ORIGINAL PAPER



Six New Complexes Based on Substituted Pyridazine Ligands: Structures and Luminescent Properties

Sheng-Bin Zhou¹ · Ceng-Ceng Du¹ · Xin-fang Wang¹ · Ying-Zhi Han¹ · Jun-Liang Dong¹ · Duo-Zhi Wang^{1,2}

Received: 18 August 2016 / Accepted: 10 August 2017 © Springer Science+Business Media, LLC 2017

Abstract Three structurally related ligands 3-chloro-6-(benzoimidazol-1-yl)pyridazine (L¹), 3-chloro-6-(1,2,4triazol-1-yl)pyridazine (L²) and 3,6-bis(imidazol-1-yl) pyridazine (L^3) were designed and synthesized, and six new Zn(II), Co(II), Cu(II) and Cd(II) complexes, namely, $[M(L^{1})_{2}Cl_{2}]$ [M = Zn (1) and Co (2)], [Cu(L^{2})_{2}(NO_{3})_{2}(H_{2}O)] (3), $[Cu(L^2)_2Cl_2]_{\infty}$ (4), $[CuL^3(CH_3COO)_2]_{\infty}$ (5) and $[CdL^{3}(SCN)_{2}]_{\infty}$ (6) were synthesized and characterized by elemental analyses, IR spectra as well as single-crystal X-ray diffraction analysis. The analysis reveals that complexes 1, 2 and 3 have a mononuclear structure, 1 and 2 have a similar structure. Complex 3 features a 1D structure with intermolecular O-H···O hydrogen bonding interactions. Complex 4 shows a 1D chain structure with bridging Cl⁻ ions. Complex 5 exhibits a 1D ladder structure. The 2D framework of 6 features are rectangular grid with a (4, 4) topology. Additionally, photoluminescence properties of ligands L^1 , L^3 and complexes 1, 2 and 6 have been studied and discussed.

Graphical Abstract Six new metal-organic complexes were synthesized and structurally characterized, complexes 1, 2 and 3 have a mononuclear structure, complexes 4 and 5 show 1D chain structure, the 2D framework of 6 has a

Electronic supplementary material The online version of this article (doi:10.1007/s10870-017-0699-6) contains supplementary material, which is available to authorized users.

- ¹ College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, People's Republic of China
- ² Key Laboratory of Energy Materials Chemistry, Ministry of Education, Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, Xinjiang, People's Republic of China

rectangle grid with a (4, 4) topology, moreover, photoluminescence properties of ligands L^1, L^3 and complexes 1, 2 and 6 have been studied and discussed.



Keywords Complexes · Substituted pyridazine · Crystal structure · Photoluminescence properties

Introduction

The past decade has witnessed a rapid development in the design and construction of metal–organic frameworks (MOFs) for their intriguing structural features and potentially useful applications such as gas adsorption and separation, luminescence, catalysis, sensors and molecular magnets [1-14]. It's worth noting that the controlled assembly of coordination polymers with particular structures and properties is still a significant challenge fraught with difficulties, due to the unpredictability of resulting compounds when modulating the chemical environment, such as metal ions, organic ligands, reagent ratio, solvents, pH value, temperature, and so on [15-22].

The synthesis of new N-donor ligands is a long-standing fascination of chemists, and so far, many N-donor ligands have been reported and studied [23–32]. Efforts have been focused on ligands based on azole heterocycles, which have both good coordination ability and diverse coordination

Duo-Zhi Wang wangdz@xju.edu.cn



Chart 1 The structure of ligands L^1-L^3

modes. Polydentate nitrogen heterocyclic ligands which contain five-membered rings (azoles) have been well used in the construction of supramolecular structures. Especially, the organic ligands triazole, imidazole and benzimidazole have an important role in the design and construction of metal–organic frameworks [33–40]. Generally, building coordination polymer materials with potential for applications mainly depends on the configuration and coordination of the ligands and the characteristics of metal ions. In particular, the conformational flexibility of the ligand is an important factor that is considered in the design of the targeted coordination polymers, because the linker could adopt various conformations in the crystallization and that further leads to structural isomerism.

Considering the above, six new complexes $[M(L^1)_2Cl_2]$ $[M = Zn (1) \text{ and Co (2)}], [Cu(L^2)_2(NO_3)_2(H_2O)] (3), [Cu(L^2)_2Cl_2]_{\infty} (4), [CuL^3(CH_3COO)_2]_{\infty} (5) \text{ and} [CdL^3(SCN)_2]_{\infty} (6) were synthesized and structurally characterized, using structurally related ligands 3-chloro-6-(benzoimidazol-1-yl)pyridazine (L^1), 3-chloro-6-(1,2,4-triazol-1-yl)pyridazine (L^2) and 3,6-bis(imidazol-1-yl) pyridazine (L^3)(Chart 1). Photoluminescence properties of ligands L¹, L³ and complexes 1, 2 and 6 have been studied and discussed.$

Experimental Section

Materials and General Methods

All reagents used for the syntheses were commercially available and employed without further purification. Elemental analysis of C, H and N were determined with a Thermo Flash EA 1112-NCHS-O analyzer. IR spectra were measured as KBr pellets using a Bruker Equinox 55 FT-IR spectrometer. ¹H NMR data were collected using an INOVA-400 NMR spectrometer and chemical shifts are reported in d relative to TMS. Solid state luminescent spectra were measured with a Hitachi F-4500 Fluorescence Spectrophotometer with a Xe arc lamp as the light source and bandwidths of 2.5 nm at room temperature.

Synthesis of Ligands L¹–L³

Preparation of 3-Chloro-6-(benzoimidazol-1-yl)pyridazine (L^1)

A mixture of benzoimidazole (1.18 g, 10 mmol), 3,6-dichloropyridazine (1.49 g, 10 mmol), sodium (0.23 g, 10 mmol) in 40 mL anhydrous THF was refluxed for 5 h under N₂. When the reaction was completed, the solution was cooled and the solvent evaporated. The crude product was purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 1:10), a pale yellow solid was obtained, yield 69.4%, m.p. 185–186 °C. ¹H NMR (CDCl₂): δ: 8.661 (s, 1H, imidazole-2), 7.442 (d, 2H, benzene), 7.747 (d, 1H, pyridazine-4), 8.138 (d, 1H, pyridazine-5), 7.913 (d, 2H, benzene). Anal. Calcd for C₁₁H₇N₄Cl: C, 57.28; H, 3.06; N, 24.29; Found: C, 57.53; H, 3.25; N, 24.46. IR (cm⁻¹, KBr pellets): 3146w, 3095 m, 3069 m, 1827w, 1793w, 1758w, 1736w, 1683w, 1608m, 1573s, 1544s, 1505s, 1456s, 1438s, 1427s, 1195s, 1171m, 1147m, 1108m, 1071s, 1010m, 988s, 938w, 883m, 858m, 842s, 781m, 769s, 745s, 647w, 636w, 620w.

Preparation of 3-Chloro-6-(1,2,4-triazol-1-yl)pyridazine (L^2)

The synthetic method of L^2 is the same as that for L^1 , except for using 1,2,4-triazole instead of benzoimidazole. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:2), a white solid was obtained, yield 68%, m.p. 167–168 °C. ¹H NMR (CDCl₃): δ : 9.367 (s, 1H, triazole-5), 8.160 (s, 2H, pyridazine), 7.746 (s, 1H, triazole-3). Anal. Calcd for C₆H₄N₅Cl: C, 39.69; H, 2.22; N, 38.57; Found: C, 39.47; H, 2.04; N, 38.36. IR (cm⁻¹, KBr pellets): 3087w, 3056w, 2830w, 2738w, 1696s, 1602s, 1516m, 1496m, 1452s, 1372m, 1303m, 1204m, 1170m, 1110w, 1009w, 970w, 933w, 885w, 830s, 764m, 739s, 696w, 627w, 579m, 501w, 482w, 424m.

Preparation of 3,6-bis(imidazol-1-yl)pyridazine (L^3)

Imidazole (3.4 g, 49.9 mmol) and sodium (1.2 g, 52.2 mmol) were added to 80 mL THF, and the solution was heated to reflux for 40 min. A solution of 3,6-dichloropyridazine (3.7 g, 24.8 mmol) in THF (10 mL) was added to the mixture within 40 min. The mixture was refluxed for 4 h under N₂, then stirred for 30 min. After the reaction mixture was cooled to room temperature, it was poured into ice water and an earthy yellow solid of L^3 was obtained after filtering

and distilling off the filtrate. The compound was recrystallized from absolute ethanol to give pure ligand L^3 as white crystals, yield 80%, m.p. 281–282 °C. ¹H NMR (DMSO): δ : 8.69 (s, 2H, imidazole-2), 8.48 (s, 2H, pyridazine), 8.11 (d, 2H, imidazole-5), 7.23 (d, 2H, imidazole-4); Anal. Calcd for C₁₀H₈N₆: C, 56.60; H, 3.80; N, 39.60; Found: C, 56.75; H, 3.75; N, 39.54. IR (cm⁻¹, KBr pellets): 3176w, 3145m, 3109m, 3047m, 3018m, 2946m, 2782w, 2621w, 2526w, 2408w, 2214w, 1991w, 1903w, 1795w, 1727w, 1692w, 1645w, 1577s, 1519s, 1490s, 1459s, 1371s, 1321s, 1277s, 1237s, 1163m, 1106m, 1059m, 1031s, 962m, 903m, 861s, 823s, 766s, 749s, 645s, 613m, 507w, 487m, 421m.

Synthesis of Complexes 1-6

Preparation of $[Zn(L^1)_2Cl_2](1)$

Complex 1 was prepared by dissolving ZnCl_2 (0.5 mmol) and \mathbf{L}^1 (0.5 mmol) in ethanol (15 mL) and subsequent refluxing for 4 h. The solution was then cooled and filtrated. Pale yellow plate-shaped crystals formed by evaporation of the solvent after 1 week (ca. 43% yield based on \mathbf{L}^1). Anal. Calcd for C₂₂H₁₄N₈Cl₄Zn: C, 44.21; H, 2.36; N, 18.75; Found: C, 44.09; H, 2.18; N, 18.56. IR (cm⁻¹, KBr pellets): 3145w, 3067w, 2973w, 2922w, 2857w, 2709w, 2584w, 2530w, 2329w, 1957w, 1784w, 1721w, 1613m, 1576m, 1548m, 1515s, 1484s, 1425s, 1356m, 1304s, 1246s, 1179m, 1158m, 1080m, 989m, 915w, 862m, 831m, 763s, 746m.

Preparation of $[Co(L^1)_2Cl_2](2)$

Pink plate-shaped crystals of **2** suitable for X-ray analysis were obtained by a similar method as described for **1**, except for using $CoCl_2 \cdot 6H_2O$ instead of $ZnCl_2$ (ca. 45% yield based on L¹). Anal. Calcd for $C_{22}H_{14}N_8Cl_4Co$: C, 44.66; H, 2.37; N, 18.95; Found: C, 44.91; H, 2.83; N, 18.51. IR (cm⁻¹, KBr pellets): 3147w, 3122w, 3065w, 1718w, 1612w, 1576m, 1548m, 1511s, 1479m, 1463s, 1425s, 1372w, 1355w, 1345w, 1303m, 1285w, 1245s, 1179w, 1158m, 1113w, 1081m, 1015w, 989w, 948w, 916w, 860w, 831m, 782w, 763m, 746m, 667w, 617w.

Preparation of $[Cu(L^2)_2(NO_3)_2(H_2O)]$ (3)

Complex **3** was prepared by dissolving Cu(NO₃)₂·3H₂O (0.4 mmol) and L^2 (0.4 mmol) in a acetonitrile solution (15 mL) and then filtrated. Blue plate-shaped crystals were obtained after several days after evaporation of the filtrate (ca. 45% yield based on L^2). Anal. Calcd for C₁₂H₁₀N₁₂O₇Cl₂Cu: C, 33.99; H, 2.48; N, 19.83; Found: C, 40.24; H, 2.29; N, 19.68. IR (cm⁻¹, KBr pellets): 3625*w*, 3162*w*, 3141*s*, 3068*m*, 1613*m*, 1568*w*, 1538*m*, 1456*s*, 1413*s*, 1438*s*, 1303*m*, 1276*m*, 1211*s*, 1188*m*, 1145*s*, 1102*w*,

1402*m*, 1023*m*, 999*m*, 971*m*, 888*w*, 858*m*, 812*m*, 708*m*, 744*w*, 664*m*.

Preparation of $[Cu(L^2)_2Cl_2]_{\infty}(4)$

This complex was obtained as purple crystals by a procedure analogous to that of **3**, but with CuCl₂·2H₂O (0.3 mmol) instead of Cu(NO₃)₂·3H₂O (ca. 28% yield based on L^2). Anal. Calcd for C₁₂H₈N₁₀Cl₄Cu: C, 28.94; H, 1.61; N, 28.13; Found: C, 28.57; H, 1.53; N, 28.31. IR (cm⁻¹, KBr pellets): 3285w, 3167m, 3158m, 3135w, 3083m, 1567m, 1522m, 1458m, 1409m, 1378m, 1339w, 1316w, 1296w, 1275w, 1193w, 1179w, 1142s, 1098m, 1040m, 1028m, 994m, 973m, 901w, 890m, 876w, 841m, 829m, 778m, 670m, 643m.

Preparation of $[CuL^3(CH_3COO)_2]_{\infty}(5)$

Complex **5** was prepared by dissolving Cu(CH₃COO)₂·H₂O (0.4 mmol) and L^3 (0.4 mmol) in CH₃OH/H₂O (1:1) and subsequent refluxing for 2 h. Blue plate-shaped crystals were obtained after several months after evaporation of the filtrate (ca. 37% yield based on L^3). Anal. Calcd for C₁₄H₁₄N₆O₄Cu: C, 42.69; H, 3.58; N, 21.34; Found: C, 42.27; H, 3.91; N, 21.02. IR (cm⁻¹, KBr pellets): 3376*w*, 3284*w*, 3150*w*, 3132*w*, 1650*w*, 1584*s*, 1535*w*, 1499*s*, 1458*s*, 1411*m*, 1387*m*, 1337*m*, 1315*m*, 1252*w*, 1150*w*, 1101*w*, 1068*s*, 1037*m*, 970*m*, 947*m*, 834*m*, 710*w*, 672*w*, 645*w*, 618*w*.

Preparation of $[CdL^3(SCN)_2]_{\infty}(6)$

A mixture of $CdSiF_6.6H_2O$ (0.4 mmol), KSCN (0.4 mmol) and L^3 (0.4 mmol) in 5 mL of H_2O was placed in a Teflon vessel in a steel autoclave, heated at 130 °C for 72 h and then cooled to room temperature at a rate of 10 °C·h⁻¹. The resulting colorless block-shaped crystals of **6** were washed several times with water. The yield is 42% based on Cd. Anal. Calcd for $C_{12}H_8N_8S_2Cd$: C, 43.89; H, 2.46; N, 34.12; Found: C, 43.58; H, 2.23; N, 34.39. IR (cm⁻¹, KBr pellets): 3158w, 3125w, 3064w, 2087s, 2069s, 1579s, 1530m, 1504s, 1453s, 1325m, 1309s, 1279m, 1248m, 1145w, 1103w, 1073s, 1038m, 971s, 948m, 827m. 813m, 738s, 644m, 620m.

X-Ray Crystallography

X-ray single-crystal diffraction data for complexes **1–6** were collected on a Bruker Smart 1000 CCD diffractometer at 293(2) K with Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) with $\omega -\varphi$ scans. The program SAINT [41] was used for integration. Semi-empirical absorption corrections were applied using SADABS program [42]. All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [43]. All non-hydrogen atoms in each

complex were located from the *E*-maps or from successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . Hydrogen atoms of carbon were included in calculated positions and refined using a riding model with U9eq being a multiple of their parent atom. The hydrogen atoms of part of water molecules were located from Fourier difference maps and refined with suitable constraints. Crystallographic data and experimental details for structural analyses are summarized in Table 1. The crystal data file in CIF format was deposited on CCDC and reference numbers 1485898–1485903 (for complexes **1–6**, respectively). This data can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ ccdc.cam.ac.uk.

Results and Discussion

Syntheses and General Characterization

In this work, our synthetic method of the ligands is similar to that reported in the literature [44]. L^1 was prepared in ca. 69.4% yield as pale yellow crystalline solid by the reaction of 3,6-dichloropyridazine with benzoimidazole, L^2 was obtained in ca. 68% yield as white crystalline solid by the reaction of 3,6-dichloropyridazine with 1,2,4-triazole, and L^3 was obtained in ca. 80% yield as white crystalline solid by the reaction of 3,6-dichloropyridazine with 1,2,4-triazole, and L³ was obtained in ca. 80% yield as white crystalline solid by the reaction of 3,6-dichloropyridazine with imidazole. All complexes 1–6 are stable at room temperature. Complexes 1, 2 and 5 were obtained in mixed solvents by refluxing, complexes 3 and 4 were obtained in organic solvents at room temperature, while complex 6 were synthesized by the hydrothermal method at 130°C.

The infrared spectra of **1–6** exhibit characteristic absorptions for corresponding ligands with a slight shift due to coordination. The absorption bands at about 1413 and 1378 cm⁻¹ indicate the existence of the NO₃⁻ ion in **3**. The characteristic bands of the coordinated acetate ions appear at 1650 and 1411 cm⁻¹ in **5**. The characteristic bands of the coordinated SCN⁻ ions appear at 2087 and 2069 cm⁻¹ in **6**. L¹–L³. **1–6** all exhibit absorption corresponding to the framework vibrations of aromatic rings at about 1420–1650 cm⁻¹.

Description of the Crystal Structure

Structure of $[M(L^2)_2Cl_2]$ [M = Zn(1) and Co(2)]

Structural analyses reveal that complexes 1 and 2 have similar mononuclear structures (Fig. 1). The coordination environment of Zn(II) ion in 1 is the same as that of Co(II) ion in 2. Complexes 1 and 2 have the general formula of $[M(L^1)_2Cl_2]$ (1) [M = Zn (1) and Co(2)]. Therefore, we just describe structure of 1.

Complex 1 crystallizes in the triclinic space group *P*-1. Crystallographic data and experimental details for the structural analyses are summarized in Table 1, selected bond distances and angles are listed in Table 2. The structure of 1 contains a four-coordinated metal ion (Fig. 1a), which is surrounded by two nitrogen atoms from two individual L^1 ligands and two Cl⁻ ions, showing a distorted tetrahedron structure, with the coordination angles varying from 103.32(6)° to 117.29(3)°. The Zn–N bond distances are 2.0326(19) and 2.0238(19) Å, respectively and in the normal range.

In complex **2** (Fig. 1b) the bond lengths of Co–N are 2.010(3) and 2.018(3) Å, shorter than complex **1**. At the same time, the coordination angles N–Co–N are in the 102.96(10)°–116.50(5)° range, slightly smaller than in complex **1**.

Structure of $[Cu(L^2)_2(NO_3)_2(H_2O)]$ (3)

Single crystal X-ray diffraction analysis reveals that complex 3 crystallizes in the monoclinic space group C2/cand the selected bond distances and angles are listed in Table 2. Complex 3 has a mononuclear structure (Fig. 2a) with one Cu(II) center, two neutral L^2 ligands, two NO₃⁻ anions and one water molecule. The Cu(II) center is seven coordinated in a distorted pentagonal bipyramidal geometry with coordination angles varying from $89.03(6)^{\circ}$ to 179.08(8)°. The Cu–O bond distances range from 1.986(30) to 2.737(32) Å, and the Cu-N bond distances are 1.9964(15) and 1.9965(14) Å. Among the donor atoms around Cu1, the O1, O2, O1^{#1}, O2^{#1} and O4 are located on the equatorial sites, while N4 and N4^{#1} atoms occupy the vertex of pentagonal bipyramid. Two L^2 ligands adopt monodentate coordination mode and two NO₃⁻ anions not only adopt bidentate coordination mode but also are used to balance the charge. It is worth noticing that a 1D structure is formed through intermolecular O-H···O hydrogen bonding interactions. As shown in Fig. 2b, the $O(2)^{\#2}$ atoms of the NO_3^- anions serves as acceptor to form $O(4)-H(1w)\cdots O(2)^{\#2}$ intermolecular hydrogen bonds with coordinated water molecules. The O···O distance of 2.958(3) Å falls into the normal range of hydrogen bond interactions (Hydrogen bonds for 3 are listed in Table 3).

Structure of $[Cu(L^2)_2Cl_2]_{\infty}(4)$

Complex 4 crystallizes in the monoclinic space group P2(1) and consists of a 1D chain structure. Selected bond distances and angles are listed in Table 2. In complex 4 Cu(II) ion coordinates two neutral L^2 ligands, and three Cl⁻ ions, two of which are symmetry equivalents. The five-coordinated

Table 1 Crystal data and structure refinement summary for complexes 1–6

	1	2	3	
Formula	$C_{22}H_{14}N_8Cl_4Zn$	C ₂₂ H ₁₄ N ₈ Cl ₄ Co	C ₁₂ H ₁₀ N ₁₂ O ₇ Cl ₂ Cu	
Formula wt	597.60	591.14	568.77	
CCDC	1485898	1485899	1485900	
Crystal system	Triclinic	Triclinic	Monoclinic	
Space group	<i>P</i> -1	<i>P</i> -1	C2/c	
T/K	293(2)	296(2)	293(2)	
a/Å	10.8698(13)	10.836(2)	28.4695(14)	
b/Å	11.2912(13)	11.271(2)	6.8125(3)	
c/Å	11.5295(15)	11.530(2)	11.3599(5)	
<i>a</i> /deg	112.524(3)	112.594(5)	90	
b/deg	100.091(3)	100.034(5)	113.282(2)	
g/deg	90.008(3)	90.194(5)	90	
V/Å ³	1283.4(3)	1276.4(5)	2023.83(16)	
Z	2	2	4	
$D/g \text{ cm}^{-3}$	1.546	1.538	1.867	
μ/mm^{-1}	1.401	1.119	1.412	
F(000)	600	594	1140	
GOF on F ²	1.054	1.011	1.067	
Reflections collected	10,978	8233	6351	
Unique refins	6554	4519	1846	
$RI^{a}, wR2^{b} [I > 2\sigma(I)]$	0.0390, 0.0911	0.0584, 0.1575	0.0233, 0.0636	
$R1^a$, $wR2^b$ (all data)	0.0601, 0.1002	0.0761, 0.1723	0.0245, 0.0646	
	4	5	6	
Formula	$C_{12}H_8N_{10}Cl_4Cu$	$C_{14}H_{14}N_6O_4Cu$	$C_{12}H_8N_8S_2Cd$	
Formula wt	497.62	393.85	440.78	
CCDC	1485901	1485902	1485903	
Crystal system	Monoclinic	Monoclinic	Triclinic	
Space group	<i>P</i> 2(1)	C2/c	<i>P</i> -1	
T/K	296(2)	293(2)	296(2)	
a/Å	9.724(4)	22.2846(12)	5.886(3)	
b/Å	7.071(3)	14.4200(12)	10.654(6)	
c/Å	13.259(5)	13.6831(9)	13.706(7)	
a/deg	90	90	94.887(15)	
b/deg	106.108(7)	110.406(3)	95.438(15)	
g/deg	90	90	95.598(15)	
V/Å ³	875.9(6)	875.88(61)	847.7(8)	
Z	2	8	2	
$D/g \text{ cm}^{-3}$	1.887	1.266	1.727	
μ/mm^{-1}	1.879	1.086	1.544	
F(000)	494	1600	432	
GOF on F^2	1.025	1.051	1.001	
Reflections collected	5043	13,039	5556	
Unique reflns	3037	3671	3671 3026	
$R1^{a}, wR2^{b} [I > 2\sigma(I)]$	0.0314, 0.0770	0.0364.0.0945 0.0208.0.0815		
$R1^a$, $wR2^b$ (all data)	0.0361, 0.0815	0.0440, 0.0982	0.0351, 0.0846	

 ${}^{a}R = \Sigma(||F_{0}| - |F_{C}||)/\Sigma|F_{0}|$ ${}^{b}wR = [\Sigma w(|F_{0}|^{2} - |F_{C}|^{2})^{2}/\Sigma w(F_{0}^{2})]^{1/2}$



Fig. 1 View of **a** the structures of **1**. **b** The structures of **2** (H atoms omitted for clarity)

Cu(II) ion connects with two nitrogen atoms from two individual L^2 ligands and three Cl⁻ ions, resulting in a distorted [CuN₂Cl₃] trigonal bipyramidal coordination geometry with the coordination angles varying from 89.27(9)° to 178.3(2)° (Fig. 3a). The Cu–N bond distances are 1.995(28) and 2.010(28) Å, and the Cu–Cl bond distances range from 2.280(14) to 2.876(17) Å. Moreover, in contrast to complex **3**, the Cu–N bond distances of complex **4** have greater bond length range and the coordination angles of complex **4** have smaller angle range. The Cu1, Cl2, Cl2^{#1} and Cl3 atoms are located on the equatorial sites, whereas the N5 and N6 atoms occupy the axial positions. Figure 3b shows a 1D chain structure along *b*-axis of **4**, in which two adjacent Cu(II) ions were linked via a μ_2 -Cl⁻ ion with the a distance of 4.565(15) Å to give a 1D chain (Fig. 3b).

Structure of $[CuL^3(CH_3COO)_2]_{\infty}(5)$

Complex 5 crystallizes in the monoclinic system, space group C2/c. Selected bond distances and angles are listed in Table 2. In this structure, Cu(II) ion coordinates two L³ ligands and two CH₃COO⁻ ions in a distorted trigonal bipyramidal fashion

involving three oxygen atoms [Cu(1)–O(2), 1.9489(18) Å; Cu(1)–O(3), 2.4161(17) Å; Cu(1)–O(3)^{#2}, 1.9746(17) Å] from three CH₃COO⁻ ions and two nitrogen atoms from L³ ligands [Cu(1)–N(2), 1.995(2) Å; Cu(1)–N(3), 2.002(2) Å]. The coordination angles of complex **5** vary from 77.91(7)° to 175.32(8)°. The O2, O3 and O3^{#2} atoms occupy the equatorial sites, whereas the N2 and N3 atoms take axial positions (Fig. 4a). Further, two Cu(II) are linked via two CH₃COO⁻ ions to form dinuclear unit, which is arranged into a 1D ladderlike structure by μ_2 -L² spacers (Fig. 4b). The Cu···Cu separation in the coordination polymer is 3.4257(4) Å.

Structure of $[CdL^3(SCN)_2]_{\infty}(6)$

The 2D metal–organic framework **6** crystallizes in the triclinic system, space group *P*-1 and selected bond distances and angles are listed in Table 2. In complex **6** contains the Cd(II) center coordinates two bridging L^3 ligands and four bridging SCN⁻ ions (Fig. 5a), thus forming a 2D network structure (Fig. 5b), different from complexes **4** and **5**. The Cd(II) center is six-coordinated by two nitrogen atoms from two liga nds[Cd(1)–N(4)=2.286(3) Å, Cd(1)–N(5)=2.319(3) Å], two

Table 2Selected bonddistances (Å) and angles (deg)for complexes 1-6

2.2338(6) 2.0238(19) 105.82(6)	
2.0238(19) 105.82(6)	
105.82(6)	
111.41(6)	
117.29(3)	
2.2446(12)	
2.018(3)	
105.21(10)	
111.53(10)	
116.50(5)	
1.9880(13)	
1.9965(14)	
2.277(2)	
90.98(6)	
89.03(6)	
89.54(4)	
2.2803(13)	
2.010(3)	
90.05(8)	
90.51(9)	
1.9746(17)	
2.002(2)	
3.4256(6)	
102.09(7)	
93.27(8)	
90.72(8)	
100.62(7)	
92.56(7)	
90.89(6)	
93.69(6)	
2.319(3)	
2.335(3)	
2.7876(17)	
2.335(3)	
90.66(9)	
89.11(12)	
90.68(9)	
N(5)-Cd(1)-S(2) 91.95(9)	
88.52(9)	
88.80(9)	

Symmetry codes, for 3: #1 -x, y, -z+1/2; for 5: #2 -x+1/2, -y+1/2, -z+1. for 6: #2 x-1, y, z; #3 x+1, y, z

Fig. 2 View of **a** the coordination environment of Cu(II) ions in **3**. **b** The 1D supermolecule structure by O–H···O hydrogen bonding interactions of **3** (symmetry codes: #2 x,y–1,z; H atoms omitted for clarity)



Table 3 Hydrogen-bonding geometry (Å, °) for 3

D–H···A	D–H	Н…А	D…A	D–H…A
O(4)–H(1W)····O(2) ^{#2}	0.84	2.24	2.958(3)	143.9

nitrogen atoms from two SCN⁻ [N(7)–Cd(1)^{#3}=2.306(3) Å, N(8)–Cd(1)^{#2}=2.335(3) Å] and two sulfur atoms from SCN⁻ [Cd(1)–S(1)=2.7876(17) Å, Cd(1)–S(2)=2.7176(16) Å] resulting in an octahedral geometry with the coordination angles varying from 87.91(12)° to 178.76(3)°. Around Cd(II) center, the N7, N8, S1 and S2 atoms are located on the equatorial sites, whereas N4 and N5 atoms occupy the axial positions. The neighboring Cd(II) ions are bridged by double $\mu_{1,3}$ -SCN⁻ ligands to form a 2D net structure with Cd···Cd separation of 5.886(3) Å. The Cd(μ -SCN)₂Cd units construct an infinite polymeric chain, and L³ acts as a bridging ligand coordinated via the two nitrogen atoms of its two imidozale rings, thus ultimately forming the 2D framework. The topological analysis reveals a 4-connected framework with the point symbol of {4⁴.6²} (Fig. 5b).

Photoluminescence Properties

Aromatic organic molecules and mixed inorganic-organic hybrid coordination polymers are promising luminescent materials for their potential applications, such as lightemitting materials (LEDs) [45, 46]. The emission spectra of L^1 , L^3 and complexes 1, 2, and 6 in the solid state at room temperature were investigated. Upon excitation with 245 nm light, complexes 1, 2 and L^1 display blue fluorescent emission bands at 402 nm (Fig. 6a). Complex 6 and L^3 exhibit blue fluorescent emission band at 403 nm upon excitation at 247 nm (Fig. 6b). The results show that the peaks of the emission spectra for 1, 2 and 6 are the same as those of the free ligands, which is likely due to the intraligand electronic transition. The significantly enhanced luminescence efficiency can be attributed to the ligand coordination to the metal centre, which enhances the rigidity of the ligand and thus reduces the loss of energy through a radiationless pathway [47].

















Fig. 6 View of a the emission spectra of L^1 , complex 1 and complex 2 in the solid state. b The emission spectra of L^3 and complex 6 in the solid state

Conclusions

A series of new metal–organic complexes have successfully been synthesized and are based on three structurally related ligands 3-chloro-6-(benzoimidazol-1-yl)pyridazine (L^1) , 3-chloro-6-(1,2,4-triazol-1-yl)pyridazine (L^2) and 3,6-bis(imidazol-1-yl)pyridazine (L^3) . These complexes show different structures including 0-D, 1-D and 2-D. Luminescence measurements reveal that complexes 1 and 6 are promising candidates for photoactive materials, due to their strong luminescence emission.

Acknowledgements This work was financially supported by the Natural Science Funds of XinJiang, China (No. 2015 211C266).

References

- 1. Chen DM, Zhang XP, Shi W, Cheng P (2015) Inorg Chem 54:5512–5518
- Liao PQ, Zhou DD, Zhu AX, Jiang L, Lin RB, Zhang JP, Chen XM (2012) J Am Chem Soc 134:17380–17383
- Elsaidi SK, Mohamed MH, Pham T, Hussein T, Wojtas L, Zaworotko MJ, Space B (2016) Cryst Growth Des 16:1071–1080

- Wang XF, Zhou SB, Du CC, Wang DZ, Jia DZ (2017) J Solid State Chem 252:72–85
- Sun GM, Song YM, Liu Y, Tian XZ, Huang HX, Zhu Y, Yuan ZJ, Feng XF, Luo MB, Liu SJ, Xu WY, Luo F (2012) CrystEng-Comm, 14:5714–5716
- 6. Arci M, Yesilel OZ, Tas M (2015) Cryst Growth Des 15:3024-3031
- 7. Wang DZ, Fan JZ, Jia DZ, Du CC (2016) CrystEngComm 18:6708–6723
- 8. Zhang T, Song FJ, Lin WB (2012) Chem Commun 48:8766–8768
- Horike S, Dinca M, Tamaki K, Long JR (2008) J Am Chem Soc 130:5854–5855;
- 10. Fan JZ, Du CC, Wang DZ (2016) Polyhedron 117:487–495
- Kong XJ, Wu YL, Long LS, Zheng LS, Zheng ZP (2009) J Am Chem Soc 131:6918–6919
- 12. Zhao JP, Zhao C, Song WC, Wang L, Xie YB, Li JR, Bu XH (2015) Dalton Trans 44:10289–10296
- Aijaz A, Lama P, Sanudo EC, Mishra R, Bharadwaj PK (2010) New J Chem 34:2502–2514
- Zhou SB, Wang XF, Du CC, Wang DZ, Jia DZ (2017) CrystEng-Comm 19:3124–3137
- Hu FL, Wang SL, Wu B, Yu H, Wang F, Liang JP (2014) Cryst-EngComm 16:6354–6363
- Dong XY, Si CD, Fan Y, Hu DC, Yao XQ, Yang YX, Liu JC (2016) Cryst Growth Des 16:2062–2073
- Maity DK, Halder A, Ghosh S, Ghoshal D (2016) Cryst Growth Des 16:4793–4804
- Xing K, Fan RQ, Gao S, Wang XM, Du X, Fang R, Yang YL (2016) Dalton Trans 45:4863–4878
- 19. Singh N, Anantharaman G (2015) Polyhedron 90:202–213
- 20. Sun D, Han LL, Yuan S, Deng YK, Xu MZ, Song DF (2013) Cryst Growth Des 13:377–385
- 21. Liu GX (2016) J Chem Crystallogr 46:213–221
- 22. Ren C, Hou L, Liu B, Yang GP, Wang YY, Shi QZ (2011) Dalton Trans 40:793–804
- Luo L, Wang P, Xu GC, Liu Q, Chen K, Lu Y, Zhao Y, Sun WY (2012) Cryst Growth Des 12:2634–2645
- 24. Wang XF, Du CC, Zhou SB, Wang DZ (2017) J Mol Struct 1128:103–110
- 25. Hu B, Geng J, Zhang L, Huang W (2014) J Solid State Chem 215:102–108
- Aricl M, Yesilel OZ, Tas M, Demiral H, Erer H (2016) Cryst Growth Des 16:5448–5459

- 27. Li JP, Fan JZ, Wang DZ (2016) J Solid State Chem 239:251-258
- Chen JQ, Cai YP, Fang HC, Zhou ZY, Zhan XL, Zhao G, Zhang Z (2009) Cryst Growth Des 9:1605–1613
- 29. Lu XX, Luo YH, Xu Y, Zhang H (2015) CrystEngComm 17:1631–1636
- 30. Liu WT, Ou YC, Lin ZJ, Tong ML (2010) CrystEngComm 12:3482–3489
- Yang F, Li BY, Xu W, Li GH, Zhou Q, Hua J, Shi Z, Feng SH (2012) Inorg Chem 51:6813–6820
- 32. Wang DZ, Li JP, Fan JZ, Jia DZ (2016) Polyhedron 111:123–131
- Tong XL, Wang DZ, Hu TL, Song WC, Tao Y, Bu XH (2009) Cryst Growth Des 5:2280–2286
- 34. Ding B, Yang P, Liu YY, Wang Y, Du GX (2013) CrystEngComm 15:2490–2503
- Guo HD, Yan YN, Guo XM, Wang N, Qi YJ (2016) J Solid State Chem 1108:134–143
- Liu QY, Guo J, Wang YL, Wei JJ, Chen Y, Hu CH (2013) J Coord Chem 66:530–538
- Jeong S, Song S, Jeong S, Oh M, Liu XF, Kim D, Moon D, Lah MS (2011) Inorg Chem 50:12133–12140
- Wang YL, Chen L, Liu CM, Zhang YQ, Yin SG, Liu QY (2015) Inorg Chem 54:11362–11368
- Li L, Hu TL, Li JR, Wang DZ, Zeng YF, Bu XH (2007) Cryst-EngComm 9:412–420
- Agarwal RA, Mukherjee S, Sanudo EC, Ghosh SK, Bharadwaj PK (2014) Cryst Growth Des 14:5585–5592
- 41. Bruker AXS (1998) SAINT software reference manual. Bruker AXS, Madison
- 42. Sheldrick GM (1994) SADABS, Siemens Area Detestor Absorption Correction Program. University of Gottingen, Gottingen
- Sheldrick GM (1997) SHELXTL NT Version 5.1. Program for solution and refinement of crystal structures. University of Göttingen, Gottingen
- 44. Jin SW, Wang DQ (2012) J Coord Chem 65:1937-1952
- 45. Shao YL, Cui YH, Gu JZ, Wu J, Wang YW (2015) RSC Adv 5:87484–87495
- Linfoot CL, Leitl MJ, Richardson P, Rausch AF, Chepelin O, White FJ, Yersin H, Robertson N (2014) Inorg Chem 53:10854–10861
- Gai YL, Jiang FL, Chen L, Bu Y, Wu MY, Zhou K, Pan J, Hong MC (2013) Dalton Trans 42:9954–9965