26,28,29]

TGA

The TGA and corresponding DTA curves of the complex heated in air from 38 to 600 °C are shown in Fig. 7. The TGA curves exhibit two distinct degradation regions: one is in the temperature range 150–180 °C and the other is in the range 260–300 °C. The thermal decomposition of the complex releases coordinated waters from the compound in the temperature range 150–180 °C. During this range a mass loss of 11.5% is observed; the expected mass loss is 11.9%. The next temperature range includes three steps of pyrolysis of organic ligands (260–280, 290–300 and 310–360 °C). A final total mass loss of 54% is observed. Because of the complicated final product, the accurate formation still has not been confirmed. Combining the TGA and DTA data with TGA experiments provides a detailed view of the decomposition process.

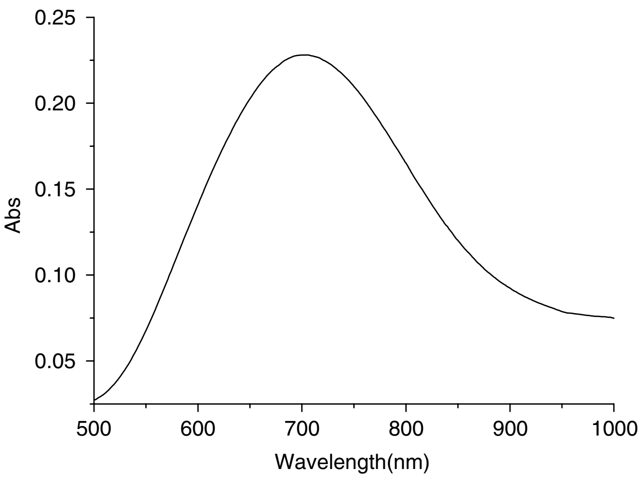

Figure 5. UV–vis spectrum of the complex in distilled water solution.

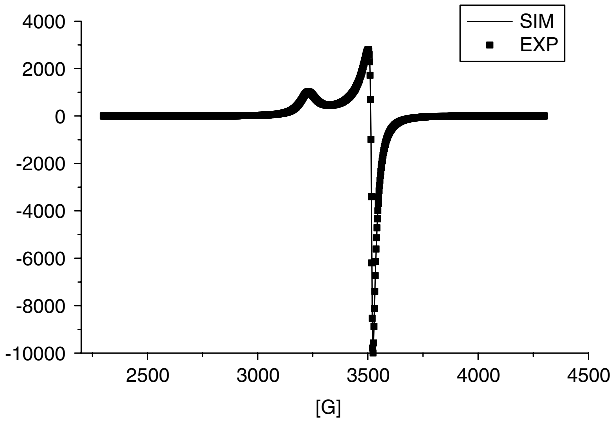

Figure 6. X-band ESR spectra of the complex in powder at room temperature.

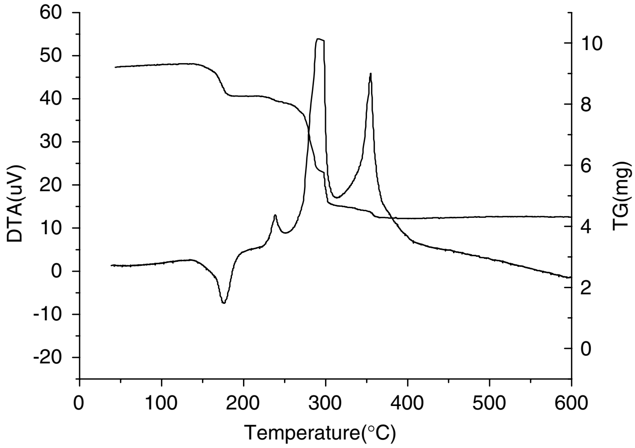

Figure 7. TGA and corresponding DTG curves of the complex from 38 to 600 °C at 10 °C/min in air.

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