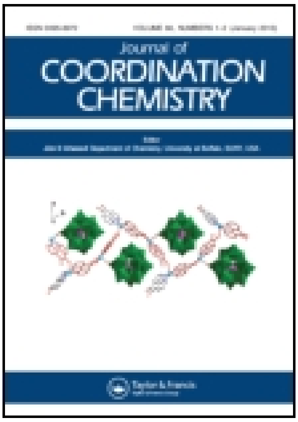
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:27
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Syntheses and characterizations of zinc(II) and copper(II) complexes with reduced Schiff base derived from salicylaldehyde and D,L-selenomethionine

Ling-Yun Wang [a] , Xue-Guang Ran [a] [b] , De-Rong Cao [a] & Jie Hao [b]
[a] School of Chemistry and Chemical Engineering, South China University of Technology , Guangzhou 510640 , China
[b] Institute of Animal Science, Guangdong Academy of Agricultural Sciences , Guangzhou 510640 , China
Published online: 27 Sep 2011.

To cite this article: Ling-Yun Wang , Xue-Guang Ran , De-Rong Cao & Jie Hao (2011) Syntheses and characterizations of zinc(II) and copper(II) complexes with reduced Schiff base derived from salicylaldehyde and D,L-selenomethionine, Journal of Coordination Chemistry, 64:18, 3245-3254, DOI: 10.1080/00958972.2011.618225

To link to this article: http://dx.doi.org/10.1080/00958972.2011.618225

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry
Vol. 64, No. 18, 20 September 2011, 3245–3254

Taylor & Francis
Taylor & Francis Group

Syntheses and characterizations of zinc(II) and copper(II) complexes with reduced Schiff base derived from salicylaldehyde and D,L-selenomethionine

LING-YUN WANG*†, XUE-GUANG RAN†‡, DE-RONG CAO† and JIE HAO‡

†School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China
‡Institute of Animal Science, Guangdong Academy of Agricultural Sciences, Guangzhou 510640, China

(*Received 13 May 2011; in final form 15 August 2011*)

New zinc(II) and copper(II) complexes with a reduced Schiff-base ligand derived from D,L-selenomethionine and salicylaldehyde have been synthesized and characterized by elemental analysis, magnetic susceptibility, IR, and NMR measurements. The single-crystal X-ray structure of the Cu(II) complex reveals that this complex is a carboxylate-bridged dimer of dinuclear copper(II) subunits and all metal centers are five-coordinate with O_4N donor sets in distorted square-pyramidal geometries. The Cu(II) complex consists of a 1-D coordination polymer.

Keywords: Reduced Schiff base; D,L-Selenomethionine; Metal complexes; Single-crystal X-ray structure

1. Introduction

Significant progress for transition metal complexes containing Schiff-base ligands has been achieved due to their applications including biological, clinical, analytical, and industrial in addition to their important roles in catalysis and organic synthesis [1–7]. However, problems of ligand instability for Schiff bases are often encountered [8–13]. These problems can be overcome by reduction of the C=N bond of the Schiff base to give an amine, which is expected to generate much more interesting coordination chemistry due to the flexible backbone of the reduced Schiff base. Further, in addition to their potential hydrogen-bond donor–acceptor functionalities, these ligands form flexible five- and six-membered rings upon complexation; the resulting metal complexes can serve as models for intermediate species in biological racemization and transamination reactions [14–19]. Structural studies on metal complexes of reduced Schiff-base ligands, derived from various amino acids and salicylaldehyde, are well

---

*Corresponding author. Email: lingyun_wr@yahoo.com.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2011.618225

documented [20–25]. On the other hand, hydrogen on the secondary amine of reduced Schiff base is expected to be significantly acidic due to metal ion coordination to the amine. Hence this N–H proton can participate in intermolecular hydrogen-bonding interactions with the carboxylate oxygen in the amino acid side arm, required for supramolecular self-assembly of the building blocks to generate interesting 2-D and 3-D coordination networks [26].

Selenium may substitute for sulfur in methionine to form selenomethionine. Selenomethionine is prepared for a variety of biological activities, predominant antioxidant, selenium supplementation, chemopreventive agent for different types of cancer, and many other diseases. Palladium(II) and platinum(II) dihalide complexes of selenomethionine have been assessed for their cytotoxicities [27]; however, there are no reports on preparation of selenomethionine reduced Schiff base and its metal complexes until now.

Recently, we reported syntheses, characterizations, and biological studies of metal complexes with Schiff base derived from aromatic aldehydes and D,L-selenomethionine [8, 9]. Instability of the D,L-selenomethionine Schiff base was encountered, which was resolved by making an equimolar metal salt of the Schiff-base ligand. The synthesis of metal complexes was carried out by one-pot reaction. As a part of extensive biological role of selenomethionine and its transition metal complexes, herein, we have begun to investigate the syntheses and characterizations of zinc(II) and copper(II) complexes with reduced Schiff base (H_2Sal-SeMet) derived from salicylaldehyde and D,L-selenomethionine. The single-crystal X-ray structure of Cu(II) complex is studied, possessing polynuclear aggregate formed by a selenomethionine reduced Schiff-base ligand.

2. Experimental

All chemicals and solvents were commercially available and used as received. D,L-selenomethionine was synthesized according to the previous method [28].

2.1. *Analytical and physical measurements*

The IR spectra were recorded using a Perkin Elmer FT-IR spectrophotometer Spectrum-one Model with KBr discs from 4000 to 400 cm^{-1}. Elemental analyses of C, H, and N were determined with an Elementar Vario EL. Metal contents were estimated using standard methods. NMR spectra were obtained on a Bruker AV-400 and TMS was used as an internal standard. Magnetic measurements were carried out on solid complexes using Gouy's method with a Sherwood Scientific Magnetic balance MSB-1 at room temperature; diamagnetic corrections were estimated from Pascal's constants and magnetic data were corrected for diamagnetic contributions of the sample holder. Conductivity measurements were made on freshly prepared 10^{-3} mol L^{-1} solutions in DMF at room temperature with a Coronation digital conductivity meter.

2.2. Preparation of H_2Sal-SeMet

D,L-Selenomethionine (0.196 g, 1 mmol) in 4 mL of absolute methanol containing $LiOH \cdot H_2O$ (0.042 g, 1 mmol) was added to a solution of salicylaldehyde (0.122 g, 1 mmol) in 2 mL of absolute methanol. The mixture was stirred overnight at room temperature. The Schiff base that formed was reduced with an excess of sodium borohydride (0.46 g, 12 mmol) stirring for another 3 h. The resulting solution was reduced *in vacuo* using a rotary evaporator to remove methanol, giving white solid. The solid was dissolved with 10 mL water and acidified with concentrated HCl to a pH of 4. The product was filtered, washed with absolute methanol three times, and further dried under vacuum at 50°C to give 0.25 g white solid in 82.8% yield. Elem. Anal. Found (%): C, 47.56; H, 5.84; N, 4.59. Calcd for $C_{12}H_{17}NO_3Se$ (%): C, 47.69; H, 5.67; N, 4.63. ^{1}H NMR (CF_3COOD-*d*, δ): 2.07 (3H, s, –SeCH_3), 2.50–2.63 (2H, m, –CHCH_2–), 2.82 (2H, t, MeSeCH_2–), 4.46 (1H, t, –C*H*–), 4.61 (2H, dd, $J = 8$ Hz, –CH_2ph), 7.01 (1H, d, $J = 4$ Hz, Ar–*H*), 7.06 (1H, t, Ar–*H*), 7.29 (1H, d, $J = 8$ Hz, Ar–*H*), 7.42 (1H, t, Ar–*H*).

2.3. General procedure for the preparation of metal complexes

H_2Sal-SeMet (0.15 g, 0.2 mmol) and KOH (0.052 g, 0.4 mmol) in 10 mL methanol were stirred for 1 h at room temperature to give transparent solution. A solution of $Zn(OAc)_2 \cdot H_2O$ or $Cu(OAc)_2 \cdot H_2O$ (0.2 mmol) dissolved in EtOH : H_2O (1 : 1 v/v, 10 mL) was added dropwise. The mixture was stirred for 1 h and the colored precipitate was filtered, washed with water, ethanol and ether, and dried *in vacuo*. The dried metal complexes were characterized by elemental analysis, IR, and NMR measurements. The filtrate was left in air at room temperature. After several weeks, green well-shaped crystals of Cu(II) complex suitable for X-ray diffraction were obtained.

Zn(II) complex: pale solid, yield: 61%. Elem. Anal. Found (%): C, 39.62; H, 4.34; N, 3.68. Calcd for $C_{12}H_{15}NO_3SeZn$ (%): C, 39.42; H, 4.14; N, 3.83. ^{1}H NMR (DMSO-d_6, δ): 1.93 (3H, s, –SeCH_3), 2.61–2.66 (2H, m, –CHCH_2–), 2.92 (2H, t, MeSeCH_2–), 3.79 (1H, t, –C*H*–), 3.94 (2H, s, –CH_2ph), 6.58 (1H, s, ph–*H*), 7.04 (2H, m, ph–*H*), 7.39 (1H, ph–*H*). ^{13}C NMR (DMSO-d_6, δ): 175.91, 165.8, 164.5, 161.9, 160.9, 155.8, 152.0, 92.3, 75.8, 60.5, 36.3, 22.3, 5.8.

Cu(II) complex: green solid, yield: 65%. Elem. Anal. Found (%): C, 39.81; H, 4.29; N, 3.64. Calcd for $C_{51}H_{70}N_4O_{14}Se_4Cu_4$ (%): C, 39.95; H, 4.60; N, 3.65.

2.4. Crystallographic studies

Single crystals of suitable quality for X-ray diffraction of the Cu(II) complex were grown in MeOH/EtOH mixture. The data were collected in the presence of mother liquor taken in a capillary. The X-ray intensity data were measured at 100 K on a Bruker-Nonius SMART APEX CCD diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). The detector was placed at 6.0 cm from the crystal. The data were reduced in SAINTPLUS, and empirical absorption correction was applied using the SADABS package. Copper was located using direct methods, and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. The structures were refined using the full matrix least-squares procedure on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions.

3. Results and discussion

3.1. *Synthesis*

To overcome general problems of ligand instability for amino acid Schiff bases, and to introduce greater ligand flexibility, an *in situ* reduction was carried out on the salicylaldehyde and D,L-selenomethionine mixture. The conditions employed gave satisfactory elemental analyses in good agreement with those calculated for the suggested formula H_2Sal-SeMet.

Cu(II) and Zn(II) complexes have been synthesized by complexation of metal salts with H_2Sal-SeMet in the presence of KOH according to procedures described in section 2. The elemental analyses obtained are in good agreement with those calculated for the suggested formulae of metal complexes. The analytical data show that the metal to ligand ratio is 1 : 1 in both complexes.

The molar conductance values in DMF for Zn(II) and Cu(II) complexes are 12.58 and 13.69 $\mathrm{S\ cm^2\ mol^{-1}}$, respectively. The relatively low values indicate non-electrolytic nature of these complexes. The bivalent metal is accommodated by the carboxylate and deprotonated phenolate.

The effective magnetic moment at room temperature for Cu(II) complex is 1.83 μ_B, indicating an $S = 1/2$ spin state and hence the +2 oxidation state of the metal ion to form electrically non-conducting complex.

3.2. *FT-IR and ^{1}H NMR characterizations*

The IR spectra of both complexes show sharp bands at ~3260 $\mathrm{cm^{-1}}$ corresponding to the N–H stretch, indicating reduction of the C = N moiety. Several weak bands at 2864–3100 $\mathrm{cm^{-1}}$ are assigned to aliphatic and aromatic C–H stretches. Strong bands at 1597–1580 and 1425–1456 $\mathrm{cm^{-1}}$ are due to the $\nu(-COO^-)$.

The ^{1}H NMR spectrum of the diamagnetic Zn(II) complex is compared with that of H_2Sal-SeMet. All protons are in their expected regions and numbers of protons calculated from the integration curves agree with those obtained from the C, H, and N elemental analyses. The benzyl protons of H_2Sal-SeMet resonate at 4.61 ppm. On complexation, this signal is shifted to 3.94 ppm, indicating involvement of imine in chelation. The signals at 7.01–7.42 ppm in the ^{1}H NMR spectrum of H_2Sal-SeMet are assigned to phenyl protons and are between 6.58 and 7.39 ppm for Zn(II) complex. The shift of the methylidyne proton in Zn(II) complex (3.79 ppm), which appears at 4.46 ppm in H_2Sal-SeMet, supports involvement of imine and carboxylate in coordination with the metal. Shifts of methylene protons from 2.50–2.63 ppm for H_2Sal-SeMet to 2.61–2.66 ppm for Zn(II) complex are observed. Methylene selenium at 2.92 ppm and methyl protons at 1.94 ppm are almost unaffected by complexation, suggesting no coordination of $-SeCH_3$ with metal.

3.3. *X-ray crystallographic analysis*

The Cu(II) complex afforded green single crystals suitable for single-crystal X-ray studies. The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are given in table 1.

Table 1. Crystal data and structure refinement parameters for [Cu_4(Sal-SeMet)$_4 \cdot$ MeOH $\cdot$ EtOH].

[Cu_4(Sal-SeMet)$_4 \cdot$ MeOH $\cdot$ EtOH]	
Chemical formula	$C_{51}H_{70}N_4O_{14}Se_4Cu_4$
Formula weight	1533.11
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions (Å, °)	
a	28.9037(14)
b	8.4866(4)
c	24.9187(12)
α	90
β	112.5740(10)
γ	90
Volume (Å^3), Z	5644.1(5), 4
Crystal size (mm^3)	$0.46 \times 0.41 \times 0.22$
Calculated density (Mg m^{-3})	1.804
Absorption coefficient (mm^{-1})	4.133
F(000)	3072
Max. and min. transmission	0.4633 and 0.2522
Refinement method	Full-matrix least-squares on F^2
θ range for data collection (°)	1.53–26.00
Index range	$-32 \leq h \leq 35$; $-10 \leq k \leq 10$; $-30 \leq l \leq 30$
Data/restraints/parameters	11,005/192/914
Temperature (K)	100
Goodness-of-fit on F^2	1.089
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0678$, $wR_2 = 0.1716$
R indices (all data)	$R_1 = 0.0901$, $wR_2 = 0.1866$

The single-crystal X-ray crystallographic analysis of Cu(II) complex reveals a tetranuclear structure, [Cu_4(Sal-SeMet)$_4 \cdot$ MeOH $\cdot$ EtOH], which consists of two dinuclear units connected by carboxylate bridges. In each dinuclear unit, the two copper centers are connected through two phenolate oxygen bridges to form a distorted Cu_2O_2 square plane. An ORTEP diagram of [Cu_4(Sal-SeMet)$_4 \cdot$ MeOH $\cdot$ EtOH] is shown in figure 1. Selected bond lengths and angles are given in table 2.

In tetranuclear Cu(II) complex, four reduced Schiff-base ligands are tridentate through imine nitrogen, phenolate oxygen, and carboxylate oxygen. Cu(1) and Cu(2) are distorted square-pyramidal geometries, coordinated by the imine nitrogen, two phenolate oxygen atoms, and carboxylate oxygen, while ethanol and methanol are coordinated at the apical position of Cu(1) and Cu(2), respectively. Ethanol and methanol are *anti* probably due to the bulkiness of the axial substitution. Cu(1) and Cu(2) are doubly bridged by two phenolates of two deprotonated H_2Sal-SeMet ligands with a Cu(1)$\cdots$Cu(2) distance of 3.015 Å. The Cu–O bond lengths due to the coordination of Cu(1) and Cu(2) to the bridging phenolate and carboxylate oxygen are 1.936–1.988 and 1.922–1.934 Å, respectively, while the Cu–N bond lengths are 1.960–1.999 Å. The Cu–O bond lengths due to the coordination of Cu(1) and Cu(2) to ethanol and methanol are Cu(1)–O(13) 2.311 Å and Cu(2)–O(14) 2.490 Å, respectively.

Cu(3) and Cu(4) are also doubly bridged by two phenolates of the other two deprotonated ligands with a Cu(3) $\cdots$ Cu(4) distance of 2.969 Å. The bond lengths of Cu(1) $\cdots$ Cu(2) and Cu(3) $\cdots$ Cu(4) are in agreement with that reported for complexes with reduced Schiff bases displaying the phenoxo-bridged dinuclear Cu(II) centers with

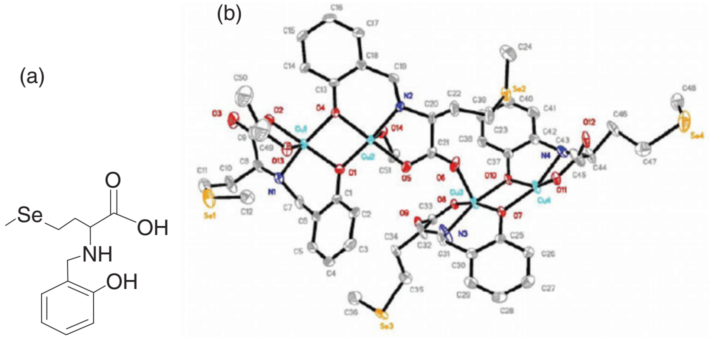


Figure 1. (a) Structural diagram of H_2Sal-SeMet and (b) an ORTEP diagram of [Cu_4(Sal-SeMet)$_4$ · MeOH · EtOH]; all hydrogen atoms are omitted for clarity.

Table 2. Selected bond distances (Å) and angles (°) for [Cu_4(Sal-SeMet)$_4$ · MeOH · EtOH].

Cu(1)–O(1)	1.945(4)	Cu(1)–O(2)	1.922(5)
Cu(1)–O(4)	1.988(4)	Cu(1)–O(13)	2.311(5)
Cu(1)–N(1)	1.999(5)	Cu(2)–O(1)	1.936(4)
Cu(2)–O(4)	1.950(4)	Cu(2)–O(5)	1.939(4)
Cu(2)–O(14)	2.490(5)	Cu(2)–N(2)	1.960(5)
Cu(3)–O(6)	2.244(5)	Cu(3)–O(7)	1.961(4)
Cu(3)–O(8)	1.959(4)	Cu(3)–O(10)	1.945(4)
Cu(3)–N(3)	1.967(6)	Cu(4)–O(7)	1.947(4)
Cu(4)–O(10)	1.975(4)	Cu(4)-O(11)	1.940(4)
Cu(4)–N(4)	2.209(13)	Cu(4)–O(12B)	2.187(15)
Cu(1)–Cu(2)	3.015(10)	Cu(3)–Cu(4)	2.969(10)
O(2)–Cu(1)–O(1)	172.8(2)	O(2)–Cu(1)–O(4)	103.8(1)
O(1)–Cu(1)–O(4)	78.4(1)	O(2)–Cu(1)–N(1)	83.2(2)
O(1)–Cu(1)–N(1)	93.6(2)	O(4)–Cu(1)–N(1)	168.9(2)
O(2)–Cu(1)–O(13)	97.0(2)	O(1)–Cu(1)–O(13)	89.7(1)
N(1)–Cu(1)–O(13)	96.4(2)	O(1)–Cu(2)–O(5)	98.3(1)
O(1)–Cu(2)–O(4)	79.5(1)	O(5)–Cu(2)–O(4)	172.1(2)
O(1)–Cu(2)–N(2)	175.6(2)	O(5)–Cu(2)–N(2)	85.9(2)
O(4)–Cu(2)–N(2)	96.4(1)	O(1)–Cu(2)–O(14)	90.7(1)
O(5)–Cu(2)–O(14)	87.4(1)	O(4)–Cu(2)–O(14)	84.9(1)
N(2)–Cu(2)–O(14)	90.8(1)	O(10)–Cu(3)–O(8)	98.8(1)
O(10)–Cu(3)–O(7)	81.4(1)	O(8)–Cu(3)–O(7)	163.1(1)
O(10)–Cu(3)–N(3)	167.4(3)	O(8)–Cu(3)–N(3)	82.9(2)
O(7)–Cu(3)–N(3)	93.3(2)	O(10)–Cu(3)–O(6)	90.9(1)
O(8)–Cu(3)–O(6)	108.6(1)	O(7)–Cu(3)–O(6)	88.2(1)
N(3)–Cu(3)–O(6)	100.4(3)	O(11)–Cu(4)–O(7)	99.4(1)
O(11)–Cu(4)–O(10)	154.2(2)	O(7)–Cu(4)–O(10)	81.0(1)
O(11)–Cu(4)–N(4)	80.0(4)	O(7)–Cu(4)–N(4)	162.2(5)
O(10)–Cu(4)–N(4)	91.8(4)	N(4B)–Cu(4)–N(4)	21.1(4)

Cu $\cdots$ Cu distance of about 3 Å [29, 30]. At Cu(3), the basal plane of the square pyramid is occupied by three oxygen atoms, one each from phenolate [Cu(3)–O(7), 1.961(4) Å], carboxylate [Cu(3)–O(8), 1.959(4) Å], and another bridged phenolate [Cu(3)–O(10), 1.945 Å] and nitrogen [Cu(3)–N(3), 1.967 Å] from the imine group. The apical site of the Cu(3) center is occupied by the carbonyl oxygen [Cu(3)–O(6), 2.244 Å] of the carboxylate from a neighboring ligand coordinated with Cu(2). Cu(4) also has distorted square-pyramidal geometry with bridging phenolate oxygen atoms (O10 and O7), one carboxylate oxygen (O11), and one nitrogen (N4) from imine group. The axial coordination of

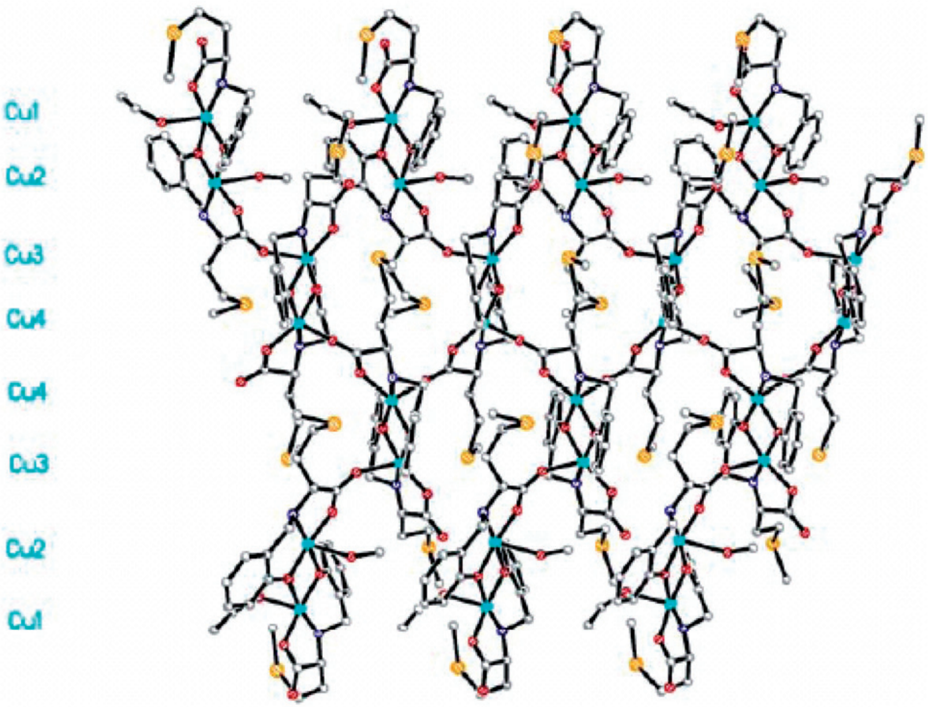


Figure 2. 1-D coordination polymer of [Cu_4(Sal-SeMet)$_4$ · MeOH · EtOH]; hydrogen atoms are omitted for clarity.

Cu(4) is provided by carbonyl oxygen (O12B) from another tetranuclear unit. Thus, Cu(II) complex contains four unique Cu centers possessing square-pyramidal geometries, different from Zn(II), Ni(II), and Cd(II) complexes with reduced amino-acid Schiff base derived from condensation of N-(2-hydroxybenzaldehyde) and L-histidine showing mononuclear structure and six-coordination with O_2N_4 donor sets in slightly distorted octahedra [24]. The Cu–O bond lengths due to coordination of Cu(4) to the bridging phenolate and carboxylate oxygen atoms are 1.947, 1.975, and 1.940 Å, respectively, while the Cu(4)–N(4) bond length is 2.209 Å. However, due to the Jahn–Teller effect, the distance of the Cu(4)–O(12B) is elongated to 2.187 Å, larger than the mean lengths of Cu–O in the equatorial plane [31, 32]. Connected by coordination of carbonyl oxygen of the carboxylate (O12B) with Cu(4), the tetranuclear unit forms a 1-D coordination polymer in the overall structure, as shown in figure 2. Similar results were also reported for Cu(II) complex with reduced Schiff base derived from N-(2-hydroxybenzaldehyde) and L-methionine with 1-D coordination polymers with the binuclear copper fragments as building blocks [25]. There are other reports on Cu(II) complexes to form 1-D polymeric chain structures [33–36]. For example, the hexanuclear unit is formed by assembly of two tetranuclear subunits *via* two copper ions coordinating simultaneously to two N,N′-2,6-pyridinedicarboxyl)-disalicylhydrazide ligands, and the 1-D chain structure of the compound is constructed by connection of hexanuclear units *via* bridging phenolic oxygens of ligands [34].

Generally, the Cu–N(imine) (1.960–2.209 Å) and the Cu–O(phenolate, carboxylate) (1.922–1.988 Å) bond lengths are comparable with bond lengths observed for copper(II)

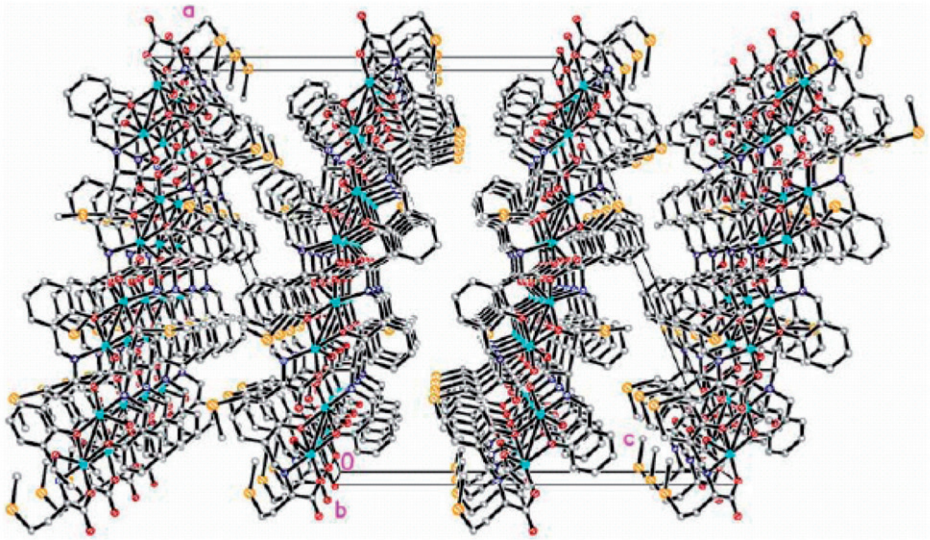


Figure 3. Packing diagram of [Cu_4(Sal-SeMet)$_4$ · MeOH · EtOH].

complexes containing the same coordinating atoms [37, 38]. Cu centers are not coordinated by selenium, which is different from coordination behavior of dichloro(*O*-methylselenomethionine)platinum(II) coordinating through two *cis* chlorides and selenium and nitrogen atoms to form a square plane [27].

The *trans* O(1)–Cu(1)–O(2), O(4)–Cu(1)–N(1), O(4)–Cu(2)–O(5), and O(1)–Cu(2)–N(2) angles are 168.9–175.6° in the Cu(1)Cu(2) dinuclear unit, while *trans* O(7)–Cu(3)–O(8), O(10)–Cu(3)–N(3), O(10)–Cu(4)–O(11), and O(7)–Cu(4)–N(4) angles are 154.2–167.4° in a Cu(3)Cu(4) dinuclear unit. Cu(1)Cu(2)O(1)O(4) and Cu(3)Cu(4)O(7)O(10) have rhomboidal geometries. The core bond angles of O(4)–Cu(1)–O(1) and O(10)–Cu(3)–O(7) are 78.4° and 81.1°, respectively. The axial Cu–O linkages are not perfectly perpendicular to every CuN_2O_2 plane with N–Cu–O and O–Cu–O angles ranging from 85.9° to 108.6°.

The structural analyses revealed that the 1-D coordination polymers further interact forming a supramolecular network through multiform non-covalent interactions and face-to-face π–π interactions between benzyl rings from different chains, as shown in figure 3. There are complicated intramolecular and intermolecular hydrogen bonds among carboxyl oxygen, phenolic oxygen, and coordinated ethanol and methanol similar to its analogous (Cu(II) complex with reduced Schiff base derived from N-(2-hydroxybenzaldehyde) and L-methionine) [25]. Although non-covalent interactions are weak compared to the metal–nitrogen and metal–oxygen coordination bonds, these interactions were important in the molecular packing [39, 40].

4. Conclusion

New zinc(II) and copper(II) complexes with reduced Schiff base derived from D,L-selenomethionine and salicylaldehyde were synthesized. A copper(II) coordination polymer with tetranuclear copper(II) units [Cu_4(Sal-SeMet)$_4 \cdot$ MeOH $\cdot$ EtOH] as secondary building blocks was confirmed by X-ray crystallographic analysis. This tetranuclear unit is further connected by carbonyl oxygen from the ligand of another tetranuclear unit at the apical position to form a 1-D coordination polymer.

Supplementary material

Crystallographic data of Cu(II) complex for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre with CCDC No. 823831. These data are available free of charge on request to the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or at http://www.ccdc.cam.ac.uk).

Acknowledgments

The support by the National Natural Science Foundation of China (20904010) and the Fundamental Research Funds for the Central Universities (2009ZM0170) is gratefully acknowledged.

References

[1] P.K. Sasmal, A.K. Patra, M. Nethaji, A.R. Chakravarty. *Inorg. Chem.*, **46**, 11112 (2007).
[2] M.Z. Wang, Z.X. Meng, B. Liu. *Inorg. Chem. Commun.*, **8**, 368 (2005).
[3] H.M. Parekha, P.K. Panchala, M.N. Patel. *Toxicol. Environ. Chem.*, **88**, 579 (2006).
[4] I. Correia, S. Marcão, K. Koci, I. Tomaz, P. Adão, T. Kiss, T. Jakusch, F. Avecilla, J. Costa Pessoa. *Eur. J. Inorg. Chem.*, 694 (2011).
[5] Y.Y. Liu, Z.H. Wang, J. Yang. *CrystEngComm*, **13**, 3811 (2011).
[6] F. Thomas, H. Arora, C. Philouze, O. Jarjayes. *Inorg. Chim. Acta*, **363**, 3122 (2010).
[7] A. Biswas, M.G.B. Drew, A. Ghosh. *Polyhedron*, **29**, 1029 (2010).
[8] X.G. Ran, L.Y. Wang, D.R. Cao, Y.C. Lin. *Appl. Organomet. Chem.*, **25**, 9 (2011).
[9] X.G. Ran, L.Y. Wang, Y.C. Lin, D.R. Cao. *Appl. Organomet. Chem.*, **24**, 741 (2010).
[10] A.G. Deibe, M.R. Bermejo, A. Sousa, C.A. McAuliffe, P. McGylnm, P.T. Ndifon, R.G. Pritchard. *J. Chem. Soc., Dalton Trans.*, 1605 (1993).
[11] C. Biswas, S. Chattopadhyay, M.G.B. Drew, A. Ghosh. *Polyhedron*, **26**, 4411 (2007).
[12] P. Mukherjee, M.G.B. Drew, A. Ghosh. *Eur. J. Inorg. Chem.*, 3372 (2008).
[13] M.S. Ray, R. Bhattacharya, S. Chaudhuri, L. Righi, G. Bocelli, G. Mukhopadhyay, A. Ghosh. *Polyhedron*, **22**, 617 (2003).
[14] B. Sreenivasulu, J.J. Vittal. *Angew. Chem. Int. Ed.*, **43**, 5769 (2004).
[15] J.J. Vittal, X.D. Yang. *Cryst. Growth Des.*, **2**, 259 (2002).
[16] R. Ganguly, B. Sreenivasulu, J.J. Vittal. *Coord. Chem. Rev.*, **252**, 1027 (2008).
[17] L. Jia, N. Tang, J.J. Vittal. *Inorg. Chim. Acta*, **362**, 2525 (2009).
[18] T.D. Tullius, J.A. Greenbaum. *Curr. Opin. Chem. Biol.*, **9**, 127 (2005).
[19] R. Singh, A. Banerjee, E. Colacio. *Inorg. Chem.*, **48**, 4753 (2009).
[20] M.A. Alan, M. Nethaji, M. Ray. *Angew. Chem. Int. Ed.*, **42**, 1940 (2003).
[21] J.D. Ranford, J.J. Vittal, D. Wu, X. Yang. *Angew. Chem. Int. Ed. Engl.*, **38**, 3498 (1999).
[22] B. Sreenivasulu, J.J. Vittal. *Cryst. Growth Des.*, **3**, 635 (2003).
[23] B. Sreenivasulu, M. Vetrichelvan, F. Zhao. *Eur. J. Inorg. Chem.*, 4635 (2005).
[24] C.Y. Gao, X.F. Ma, J.L. Tian, D.D. Li, S.P. Yan. *J. Coord. Chem.*, **63**, 115 (2010).
[25] C.Y. Gao, X.F. Ma, J. Lu, Z.G. Wang, J.L. Tian, S.P. Yan. *J. Coord. Chem.*, **64**, 2157 (2011).

[26] B.Y. Lou, D.Q. Yuan, S.Y. Gao. *J. Mol. Struct.*, **707**, 231 (2004).
[27] M. Carland, B.F. Abrahams, T. Rede. *Inorg. Chim. Acta*, **359**, 3252 (2006).
[28] X.G. Ran, D.R. Cao, L.Y. Wang. *Polish J. Chem.*, **86**, 431 (2009).
[29] C.S. Chan, L.L. Koh, P.H. Leung. *Inorg. Chim. Acta*, **236**, 101 (1995).
[30] P. Li, N.K. Solanki, H. Ehrenberg. *J. Chem. Soc., Dalton Trans.*, 1559 (2000).
[31] X. Li, D. Cheng, J. Lin, Z. Li, Y. Zheng. *Cryst. Growth Des.*, **8**, 2853 (2008).
[32] L. Cañadillas-Delgado, A. Labrador, F.S. Delgado, C. Ruiz-Pérez, F. Lloret, M. Julve. *Inorg. Chem.*, **48**, 6630 (2009).
[33] Y.K. Lee, S.W. Lee. *J. Korean Chem. Soc.*, **5**, 46 (2002).
[34] S.N. Qin, Z.L. Chen, D.C. Liu, W.Y. Huang, F.P. Liang. *Inorg. Chem. Commun.*, **14**, 784 (2011).
[35] L.F. Marques, M.V. Marinho, C.C. Correa, N.L. Speziali, R. Diniz, F.C. Machado. *Inorg. Chim. Acta*, **368**, 242 (2011).
[36] J.F. Eubank, R.D. Walsh, M. Eddaoudi. *Chem. Commun.*, 2095 (2005).
[37] V.K. Muppidi, P.S. Zacharias, S. Pal. *Chem. Commun.*, 2515 (2005).
[38] V.-K. Muppidi, S. Pal. *Eur. J. Inorg. Chem.*, 2871 (2006).
[39] R. Kumai, S. Horiuchi, H. Sagayama, T.-H. Arima, M. Watanabe, Y. Noda, Y. Tokura. *J. Am. Chem. Soc.*, **129**, 12920 (2007).
[40] W. Huang, X.K. Xie, K. Cui, S.-H. Gou, Y.Z. Li. *Inorg. Chim. Acta*, **358**, 875 (2005).