ELSEVIER

Note

Metal–N-saccharide chemistry: synthesis and structure determination of two Cu(II) complexes containing glycosylamines

Wei Zhang,[a] Tao Jiang,[a,*] Sumei Ren,[a] Zhongwei Zhang,[a] Huashi Guan[a] and Jingsheng Yu[b]

[a]*Marine Drug and Food Institute, Ocean University of China, Qingdao 266003, China*
[b]*The Key Laboratory for Supramolecular Structure and Materials of Ministry of Education,
Jilin University, Changchun 130023, China*

Abstract—Two new complexes $[Cu(N,N',N''-(D\text{-}Glc)_3\text{-}tren)Cl]Cl$ (**1**) and $[Cu(N,N',N''-(maltose)\text{-}tren)]Cl_2 \cdot H_2O$ (**2**), have been synthesized and characterized by elementary analysis, and the IR and UV spectra suggest that complex **1** and complex **2** are arranged in trigonal bipyramidal configuration and square-pyramidal configuration, respectively. The crystal structure of complex **1** has been determined by X-ray diffraction as: $a = 9.3476(8)$, $b = 17.4236(13)$, $c = 9.7836(8)$ Å, $\beta = 91.197(3)°$, $V = 1593.1(2)$ Å^3, $Z = 2$, and $R = 0.0325$, which shows that three secondary amine groups (N-1, N-2, N-3) of the glycosylamine ligand forms the equatorial plane, and the tertiary amine (N-4) and one Cl$^-$ are located at the apical positions.
© 2004 Elsevier Ltd. All rights reserved.

1. Introduction

Carbohydrates and carbohydrate derivatives play important roles in various biological processes.[1] Some important enzymatic reactions involve metal–N-sugar interactions with alkali, alkaline earth, and some transition metal ions.[2,3] Study of the coordination behavior of sugar molecules is difficult because of their complicated stereochemistry and sensitive hygroscopic properties.

Yano et al. have studied the synthesis and characterization of nickel(II) and cobalt(III) complexes containing glycosylamines formed by reaction of sugars and diamines.[4–6] Their research suggests that the stereochemical structure of the sugar complexes can be changed by using different metal ions. We report here the first successful synthesis and X-ray crystal structure

analysis of a Cu(II) complex containing a glycosylamine derived from D-glucose and tris(2-aminoethyl)amine. The results of elemental analysis, and FT-IR and UV measurements, are also discussed.

2. Results and discussion

The synthesis of **1** *and* **2**. The polarity of the ligands and complexes is very similar, which made it extremely difficult to obtain suitable crystals for X-ray analysis. We purified the reaction solution by loading it on a Sephadex LH-20 gel-permeation column and then the blue major band was collected, left standing overnight, and single crystals suitable for X-ray diffraction studies were grown.

FT-IR studies. The absorption bands and tentative assignments for **1** and **2** are given in Table 1.

In the IR spectra, besides a broad band for the hydroxyl groups, a moderate peak corresponding to δ_{NH} was observed around 1634 cm^{-1}, which is shifted to a

* Corresponding author. Tel.: +86-532-2032712; e-mail: jiangtao@
  mail.ouc.edu.cn

Table 1. IR data for **1** and **2**

1	2	Possible assignments[7]
3384	3384	ν_{OH}
2924	2924	ν_{CH}
2888	2883	
1633	1634	δ_{NH}
1459	1460	δ_{CH}
1397	1403	
1362	1362	ω_{CH}
1280	1259	τ_{CH}
1081	1075	ν_{CO}
1044	1037	δ_{COH}
906	906	ν_{CC}
819	844	δ_{CCO}

δ, bending mode; ν, stretching mode; τ, twisting; ω, wagging.

higher energy region as compared with that of the complex [Cu (tren)]$^{2+}$. This observation indicates the successful formation of the glycosylamine.

UV–vis studies. UV–vis spectra of **1** and **2** were measured in MeOH, and the corresponding data are provided in Table 2.

The absorption spectrum of **1** shows a main band at 11261 cm^{-1} and a shoulder at 13870 cm^{-1}. This absorption pattern, one peak accompanied by a higher

**Table 2.** UV–vis data for **1** and **2**

| Complexes	Absorption ν_{max}/cm^{-1} (ε/L mol^{-1} cm^{-1})
1	11261 (159), 13870sh
2	14514 (182), 11614sh

energy (less intense) shoulder, is typical of a trigonal bipyramidal copper(II) geometry[8,9] and consistent with its crystal structure determined by the X-ray analysis. These two bands are assigned to the $A_1' \rightarrow E'$ (main) and $A_1'' \rightarrow E''$ (sh) transitions with an approximate D_{3h} symmetry.[10,11]

The absorption spectrum of **2** shows a main band at 14514 cm^{-1} with a shoulder at 11614 cm^{-1}, which is significantly different from that of **1**. This absorption pattern, a broad main band with a lower-energy shoulder, has often been observed for square-pyramidal copper(II) complexes.[12]

Single-crystal X-ray studies. The molecular structure of the complex [Cu(N,N',N''-(D-Glc)$_3$-tren)Cl]Cl is shown in Figure 1, Figure 2 is the unit cell of the crystal structure of **1**. The crystal data and structure refinements are listed in Table 3; selected bond lengths, angles, and torsion angles in Table 4.
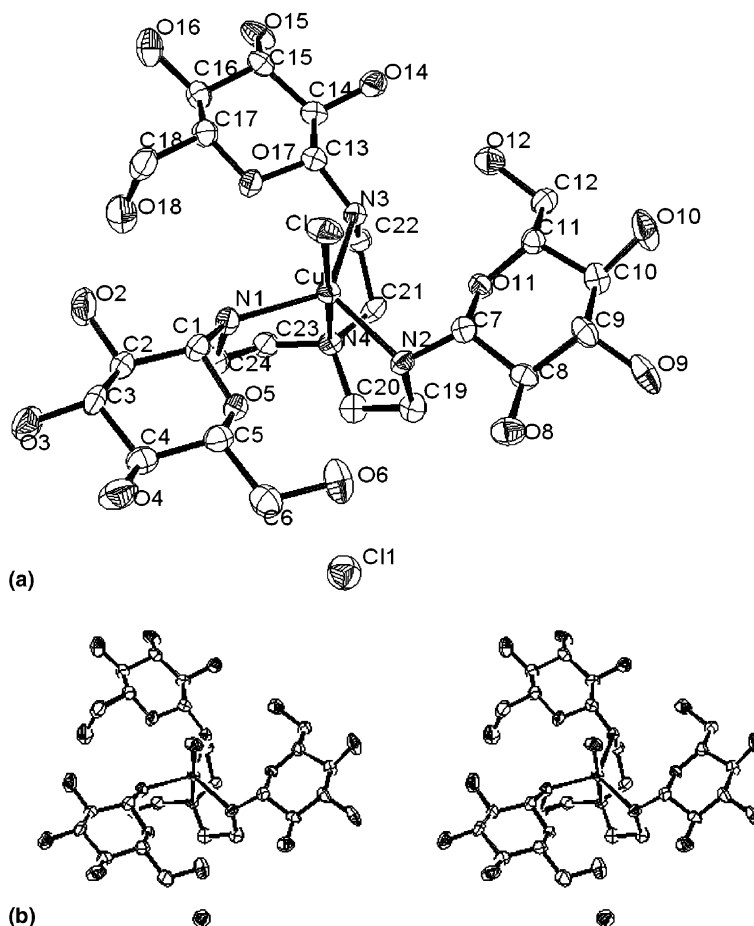
Figure 1. (a) The molecular structure of complex **1** showing 50% probability thermal ellipsoids using ORTEP and (b) the stereo view of **1**.
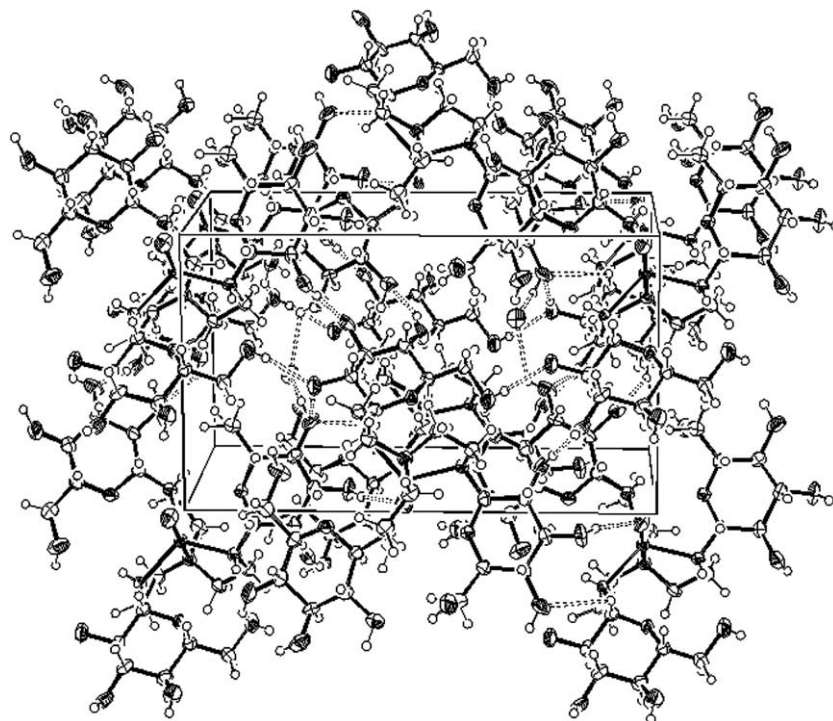
Figure 2. The unit cell of crystal structure of complex **1**. Key: ⊘, chlorine; ⊘, oxygen; ○, hydrogen; ⁓, hydrogen-bonds.

Table 3. Crystal data and structure refinements for **1**

Empirical formula	$C_{24}H_{48}Cl_2N_4O_{15}Cu$
Formula weight	767.10
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2(1)$
Unit cell dimensions	$a = 9.3476(8)$ Å, alpha = 90°
	$b = 17.4236(13)$ Å, beta = 91.197°
	$c = 9.7836(8)$ Å, gamma = 90°
Volume	1593.1(2) Å³
Z, calculated density	2, 1.599 Mg/m³
Absorption coefficient	0.930 mm⁻¹
$F(0\,0\,0)$	806
Crystal size	$0.57 \times 0.35 \times 0.29$ mm
Theta range for data collection	2.08–27.42°
Limiting indices	$0 \leqslant h \leqslant 20$, $0 \leqslant k \leqslant 22$,
	$-12 \leqslant l \leqslant 12$
Reflections collected/unique	3749/3749 [$R_{int} = 0.0000$]
Completeness to theta = 27.42	99.9%
Absorption correction	Empirical
Max. and min. transmission	0.7716 and 0.6188
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3749/1/598
Goodness-of-fit on F^2	0.864
Final R indices [$I > 2$ sigma (I)]	$R1 = 0.0325$, $wR2 = 0.0659$
R indices (all data)	$R1 = 0.0413$, $wR2 = 0.0715$
Absolute structure parameter	0.106 (16)
Largest diff. peak and hole	0.452 and -0.732 e Å⁻³

The core (CuN_4Cl) geometry of the cation is best described as an approximate regular trigonal bipyramid (TBP) for complex **1**. Three secondary amine groups (N-1, N-2, N-3) of the glycosylamine ligand form the equatorial plane with trigonal bond angles of 118.95(15)°, 119.92(15)°, and 117.60(15)°, and the tertiary amine (N-4) and one Cl⁻ are located at the apical positions. The Cl–Cu–N-4 group, is approximately linear with an angle of 179.16(12)°, and all of the axial/equatorial bond angles fall in the range 82–97°. The axial Cu–N-4 bond (2.008 Å) is shorter than any of the in-plane Cu–N bonds, as is typical for TBP copper(II) geometry,[8] the Cu–N-3 bond length (2.125 Å) is in the normal range for Cu–amine in-plane distances with a TBP structure, however, the bond lengths for Cu–N-1 (2.146 Å) and Cu–N-2 (2.142 Å) bonds are slightly longer.

The molecular structure of **1** (Fig. 1) reveals the pyranose form of the saccharide moiety and C-1 modified via glycosylamine formation. A stereo view of the molecule (Fig. 1) reveals the chair conformation of three six-membered rings and the presence of the saccharide moiety in the $^4C_1$ conformation. Torsion angles (Table 4) supports the β-anomeric form of the saccharide moiety. Three Cremer–Pople parameters, obtained using the program PLATON, are, respectively as follows: Q, 0.565 Å; θ, 7.6°; φ, 18.37°; ΔCs (C-1, C-4), 0°; ΔCs (C-2, C-5), 0°; ΔCs (C-3, O-5), 0°; Q, 0.578 Å; θ, 9.5°; φ, 81.19°; ΔCs (C-7, C-10), 0°; ΔCs (C-8, C-11), 0°; ΔCs (C-9, O-11), 0°; Q, 0.593 Å; θ, 11.5°; φ, 296.72°; ΔCs (C-13, C-16), 0°; ΔCs (C-14, C-17), 0°; ΔCs (C-15, O-17), 0°. The hydroxyl groups in the crystal structure of the complex **1**, form an extensive hydrogen-bond network (Fig. 2); the bond lengths and angles are given in Table 5.

Table 4. Selected bond lengths (Å), bond angles (°) and torsion angles (°) of **1**

Bond lengths (Å)			
Cu–N(4)	2.008 (3)	N(2)–C(7)	1.455 (5)
Cu–N(3)	2.125 (4)	N(2)–C(19)	1.487 (5)
Cu–N(1)	2.146 (4)	N(3)–C(13)	1.447 (5)
Cu–N(2)	2.142 (4)	N(3)–C(22)	1.484 (5)
Cu–Cl	2.2576 (10)	N(4)–C(20)	1.475 (6)
N(1)–C(1)	1.441 (5)	N(4)–C(21)	1.490 (6)
N(1)–C(24)	1.482 (6)	N(4)–C(23)	1.492 (5)
Bond angles (°)			
N(4)–Cu–N(3)	84.96 (16)	C(7)–N(2)–Cu	111.8 (2)
N(4)–Cu–N(2)	83.46 (14)	C(19)–N(2)–Cu	108.2 (3)
N(3)–Cu–N(2)	119.92 (15)	C(13)–N(3)–C(22)	116.2 (3)
N(4)–Cu–N(1)	82.77 (14)	C(13)–N(3)–Cu	111.8 (3)
N(3)–Cu–N(1)	117.60 (15)	C(22)–N(3)–Cu	107.5 (3)
N(2)–Cu–N(1)	118.95 (15)	C(20)–N(4)–C(21)	112.0 (3)
N(4)–Cu–Cl	179.16 (12)	C(20)–N(4)–C(23)	111.3 (4)
N(3)–Cu–Cl	95.62 (10)	C(21)–N(4)–C(23)	111.0 (4)
N(2)–Cu–Cl	96.77 (10)	C(20)–N(4)–Cu	107.7 (3)
N(1)–Cu–Cl	96.41 (11)	C(21)–N(4)–Cu	106.4 (3)
C(1)–N(1)–C(24)	114.5 (4)	C(23)–N(4)–Cu	108.2 (2)
C(1)–N(1)–Cu	117.0 (3)	O(5)–C(1)–N(1)	105.0 (3)
C(24)–N(1)–Cu	109.8 (3)	O(11)–C(7)–N(2)	105.9 (3)
C(7)–N(2)–C(19)	113.5 (3)	O(17)–C(13)–N(3)	106.0 (3)
Torsion angles (°)			
N(1)–C(1)–C(2)–C(3)	175.4	O(10)–C(10)–C(11)–O(11)	−169.9
O(2)–C(2)–C(3)–C(4)	−171.9	C(12)–C(11)–O(11)–C(7)	179.4
O(3)–C(3)–C(4)–C(5)	169.0	N(3)–C(13)–C(14)–C(15)	169.0
O(4)–C(4)–C(5)–O(5)	179.6	O(14)–C(14)–C(15)–C(16)	−169.0
C(6)–C(5)–O(5)–C(1)	−176.8	O(15)–C(15)–C(16)–C(17)	174.3
N(2)–C(7)–C(8)–C(9)	−178.1	O(16)–C(16)–C(17)–O(17)	174.4
O(8)–C(8)–C(9)–C(10)	179.2	C(18)–C(17)–O(17)–C(13)	−163.6
O(9)–C(9)–C(10)–C(11)	170.8		

Table 5. Hydrogen-bond data for **1**

D–H⋯A	d (D–H) (Å)	d (H⋯A) (Å)	d (D⋯A) (Å)	<(DHA) (°)	Symmetry
O(4)–H(9)⋯O(12)	1.28 (11)	1.88 (11)	2.884 (6)	131 (8)	$-x, y - 1/2, -z$
O(14)–H(21)⋯O(9)	0.75 (5)	1.95 (5)	2.697 (5)	171 (5)	$-x, y + 1/2, 1 - z$
O(12)–H(22)⋯O(8)	0.73 (8)	2.18 (8)	2.908 (7)	175 (9)	$-x, y + 1/2, 1 - z$
O(10)–H(25)⋯O(2)	0.65 (7)	2.43 (9)	2.891 (5)	130 (10)	$x - 1, y, z + 1$
O(9)–H(26)⋯O(3)	0.88 (6)	1.91 (6)	2.734 (6)	155 (5)	$x - 1, y, z + 1$
O(8)–H(29)⋯O(16)	0.52 (6)	2.23 (6)	2.731 (6)	164 (10)	$-x, y - 1/2, -z$
O(3)–H(10)⋯Cl(1)	0.54 (6)	2.53 (8)	2.998 (7)	147 (8)	$x, y, -1 + z$
O(16)–H(15)⋯Cl(1)	0.96 (5)	2.25 (7)	3.125 (6)	152 (7)	$1 - x, y + 1/2, -z$

3. Experimental

3.1. General methods

Tris(2-aminoethyl)amine was purchased from Acros Organic Co. All other chemicals were purchased from local chemical companies. The abbreviations, D-Glc and tren refer to D-glucose and tris(2-aminoethyl)amine, respectively. Elemental analysis was carried out on a P-E 240 elemental analyzer. FT-IR spectra were recorded on a Nicolet Nexus 470 instrument using KBr. The solution electronic spectrum was recorded on a Unico UV2102 PC spectrophotometer.

3.2. Preparation of [Cu(*N,N′,N″*-(D-Glc)₃-tren)Cl]Cl (1)

A methanolic solution (50 mL) containing D-Glc (2.16 g, 12.0 mmol) and tren (0.45 mL, 3.0 mmol) was incubated at 65 °C for 1 h. Then, a methanolic solution (10 mL) of CuCl₂·2H₂O (0.51 g, 3.0 mmol) was added to the foregoing mixture at room temperature. The resulting bluish-green solution was concentrated and chromatographed on a Sephadex LH-20 gel-permeation column eluted with MeOH, whereupon the mixture was separated into two bands. The blue band was collected, left standing overnight, and single crystals suitable for X-ray diffraction studies were grown. Yield 1.19 g (52%);

mp 90–92 °C; Anal. Calcd for $C_{24}H_{48}N_4O_{15}Cl_2Cu$: C, 37.58; H, 6.31; N, 7.30; Cu, 8.28. Found C, 37.21; H, 6.53; N, 7.32; Cu, 8.01. Single crystals suitable for X-ray diffraction were grown from MeOH solution at room temperature.

3.3. Preparation of [Cu(*N*,*N'*,*N''*-(maltose)₃-tren)]-Cl₂·H₂O (2)

The complex was prepared by adopting the procedure given for **1** but by using maltose (4.11 g, 12.0 mmol) in MeOH. Yield 1.95 g (51%); mp 150–153 °C; Anal. Calcd for $C_{42}H_{80}N_4O_{31}Cl_2Cu$: C, 39.67; H, 6.34; N, 4.41; Cu, 5.00. Found C, 39.23; H, 6.62; N, 4.40; Cu, 4.87.

3.4. Single-crystal X-ray structure determinations

A single crystal ($0.57 \times 0.35 \times 0.29$ mm) of **1** was mounted on a glass capillary, and data collection was conducted on a Rigaku RAXIS-RAPID diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) in the θ range from 2.08° to 27.42° at 293 K. Full-matrix least-squares refinement on F^2 with anisotropic thermal parameters for all nonhydrogen atoms was used. The hydrogen atoms were geometrically fixed and were treated as riding atoms with fixed thermal parameters. The hydrogen atom data is given as supplementary data. Calculations were completed with SHELX-97 program.

Supplementary material

CCDC 234422 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033.

References

1. Carolyn, R. B.; Laura, L. K. *Science* **2001**, *291*, 2357–2376.
2. Nagy, L.; Szorcsik, A. *J. Inorg. Biochem.* **2002**, *89*, 1–12.
3. Whilm-Christian, H.; Martin, N.; Karl, Heinz Dotz *J. Organomet. Chem.* **2003**, *684*, 153–169.
4. Yano, S.; Kato, M.; Shioi, H. *J. Chem. Soc., Dalton Trans.* **1993**, 1699–1706.
5. Tanase, T.; Doi, M.; Nouchi, R. *Inorg. Chem.* **1996**, *35*, 4848–4857.
6. Ishida, K.; Nonoyama, S.; Hirano, T. *J. Am. Chem. Soc.* **1989**, *111*, 1599–1604.
7. Yang, L. M.; Zhao, Y.; Xu, Y. Z. *Carbohydr. Res.* **2001**, *334*, 91–95.
8. Duggan, M.; Ray, N.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1980**, 1342–1347.
9. Tuagi, S.; Hathaway, B.; Kremer, S. *J. Chem. Soc., Dalton Trans.* **1984**, 2087–2091.
10. Reinen, D.; Friebel, C. *Inorg. Chem.* **1984**, *23*, 791–798.
11. Utsuno, S.; Miyamae, H.; Horikoshi, S. *Inorg. Chem.* **1985**, *24*, 1348–1354.
12. Bew, M. J.; Hathaway, B. J.; Fereday, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1229–1237.