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Supramolecular Self-Assembly and Crystal Structures of New Zinc(II) Complexes Derived from 4-Methyl-2-[(2-Methylaminoethylimino)methyl]phenol[1]

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Abstract—A new dinuclear zinc(II) complex, $[Zn_2Br_2L_2]$ (**I**), was prepared from 4-methyl-2-[(2-methylaminoethyl-imino)methyl]phenol (HL) with zinc bromide in methanol. Self-assembly of **I** with ammonium thiocyanate in methanol afforded the mononuclear complex $[Zn(L)(HL)]_2[Zn(NCS)_4]$ (**II**). Structures of complexes **I**, **II** have been characterized by elemental analysis, IR spectra and single crystal X-ray diffraction (CIF files CCDC nos. 1046617 (**I**), 1046618 (**II**)). Complex **I** possesses a crystallographic two-fold rotation axis symmetry, with Zn···Zn separation of 3.106(1) Å. Complex **II** contains two mononuclear zinc(II) complex cations and one $[Zn(NCS)_4]$ complex anion. The Zn(1) atom in **I** is in a tetrahedral coordination. The Zn(2) atom in **I** and the Zn atoms in **II** are in octahedral coordination. Crystals of **I**, **II** complexes are stabilized by hydrogen bonds.

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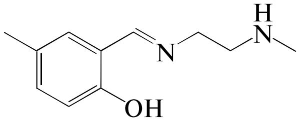
INTRODUCTION

Schiff bases are a kind of versatile ligands in coordination chemistry which are readily synthesized from the reaction of primary amines with carbonyl-containing compounds. In recent years, much work has been carried out on the syntheses and properties of Schiff bases and their complexes [1–5]. Schiff bases derived from salicylaldehyde and primary amines constitute one of the most relevant synthetic ligand systems with importance in asymmetric catalysis and they appear to be of importance for a broad range of transition-metal catalyzed reactions including lactide polymerization, epoxidation of olefins, hydroxylation and asymmetric ring opening of epoxides [6–10]. Although a number of Schiff bases and their complexes have been studied, the relationship between the self-assembly processes and structures has seldom been reported. In the present work, we report the synthesis, structural and spectroscopic properties of two new Schiff base zinc(II) complexes, $[Zn_2Br_2L_2]$ (**I**) and $[Zn(L)(HL)]_2[Zn(NCS)_4]$ (**II**), where L is the monoanionic form of 4-methyl-2-[(2-methylaminoethylimino)methyl]phenol (**HL**):



(HL)

EXPERIMENTAL

Materials and physical measurements. 5-Methylsalicylaldehyde and *N*-methylethane-1,2-diamine with AR grade were purchased from Lancaster. Other reagents and solvents were purchased from Shanghai Chemical Reagent Company and used as received. The mono-Schiff base HL was prepared according to the literature method [11]. C, H, and N elemental analyses were performed on a PerkinElmer 240C elemental analyzer. IR spectra were measured with a Nicolet FT-IR 170-SX spectrophotometer.

Synthesis of I. HL (2.0 mmol, 0.385 g) and zinc bromide (2.0 mmol, 0.450 g) were mixed in methanol. The mixture was stirred at room temperature for 30 min to give a slight yellow solution. Yellow block-like single crystals of complex **I**, suitable for X-ray dif-

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fraction, were obtained after slow evaporization of the solution in air. The yield was 72%.

For $C_{22}H_{30}N_4O_2Br_2Zn_2$

anal. calcd., %:	C, 39.26;	H, 4.49;	N, 8.32.
Found, %:	C, 39.39;	H, 4.56;	N, 8.17.

IR data (KBr; ν, cm^{-1}): 3231 w ν(N–H), 1623 s, ν(C=N).

Synthesis of II. Complex **I** (0.1 mmol, 67.3 mg) and ammonium thiocyanate (0.2 mmol, 15.2 mg) were mixed in methanol. The mixture was stirred at room temperature for 30 min to give a slight yellow solution. Slight yellow block-like single crystals of complex **II**, suitable for X-ray diffraction, were obtained after slow evaporization of the solution in air. The yield was 31%.

For $C_{48}H_{62}N_{12}O_4S_4Zn_3$

anal. calcd., %:	C, 48.22;	H, 5.23;	N, 14.06.
Found, %:	C, 48.08;	H, 5.35;	N, 13.97.

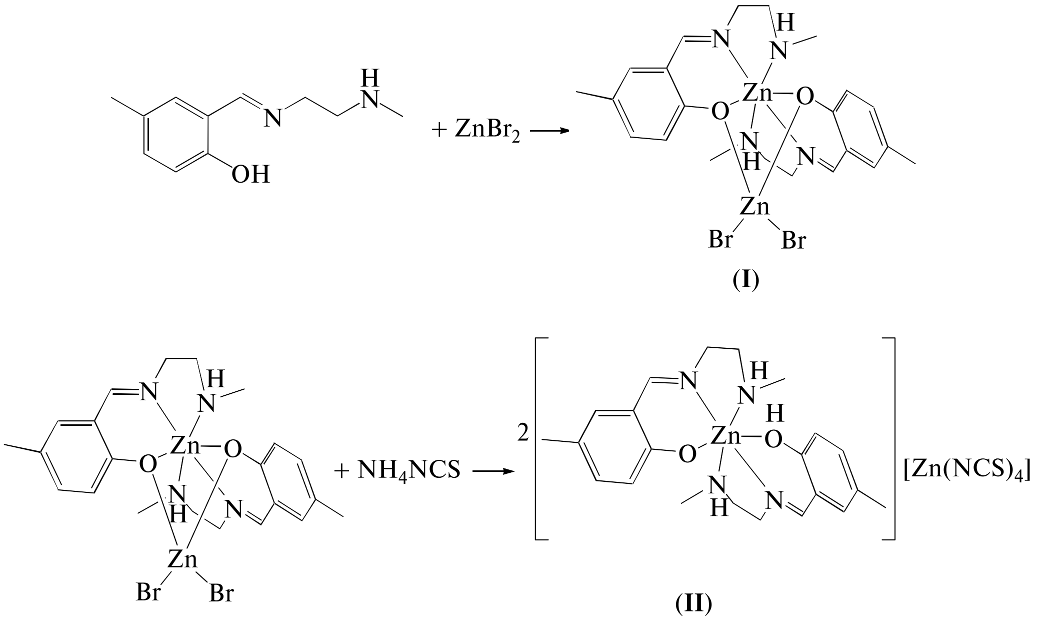
IR data (KBr; ν, cm^{-1}): 3210 w ν(N–H), 2077 s ν(NCS), 1622 s ν(C=N).

X-ray crystallography of I, II. Diffraction intensities for the complexes were collected at 298(2) K using Bruker SMART CCD detector with MoK_α radiation ($\lambda = 0.071073$ nm). The collected data were reduced using SAINT [12], and multi-scan absorption corrections were performed using SADABS [13]. Structures were solved by direct method and refined against F^2 by full-matrix least-squares method using SHELXTL [14]. All non-hydrogen atoms were refined anisotropically. The amino and hydroxyl H were located from difference Fourier maps and refined isotropically, with N–H and O–H distances restrained to 0.90(1) and 0.85(1) Å, respectively. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. A summary of the crystallographic data are given in Table 1. Coordinate bond lengths and angles are listed in Table 2.

Supplementary data for the structures have been deposited with the Cambridge Crystallographic Data Centre (nos. 1046617 (**I**) and 1046618 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The synthesis procedures for complexes **I**, **II** are shown in Scheme. Complex **I** was prepared by reaction of the mono-Schiff base with zinc bromide in methanol. Complex **II** was prepared by reaction of **I** with ammonium thiocyanate in methanol.



Scheme.

Table 1. Crystallographic data and structure refinement information for complexes **I** and **II**

Parameter	Value	
	I	**II**
Fw	673.06	1195.45
Crystal shape/colour	Block/yellow	Block/slight yellow
Crystal size (mm)	0.25 × 0.23 × 0.22	0.17 × 0.13 × 0.13
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$Pna2_1$
a, Å	23.463(3)	21.060(1)
b, Å	8.896(1)	15.3115(7)
c, Å	16.733(2)	17.0041(8)
β, deg	131.748(3)	
V, Å^3	2605.9(6)	5483.2(4)
Z	4	4
$\mu(\text{Mo}K_\alpha)$, mm^{-1}	4.933	1.507
$T_{\min}/T_{\max}$	0.3719/0.4100	0.7837/0.8281
ρ_{calcd}, g cm^{-3}	1.716	1.448
Reflections collected	11174	48054
Independent reflections (R_{int})	2418 (0.0542)	8998 (0.0496)
Observed reflections ($I \ge 2\sigma(I)$)	1832	7182
Numbers of parameters	151	658
Restraints	1	5
Goodness of fit on F^2	1.058	1.059
R_1, wR_2 ($I \ge 2\sigma(I)$)	0.0520, 0.1341	0.0501, 0.1102
R_1, wR_2 (all data)	0.0742, 0.1459	0.0705, 0.1186
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$, e Å^{-3}	0.906, –1.037	0.571, –0.437

The molecular structure of complex **I** is shown in Fig. 1a. X-ray crystallography reveals that the complex possesses a two-fold ratation axis symmetry with the axis passesses through the two Zn atoms. The two Zn atoms are bridged by two phenolate groups. The Zn···Zn separation is 3.106(1) Å. The Zn(1) atom is coordinated by two phenolate O atoms from two Schiff base ligands and two Br atoms, forming a tetrahedral coordination. The Zn(2) atom is coordinated by two phenolate O, two imino N and two amino N atoms from two Schiff base ligands, forming an octahedral coordination. The coordinate bond lengths in complex **I** are comparable to those reported in similar zinc(II) complexes [15, 16]. Molecule of **I** is butterfly-shaped with the dihedral angle formed by the two benzene rings of 70.8(3)°.

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

Bond	*d*, Å	Bond	*d*, Å
		I	
Zn(1)–O(1)	1.974(4)	Zn(1)–Br(1)	2.3566(9)
Zn(2)–N(1)	2.111(5)	Zn(2)–O(1)	2.163(4)
Zn(2)–N(2)	2.195(5)		
		II	
Zn(1)–N(1)	2.103(5)	Zn(1)–O(1)	2.109(3)
Zn(1)–N(3)	2.112(4)	Zn(1)–O(2)	2.151(4)
Zn(1)–N(2)	2.201(5)	Zn(1)–N(4)	2.214(6)
Zn(2)–O(3)	2.078(3)	Zn(2)–N(5)	2.090(4)
Zn(2)–N(7)	2.111(5)	Zn(2)–N(6)	2.177(5)
Zn(2)–O(4)	2.184(4)	Zn(2)–N(8)	2.225(5)
Zn(3)–N(11)	1.944(8)	Zn(3)–N(10)	1.955(9)
Zn(3)–N(9)	2.003(8)	Zn(3)–N(12)	2.026(8)
Angle	ω, deg	Angle	ω, deg
		I	
O(1)Zn(1)O(1*A*)	87.4(2)	O(1)Zn(1)Br(1*A*)	112.59(11)
O(1)Zn(1)Br(1)	114.71(12)	Br(1)Zn(1)Br(1*A*)	112.62(6)
N(1)Zn(2)O(1)	82.42(16)	O(1)Zn(2)O(1*A*)	78.2(2)
O(1)Zn(2)N(2)	159.63(17)	N(1)Zn(2)N(2)	79.32(18)
N(2)Zn(2)N(2*A*)	96.9(3)	O(1)Zn(2)N(2*A*)	95.30(17)
		II	
N(1)Zn(1)O(1)	84.31(16)	N(1)Zn(1)N(3)	174.96(19)
O(1)Zn(1)N(3)	95.77(15)	N(1)Zn(1)O(2)	102.30(17)
O(1)Zn(1)O(2)	85.89(14)	N(3)Zn(1)O(2)	82.72(15)
N(1)Zn(1)N(2)	79.5(2)	O(1)Zn(1)N(2)	161.8(2)
N(3)Zn(1)N(2)	101.1(2)	O(2)Zn(1)N(2)	89.5(2)
N(1)Zn(1)N(4)	96.94(19)	O(1)Zn(1)N(4)	94.15(18)
N(3)Zn(1)N(4)	78.03(19)	O(2)Zn(1)N(4)	160.66(18)
N(2)Zn(1)N(4)	96.0(3)	O(3)Zn(2)N(5)	86.30(16)
O(3)Zn(2)N(7)	96.93(16)	N(5)Zn(2)N(7)	176.13(18)
O(3)Zn(2)N(6)	164.7(2)	N(5)Zn(2)N(6)	80.4(2)
N(7)Zn(2)N(6)	96.1(2)	O(3)Zn(2)O(4)	85.75(14)
N(5)Zn(2)O(4)	95.85(16)	N(7)Zn(2)O(4)	82.32(15)
N(6)Zn(2)O(4)	88.12(19)	O(3)Zn(2)N(8)	90.60(17)
N(5)Zn(2)N(8)	101.68(19)	N(7)Zn(2)N(8)	80.47(18)
N(6)Zn(2)N(8)	99.4(2)	O(4)Zn(2)N(8)	161.83(18)
N(11)Zn(3)N(10)	115.1(3)	N(11)Zn(3)N(9)	110.3(3)
N(10)Zn(3)N9	105.6(3)	N(11)Zn(3)N(12)	109.6(3)
N(10)Zn(3)N(12)	104.1(4)	N(9)Zn(3)N(12)	112.1(3)

* Symmetry code for A: $-x$, y, $1/2 - z$.

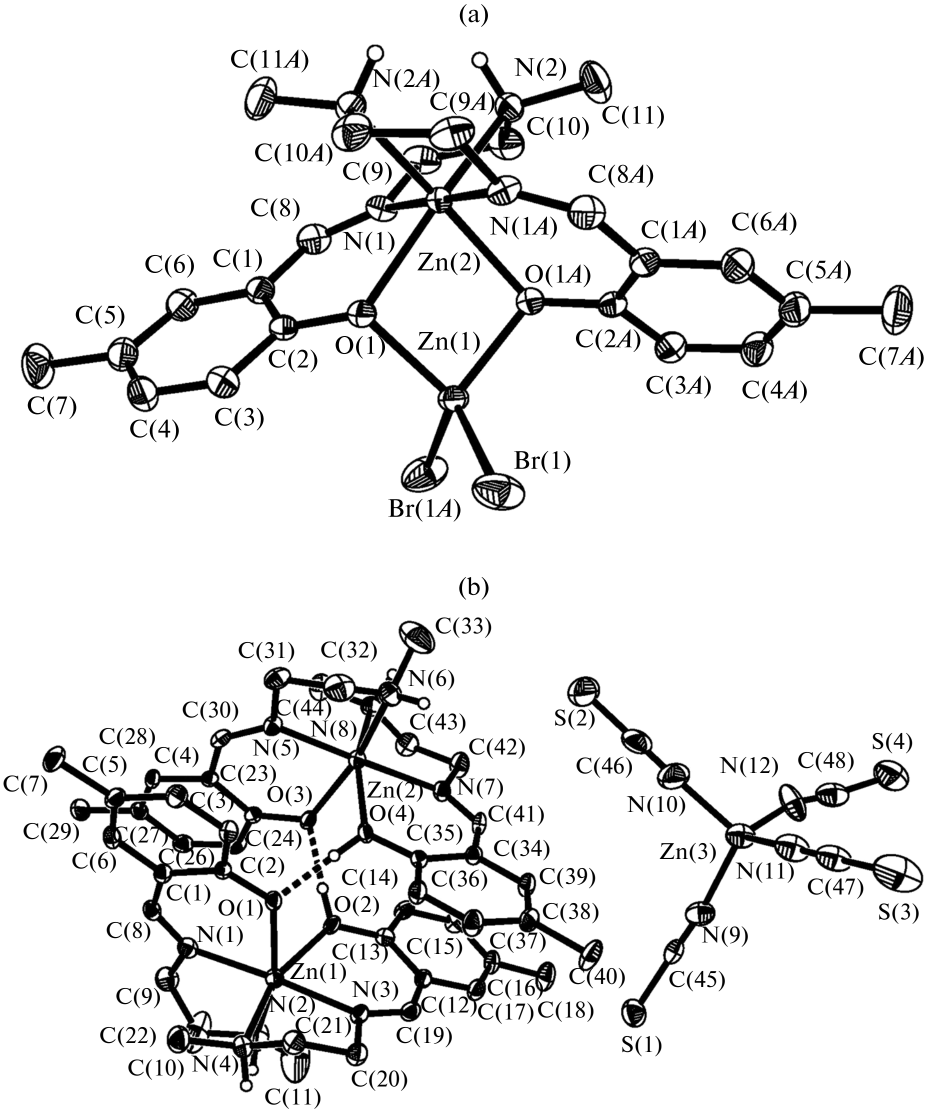


Fig. 1. The molecular structure of complexes **I** (a) and **II** (b). In **I**, atoms labeled with the suffix *A* are at the symmetry position $-x, y, 1/2 - z$. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms except for the amino H (for **I**, **II**) and hydroxyl H (for **II**) are omitted for clarity.

In the crystal structure of complex **I**, molecules are linked via intermolecular N(2)–H(2)···Br(1) hydrogen bonds (N(2)–H(2) 0.90(1), H(2)···Br(1)^i 2.76(3), N(2)···Br(1)^i 3.607(5) Å, N(2)–H(2)···Br(1)^i 158(7)°; symmetry code: ^{i} $-x$, y, $1/2 - z$), forming 1D chains running along *y* axis (Fig. 2a).

The molecular structure of complex **II** is shown in Fig. 1b. X-ray crystallography reveals that the complex contains two [Zn(L)(HL)] cations and one [Zn(NCS)$_4$] anion. The difference Fourier map of the complex reveals that there are H atoms attached to O(2) and O(4) atoms. The two [Zn(L)(HL)] units are linked together by intermolecular O(2)–H(2)···O(3) and O(4)–H(4*A*)···O(1) hydrogen bonds (O(2)–H(2) 0.85(1), H(2)···O(3) 1.61(1), O(2)···O(3) 2.455(5) Å, O(2)–H(2)···O(3) 176(8)°; O(4)–H(4*A*) 0.85(1), H(4*A*)···O(1) 1.62(2), O(4)···O(1) 2.456(5) Å, O(4)–H(4*A*)···O(1) 169(8)°). The Zn atoms in the cations are coordinated by two phenolate O, two imino N and two amino N atoms from two Schiff base ligands, forming octahedral coordination. The Zn atom in the anion is coordinated by four N atoms from four thiocyanate ligands, forming tetrahedral coordination. The coordinate bond lengths in complex **II** are comparable to those reported in similar zinc(II) complexes [17, 18].

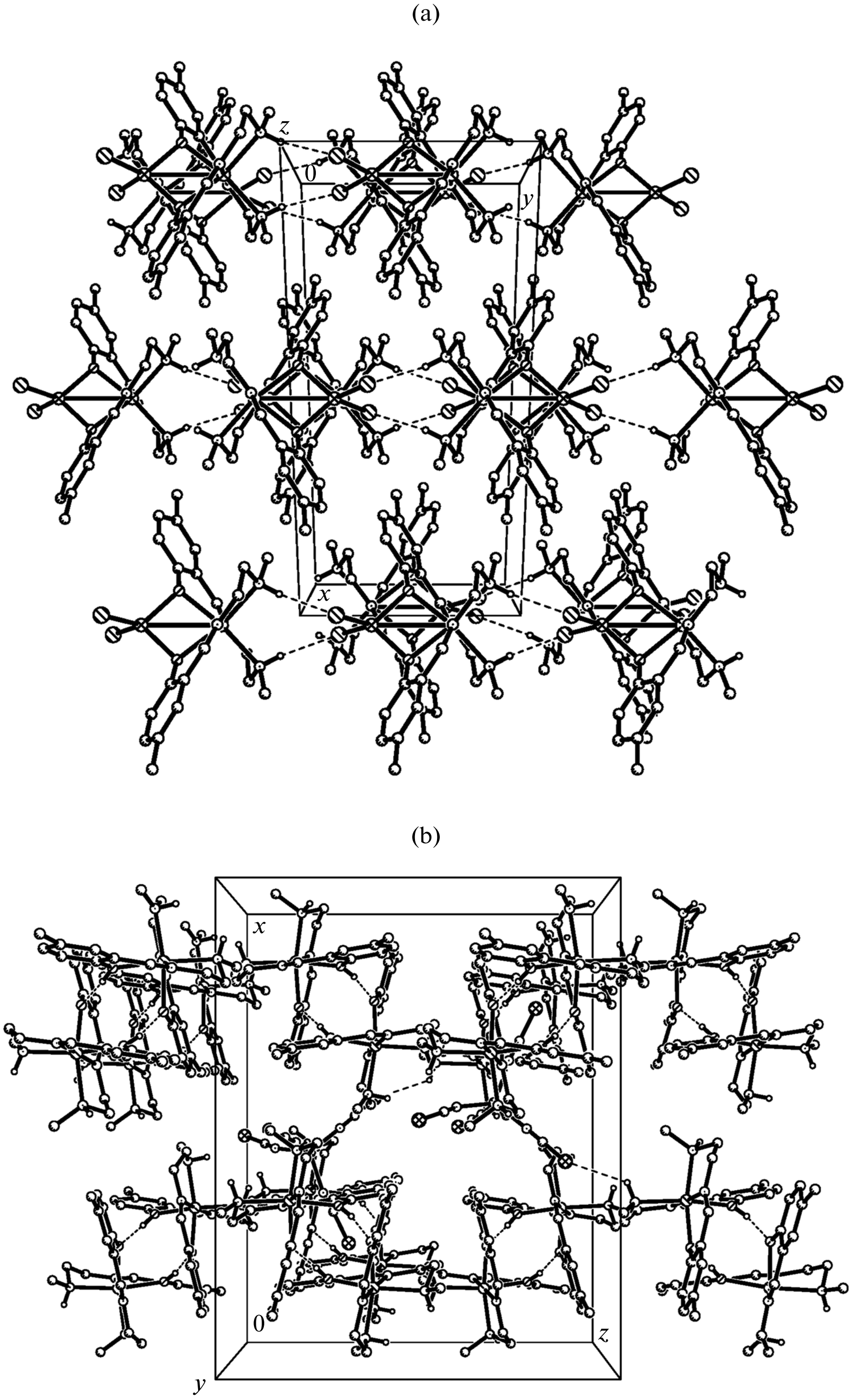


Fig. 2. Molecular packing of complexes **I** viewed along the *z* axis (a) and **II** viewed along the *y* axis (b). Hydrogen bonds are drawn as dashed lines.

The dihedral angles between the benzene rings are 69.8(3)° for Zn(1) molecule and 65.3(3)° for Zn(2) molecule.

In the crystal structure of complex **II**, molecules are linked via intermolecular N(8)–H(8*A*)···S(3)$^{\text{ii}}$ and N(4)–H(4)···N(12)$^{\text{iii}}$ hydrogen bonds (N(8)–H(8*A*)

0.91, H(8*A*)···S(3)^{ii} 2.82, N(8)···S(3)^{ii} 3.479(6) Å, N(8)–H(8*A*)···S(3)^{ii} 131(5)°; N(4)–H(4) 0.90(1), H(4)···N(12)^{iii} 2.68(3), N(4)···N(12)^{iii} 3.559(9) Å, N(4)–H(4)···N(12)^{iii} 163(6)°; symmetry codes: ^{ii} $1 - x$, $1 - y$, $-1 - z$; ^{iii} $3/2 + x$, $-1/2 - y$, z), forming a 3D network (Fig. 2b).

In the IR spectra of complexes **I**, **II**, there exist characteristic N–H vibrations in the region 3210–3230 cm^{-1}. The strong absorption bands at about 1622 cm^{-1} can be attributed to the vibration of the azomethine groups, ν(C=N) . The intense band centered at 2077 cm^{-1} for **II** is attributed to the strecting vibration of the thiocyanate ligands.

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