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Synthesis, Characterization, and Structures of Two New Tetranuclear Copper Complexes with Azido/Dicyanamide Bridges Containing Chiral Schiff Base Ligand[1]

Z. Zhou[a], **X. K. Hou**[b], **C. C. Xue**[b], **and Z. X. Wang**[b], *

[a] *Department of Chemistry, College of Science, South Agricultural University, Guangzhou, 510642 P.R. China*

[b] *Department of Chemistry, College of Science, Shanghai University, Shanghai, 200444 P.R. China*

**e-mail: zxwang@shu.edu.cn*

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Abstract—Two new copper complexes $[Cu_4(\mu\text{-}L)_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$ (**I**) and $[Cu_4(\mu\text{-}L)_2(\mu_{1,5}\text{-Dca})_2(\text{Dca})_2]$ (**II**) (H_2L = (1*R*,3*S*)-*N*',*N*''-bis[5-methoxysalicylidene]-1,3-diamino-1,2,2-trimethylcyclopentane, Dca = dicyanamide ions) were synthesized and structurally characterized by elemental analyses, IR spectroscopy and single-crystal X-ray diffraction (CIF files CCDC nos. 1013673 (**I**), 1013672 (**II**)). The two complexes crystallize in monoclinic $P2_1/c$ and triclinic $P\bar{1}$ space group, respectively. Both the complexes consist of two crystallographically independent copper ions connected by a double phenoxo bridges, which are further linked to the other symmetry-related half of the molecule by two end-on azido bridges or $\mu_{1,5}$-dca groups.

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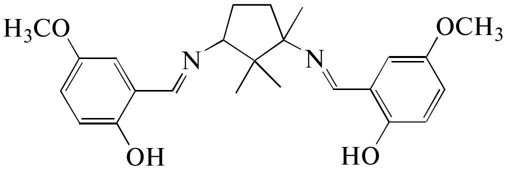
INTRODUCTION

Chiral Schiff base ligands, obtained by condensing between a number of chiral amines and aldehydes or ketones, are a very important class of ligands to construct molecule materials with various novel structures and interesting properties [1–3]. In their family, tetradentate Schiff-base ligands containing N, O donors have been widely utilized to form polynuclear complexes with interesting structures [4–6]. Camphoric diamine is a very useful material to construct chiral compounds [7]. Chiral Schiff base ligand condensation of camphoric diamine with a variety of aldehydes is also exploited to synthesize functional molecular materials [8]. Recently, we prepared a series of chiral Schiff base ligands based on camphoric diamine and used azide or dicyanamide ions as a small conjugated ligand bridging to connect partially blocked dinuclear copper to form a series of compounds exhibiting 0D [9], 1D and 2D structures [10]. To continue our previous work, we synthesized a new chiral Schiff base ligand (1*R*,3*S*)-*N*',*N*''-bis[5-methoxysalicylidene]-1,3-diamino-1,2,2-trimethylcyclopentane (H_2L) obtained by reaction with 5-methoxysalicylaldehyde and camphoric diamine and harvested two new tetranuclear copper complexes with doubly phenoxo and end-on azido or dicyanamide bridges. Herein, we describe the details of syntheses, characterization and crystal structures of the complexes, $[Cu_4(\mu\text{-}L)_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$ (**I**) and $[Cu_4(\mu\text{-}L)_2(\mu_{1,5}\text{-Dca})_2(\text{Dca})_2(CH_3OH)_2]$ (**II**), where Dca are dicyanamide ions.



(H_2L)

EXPERIMENTAL

Materials and methods. All chemicals used during the course of this work were of reagent grade and used as received from commercial sources without further purification. Schiff base ligands H_2L was prepared according to the literature methods [11, 12]. Elemental analyses for carbon, hydrogen, and nitrogen were carried out with a Vario EL III elemental analyzer. Infrared spectra were recorded with a Nicolet A370 FT-IR spectrometer using KBr pellets in the 4000–400 cm^{-1} region.

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[1] The article is published in the original.

Caution! Azide derivatives are potentially explosive, only a small amount of material should be prepared, and it should be handled with proper care.

Synthesis of complex I. This complex was prepared by a similar procedure to that described in reference [9] except that H_2L was used. Due to the low yield, only several crystals were picked up by handy to do Infrared spectra.

IR (KBr; ν, cm^{-1}): 2955, 2068, 2039, 1604, 1482, 1288, 815.

Synthesis of complex II. Solid of $CuCl_2 \cdot 2H_2O$ (34.6 mg, 0.200 mmol) was added to 5 mL of a methanolic solution dissolved H_2L (18.4 mg, 0.050 mmol) with stirring for 10 min. Then Na(Dca) (28.6 mg, 0.300 mmol) dissolved in 5 mL of CH_3OH was added slowly to the above mixture, and the resulting brown solution was stirred for 5 min followed by filtration. The filtrate was left at room temperature, and dark crystals appeared after 3 days. They were collected by filtration, washed with methanol (the yeld was 42% based on Cu) and a well-shaped crystal of **II** was selected for X-ray single-crystal diffraction analysis.

For $C_{58}H_{62}N_{16}O_{10}Cu_4$

anal. calcd., %:	C, 49.78;	H, 4.43;	N, 16.02;
Found, %:	C, 49.97;	H, 4.42;	N, 16.15.

IR (KBr; ν, cm^{-1}): 2964, 2306, 2239, 2168, 1607, 810.

X-ray crystallography. Crystallographic data of complexes **I** and **II** were collected using a Bruker SMART APEXII CCD diffractometer operating at room temperature. Intensities were collected with graphite monochromatized MoK_α radiation (λ = 0.71073 Å), using the φ and ω scan technique. Data reduction was made with the Bruker SAINT package [13]. Absorption correction was performed using the SADABS program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXL-2000 with anisotropic displacement parameters for all non-hydrogen atoms [14]. H atoms were introduced in calculations using the riding model. All computations were carried out using the SHELXTL-2000 program package [15]. X-ray crystallographic data and refinement details are summarized in Table 1. The selected bond lengths and angles for the two complexes are given in Table 2.

Crystallographic data for the structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1013673 (**I**), 1013672 (**II**); www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The infrared spectra exhibit characteristic vibration bands of the chiral Schiff base ligand in both complexes. The bands presenting at 2955 and 1604 cm^{-1} in **I**, 2964 and 1607 cm^{-1} in **II** are designated to the stretching vibrations of the methyl groups and the ν(C=N) stretching frequencies, respectively. In addition, absorption of 815 and 810 cm^{-1} is assigned to the δ(CH) bending vibrations of phenyl rings for **I** and **II**. Meanwhile, the spectra of **I** show strong sharp double characteristic absorptions of the ν(N=N) at 2068 and 2039 cm^{-1}, together with the presence of a band at about 1288 cm^{-1} indicating the presence of both EO bridging and terminal azido ligands [16, 17], which are in agreement with the crystal structure. While the appearance of three sharp and strong stretching frequencies in the 2310–2160 cm^{-1} region confirms the presence of dicyanamide anions in complex **II**. The peaks at 2306, 2239 and 2168 cm^{-1} are characteristic for expected absorption of asymmetric and symmetric vibrations of the ν(C≡N) groups [18, 19].

The single crystal X-ray structural analysis shows that both of the two complexes are centrosymmetrical tetranuclear structures. As showing in Fig. 1, both the complexes consist of two crystallographically independent copper ions connected by a double phenoxo bridges, which are further linked to the other symmetry-related half of the molecule by two EO azido bridges or $\mu_{1,5}$-Dca ions. This array of the copper ions leads to very similar to the tetranuclear units [9, 20–22]. In complex **I**, the terminal copper Cu(1) ions present a slightly distorted square plane geometry which is coordinated to two phenoxo oxygen atoms, two imine nitrogen atoms from one ligand. While the terminal Cu(1) ions in **II** show a square pyramid geometry with two phenoxo oxygen atoms and two nitrogen atoms from one L^{2-}. The O(3) atom of the methanol molecule is located on the apical site of the square pyramid. With the different coordination environment, the Cu(2) ions of both complexes take on a square pyramid geometry with two phenoxo oxygen atoms from one ligand and three nitrogen atoms from one terminal azido/Dca ion and two EO azido/Dca groups for **I** and **II**, respectively. The apical site of square pyramid is occupied by a relatively longer Cu(2)–O(1) bond with the bridging phenoxo oxygen atom of L^{2-} for **I**, or by one nitrogen atom from the terminal Dca unit for **II**. The bond lengths of Cu–O of complex **I** are in the range of 1.911(5)–2.284(5) Å which are very similar to those of in complex **II** (Table 2). The Cu–N bond distances range from 1.929(10) to 1.992(6) Å in **I** which are slightly shorter than those of in **II**. All the bond lengths of the two complexes are compared to those of other tetranuclear complexes bridged by azido anions

Table 1. Crystallographic data and structural refinement details of complexes **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{48}H_{56}N_{16}O_8Cu_4$	$C_{58}H_{62}N_{16}O_{10}Cu_4$
Formula weight	1239.25	1397.40
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a, Å	12.1061(14)	9.956(3)
b, Å	14.6540(17)	11.740(3)
c, Å	16.5782(15)	14.769(4)
α, deg	90	90.078(5)
β, deg	115.998(6)	94.292(5)
γ, deg	90	115.015(4)
V, Å^3	2643.4(5)	1558.9(7)
Z	2	1
ρ_{calcd}, g/cm^3	1.557	1.491
μ, mm^{-1}	1.655	1.415
F(000)	1272	720
Reflections collected/unique	18158/4622	8722/5495
R_{int}	0.0373	0.0404
Limiting indices	$-14 \le h \le 14$, $-17 \le k \le 17$, $-19 \le l \le 19$	$-11 \le h \le 11$, $-14 \le k \le 14$, $-17 \le l \le 17$
Data/restraints/parameters	4622/70/343	5495/10/403
GOOF (all reflections)	1.029	1.004
R_1, wR_2 ($I > 2\sigma(I)$)	0.0877, 0.2283	0.0774, 0.2093
R_1, wR_2 (all data)	0.1044, 0.2378	0.1062, 0.2289
Largest diff. peak/hole, e Å^{-3}	1.041 and –0.695	1.460 and –0.764

Table 2. Selected bond lengths (Å) and bond angles (deg) for complexes **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
Cu(1)–N(1)	1.929(10)	Cu(2)–O(1)	2.284(5)
Cu(1)–N(2)	1.978(7)	Cu(2)–O(2)	2.006(5)
Cu(1)–O(1)	1.911(5)	Cu(2)–N(3)	1.992(6)
Cu(1)–O(2)	1.931(5)	Cu(2)–N(3)$^{\#1}$	1.977(7)
		II	
Cu(1)–N(1)	1.966(5)	Cu(2)–O(1)	2.003(4)
Cu(1)–N(2)	1.966(5)	Cu(2)–O(2)	1.986(4)
Cu(1)–O(1)	1.950(4)	Cu(2)–N(3)	1.979(7)
Cu(1)–O(2)	1.950(4)	Cu(2)–N(6)	2.228(6)
Cu(1)–O(3)	2.354(5)	Cu(2)–N(8)$^{\#1}$	1.992(6)
Angle	ω, deg	Angle	ω, deg
		I	
Cu(1)O(1)Cu(2)	98.5(2)	Cu(1)O(2)Cu(2)	108.1(3)
Cu(2)N(3)Cu(2)$^{\#1}$	103.4(3)	O(1)Cu(1)O(2)	80.3(2)
O(1)Cu(1)N(1)	93.1(3)	N(1)Cu(1)O(2)	165.7(3)
O(1)Cu(1)N(2)	164.6(3)	N(1)Cu(1)N(2)	96.2(3)
O(2)Cu(1)N(2)	93.2(3)	N(6)Cu(2)N(3)$^{\#1}$	160.5(3)
N(6)Cu(2)N(3)	94.7(3)	N(3*A*)Cu(2)N(3)	76.6(3)
N(6)Cu(2)O(2)	93.4(3)	N(3*A*)Cu(2)O(2)	93.8(2)
N(3)Cu(2)O(2)	169.9(2)	N(6)Cu(2)O(1)	95.8(3)
N(3)$^{\#1}$Cu(2)O(1)	103.7(3)	N(3)Cu(2)O(1)	115.0(3)
O(2)Cu(2)O(1)	70.2(2)		
		II	
Cu(1)O(1)Cu(2)	102.35(19)	Cu(1)O(2)Cu(2)	102.95(18)
O(1)Cu(1)O(2)	76.20(17)	O(1)Cu(1)N(1)	93.0(2)
O(2)Cu(1)N(1)	166.5(2)	O(1)Cu(1)N(2)	164.4(2)
O(2)Cu(1)N(2)	91.99(18)	N(1)Cu(1)N(2)	97.1(2)
O(1)Cu(1)O(3)	90.7(2)	O(2)Cu(1)O(3)	90.99(19)
N(1)Cu(1)O(3)	97.2(3)	N(2)Cu(1)O(3)	99.8(2)
N(3)Cu(2)O(2)	150.1(3)	N(3)Cu(2)N(8)$^{\#1}$	93.4(3)
O(2)Cu(2)N(8)$^{\#1}$	93.9(2)	N(3)Cu(2)O(1)	91.7(2)
O(2)Cu(2)O(1)	74.21(16)	N(8)$^{\#1}$Cu(2)O(1)	163.5(2)
N(3)Cu(2)N(6)	100.7(3)	O(2)Cu(2)N(6)	108.3(2)
N(8)$^{\#1}$Cu(2)N(6)	89.7(2)	O(1)Cu(2)N(6)	104.7(2)

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, -y + 1, -z + 1$ (**I**); $^{\#1}$ $-x + 1, -y + 2, -z$ (**II**).

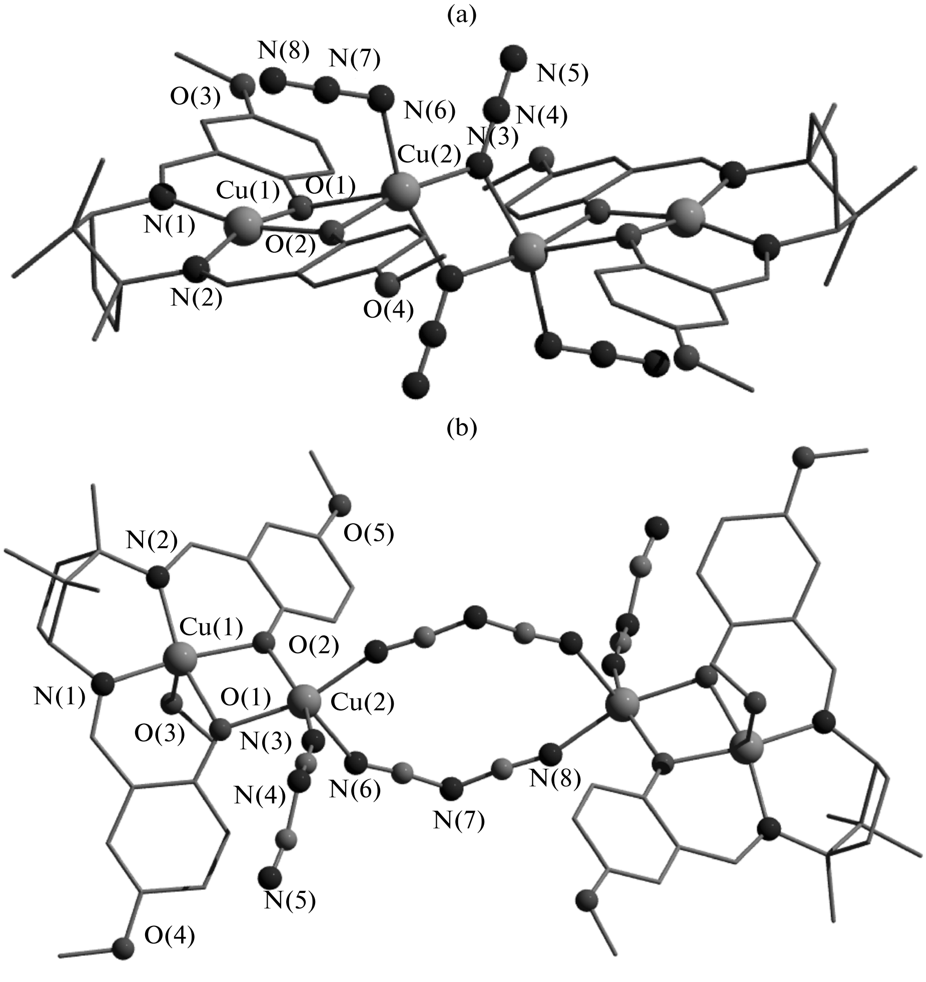

Fig. 1. Molecular structures of **I** (a) and **II** (b). All hydrogen atoms are been omitted for clarity.

[23, 24]. The Cu(1)O(1)Cu(2), Cu(1)O(2)Cu(2) and Cu(2)N(3)Cu(2)$^{\#1}$ bond angles are 98.5(2)°, 108.1(3)° and 103.4(3)° in complex **I**. For complex **II**, the bond angles of Cu(1)O(1)Cu(2) and Cu(1)O(2)Cu(2) are 102.35(19)° and 102.95(18)°. The central copper(II) atom Cu(2) and Cu(2)$^{\#1}$ connected by double bridges of EO azido/Dca to generate a tetranuclear cluster. Due to the different coordination modes of the bridging ligands, the Cu(2)–Cu(2)$^{\#1}$ distance is 3.115 Å in **I** and 7.382 Å in **II**, respectively.

In the reported tetranuclear azido-copper(II) complexes $[Cu_4(\mu\text{-}L^1)_2(\mu_{1,1}\text{-}N_3)_2(CH_3O)_2]$ and $[Cu_4(\mu\text{-}L^2)_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2] \cdot 2H_2O$ (H_2L^1 = (1*R*,3*S*)-*N*',*N*''-bis[salicylidene]-1,3-diamino-1,2,2-trimethylcyclopentane and H_2L^2 = (1*R*,3*S*)-*N*',*N*''-bis[5-methylsalicylidene]-1,3-diamino-1,2,2-trimethyl-cyclopentane) [9], the two phenyl rings of the chiral Schiff base ligands are nearly coplanar. However, the two phenyl rings of L^{2-} significantly deviate from coplanar with a dihedral angle of 37.33° and 39.13° in **I** and **II**, respectively, due to the effect of the substituents ($-OCH_3$) on the phenyl rings. In the solid state of **I**, the tetranuclear units are interlinked via weak hydrogen bonding and π–π stacking of the phenyl rings from the L^{2-} ligands to form a 3D supramolecular structure (Fig. 2). In contrast with complex **I**, the tetranuclear molecules are linked by O(3)–H(3*A*)···N(5) (symmetrical code: *x, y* – 1, *z*) hydrogen bonds, involving the coordinated methanol molecules and the terminal N atom of the Dca groups, to form a 1D infinite chain structure along the *y* axis in the crystal structure of **II** (Fig. 3a). Furthermore, the neighboring chains are extended to 3D supramolecular architecture by the collaboration with weak hydrogen bonding and π–π stacking (Fig. 3b).

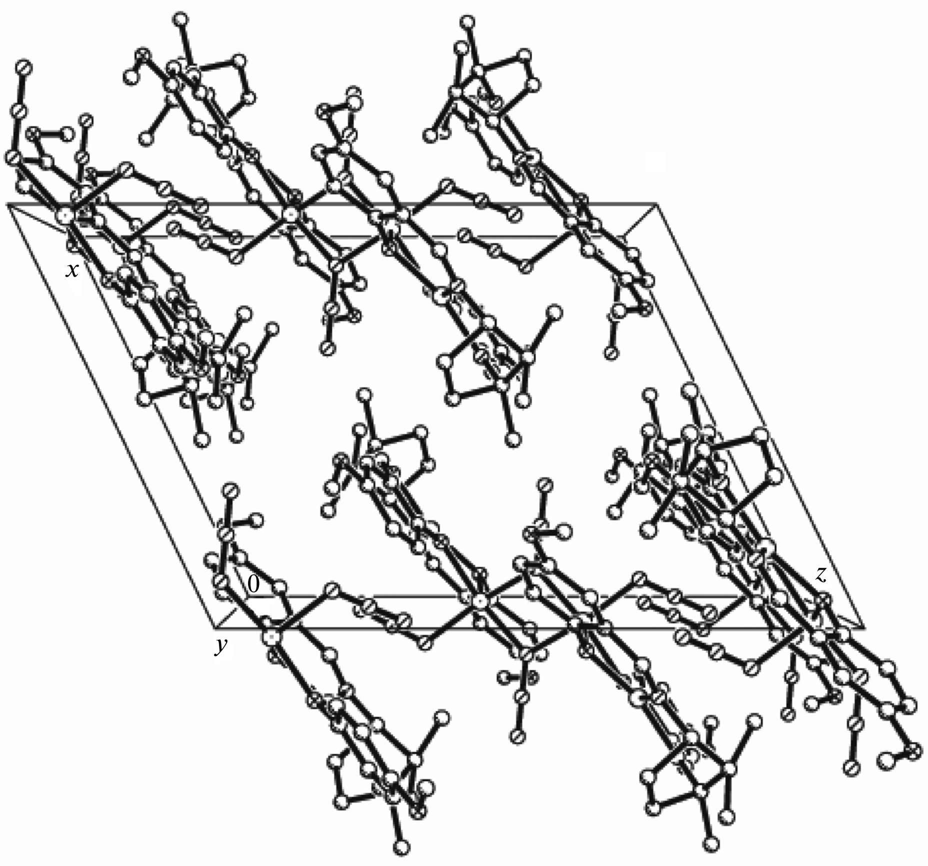

Fig. 2. 3D supramolecular architecture of **I**.

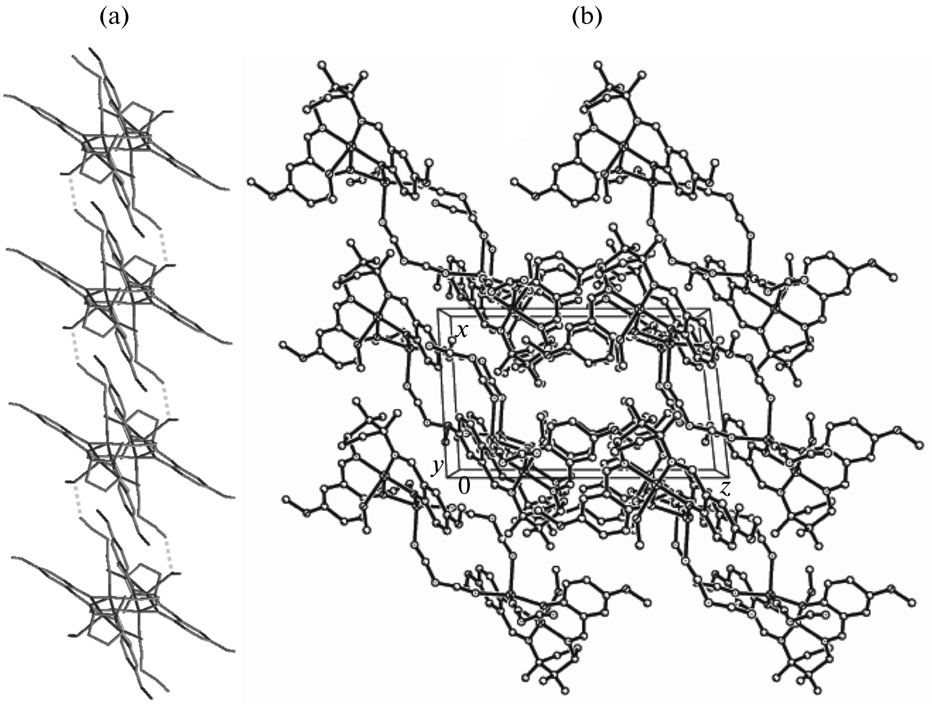

Fig. 3. A 1D infinite chain structure formed by hydrogen bonds along the *y* axis in **II** (a) and 3D supramolecular architecture of **II** (b).

REFERENCES

1. Li, G., Zhang, J., Xu, Z.,et al., *Organometallics*, 2006, vol. 25, p. 1676.
2. Li, D., Wang, T., Li, C., et al., *Chem. Commun.*, 2010, vol. 46, p. 2929.
3. Liu, C.M., Xiong, R.G., Zhang, D.Q., et al., *J. Am. Chem. Soc.*, 2010, vol. 132, p. 4044.
4. Bhar, K., Choubey, S., Mitra, P., et al., *J. Mol. Struct.*, 2011, vol. 988, p. 128.
5. Lu, G., Yoshino, T., Morimoto, H., et al., *Angew. Chem. Int. Ed.*, 2011, vol. 50, p. 4382.
6. Sutradhar, M., Barman, T.R., Drew, M.G.B., et al., *J. Mol. Struct.*, 2013, vol. 1041, p. 44.
7. Wang, Z.-X., Wei, J., Li, Y.-Z., et al., *J. Mol. Struct.*, 2008, vol. 875, p. 198.
8. Jiang, J.C., Chu, Z.L., Huang,W., et al., *Inorg. Chem.*, 2010, vol. 49, p. 5897.
9. Hou, X.-K., Wu, L.-F., Xiao, H.-P., et al., *Z. Anorg. Allg. Chem.*, 2013, vol. 639, p. 633.
10. Wang, Z.-X., Wu, L.-F., Hou, X.-K., et al., *Z. Anorg. Allg. Chem.*, 2014, vol. 640, p. 229.
11. Yang, Z.H., Wang, L.X., Zhou, Z.H., et al., *Tetrahedron: Asymmetry*, 2001, vol. 12, p. 1579.
12. Serra, M.E.S., Murtinho, D., Goth, A., et al., *Chirality*, 2010, vol. 22, p. 425.
13. *Software packages SMART*, Madison (WI, USA): Siemens Analytical X-ray Instruments Inc., 1996.
14. Sheldrick, G.M., *SADABS*, *Version 2008/1*, Göttingen (Germany): Univ. of Göttingen, 2008.
15. Sheldrick,G.M., *SHELXL-97*, *Program for the Refinement of Crystal Structures from Diffraction Data*, Göttingen (Germany): Univ. of Göttingen, 1997.
16. Wang, X.-T., Wang, X.-H., Wang, Z.-M., et al., *Inorg. Chem.*, 2009, vol. 48, p. 1301.
17. Beheshti, A., Lalegani, A., Bruno, G., et al., *J. Mol. Struct.*, 2014, vol. 1071, p. 18.
18. Mautner, F.A., Albering, J.H., Mikuriya, M., et al., *Inorg. Chem. Commun.*, 2010, vol. 13, p. 796.
19. Talukder, P., Shit, S., Sasmal, A., et al., *Polyhedron*, 2011, vol. 30, p. 1767.
20. Koner, S., Saha, S., Okamoto, K.-I., et al., *Inorg. Chem.*, 2003, vol. 42, p. 4668.
21. Khalaji, A.D. and Evans, H.S., *Polyhedron*, 2009, vol. 28, p. 3769.
22. Khalaji, A.D., Hadadzadeh, H., Fejfarova, K., et al., *Polyhedron*, 2010, vol. 29, p. 807.
23. Kunduracl, S., Öz, M., Kurtaran, R., et al., *J. Therm. Anal. Calorim.*, 2010, vol. 101, p. 221.
24. Ray, A., Mitra, S., Khalaji, A.D., et al., *Inorg. Chim. Acta*, 2010, vol. 363, p. 3580.