

Interactions between metal ions and carbohydrates: the coordination behavior of neutral erythritol to transition metal ions

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Abstract

The single crystals of coordinated complexes of neutral erythritol ($C_4H_{10}O_4$) with various transition metal ions were synthesized and studied using FT-IR and single crystal X-ray diffraction analysis. Two $CuCl_2$ -erythritol complexes (denoted as CuE(I) and CuE(II)) were obtained. In CuE(I), Cu^{2+} coordinates with two chloride ions and four OH groups from two erythritol molecules. Two copper centers are linked by one erythritol molecule to form a zigzag chain. For CuE(II), each Cu^{2+} coordinates with two OH groups from an erythritol molecule and two chloride ions. The crystal of CuE(II) contains complexed and free erythritol, the dimers of $[Cu_2Cl_4(C_4H_{10}O_4)]$ further form a $[Cu_2Cl_4(C_4H_{10}O_4)]_\infty$ chain via secondary $Cu \cdots Cl$ bonds, both the dimer unit of $[Cu_2Cl_4 \cdot (C_4H_{10}O_4)]$ and non-coordinated $C_4H_{10}O_4$ unit exist side by side in the crystal. $MnCl_2$ -erythritol complex whose structure is similar to CuE(I) is also acquired. The OH groups of erythritol act as ligand to coordinate to metal ions on one hand, on the other hand, OH groups form hydrogen bonds network that link chain and layer together to build three-dimensional structures.

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1. Introduction

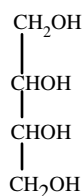
Although carbohydrates are very important biomolecules, carbohydrate research is a challenge topic and its progress is much slower than that of proteins, amino acids, DNA and RNA. On the other hand, many metal ions such as Cu^{2+} , Mn^{2+} , etc., occur in biological systems and play a vital role in various metabolic activities. Coordination among metal and carbohydrate may involve in many biochemical processes [1–4]. Therefore, the studies on the interaction between saccharides and metal ions, being an important branch of bioinorganic chemistry, provide an accessible route to

enhance our understanding on the chemical/biological nature of carbohydrate molecules.

The acquisition of reliable structural information on bond distances and bond angles for transition metal-sugar complexes is hampered by difficulties in the preparation of single crystals in these systems [5–11]. Functionalization and deprotonation are often applied on carbohydrate so that stable complex can be obtained [12–18]. As a result, very few papers about the metal complexes were published where non-functionalized and neutral carbohydrates are involved [19–24]. In our previous work, we found an effective approach to prepare a series of complexes with non-functionalized and neutral saccharide and alditol [25–30]. Those works provide abundant information on the coordination behavior between metal and hydroxyl groups, which is very important to understand the physiological role of metal

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Scheme 1. Structural formula of erythritol.

ions. For example, the coordination of biological important surfactant having important role in the digestion process, cholic acid to metal ion involves in the coordination of hydroxyl groups [31].

Erythritol (denoted as E, depicted in Scheme 1), being one of the simplest representatives of carbohydrates, was chosen as a model to study the coordination of hydroxyl groups to metal ions. The paper reported here demonstrates the multiple forms of coordination complexes between metal ions and erythritol within one system.

2. Experimental

2.1. Materials and methods

Erythritol ($\text{C}_4\text{H}_{10}\text{O}_4$, Sigma) and the other reagents were obtained from commercial sources and used as supplied. The procedure of preparation of copper chloride–erythritol complexes is as follows: 3 mmol erythritol (0.3663 g) and 3 mmol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.51 g) were dissolved in a 1:1 $\text{H}_2\text{O}/\text{EtOH}$ (10 ml) mixture. The solution was put on a water bath and the temperature was 80 °C. Small amount of EtOH (Analytical Reagent) was kept being added into the solution during the heating process to make reaction time longer and the complexes form. The resultant concentrated solution was filtered and cooled down for crystallization at room temperature. Single crystals of $\text{CuCl}_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4[\text{CuE(I)}]$ and $\text{CuCl}_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4[\text{CuE(II)}]$ were obtained, respectively. Our experiment process was as follows: two CuCl_2 –erythritol complexes were found in the bottle of a reaction and obtained from the same equimolar solution, CuE(II) as polycrystalline powder and CuE(I) in block single crystal form, respectively, and the two complexes were easy to be separated for that they had dramatically different colors and shapes. The IR spectra of block single crystal of CuE(I) and polycrystalline powders of CuE(II) indicated that they are different complexes, the structure of block single crystal of CuE(I) was determined and many times of repeated experiments were done to prepare the single crystal of CuE(II), finally, one experiment with longer reaction time was successful and the single crystal structure of CuE(II) was determined later.

The same processes were utilized to prepare $\text{MnCl}_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4$ (MnE), $\text{CoCl}_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4$ (CoE),

$\text{NiCl}_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4$ (NiE) and $\text{ZnCl}_2 \cdot \text{C}_4\text{H}_{10}\text{O}_4$ (ZnE) with erythritol and corresponding metal salts.

2.2. Physical measurements

Infrared spectra of the resultant complexes were measured on a Nico-plan infrared microscope attached on a Nicolet Magna-IR 750 FT-IR spectrometer. All the spectra were recorded at a resolution of 4 cm^{-1} and 64 scans were co-added. Elemental analysis data were satisfactory within 0.4% for Cu, Mn, Co and Ni complexes. Elemental analysis data for Zn complex were not obtained because the sample was utilized to prepare a single crystal but failed. The magnetic susceptibility for crystalline sample CuE(I) was measured on a Quantum Design SQUID XL7 magnetometer with a 1 kOe field in a temperature range of 2–300 K. The magnetic susceptibility for crystalline sample CuE(II) was measured on a MagLab2000 magnetometer (Oxford Instruments) with a 10 kOe field in a temperature of 2–300 K. Field dependence of magnetization for the two samples was measured at low temperature using the MagLab2000.

2.3. X-ray crystallographic analysis

Data for three transition metal chlorides–erythritol complexes, CuE(I), CuE(II) and MnE were collected on a NONIUS KappaCCD Diffractometer with graphite monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature (293K). The structures were resolved by direct methods with SHELX-97 and refined using the full-matrix least-squares on F^2 method. Empirical absorption corrections were applied and anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 203547–203549. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK [fax: (internat) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

3. Results and discussion

In this work, three single crystals of the metal–erythritol complexes (CuE(I), CuE(II) and MnE) are obtained and their structures are determined using single crystal X-ray diffraction analysis. Crystal parameters and details of the data collection and refinement of the complexes are given in Table 1. Selected bond length and angles are listed in Table 2. The geometric param-

Table 1
Crystal and structure refinement for transition metal–erythritol complexes

	CuE(II)	CuE(I)	MnE
Crystal size (mm ³)	0.45 × 0.15 × 0.03	0.40 × 0.25 × 0.15	0.43 × 0.25 × 0.15
Crystal shape/crystal colour	Plate/light green	Column/light blue	Column/light pink
Chemical formula	CuCl ₂ · C ₄ H ₁₀ O ₄	CuCl ₂ · C ₄ H ₁₀ O ₄	MnCl ₂ · C ₄ H ₁₀ O ₄
Formula weight	256.56	256.56	247.96
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> ₂ / <i>c</i>	<i>C</i> ₂ / <i>c</i>
<i>a</i> (Å)	6.2587(2)	14.9403(5)	15.3749(7)
<i>b</i> (Å)	7.5076(3)	7.0436(3)	7.1276(4)
<i>c</i> (Å)	9.7094(4)	10.2343(4)	9.8948(6)
α (°)	104.1589(13)	90	90
β (°)	105.6192(14)	131.220(3)	129.244(2)
γ (°)	99.646(2)	90	90
<i>Z</i>	2	4	4
<i>V</i> (Å ³)	412.50(3)	810.10(5)	839.77(8)
<i>D_c</i> (g/cm ³)	2.066	2.104	1.961
μ (mm ⁻¹)	3.257	3.317	2.171
<i>F</i> (000)	258	516	500
Reflections collected/unique [<i>R</i> _{int}]	7540/1864 [0.0719]	7138/885 [0.0516]	7826/943 [0.0823]
Reflections with <i>I</i> > 2σ(<i>I</i>)	1404	781	704
Data/restraints/parameters	1864/4/109	885/4/59	943/4/59
Goodness-of-fit on <i>F</i> ²	1.031	1.115	1.037
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0468	0.0273	0.0347
<i>WR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1119	0.0606	0.0699

Table 2
Selected bond lengths (Å) and angles (°) for CuE(II), CuE(I) and MnE^a

CuE(II)		CuE(I)		MnE	
<i>Bond lengths</i>					
Cu(1)–O(1)	1.984(3)	Cu(1)–O(1)	2.3522(17)	Mn(1)–O(1)	2.2035(18)
Cu(1)–O(2)	1.997(3)	Cu(1)–O(1)#1	2.3522(17)	Mn(1)–O(1)#1	2.2035(18)
Cu(1)–Cl(2)	2.2324(11)	Cu(1)–O(2)#1	2.0382(17)	Mn(1)–O(2)	2.2472(19)
Cu(1)–Cl(1)	2.2465(11)	Cu(1)–O(2)	2.0382(17)	Mn(1)–O(2)#1	2.2472(19)
O(1)–C(1)	1.430(4)	Cu(1)–Cl(1)#1	2.2630(6)	Mn(1)–Cl(1)#1	2.4505(8)
O(2)–C(2)	1.453(5)	Cu(1)–Cl(1)	2.2630(6)	Mn(1)–Cl(1)	2.4505(7)
O(3)–C(3)	1.437(5)	O(1)–C(1)	1.436(3)	O(1)–C(1)	1.444(3)
O(4)–C(4)	1.425(5)	O(2)–C(2)	1.445(3)	O(2)–C(2)	1.432(3)
C(1)–C(2)	1.511(5)	C(1)–C(2)	1.506(3)	C(1)–C(2)	1.509(4)
C(1)–C(1)#1	1.526(7)	C(1)–C(1)#2	1.520(5)	C(1)–C(1)#2	1.527(5)
C(3)–C(4)	1.508(6)				
C(3)–C(3)#2	1.520(8)				
<i>Bond angles</i>					
O(1)–Cu(1)–O(2)	79.23(11)	O(2)#1–Cu(1)–O(2)	86.18(10)	O(1)–Mn(1)–O(1)#1	147.77(11)
O(1)–Cu(1)–Cl(2)	90.99(8)	O(2)#1–Cu(1)–Cl(1)#1	170.98(5)	O(1)–Mn(1)–O(2)	72.56(7)
O(2)–Cu(1)–Cl(2)	169.65(9)	O(2)–Cu(1)–Cl(1)#1	90.74(5)	O(1)#1–Mn(1)–O(2)	84.76(7)
O(1)–Cu(1)–Cl(1)	160.64(9)	O(2)#1–Cu(1)–Cl(1)	90.74(5)	O(1)–Mn(1)–O(2)#1	84.76(7)
O(2)–Cu(1)–Cl(1)	90.04(8)	O(2)–Cu(1)–Cl(1)	170.98(5)	O(1)#1–Mn(1)–O(2)#1	72.56(7)
Cl(2)–Cu(1)–Cl(1)	100.30(4)	Cl(1)#1–Cu(1)–Cl(1)	93.52(3)	O(2)–Mn(1)–O(2)#1	90.40(10)
C(1)–O(1)–Cu(1)	116.8(2)	O(2)#1–Cu(1)–O(1)	84.05(7)	O(1)–Mn(1)–Cl(1)#1	102.00(5)
C(2)–O(2)–Cu(1)	112.1(2)	O(2)–Cu(1)–O(1)	73.12(6)	O(1)#1–Mn(1)–Cl(1)#1	100.07(6)
		Cl(1)#1–Cu(1)–O(1)	103.18(5)	O(2)–Mn(1)–Cl(1)#1	174.54(5)
		Cl(1)–Cu(1)–O(1)	98.14(5)	O(2)#1–Mn(1)–Cl(1)#1	88.63(5)
O(1)–C(1)–C(2)	107.0(3)	O(2)–Cu(1)–O(1)#1	84.05(7)	O(1)#1–Mn(1)–Cl(1)	102.00(5)
O(1)–C(1)–C(1)#1	108.0(4)	Cl(1)#1–Cu(1)–O(1)#1	98.14(5)	O(2)–Mn(1)–Cl(1)	88.63(5)
C(2)–C(1)–C(1)#1	112.4(4)	Cl(1)–Cu(1)–O(1)#1	103.18(5)	O(2)#1–Mn(1)–Cl(1)	174.54(5)
O(2)–C(2)–C(1)	105.3(3)	O(1)–Cu(1)–O(1)#1	148.70(9)	Cl(1)#1–Mn(1)–Cl(1)	92.82(4)
O(3)–C(3)–C(4)	111.3(3)	O(1)–C(1)–C(2)	107.11(19)	O(1)–C(1)–C(2)	107.1(2)
O(3)–C(3)–C(3)#2	109.5(4)	O(1)–C(1)–C(1)#2	108.2(2)	O(1)–C(1)–C(1)#2	108.1(3)
C(4)–C(3)–C(3)#2	112.8(4)	C(2)–C(1)–C(1)#2	112.6(3)	C(2)–C(1)–C(1)#2	112.4(3)
O(4)–C(4)–C(3)	112.1(3)	O(2)–C(2)–C(1)	106.61(19)	O(2)–C(2)–C(1)	106.7(2)

^aSymmetry transformations used to generate equivalent atoms. CuE(II): #1 *x* + 1, *−y* + 1, *−z*; #2 *−x*, *−y* + 1, *−z* − 1. CuE(I): #1 *−x*, *y*, *−z* + 1/2; #2 *−x*, *−y*, *−z*. MnE: #1 *−x* + 1, *y*, *−z* + 1/2; #2 *−x* + 1, *−y*, *−z*.

Table 3
Hydrogen bond lengths (Å) and angles (°) in CuE(II), CuE(I) and MnE^a

	D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
CuE(II)	O(1)–H(1)···O(4)	0.813(18)	1.81(2)	2.613(4)	167(3)
	O(2)–H(2)···O(3)#3	0.812(18)	1.84(2)	2.633(4)	165(3)
	O(3)–H(3)···Cl(1)#4	0.82	2.39	3.158(3)	155.3
	O(4)–H(4)···Cl(1)#5	0.82	2.40	3.158(3)	153.3
CuE(I)	O(1)–H(1)···Cl(1)#3	0.793(17)	2.403(19)	3.1894(19)	172(3)
	O(2)–H(2)···Cl(1)#4	0.783(17)	2.42(2)	3.1314(18)	152(3)
MnE	O(1)–H(1)···Cl(1)#3	0.802(17)	2.314(19)	3.111(2)	172(2)
	O(2)–H(2)···Cl(1)#4	0.806(17)	2.37(2)	3.1185(19)	155(3)

^aSymmetry transformations used to generate equivalent atoms. CuE(II): #1 $-x + 1, -y + 1, -z$; #2 $-x, -y + 1, -z - 1$; #3 $-x, -y + 1, -z$; #4 $x - 1, y, z - 1$; #5 $-x, -y, -z$. CuE(I): #1 $-x, y, -z + 1/2$; #2 $-x, -y, -z$; #3 $x, -y + 1, z - 1/2$; #4 $x + 1/2, -y + 1/2, z + 1/2$. MnE: #1 $-x + 1, y, -z + 1/2$; #2 $-x + 1, -y, -z$; #3 $-x + 1, -y + 1, -z$; #4 $-x + 1/2, -y + 1/2, -z$.

eters for hydrogen bonding systems for the three complexes are shown in Table 3.

3.1. Crystal structures of three transition metal chlorides–erythritol complexes

The structure and atom-numbering scheme of CuE(I) is shown in Fig. 1. Cu²⁺ coordinates with two chloride ions and four OH groups from two erythritol molecules. Two copper centers are linked by one erythritol molecule to form zigzag chain. A layer is thus formed by the interwoven zigzag chains via O(1)–H(1)···Cl(1)#3 hydrogen bonds (O···Cl distance is 3.1894 Å) (#1 $-x, y, -z + 1/2$; #2 $-x, -y, -z$; #3 $x, -y + 1, z - 1/2$; #4 $x + 1/2, -y + 1/2, z + 1/2$) (Fig. 1, the structure of CuE(I)). Because of the existence of C2 axis, there are only two types of OH groups in the complex. For CuE(II), Cu is in a planar square environment, each Cu²⁺ coordinates with two OH groups from an erythritol molecule and two chlorides. On the other hand, for the coordinated erythritol molecule, each alditol provides two hydroxyl groups to one Cu²⁺ and the other two hydroxyl groups to coordinate with another Cu²⁺. The dimers of [Cu₂Cl₄(C₄H₁₀O₄)] further form a [Cu₂Cl₄(C₄H₁₀O₄)]_∞ chain via secondary Cu···Cl bonds (dashed lines, 2.827 Å) (Fig. 2). The interesting feature of the complex is that both coordinated and free erythritol co-exist in the crystal. The coordinated chain is surrounded by the non-coordinated erythritol units via a series of hydrogen bonds listed in Table 3. Strong hydrogen bond with O···O distance of 2.613 and 2.633 Å are formed among the above hydrogen bonding system. Although the coordinated structures of CuE(I) is dramatically different from that of CuE(II), the chemical formula of the two complexes are the same, CuCl₂·C₄H₁₀O₄.

The crystal structures of metal ion-deprotonated erythritol complexes crystallized from alkaline solutions have been reported [15–18]; the crystal structure of Na₂[Cu(Eryt H₋₄)·Eryt·12H₂O] [15] contains fully

deprotonated erythritol and free non-deprotonated erythritol exists side by side. Cu²⁺ binds to four O⁻ from two deprotonated erythritol molecules. The two CuCl₂–erythritol complexes in neutral form reported here exhibit different coordination structures. The coordination bonds between copper and chloride co-occur with the Cu–O bonds in the complex between copper ions and neutral erythritol, while the Cu–Cl bonds are replaced by Cu–O bonds in copper deprotonated erythritol complex. On the other hand, hydrogen bonds, as an important form of weak bond interactions, are crucially important in various biological processes. Here, significant differences are found among CuE(I), CuE(II) and the copper deprotonated erythritol complex as far as the pattern of hydrogen bond networks is concerned.

Only one MnCl₂–erythritol complex has been obtained. The structure of MnCl₂·C₄H₁₀O₄ MnE is similar to CuE(I) (Fig. 3). Erythritol is coordinated to two Mn²⁺ ions, and Mn²⁺ coordinates to four hydroxyl groups of two erythritol molecules and two chloride ions. Layer formed by zigzag chains of [Mn(C₄H₁₀O₄)Cl₂] interwoven together and linked via the hydrogen bonds among different chains O(1)–H(1)···Cl(1)#3 (3.111 Å) and among different layers O(2)–H(2)···Cl(1)#4 (3.1185 Å).

Mn–O bond lengths are 2.2035 and 2.2472 Å. The differences of two bond lengths of Mn–O are smaller than two corresponding Cu–O bonds in CuE(I) (2.0382 and 2.3522 Å). Jahn–Teller effect that brought about significant aberrance of octahedron around copper ions in CuE(I) accounts for the phenomenon. Mn–Cl distances are 2.4505 Å and Cu–Cl distances are 2.2630 Å, which show a larger difference.

For CuE(II), Cu–O bond lengths are 1.984 and 1.997 Å, which are shorter than the corresponding bond lengths in CuE(I). Cu–Cl distances are 2.2324 and 2.2465 Å, which are also shorter than the distances in CuE(I) for that Cu²⁺ is 4-coordinated in CuE(II). As far as the conformations of erythritol in the complexes are

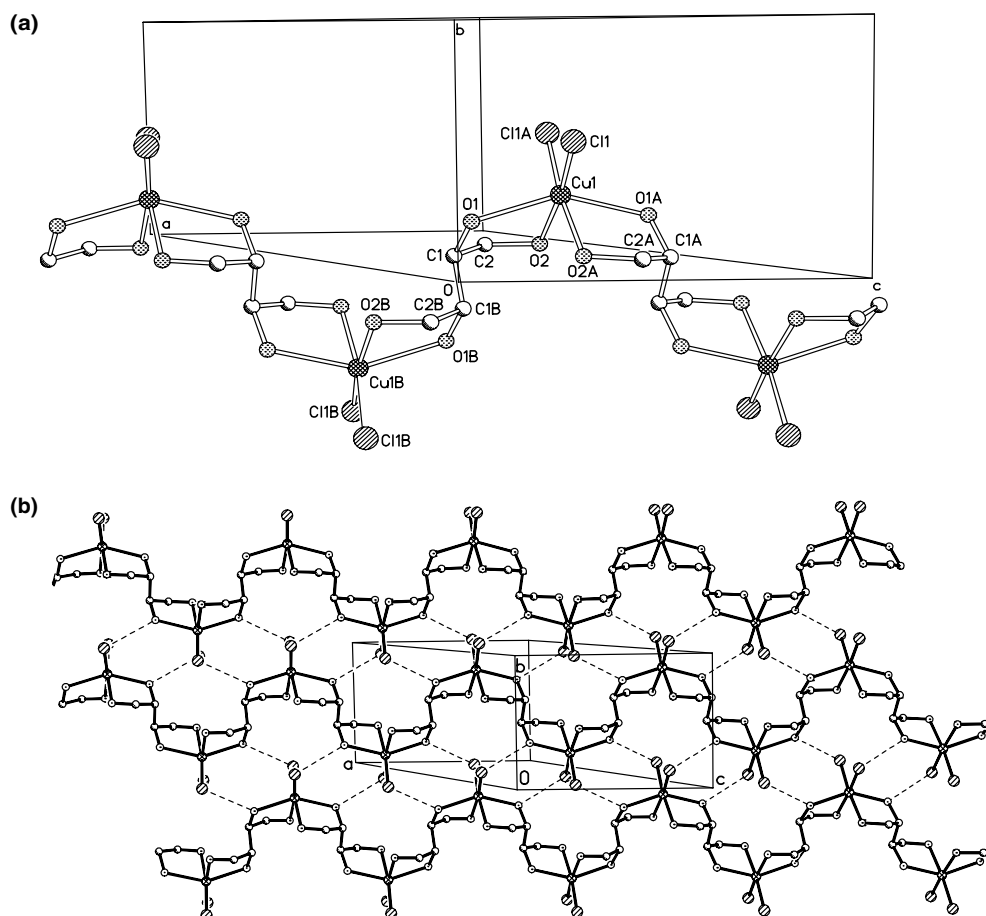


Fig. 1. The crystal structure of CuE(I). (a) Zigzag chain of $[\text{Cu}(\text{C}_4\text{H}_{10}\text{O}_4)\text{Cl}_2]$. (b) Layer formed by above chains interwoven together and linked through $\text{O}(1)\text{-H}(1)\cdots\text{Cl}(1)$ bonds between chains.

concerned, the four carbon atoms in erythritol are in a plane for CuE(I) and MnE. The geometric parameters of erythritol in the above three complexes are listed in Table 2, the conformation of erythritol in CuE(I) and MnE are similar. However, large differences on the conformation of erythritol can be found between CuE(I) and CuE(II). For example, the changes of bond lengths and angles of erythritol are different: O–C, C–C distances and O–C–C, C–C–C#2 are close for CuE(I) and MnE: O–C–C bond angles are from 106.61° to 108.2° , C–C–C angles are from 112.4° to 112.6° , which have differences with erythritol itself [32]; for CuE(II), O–C distances are from 1.425 to 1.453 Å, C–C distances are from 1.508 to 1.526 Å, O–C–C angles are from 105.3° to 112.1° , C(2)–C(1)–C(1)#1 are from 112.4° to 112.8° , which have larger differences with CuE(I) and MnE for that CuE(II) has different structure.

3.2. FT-IR spectra of transition metal chlorides–erythritol complexes

The FT-IR spectra of CuE(I), CuE(II), MnE, CoE, NiE and ZnE are shown in Fig. 4. No H–O–H defor-

mational band of H_2O is found between 1700 cm^{-1} and 1600 cm^{-1} in the FT-IR spectra of CuE(I) and CuE(II), indicating that water is not involved in the two complexes. The $\nu(\text{OH})$ bands of CuE(I) split into two peaks, which are consistent with two types of hydroxyl groups in the structure. For CuE(II), a broad $\nu(\text{OH})$ band around $\sim 3000\text{ cm}^{-1}$ occurs with two OH stretching bands locating at higher frequency. Strong hydrogen bonds with O \cdots O distance of 2.613 and 2.633 Å result in the OH stretching band around 3000 cm^{-1} . In comparison with CuE(I), the presence of two types of erythritol molecules in the structure of CuE(II) results in more complex bands between 1500 and 650 cm^{-1} in FT-IR spectra.

The IR spectra of MnCl_2 , CoCl_2 , NiCl_2 , ZnCl_2 –erythritol (MnE, CoE, NiE and ZnE) in the 1500 – 650 cm^{-1} region are similar to CuE(I) in band positions and relative intensities, which indicate that Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} would form the same coordination structures with erythritol just like CuE(I) according to the previous results that similar IR spectra correspond to analogous structures (Fig. 4) [25–30]. But the bands in the 1500 – 650 cm^{-1} region especially those located at

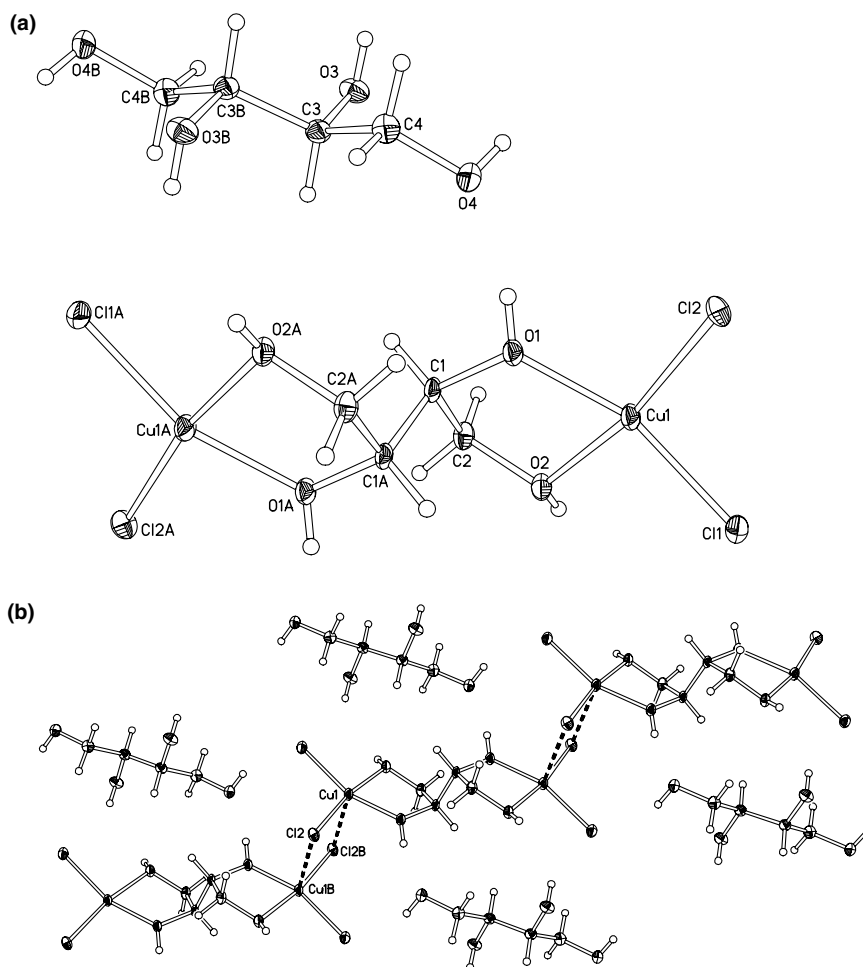


Fig. 2. The crystal structure of CuE(II). (a) The dimer unit of $[\text{Cu}_2\text{Cl}_4(\text{C}_4\text{H}_{10}\text{O}_4)]$ and one non-coordinated $\text{C}_4\text{H}_{10}\text{O}_4$ unit. (b) The dimers of $[\text{Cu}_2\text{Cl}_4(\text{C}_4\text{H}_{10}\text{O}_4)]$ further form a $[\text{Cu}_2\text{Cl}_4(\text{C}_4\text{H}_{10}\text{O}_4)]_\infty$ chain via secondary $\text{Cu}\cdots\text{Cl}$ bonds (dashed lines, 2.827 Å), together with the surrounding non-coordinated $\text{C}_4\text{H}_{10}\text{O}_4$ units.

~ 1256 , 1239 and ~ 1410 cm^{-1} for five transition metal complexes have minor disparity in band positions and relative intensities, which reflect the conformations of erythritol have some differences in the five structures. It is the same that $\nu(\text{OH})$ split into two peaks for CuE(I), MnE and ZnE, but the $\nu(\text{OH})$ positions are different: 3390, 3321 cm^{-1} for CuE(I), 3321, 3236 cm^{-1} for MnE and 3347, 3276 cm^{-1} for ZnE.

3.3. Magnetic properties of two copper chlorides–erythritol complexes

The variable-temperature magnetic susceptibility χ_m for CuE(I) and CuE(II) is shown in Fig. 5a. The χ_m increases as the temperature is lowered, reaching a maximum at ca. 12 and 8.2 K, respectively, indicative of antiferromagnetic interaction between Cu(II) ions. The Neel temperatures, T_N , of CuE(I) and CuE(II) were determined as the sharp peak of $d(\chi_m T)/dT$ at 7 and 5 K, respectively [33,34]. The magnetic susceptibility

above 50 K obeys the Curie–Weiss law ($\chi_m = C/(T\theta)$) well with a Weiss constant, $\theta = -7.5(1)$ K, and a Curie constant, $C = 0.440(6)$ $\text{cm}^3 \text{mol}^{-1} \text{K}$ for CuE(I), and $\theta = -14(1)$ K, $C = 0.474(8)$ $\text{cm}^3 \text{mol}^{-1} \text{K}$ for CuE(II). The C values correspond to a spin-only Cu(II) ions with $S = 1/2$ and $g = 2.17$ for CuE(I), and $g = 2.25$ for CuE(II).

The field dependence of the magnetization at 1.85 K for CuE(I) or 1.79 K for CuE(II) is shown in Fig. 5b. For CuE(I), the magnetization increases very slowly with increasing field due to antiferromagnetic ordering, and then increases quickly for a transition from an antiferromagnet to a spin-flop state at a transition field around 60 kOe. The magnetization is only 0.114 N at 70 kOe, far from the saturation value of 1.0 $N\beta$ for a spin only Cu(II) ion, suggesting an antiferromagnetic ordering again. In contrast to CuE(I), the field dependence of the magnetization for CuE(II) also shows a linear increase but with a more slow speed, and the transition to a spin flop state needs more large field (>70 kOe). The

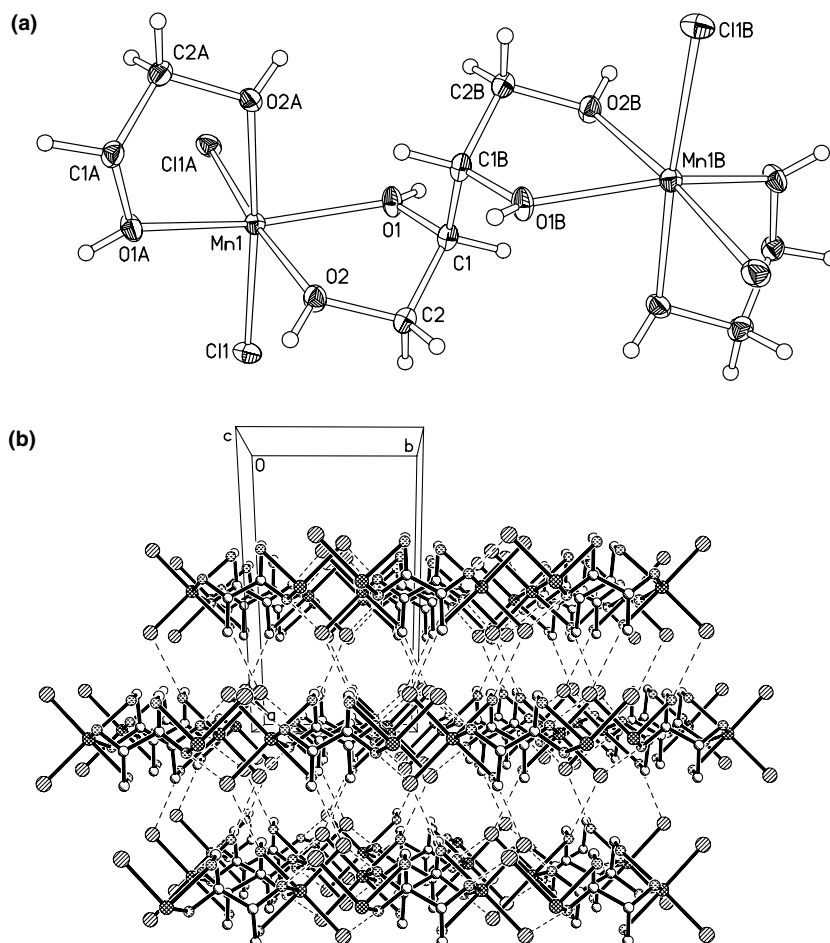


Fig. 3. The crystal structure of MnE. (a) Two Mn centers linked by one $C_4H_{10}O_4$. (b) Packing of the layers down the c axis, between layers are $O(2)–H(2) \cdots Cl(1)$ hydrogen bonds.

magnetization under 70 kOe at 1.79 K is only $0.093 N\beta$, also far from the saturation value of $1.0 N\beta$ expected for a spin only Cu(II) ion, being another evidence supporting the antiferromagnetic ordering of CuE(II).

Based on the structural data, for CuE(I), the Cu(II) ions are bridged by E (5.637 Å) and by hydrogen bond (5.740 Å) to form a quadratic layer, and the layers are connected further by rich interlayer hydrogen bonds with 6.9–8.5 Å separations. For CuE(II), Cu(II) ions are bridged by Cl (3.683, 4.157 Å) and by E (6.259 and 6.460 Å) to form a chain, the chains are connected further by rich hydrogen bonds to result a three-dimensional network with interchain separations 7.3–8.5 Å. The magnitude of antiferromagnetic interactions between Cu(II) ions was not obtained, since no suitable model available for magnetic analysis of such complicated hydrogen bonded 3D networks.

Although the hydrogen bonding between layers or chains in CuE(I) and CuE(II) could have a crucial contribution to the magnetic ordering, the antiferromagnets possess obviously low-dimensional characters,

as the ratio of $T_N/T_{Z_{max}}$, 0.58 and 0.61 for CuE(I) and CuE(II), respectively, is quite low.

Erythritol is an open-chain molecule. Its structural characteristic makes it possible to use two hydroxyl groups to coordinate to one metal ion and the other two to another metal ion. A chained structure is thus formed. The OH groups of erythritol act as ligand to coordinate to metal ions on one hand, one the other hand, OH groups form hydrogen bonds network that link molecular chain and molecular layer together to build three-dimensional structures. The study of the coordination modes and stability of the complexes in solution indicated that the interaction between metal ions and erythritol in solution is weak [35]. The results of alkaline earth ion, transition metal ions and lanthanide ion–erythritol complexes [30] indicate that erythritol may be two bidentate ligands, non-coordinated molecule or as three hydroxyl donor.

The above results provide us clear evidences to support that versatile structural features may be observed in metal carbohydrate complexes. This implies complex

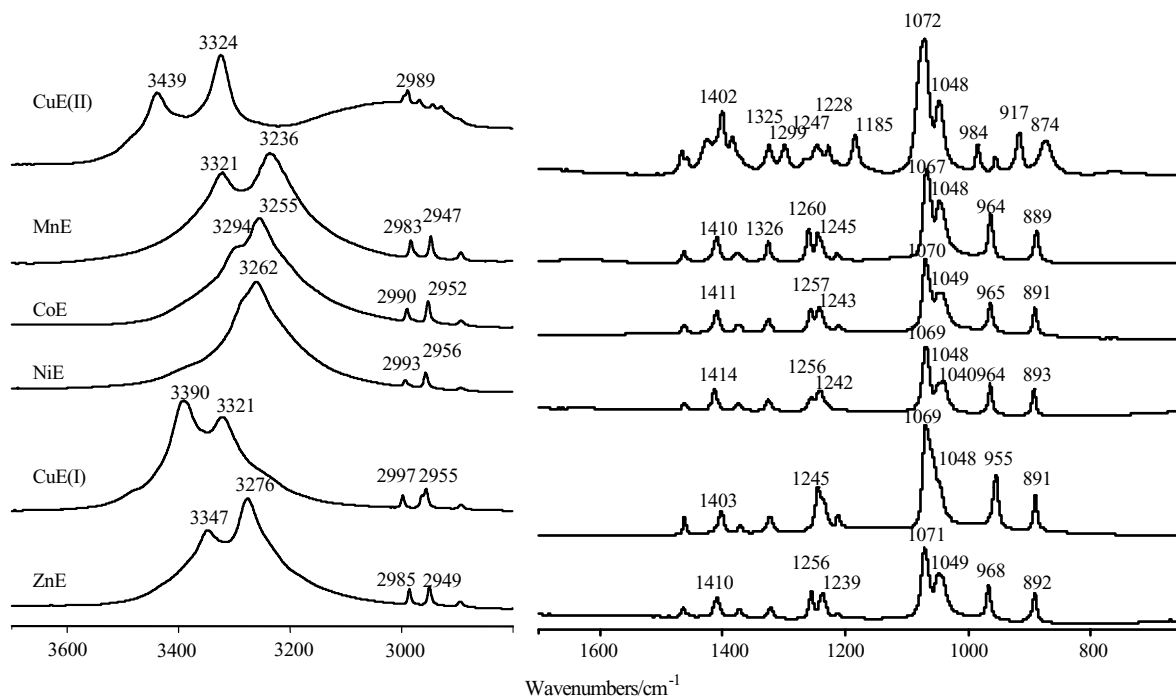


Fig. 4. The IR spectra of transition metal ions-erythritol complexes in the 3700–2800 and 1700–650 cm⁻¹ regions.

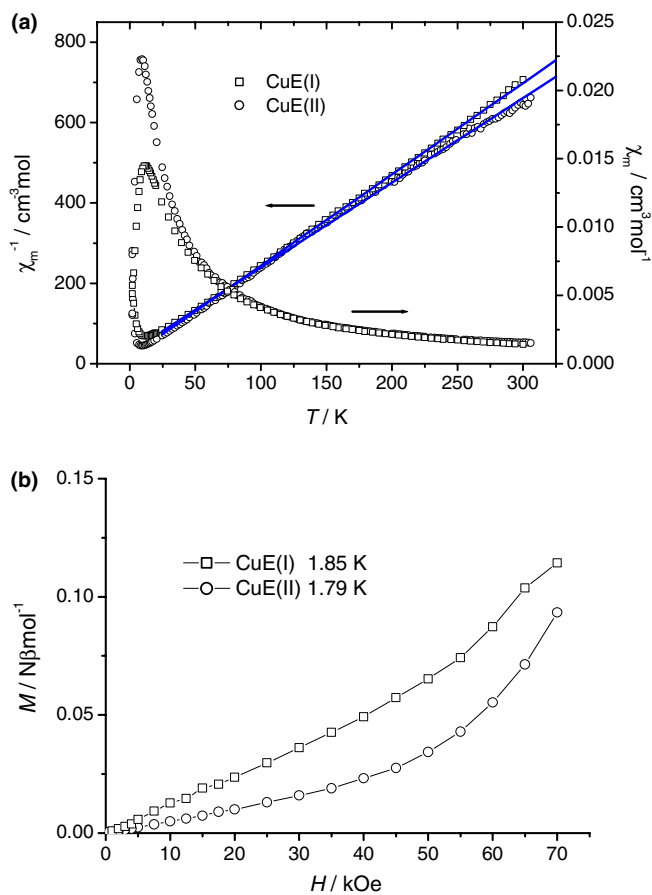


Fig. 5. (a) Temperature dependence of the magnetic susceptibility for crystalline sample CuE(I) and CuE(II). (b) Field dependence of magnetization for CuE(I) and CuE(II).

and diverse structures are expected in the supra-molecular complexes between metal ion and bio-molecules with residue having hydroxyl groups. The variety of coordination feature may serve as information storage and transmission in biological activities.

In conclusion, we have shown that three metal ion–erythritol complexes serve as examples of hydroxyl group coordination towards metal ions. Coordination structure, as well as hydrogen bonding network play an important role to determine the structural features of the complexes. In comparison with other kind of coordination complexes, interaction between metal ions and neutral carbohydrate is quite weak and the chemistry of metal–neutral saccharide complexes is still in developing stage. The investigation presented here contributes to a deeper understanding of the coordination modes of hydroxyl groups to transition metal ions.

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