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Synthesis and Crystal Structure of Supramolecular Trinuclear Nickel(II) Complex with 5-Methoxy-4'-chloro-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol

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A new trinuclear Ni(II) complex has been synthesized through the reaction of an asymmetric Salamo-type ligand of 5-methoxy-4'-chloro-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol (H_2L) with Ni(II) acetate tetrahydrate in *n*-butanol/acetonitrile solution and characterized by X-ray diffraction methods. The X-ray crystallography of the Ni(II) complex shows that the unit cell contains two crystallographically independent but chemically identical trinuclear Ni(II) complex (molecules A and B) and each molecule comprises three Ni(II) atoms, two deprotonated L^{2-} units, two acetate anions and two coordinated *n*-butanol molecules. In the crystal, the complex molecules are linked to form an infinite sandwich supramolecular structure through intermolecular O-H···O and C-H···O hydrogen bond interactions.

Keywords: Asymmetric Salamo-type ligand, Ni(II) complex, Synthesis, Crystal structure.

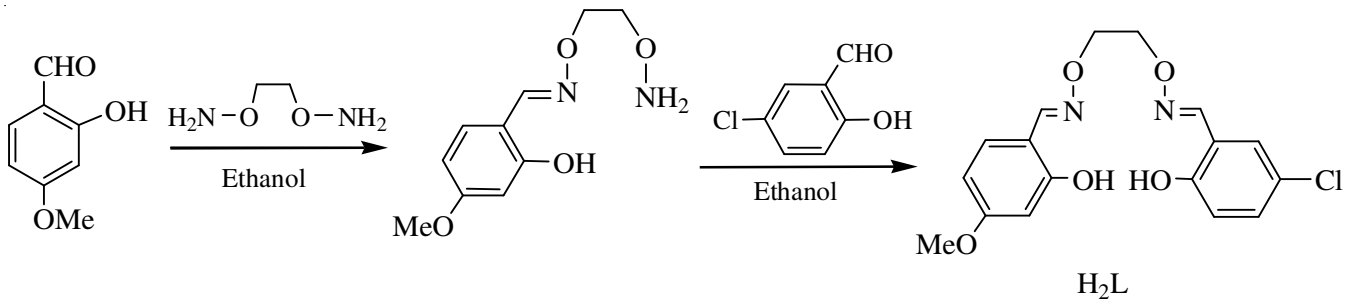
INTRODUCTION

Transition metal complexes having Salen-type ligands or its analogues are extensively investigated, because not only these series of complexes played an important role in the development of modern coordination chemistry[1], but they can also be found at key points in the development of their unique catalytic activity[2], buliding blocks for cyclic supramolecular structures[3], interesting magnetic properties[4-6], nonlinear optical materials[7,8], thin films[9] and excellent biological activity[10,11], such as anticancer and anticoagulant activity[12]. Although some advance has been made in the studies of Ni(II) complexes with Salen-type and Salamo-type ligands[13-16b], it still seems there could be new and specific applications for such unique complexes, which can introduce a variety of solvent effect. Meanwhile, comparing with symmetric complexes, transition metal complexes derived from asymmetric Salamo-type ligands sometimes exhibit better ways to control supramolecular interactions[16c,d].

Herein, we report the synthesis and crystal structure of a supramolecular trinuclear Ni(II) complex with an asymmetric ligand 5-methoxy-4'-chloro-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol (H_2L).

EXPERIMENTAL

2-Hydroxy-4-methoxybenzaldehyde (≥ 99 %) and 2-hydroxy-5-chlorobenzaldehyde (≥ 99 %) were purchased from Alfa Aesar and used without further purification. 1,2-*Bis*-(aminooxy)ethane was synthesized according to an analogous method reported earlier[17-19]. The others are the same as reported in literature[16e].



Scheme-I: Synthetic route to the asymmetrical salamo-type ligand H_2L

General procedure

Synthesis of the ligand H_2L: The major reaction steps involved in the synthesis of H_2L are given in **Scheme-I**.

H_2L was synthesized according to an analogous method reported earlier[16,20]. Yield 87.0 %. m.p. 383-385 K. Anal. calcd. for $C_{17}H_{17}N_2O_5Cl$ (%): C, 55.97; H, 4.70; N, 7.68. Found: C, 55.81; H, 4.86; N, 7.53.

Synthesis of the Ni(II) complex: A solution of $Ni(OAc)_2{\cdot}4H_2O$ (3.70 mg, 0.015 mmol) in *n*-butanol (2 mL) was added dropwise to a solution of H_2L (3.65 mg, 0.01 mmol) in acetonitrile (2 mL) at room temperature. The colour of the mixing solution turned to green immediately, then stirred for 2 h at room temperature. The mixture was filtered and the filtrate was allowed to stand at room temperature for about three months, the solvent was partially evaporated and obtained green block-like single crystals suitable for X-ray crystallographic analysis. Anal. Calcd. for $C_{154}H_{212}N_{12}O_{54}Ni_9Cl_6$ (%): C, 48.21; H, 5.57; N, 4.38; Ni, 13.77. Found: C, 48.38; H, 5.72; N, 4.19; Ni, 13.61.

X-Ray structure determination: The X-Ray structure determination is the same as literature early[16]. Details of the data collection and refinements of the Ni(II) complex are listed in Table-1. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically. CCDC: 954018.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE Ni(II) COMPLEX

Empirical formula	$C_{154}H_{212}N_{12}O_{54}Ni_9Cl_6$
Formula weight	3836.45
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Cell dimensions, (Å, deg)	a = 15.347(1), b = 16.665(1), c = 19.393(2), α = 67.854(1), β = 80.978(2), γ = 73.714(1)
Volume (Å^3)	4402.4(7)
Z	1
Density (calculated) (mg/m^3)	1.447
Absorption coefficient (mm^{-1})	1.115
$F_{(000)}$	2006
Crystal size	0.30 × 0.21 × 0.18
Index ranges	-18 ≤ h ≤ 14, -19 ≤ k ≤ 19, -23 ≤ l ≤ 19
Reflections collected	22325/15241 [R(int) = 0.0599]
Independent reflections	2295
Data/restraints/parameters	15241/1/987
Goodness of fit indicator	1.092
R [I > 2σ(I)]	R_1 = 0.0665, wR_2 = 0.1360
Largest diff. peak and hole (e Å^{-3})	1.353 and -1.632

RESULTS AND DISCUSSION

Crystal structure of the Ni(II) complex: ORTEP representation of the Ni(II) complex is shown in Fig. 1. Selected bond lengths and angles are listed in Table-2. X-ray crystallographic analysis reveals that the Ni(II) complex crystallizes in the triclinic system, space group *P*-1 with two crystallographically independent but chemically identical trinuclear Ni(II) complex (molecules A and B) and each molecule comprises three Ni(II) atoms, two deprotonated L^{2-} units, two acetate anions and two coordinated *n*-butanol molecules, as well as one non-coordinated water and two non-coordinated *n*-butanol molecules.

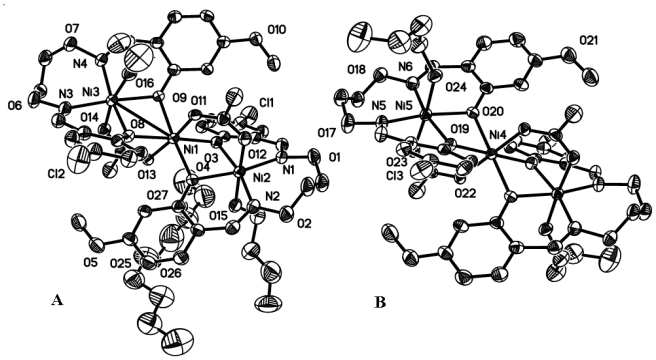


Fig. 1. ORTEP-style drawing of the Ni(II) complex. (Thermal ellipsoids are plotted at 30 % probability level)

As shown in Fig. 1, all the Ni(II) atoms of the Ni(II) complex are hexa-coordinated and have a slightly distorted octahedral coordinated polyhedron. All the terminal Ni(II) (Ni2, Ni3, Ni5 and Ni5$^{\#1}$) atoms are located in the *cis*-N_2O_2 coordinated sphere of the deprotonated L^{2-} units and coordinated to oxygen atoms from the μ-acetato anion and oxygen atoms from the coordinated *n*-butanol molecules in the axial positions, respectively. Meanwhile, the central Ni(II) atoms (Ni1 and Ni4) are hydrogen-bonded to μ-phenoxo oxygen (O3, O4, O8, O9 and O19, O20, O19$^{\#1}$, O20$^{\#1}$) atoms from deprotonated L^{2-} units and μ-acetato oxygen (O11, O13 and O22, O22$^{\#1}$) atoms in the axial positions. In addition, the terminal Ni(II) (Ni2) atom deviates by 0.046 (3) Å from the coordination plane defined by the O4, O3, N1, N2 atoms, while the Ni3 atom deviates by 0.113(2) Å from that of N_2O_2 plane in molecule A, which are different from the molecule B with both of the terminal Ni(II) (Ni5 and Ni5$^{\#1}$) atoms deviating by 0.021(3) Å from the coordination planes defined by the O19, O20, N5, N6 and O19$^{\#1}$, O20$^{\#1}$, N5$^{\#1}$, N6$^{\#1}$ atoms. And the dihedral angle between the two mean planes of N_2O_2 is 15.69(4)° in the molecule A, while in the molecule B, the two mean planes are parallel to each other.

Intermolecular interactions of Ni(II) complex: In the crystal structure, the Ni(II) complex contains abundant intramolecular and intermolecular hydrogen bonding interactions and hydrogen bond data are summarized in Table-3.

In the crystal structure, the molecule A is stabilized by six intramolecular C2-H2A···O12, C6-H6···O13, C13-H13···O13, C16-H16···O11, C18-H18B···O14 and C30-H30···O3 hydrogen bonding interactions, as shown in Fig. 2,

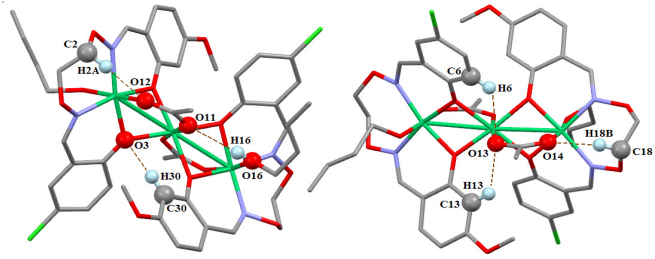


Fig. 2. View of the intramolecular hydrogen-bonding interactions of the molecule A

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE Ni(II) COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Ni1-O11	2.028(5)	Ni2-N1	2.076(5)	Ni4-O19	2.079(4)
Ni1-O4	2.044(4)	Ni2-O15	2.113(5)	Ni4-O19$^{\#1}$	2.079(4)
Ni1-O3	2.074(4)	Ni3-O8	1.998(4)	Ni4-O22	2.090(4)
Ni1-O9	2.075(4)	Ni3-N4	2.001(5)	Ni4-O22$^{\#1}$	2.090(4)
Ni1-O13	2.080(4)	Ni3-O9	2.020(4)	Ni5-O19	2.003(4)
Ni1-O8	2.084(4)	Ni3-O14	2.044(5)	Ni5-O20	2.031(4)
Ni1-Ni3	2.990(1)	Ni3-N3	2.052(5)	Ni5-O23	2.035(5)
Ni2-O4	2.017(4)	Ni3-O16	2.198(5)	Ni5-N6	2.057(5)
Ni2-O3	2.020(4)	Ni4-O20$^{\#1}$	2.047(4)	Ni5-N5	2.067(5)
Ni2-O12	2.029(5)	Ni4-O20	2.047(4)	Ni5-O24	2.092(5)
Ni2-N2	2.046(5)				
Bond	Angles	Bond	Angles	Bond	Angles
O11-Ni1-O4	90.6(2)	O8-Ni3-N3	87.4(2)	O23-Ni5-O24	175.7(2)
O11-Ni1-O3	93.0(2)	N4-Ni3-N3	96.4(2)	N6-Ni5-O24	90.0(2)
O4-Ni1-O3	77.2(2)	O9-Ni3-N3	173.8(2)	N5-Ni5-O24	86.8(2)
O11-Ni1-O9	88.1(2)	O14-Ni3-N3	91.6(2)	C3-N1-Ni2	123.8(5)
O4-Ni1-O9	175.4(2)	O8-Ni3-O16	80.1(2)	O1-N1-Ni2	128.5(4)
O3-Ni1-O9	98.5(2)	N4-Ni3-O16	87.7(2)	C10-N2-Ni2	123.1(4)
O11-Ni1-O13	174.0(2)	O9-Ni3-O16	83.6(2)	O2-N2-Ni2	128.0(4)
O4-Ni1-O13	92.7(2)	O14-Ni3-O16	168.5(2)	C20-N3-Ni3	124.0(4)
O3-Ni1-O13	92.6(2)	N3-Ni3-O16	94.9(2)	O6-N3-Ni3	126.0(4)
O9-Ni1-O13	89.1(2)	O8-Ni3-Ni1	44.0(1)	C27-N4-Ni3	124.2(4)
O11-Ni1-O8	88.9(2)	N4-Ni3-Ni1	133.4(2)	O7-N4-Ni3	121.6(4)
O4-Ni1-O8	101.6(2)	O9-Ni3-Ni1	43.8(1)	C49-N5-Ni5	122.7(4)
O3-Ni1-O8	177.7(2)	O14-Ni3-Ni1	81.0(1)	O17-N5-Ni5	129.6(4)
O9-Ni1-O8	82.8(2)	N3-Ni3-Ni1	130.2(2)	C56-N6-Ni5	124.7(4)
O13-Ni1-O8	85.5(2)	O16-Ni3-Ni1	87.6(1)	O18-N6-Ni5	126.5(4)
O11-Ni1-Ni3	96.3(1)	O20$^{\#1}$-Ni4-O20	180.0(1)	C5-O3-Ni2	126.8(4)
O4-Ni1-Ni3	142.2(1)	O20$^{\#1}$-Ni4-O19	103.2(2)	C5-O3-Ni1	133.6(4)
O3-Ni1-Ni3	139.0(1)	O20-Ni4-O19	76.8(2)	Ni2-O3-Ni1	97.0(2)
O9-Ni1-Ni3	42.37(1)	O20$^{\#1}$-Ni4-O19$^{\#1}$	76.8(2)	C12-O4)-Ni2	128.3(4)
O13-Ni1-Ni3	78.1(1)	O20-Ni4-O19	103.2(2)	C12-O4-Ni1	133.1(4)
O8-Ni1-Ni3	41.8(1)	O19-Ni4-O19	180.0(2)	Ni2-O4-Ni1	98.1(2)
O4-Ni2-O3	79.0(2)	O20$^{\#1}$-Ni4-O22	91.9(2)	C22-O8-Ni3	121.6(4)
O4-Ni2-O12	92.3(2)	O20-Ni4-O22	88.1(2)	C22-O8-Ni1	134.2(4)
O3-Ni2-O12	91.8(2)	O19-Ni4-O22	89.910(2)	Ni3-O8-Ni1	94.2(2)
O4-Ni2-N2	88.7(2)	O19$^{\#1}$-Ni4-O22	90.110(2)	C29-O9-Ni3	125.4(4)
O3-Ni2-N2	167.5(2)	O20$^{\#1}$-Ni4-O22$^{\#1}$	88.1(2)	C29-O9-Ni1	131.8(3)
O12-Ni2-N2	90.8(2)	O20-Ni4-O22	91.9(2)	Ni3-O9-Ni1	93.8(2)
O4-Ni2-N1	165.6(2)	O19-Ni4-O22	90.1(2)	C35-O11-Ni1	128.6(5)
O3-Ni2-N1	86.8(2)	O19$^{\#1}$-Ni4-O22$^{\#1}$	89.9(2)	C35-O12-Ni2	128.5(4)
O12-Ni2-N1	90.5(2)	O22-Ni4-O22	180.0(2)	C37-O13-Ni1	127.7(5)
N2-Ni2-N1	105.3(2)	O19-Ni5-O20	78.9(2)	C37-O14-Ni3	125.7(4)
O4-Ni2-O15	88.7(2)	O19-Ni5-O23	91.9(2)	C39-O15-Ni2	130.7(5)
O3-Ni2-O15	89.3(2)	O20-Ni5-O23	92.1(2)	C43-O16-Ni3	139.9(4)
O12-Ni2-O15	178.6(2)	O19-Ni5-N6	166.7(2)	C51-O19-Ni5	126.5(4)
N2-Ni2-O15	88.2(2)	O20-Ni5-N6	87.8(2)	C51-O19-Ni4	133.1(3)
N1-Ni2-O15	88.8(2)	O23-Ni5-N6	89.7(2)	Ni5-O19-Ni4	98.5(2)
O8-Ni3-N4	167.5(2)	O19-Ni5-N5	88.4(2)	C58-O20-Ni5	126.5(4)
O8-Ni3-O9	86.5(2)	O20-Ni5-N5	167.3(2)	C58-O20-Ni4	133.5(4)
N4-Ni3-O9	89.5(2)	O23-Ni5-N5	89.2(2)	Ni5-O20-Ni4	98.7(2)
O8-Ni3-O14	90.7(2)	N6-Ni5-N5	104.9(2)	C64-O22-Ni4	130.5(5)
N4-Ni3-O14	101.0(2)	O19-Ni5-O24	89.3(2)	C64-O23-Ni5	128.4(4)
O9-Ni3-O14	88.9(2)	O20-Ni5-O24	92.2(2)	C66-O24-Ni5	127.2(4)

Symmetry transformations used to generate equivalent atoms:$^{\#1}$ –x + 1,-y + 1,-z

while the molecule B is stabilized by three pairs of intramolecular C48-H48A···O23, C52-H52···O22 and C59-H59···O22 hydrogen bonding interactions, as shown in Fig. 3. Furthermore, each molecule B links two molecules A through seven pairs of intermolecular O-H···O and C-H···O hydrogen bonding interactions among the molecule A, B, crystallizing water and *n*-butanol molecules to form a sandwich A-B-A type structure (Fig. 4). In addition to, the molecule B is further stabilized by two pairs of intermolecular C68-H68A···Cl3 hydrogen bonding interactions between the -C68H68A unit of the coordinated

n-butanol molecule and the Cl3 atom of the benzene ring to form an infinite 1D chain along the a axis, as illustrated in Fig. 5. Thus, the molecule A, B, crystallizing water and *n*-butanol molecules are linked to form an infinite sandwich supramolecular structure through intermolecular O-H···O and C-H···O hydrogen bond interactions.

TABLE-3
DATA FOR HYDROGEN-BONDING INTERACTIONS (Å, º)

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A
C2-H2A···O12	0.97	2.37	3.245(10)	149
C6-H6···O13	0.93	2.56	3.212(8)	128
C13-H13···O13	0.93	2.55	3.242(8)	132
O16-H16···O11	0.82	2.35	3.126(6)	158
C18-H18B···O14	0.97	2.21	3.131(9)	159
C30-H30···O3	0.93	2.47	3.230(8)	139
C48-H48A···O23	0.97	2.32	3.196(9)	150
C52-H52···O22	0.93	2.58	3.210(8)	126
C59-H59···O22	0.93	2.57	3.248(8)	130
O15-H15···O27	0.82	1.84	2.663(6)	175
O24-H24···O26	0.82	1.84	2.663(6)	176
O25-H25···O26	0.82	1.99	2.763(10)	157
O26-H26···O22	0.82	1.92	2.732(8)	171
O27-H27C···O13	0.85	1.89	2.734(7)	174
O27-H27D···O25	0.85	1.88	2.726(10)	174
C68-H68A···Cl3	0.97	2.87	3.394(9)	114
C75-H75A···O27	0.97	2.19	2.770(13)	117

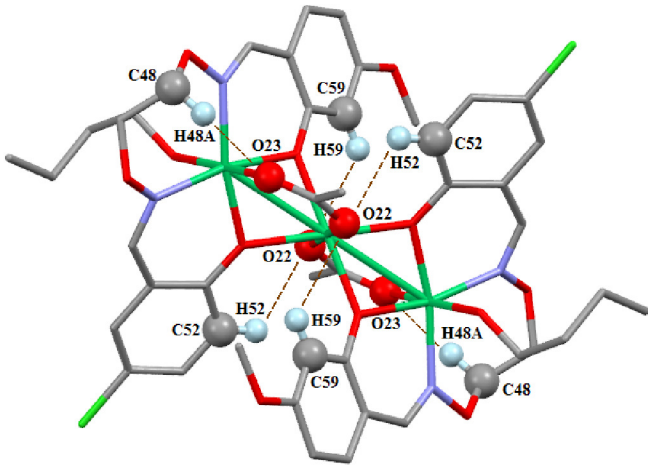


Fig. 3. View of the intramolecular hydrogen-bonding interactions of the molecule B

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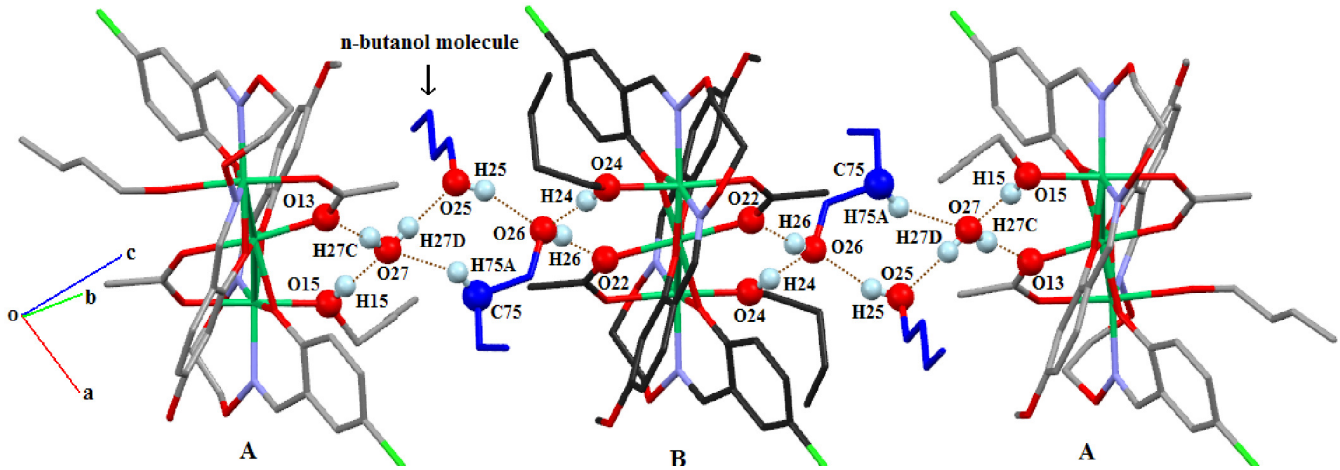

Fig. 4. View of the sandwich A-B-A type structure of the Ni(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

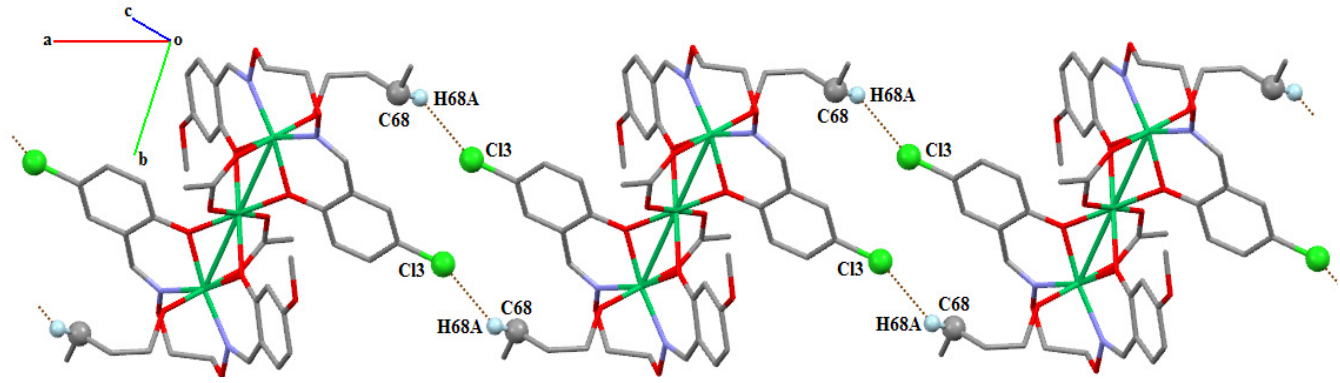

Fig. 5. (colour online). View of the 1D chain motif of the molecule B units along the a axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

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