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Syntheses, Structures, and Luminescent Properties of Zinc(II) Complexes Based on Imidazole Derivative[1]

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Abstract—Two new Zn(II) coordination complexes $[ZnL_2(SCN)_2]$ (**I**) and $[ZnL_2Cl_2]$ (**II**) have been prepared by self-assembly of corresponding metal salts with (*E*)-2-(3-(4-(1*H*-imidazole-1-yl)styryl)-5,5-dimethylcyclohexo-2-enylidene) malononitrile (L) and characterized by IR spectrum, elemental analysis and single-crystal X-ray diffraction. Complexes **I** and **II** are two-dimensional (2D) networks with different topology structures. The luminescence properties were investigated.

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INSTRUCTION

The construction of supramolecular coordination complexes with novel topologies is of great interest because of their structural diversity and the applications of fluorescent sensing, molecular magnetism, nonlinear optics, catalysis, and gas sorption [1–6]. However, the factors influencing the construction of supramolecular coordination complexes are complicated. The general thought is that solvent system, different metal ions, organic ligands and counterions [7–11] may have a great influence on the self-assembly process. Among these, organic ligands, especially those with proper organic bridging linkers, have significant influences on the desirable supramolecular coordination complexes because of the different spacer lengths, steric hindrance effects, flexibility, conformational preferences and so on. Therefore, considerable efforts have been devoted to choose or design various multifunctional bridging ligands [12, 13].

Recently, the N,N'-bidentate donors ligands have attracted increasing attention in preparation of interesting supramolecular complexes due to their outstanding features of versatile coordination fashions [14–17]. Owing to these advantages, we designed and synthesized the ligand (*E*)-2-(3-(4-(1*H*-imidazole-1-yl)styryl)-5,5-dimethylcyclohexo-2-enylidene) (L) malononitrile which contain a π-conjugated system, imidazolyl, dicyano and isophorone groups. Structurally, imidazole and dicyano groups with electron-donating and electron-withdrawing ability are incorporated into molecular end, which is intended to enrich the π-electron density, increase the dimension of π-electron delocalization of the system and endow excellent optical properties. The isophorone structure provides an advantage that the steric hindrance associated with the ring structure as well as the dimethyl substituents of an isophorone unit is expected to hinder the formation of intermolecular π···π interactions, which may effectively avoid fluorescence quenching of complex in the solid state. On the other hand, the anions play an important role in the construction of coordination complexes with distinctive structures [18, 19]. In order to investigate the effect of anions on the complex structures based on the ligand and the changes of the optical properties, two anions (SCN^- and Cl^-) were used and a remarkable class of Zn(II)-containing coordination complexes were successfully synthesized: $ZnL_2(SCN)_2$ (**I**) and ZnL_2Cl_2 (**II**). Their syntheses, crystal structures and solid state luminescent properties were discussed in detail.

EXPERIMENTAL

General methods. All the reagents and solvents were commercially available and used without further purification. IR spectra were recorded from KBr discs in the 4000–40 cm^{-1} range on a nicolet Nexus 870 spectrophotometer. Elemental analyses were carried out on Vario EL III analyzer. The solid state luminescence spectra were measured on the Hitachi F-7000 fluorescence spectrophotometer. Time-resolved fluorescence measurements were performed on a HORIB Fluoro-Max-4P fluorescence spectrofluorometer. The decays were analyzed by least-squares. The quality of the exponential fits was evaluated by the goodness of fit (χ^2).

[1] The article is published in the original.

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

Parameter	Value	
	I	**II**
Formula weight	862.37	817.11
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a, Å	44.253(5)	9.249(5)
b, Å	5.587(5)	10.118(5)
c, Å	18.236(5)	22.442(5)
α, deg	90	88.499(5)
β, deg	98.257(5)	85.634(5)
γ, deg	90	82.282(5)
V, Å^3	4462(4)	2074.8(16)
Z	4	2
ρ_{calcd}, g cm^{-3}	1.284	1.308
μ, mm^{-1}	0.688	0.762
θ, Range, deg	0.93–25.94	0.91–25.00
F(000)	1792	848
Reflections collected/unique	15038/3933	14801/7217
R_{int}	0.0556	0.0251
GOOF on F^2	1.053	1.033
Final R indices, $I > 2\sigma(I)$	$R_1 = 0.0658$, $wR_2 = 0.1796$	$R_1 = 0.0394$, $wR_2 = 0.1151$
R indices, all data	$R_1 = 0.1362$, $wR_2 = 0.2355$	$R_1 = 0.0540$, $wR_2 = 0.1242$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.300/–1.031	0.513/–0.474

Synthesis of L was carried out as described in [20].

Synthesis of complex I. A solution of $Zn(SCN)_2$ (0.04 g, 0.22 mmol) in methanol (10 mL) was added to a solution of L (0.15 g, 0.44 mmol) in chloroform (10 mL) and the resulting mixed solution was stirred at room temperature. Yellow solid were separated out from the solution at once. The solid were dissolved in acetonitrile and the solution was left to evaporate slowly at room temperature. After one week, yellow block crystals were isolated with a yield of 0.10 g (40%).

For $C_{46}H_{40}N_{10}S_2Zn$

anal. calcd. %:	C, 64.06;	H, 4.68;	N, 16.24.
Found %:	C, 63.90;	H, 4.59;	N, 15.92.

IR (ν, cm^{-1}): 3436 ν(NH), 3123 ν(=CH), 2959 ν(CH_3), 2221 ν(CN), 1567 ν(C_6H_6), 1524 ν(C_6H_6).

Synthesis of complex II. A methanol solution (10 mL) of $ZnCl_2$ (0.03 g, 0.22 mmol) was carefully layered onto a solution of L (0.15 g, 0.44 mmol) in chloroform (10 mL) at room temperature. After a week, orange block crystals of **II** were collected by filtration with a yield of 0.11 g (61%).

For $C_{44}H_{40}N_8Cl_2Zn$

anal. calcd. %:	C, 64.67;	H, 4.93;	N, 13.71.
Found %:	C, 64.52;	H, 4.87;	N, 13.63.

IR (ν, cm^{-1}): 3435 ν(NH), 3142 ν(=CH), 2958 ν(CH_3), 2221 ν(CN), 1567 ν(C_6H_6), 1523 ν(C_6H_6).

X-ray crystallography. The X-ray diffraction measurements were performed on Bruker SMART CCD area detector using graphite monochromated MoK_α radiation (λ = 0.71069 Å) at 298(2) K. Intensity data were collected in the variable ω-scan mode. The structures were solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with SHELXTL program package [21]. Details of the crystal parameters, data collections and refinements are listed in Table 1, and selected bond distances and angles are given in Table 2.

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

Bond	*d*, Å	Bond	*d*, Å
		I	
Zn(1)–N(4)	1.979(5)	Zn(1)–N(5)	1.929(8)
		II	
Zn(1)–N(5)	2.024(2)	Zn(1)–N(4)	2.028(2)
Zn(1)–Cl(1)	2.2338(12)	Zn(1)–Cl(2)	2.2397(11)
Angle	ω, deg	Angle	ω, deg
		I	
$N(5)^{\#1}Zn(1)N(5)$	112.8(4)	$N(5)Zn(1)N(4)^{\#1}$	114.4(3)
N(5)Zn(1)N(4)	102.2(2)	$N(4)Zn(1)N(4)^{\#1}$	111.3(3)
		II	
N(5)Zn(1)N(4)	101.70(9)	N(5)Zn(1)Cl(1)	109.26(7)
N(4)Zn(1)Cl(1)	109.33(7)	N(5)Zn(1)Cl(2)	106.51(7)
N(4)Zn(1)Cl(2)	114.83(7)	Cl(1)Zn(1)Cl(2)	114.30(4)

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

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (no. 957854 (**I**), 957864 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In complex **I**, crystallizes in the monoclinic system, space group *C*2/*c*. And one Zn^{2+} ion, two L ligands and two SCN^- anions constitute a V-type structure. The crystallographically unique Zn^{2+} ion is four-coordinated by two N atoms from imidazolyl groups of two distinct L ligands and two N atoms from two distinct SCN anions (Zn(1)–N(4) 1.979 Å and Zn(1)–N(5) 1.929 Å), showing a distorted tetrahedral geometry ($ZnL_2(SCN)_2$) (Fig. 1a). The bond angles around the Zn^{2+} ion are in the range of 102.20(9)°–114.40(7)°. The selected bond distances and angles are shown in Table 2. Two adjacent unit cells are linked by two kinds of C(5)–H(5A)···π(C(12)–C(13)) hydrogen bonds (the distance of H···centroid is 2.75 Å and the angle of C–H···centroid is 156.15°) and C(22)–H(22)···S(1) hydrogen bonds (the distance of H···S is 2.85 Å and the angle of C–H···S is 170°), and such structural units are further extended to a 1D chain along the y axis (Fig. 1a). Through two kinds of C–H···N hydrogen bonds (the distance of H(13)···N(2) is 2.652 Å, H(19)···N(2) is 2.607 Å, and the angle of C–H···N is 149.0° and 152.3°), these 1D chains are further assembled into the 2D supramolecular layer (Fig. 1b).

As illustrated in Fig. 2, the asymmetric unit of **II** consists of one Zn(II) atom, two L ligands and two chlorine ions. The central Zn^{2+} ion is also four-coordinated by two terminal chlorine ions and two N atoms of imidazolyl groups from two ligands to from a slightly distorted tetrahedral geometry. The bond angles around the Zn^{2+} ion are in the range of 101.70(9)°–114.83(7)°. The selected bond distances and angles are shown in Table 2. In the molecular packing structure of complex **II**, the C–H···Cl, C–H···N hydrogen bonding interactions and the C–H···π interactions play a significant role. As shown in Fig. 2a, two molecules of the complex are interconnected by C(23)–H(23)···Cl(1) hydrogen bonding interaction (the distance of H···Cl is 2.88 Å and the angle of C–H···Cl is 160°) and C(16)–H(16)···π interaction (the H(16)···centroid distances is 2.91 Å) to form a dimmer. The neighboring dimmers are further linked by C(21)–H(21)···N(2), C(18)–H(18)···N(2) hydrogen bonding interactions and C(38)–H(38*B*)···π interactions (the H(21)···N(2), H(18)···N(2), and H(38*B*)···π centroid distances are 2.52, 2.50, and 3.25 Å, respectively), giving rise to an extended 1D chain, as shown in Fig. 2b. The adjacent chains are stacked through C(24)–H(24)···Cl(2) hydrogen bonding interactions (H(24)···Cl(2) 2.92 Å) to form 2D supramolecular structure (Fig. 2c).

From the above-mentioned structural descriptions, it can be seen that L ligands show similar structural features and the same coordination modes. In complexes **I** and **II**, because of the steric repulsion formed by the isophorone group, neutral L coordinates to one

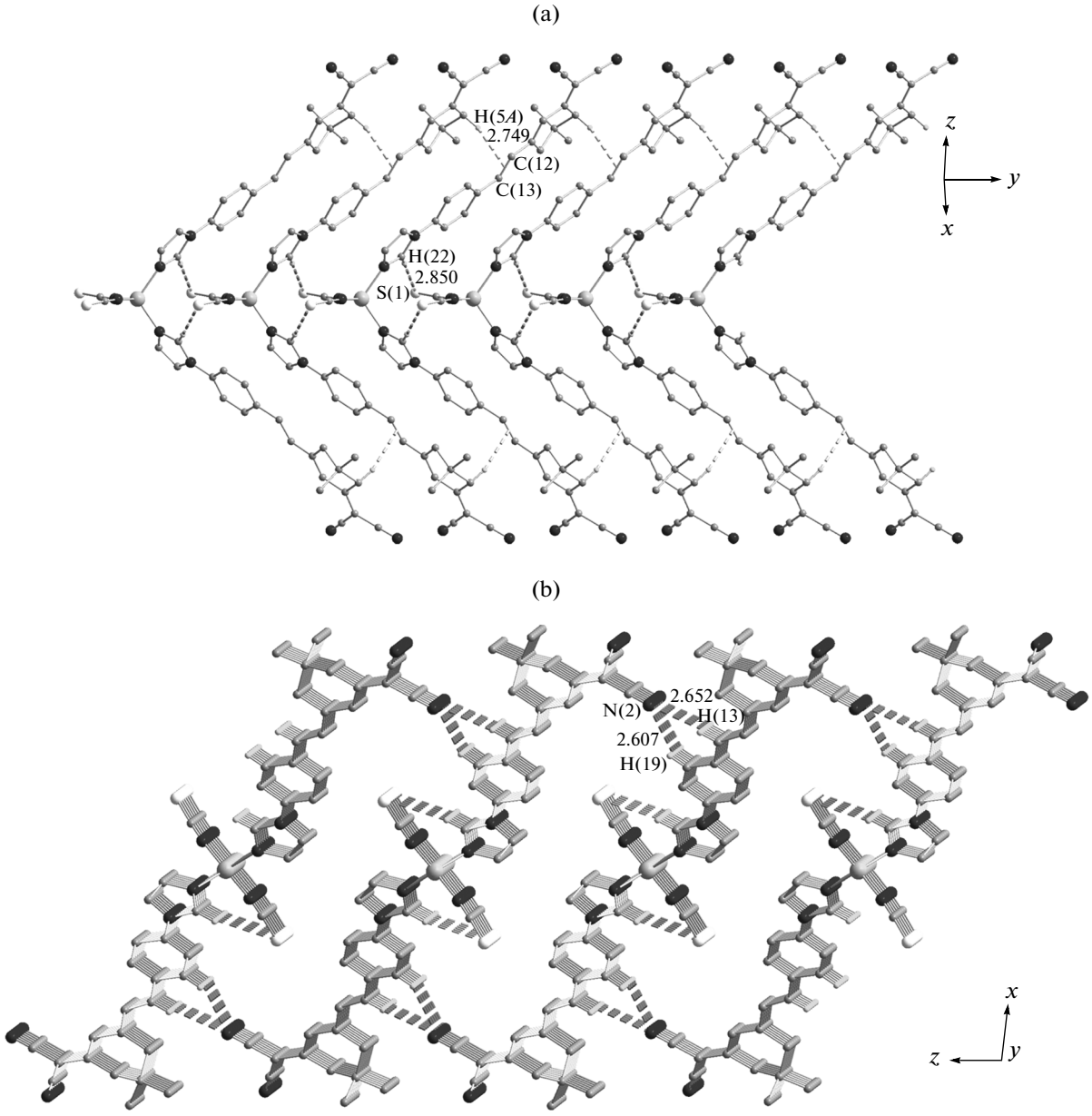

Fig. 1. The one-dimensional structure of complex **I** (a); the two-dimensional structure of complex **I** viewed along *y* axis (b).

metal center with one N atom from each imidazole group. So complexes **I** and **II** show the similar 1D chain structures. Additionally, the cyano N atoms of the ligand are not directly involved in coordination, but play an important role in the formation of higher-dimensional structures through C–H···N hydrogen bonding interactions. The anion also acts as a key role in determining the structures of the resultant complexes. The complexes **I** and **II** show the effect of anions (SCN^- and Cl^-) on their complex structures. The coordination ability and the size of the anions influence the angles, which further result in the structural distinction of the Zn(II) atoms.

Metal-organic complexes consisting of d^{10} metal atoms and organic ligands are promising candidates for applicable hybrid photoactive materials such as light-emitting diodes (LEDS) [22–24]. Therefore, the solid-state luminescent spectra of the neutral ligand and the complexes **I** and **II** have been investigated at room temperature (Fig. 3). The main emission peak of L is at 521 nm, which may be attributed to π–π* transition. Compared to that of L, the maximum emission peaks of **I** and **II** are red shifted to 536 and 530 nm, respectively. The red shifts may be attributed to the cooperative effects of the neutral ligand and metal salts.

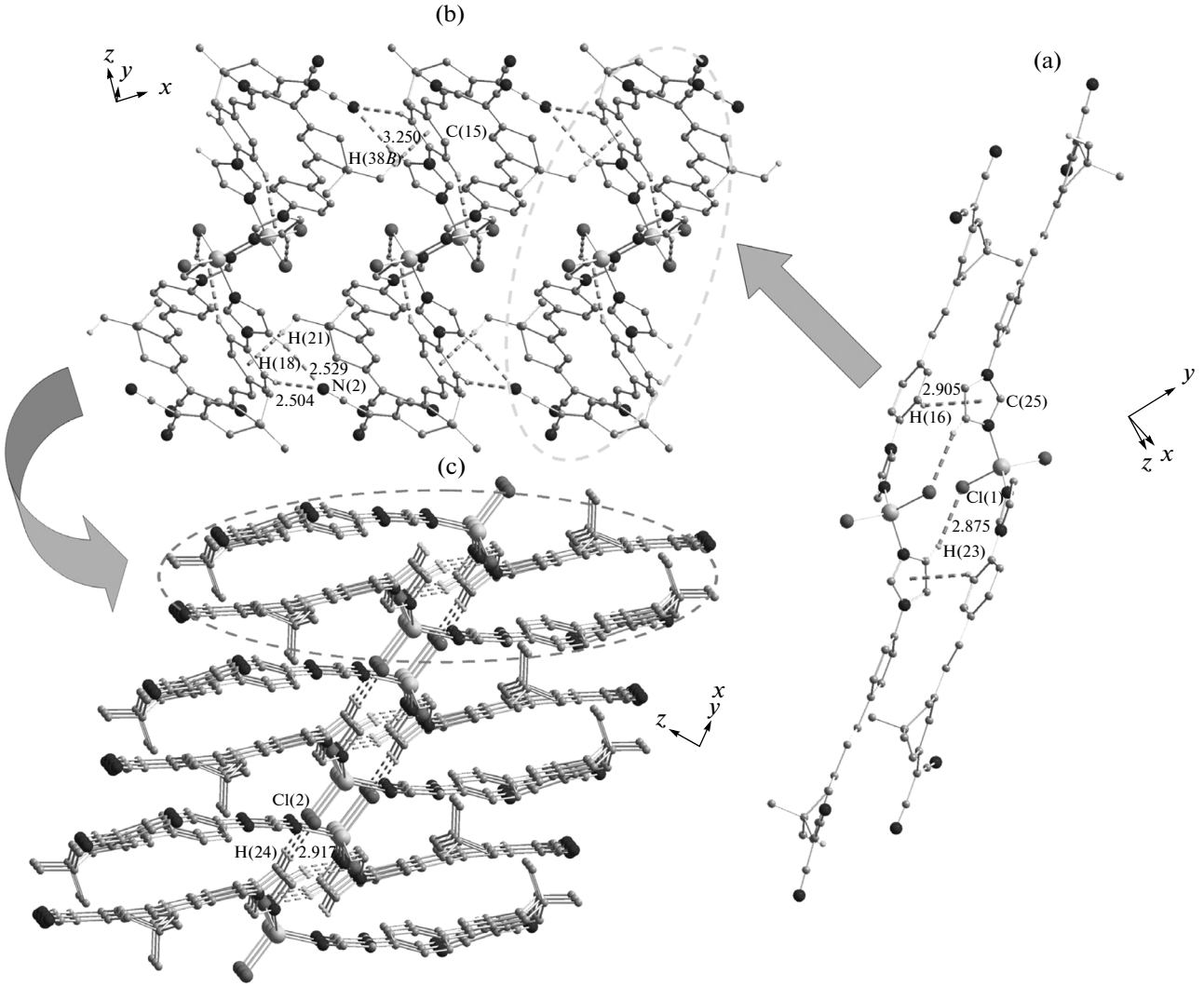

Fig. 2. Two molecules of complex **II** are interconnected though intermolecular weak interactions (a); the one-dimensional structure of complex **II** (b); the two-dimensional structure of complex **II** (c).

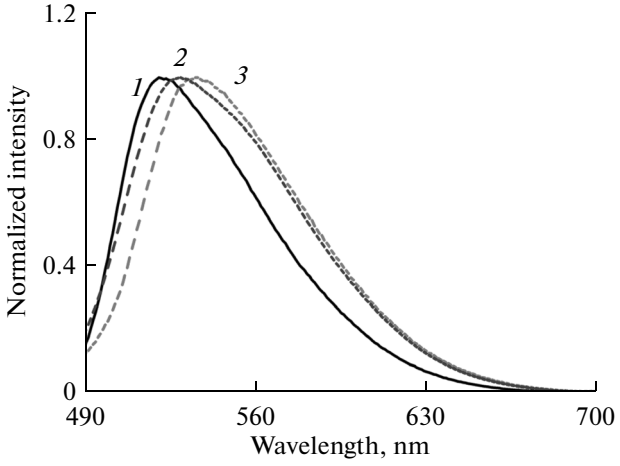

Fig. 3. Solid-state emission spectra of L (*1*) and complexes **I** (*2*), **II** (*3*) at room temperature.

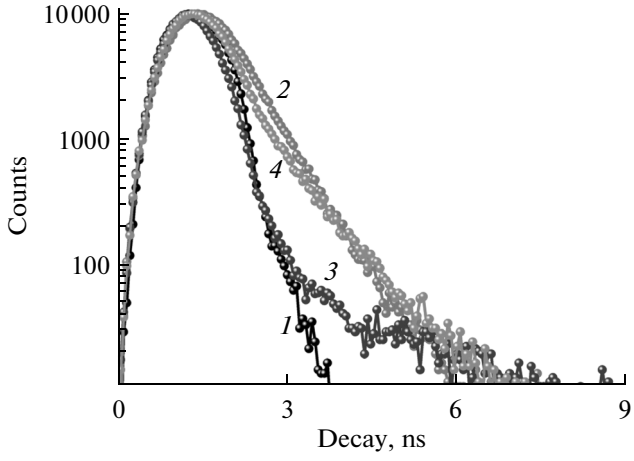

Fig. 4. Time-resolved fluorescence curves: SiO_2 (*1*), L (*2*) and complexes **I** (*3*), **II** (*4*) in the solid state at room temperature.

The fluorescence decay profiles of L and complexes **I** and **II** were measured at their optical excitation wavelengths in the solid state at room temperature (Fig. 4). The fluorescence lifetime of **I** is less than 0.1 ns. The fluorescence lifetimes of L and **II** are 0.27 and 0.1 ns, respectively. The different anions and coordination environments of metal centres would have an effect on the emission wavelength, intensity, and fluorescence lifetimes of the complexes.

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