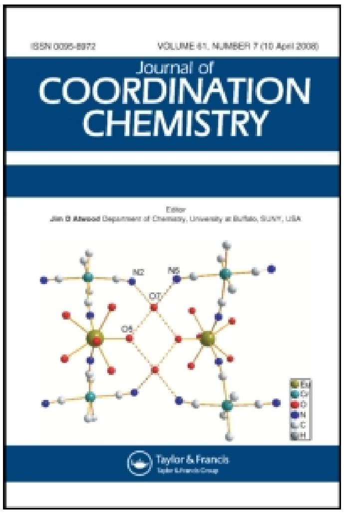

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Synthesis, structure and spectroscopy of a copper complex of the chiral pendant-arm macrocycle *N,N',N''*-tris[2*S*-2-hydroxypropyl]- 1,4,7-triazacyclononane

Wei Han[a]; Ling Li[a]; Wen Gu[a]; Zhan-Quan Liu[a]; Shi-Ping Yan[a]; Dai-Zheng Liao[a]; Zong-Hui Jiang[a]; Peng Cheng[a]
[a] Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

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SYNTHESIS, STRUCTURE AND SPECTROSCOPY OF A COPPER COMPLEX OF THE CHIRAL PENDANT-ARM MACROCYCLE *N,N′,N″*-TRIS[2*S*-2-HYDROXYPROPYL]-1,4,7-TRIAZACYCLONONANE

WEI HAN, LING LI, WEN GU, ZHAN-QUAN LIU, SHI-PING YAN*,
DAI-ZHENG LIAO, ZONG-HUI JIANG and PENG CHENG

Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

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The preparation, crystal structure and spectroscopy of $[Cu(H_3L)](ClO_4)_2]$ ($H_3L = N,N',N''$-tris[2*S*-hydroxypropyl]-1,4,7-triazacyclononane) is presented. The complex crystallizes in the monoclinic space group $P2_1/c$, $a = 13.954(5)$, $b = 9.700(4)$, $c = 17.883(7)$ Å, $\beta = 99.548(8)^\circ$, $Z = 4$; $R1 = 0.0665$, $wR2 = 0.1826$. The central copper ion is coordinated to three nitrogen atoms of the macrocycle and three oxygen atoms from the pendant hydroxypropyl groups, forming a distorted octahedral coordination sphere.

Keywords: Copper; Crystal structure; Macrocycle; Spectroscopic properties

INTRODUCTION

The "small" macrocyclic ligand 1,4,7-triazacyclononane (tacn) has a rich chemistry [1]. Unlike tetraazamacrocycles, tacn is readily coordinated to transition metal ions to form "sandwich" complexes. On the other hand, tacn is much more easily derivatized at the nitrogen atoms to give *N*-alkylated ligands. Recently we have investigated the chemistry of the ligand with hydroxypropyl arms. This is particularly interesting because it forms complexes in which the OH can remain protonated and act as an alcohol or can be deprotonated and act as an alkoxide. Peacock *et al.* have reported the hydrogen-bridged dimer $[Co^{III}LH_3LCo^{III}]^{3+}$ [2], $[Cr^{III}LH_3LCr^{III}]^{3+}$ [3], the mixed-valence manganese dimer $[Mn^{II}(H_3L)LMn^{IV}]^{3+}$ [4] and a mixed-metal dimer $[Zn^{II}(H_3L)LV^{IV}]^{3+}$ [5]. In addition, a series of monomeric Mn(II) [6], Ni(II) [7], and Zn(II) [8] complexes were also synthesized and characterized. However, the crystal structure of the monomeric copper complex of this ligand is not documented

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*Corresponding author. E-mail: yansp@nankai.edu.cn

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and in this article we report the synthesis, structural and spectroscopic characterization of the Cu(II) complex.

EXPERIMENTAL

Starting Materials

1,4,7-triazacyclononane (tacn) was prepared according to a published procedure [9]. *N*,*N*′,*N*″-Tris[(2*S*)-hydroxypropyl]-1,4,7-triazacyclononane was prepared as the hydrochloride salt from tacn · 3HCl and (*S*)-(−)-propylene oxide as previously published [2]. All other chemicals were of reagent grade and used as commercially obtained.

Preparation of $[Cu(H_3L)](ClO_4)_2$

To a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) in 10 cm^3 of methanol was added $LH_3 \cdot 3HCl$ (0.34 g, 1 mmol) in 10 cm^3 of methanol. The title complex slowly precipitated as a blue microcrystalline powder. It was then dissolved in 20 cm^3 of distilled water to form a deep-blue, clear solution which was allowed to stand for a few weeks. Deep-blue block-shaped crystals suitable for X-ray crystallography were obtained. Anal. Calcd. for $C_{15}H_{33}Cl_2CuN_3O_{11}$ (%): C, 31.81; H, 5.83; N, 9.91. Found: C, 32.07; H, 5.54; N, 9.01.

Physical Measurements

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 instrument. IR spectra were recorded on a Nicolet 5DX FTIR spectrophotometer using KBr pellets in the range 4000–400 cm^{-1}. Electronic spectra were recorded on a Shimadzu UV-2101PC scanning spectrophotometer using DMF solutions.

X-ray Crystallography

Data collection was performed on a Siemens Smart diffractometer equipped with a CCD area detector (Mo Kα radiation, $\lambda = 0.71073$ Å) by the φ-ω scan technique at 293(2) K. The structure was solved by direct methods using SHELX-97 [10] and refined by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atom on F^2. The hydrogen atoms were added theoretically, riding on the atoms concerned and refined with fixed thermal parameters. Crystal data and structure refinement details are listed in Table I. Final atomic coordinates for non-hydrogen atoms and equivalent thermal parameters are listed in Table II.

RESULTS AND DISCUSSION

Crystal Structure

The crystal structure of the title complex consists of a $[Cu(H_3L)]^{2+}$ cation as shown in Fig. 1 and two ClO_4^- anions. Selected bond lengths and angles are listed in Table III. In Fig. 1, the central copper ion is seen to show distorted octahedral coordination

TABLE I Crystal data and structure refinement details for the title compound

Empirical formula	$C_{15}H_{33}C_{12}CuN_3O_{11}$
Formula mass ($g\,mol^{-1}$)	565.88
Temperature (K)	293(2)
λ (Mo Kα) (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.954(5)
b (Å)	9.700(4)
c (Å)	17.883(7)
β (°)	99.548(8)
V (Å^3)	2387.0(16)
Z	4
Crystal size (mm)	0.32 × 0.20 × 0.18
D_{calcd} ($Mg\,m^{-3}$)	1.575
Abs. Coeff. (mm^{-1})	1.197
$F(000)$	1180
2θ range (°)	1.48–25.00
Reflections collected	9825
R(int)	0.0969
Completeness to θ (%)	99.9
Goodness-of-fit on F^2	0.996
Max./min. transmission	1.000, 0.884
Data/restraints/parameters	4198/152/329
$R_1[I > 2\sigma(I)]$	0.0665
wR_2 (all data)	0.1826
Largest diff. peak hole (e Å^{-3})	0.516, −0.381

geometry by bonding to three nitrogen atoms from tacn and three oxygen atoms from pendant 2-hydroxypropyl arms. The octahedral geometry is distorted with coordination bond angles ranging from 73.0(2)° to 124.2(3)°. The OH groups in the ligand remain protonated and the average Cu–O bond distance is 2.132(5) Å [Cu–N 2.101(6) Å], indicating that $[Cu(H_3L)]^{2+}$ is a typical Cu(II) species.

A view of the $[Cu(H_3L)]^{2+}$ looking down the *quasi* C_3 axis is shown in Fig. 2 and a comparison of selected geometric parameters with those of other relevant complexes is summarized in Table IV. The upper donor set of the copper ion (O_3) is twisted in a clockwise direction relative to the lower set (N_3) when viewed down the C_3 axis. The three twist φ angle, (φ is defined as the angle of twist away from an exactly staggered arrangement of ligating atoms as viewed down the C_3 axis; thus φ is 0° for octahedral geometry and 60° for trigonal prismatic geometry) are 26.8, 28.8 and 0.9°. That is to say that the N(2)–O(2) pair remain in the eclipsed arrangement, while the N(1)–O(1) and N(3)–O(3) have relatively large twist angles that form staggered conformations. The average twist angle, 18.1(7)° is somewhat larger than in the Cr^{III} dimer (15°) [3] and in the Co^{III} dimer (10–11°) [2] (Table IV). In addition to the twist angles mentioned above, the angle between the C_3 axis and the Cu–N bond is less than half the tetrahedral angle, indicating trigonal elongation, while that between the C_3 axis and the Cu–O bond is greater than the tetrahedral angle, indicating trigonal compression. Thus the "tacn" half of the molecule is trigonally elongated while the "hydroxypropyl" part is trigonally compressed. The endocyclic chelate rings are all in the λ conformation while the exocyclic ones adopt the δ conformation with equatorial methyl groups. Therefore the overall chirality description of the title complex (using the nomenclature of Taylor *et al.* [11]) is $[\Delta(\lambda\delta)]$.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the non-hydrogen atoms

	x/a	y/b	z/c	U_{eq}
Cu(1)	2799(1)	8359(1)	6572(1)	45(1)
N(1)	1992(4)	7179(6)	7213(4)	50(2)
N(2)	3267(4)	6545(7)	6210(4)	61(2)
N(3)	1544(4)	8047(7)	5662(4)	54(2)
O(1)	2383(3)	9896(5)	7203(3)	52(1)
O(2)	4267(3)	8749(6)	6872(4)	87(2)
O(3)	2944(4)	9944(7)	5626(4)	94(2)
C(1)	2620(5)	5922(8)	7375(5)	60(2)
C(2)	2900(6)	5390(8)	6635(5)	64(2)
C(3)	2846(6)	6475(9)	5372(5)	72(3)
C(4)	1775(6)	6798(9)	5240(5)	70(3)
C(5)	736(5)	7818(9)	6096(5)	57(2)
C(6)	1029(5)	6856(8)	6777(5)	59(2)
C(7)	1952(5)	8001(8)	7899(4)	55(2)
C(8)	1708(5)	9475(7)	7710(4)	49(2)
C(9)	1834(6)	10 388(8)	8402(4)	73(3)
C(10)	4359(6)	6570(10)	6382(7)	89(3)
C(11)	4756(7)	7901(14)	6404(7)	113(4)
C(12)	5878(5)	7916(11)	6660(6)	98(4)
C(13)	1356(6)	9274(10)	5172(5)	68(3)
C(14)	2248(6)	9827(11)	4941(5)	80(3)
C(15)	2044(8)	11 179(12)	4541(7)	123(4)
Cl(1)	772(1)	2729(2)	6549(1)	59(1)
O(4)	216(4)	1481(5)	6508(4)	78(2)
O(5)	613(5)	3515(6)	7192(4)	102(2)
O(6)	509(5)	3534(7)	5897(4)	107(2)
O(7)	1784(4)	2414(6)	6643(4)	90(2)
Cl(2)	4984(2)	2402(3)	5936(2)	83(1)
O(8)	4410(20)	3540(20)	5612(16)	280(20)
O(9)	5983(8)	2630(30)	5920(15)	166(14)
O(10)	4662(18)	1219(17)	5462(11)	123(11)
O(11)	4820(20)	2140(30)	6685(7)	201(18)
O(8′)	5681(11)	1466(12)	5729(8)	143(7)
O(9′)	4344(11)	2911(18)	5303(7)	204(10)
O(10′)	5511(10)	3541(10)	6326(8)	144(6)
O(11′)	4452(12)	1752(17)	6447(8)	200(10)

TABLE III Selected bond lengths (Å) and angles (°) for the title compound

Cu(1)–O(1)	2.012(5)	Cu(1)–N(2)	2.020(6)
Cu(1)–O(2)	2.064(5)	Cu(1)–N(1)	2.078(6)
Cu(1)–O(3)	2.320(6)	Cu(1)–N(3)	2.205(6)
O(1)–Cu(1)–N(2)	164.5(3)	O(2)–Cu(1)–N(3)	148.1(3)
O(1)–Cu(1)–O(2)	94.8(2)	N(1)–Cu(1)–N(3)	84.0(2)
N(2)–Cu(1)–O(2)	83.3(2)	O(1)–Cu(1)–O(3)	89.2(2)
O(1)–Cu(1)–N(1)	82.3(2)	N(2)–Cu(1)–O(3)	105.7(3)
N(2)–Cu(1)–N(1)	86.0(3)	O(2)–Cu(1)–O(3)	82.2(2)
O(2)–Cu(1)–N(1)	124.2(3)	N(1)–Cu(1)–O(3)	152.6(2)
O(1)–Cu(1)–N(3)	104.4(2)	N(3)–Cu(1)–O(3)	73.0(2)
N(2)–Cu(1)–N(3)	84.4(3)		

IR and Electronic Spectra

IR spectra of the complex show a strong broad absorption band at about 1060 cm^{-1}, characteristic of ClO_4^- anions. The ν(C–H) stretches in tacn are indicated by sharp

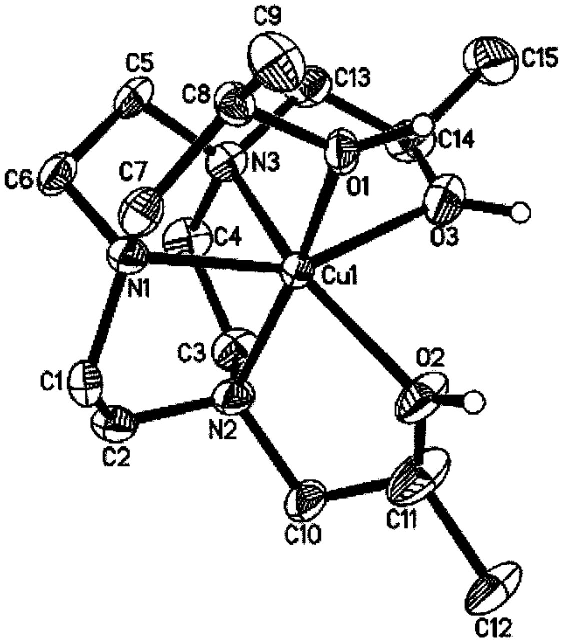

FIGURE 1 Molecular structure of the complex cation $[Cu(H_3L)]^{2+}$ showing the atom numbering scheme. Thermal ellipsoids represent 20% probabililty.

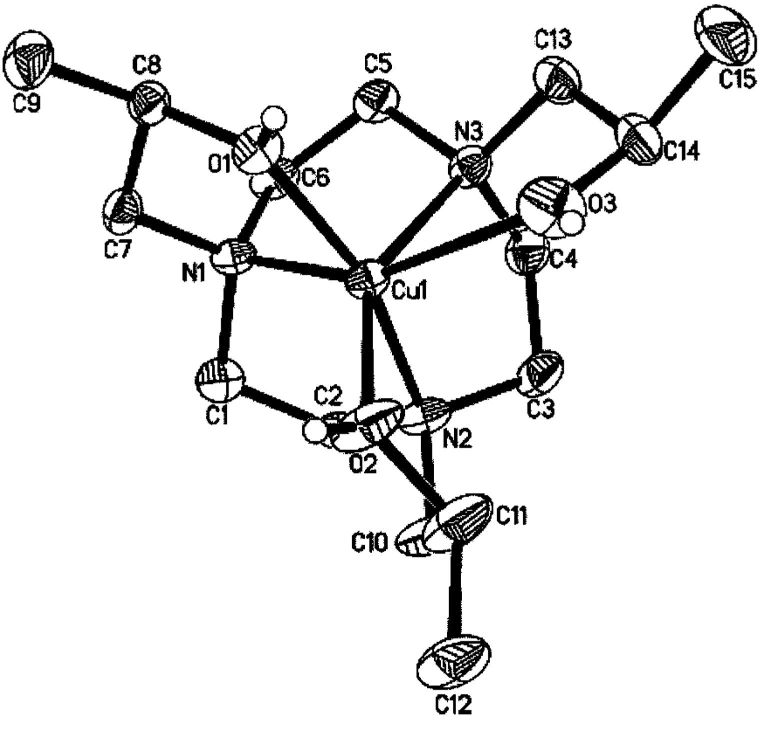

FIGURE 2 View of the $[Cu(H_3L)]^{2+}$ cation looking down the *quasi* C_3 axis.

TABLE IV Bond lengths (Å) and twists away from octahedral geometry, φ (°), for $[Cu(H_3L)]^{2+}$ and related complexes

Complex	*M–N*	*M–O*	*O–H*	φ	*Ref.*
$[Cu(H_3L)]^{2+}$	2.101[a]	2.132[a]	0.93[a]	18[a]	This work
$[Cr^{III}LH_3LCr^{III}]^{3+}$	2.071[a]	1.857[a]	1.841[a]	15[a]	[3]
$[Mn^{II}LH_3]^{2-}$ (half)	2.251	2.142		60.0	[6]
$[Mn^{IV}L]^{+}$ (half)	2.051	1.857	1.841	11	[6]
$[Mn^{II}LH_3]^{2+}$	2.245[a]	2.166[a]		37.4	[6]
[CoL] (half)	1.944	1.939	1.62	11	[2]
$[Co(LH_3)]^{3+}$ (half)	1.954	1.939	0.90	10	[2]
$[Ni(H_3L)]^{2+}$	2.064	2.083		17.5	[7]

[a] Average values.

bands involving splitting at 2900 and 2800 cm^{-1}. A broad absorption with shoulders ranging from 3650 to 3150 cm^{-1} can be ascribed to the ν(O–H) stretches of the hydroxypropyl groups. Electronic spectra show a very strong absorption band at 37 313 cm^{-1} ($\varepsilon = 5.00 \times 10^4\ M^{-1}\,cm^{-1}$), which may be attributed to a charge-transfer transition of the ligand and a weak band at about 14 534 cm^{-1} ($\varepsilon = 956\ M^{-1}\,cm^{-1}$) represents the typical d–d transition in Cu^{II}.

ESR Spectra

The X-band powder ESR spectrum of $[Cu(H_3L)](ClO_4)_2$ at room temperature displays a broad asymmetric absorption. The ESR spectrum at 110 K shows three different g tensors with hyperfine structure in the g_z signal. A computer simulation gave $g_x = 2.055$, $g_y = 2.10$, $g_z = 2.225$.

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Supplementary Data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 219829. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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