

基于香豆素 N_2O_2 配体构筑的单核铜(II)和三核钴(II) 配合物:合成、结构及荧光性质

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摘要: 合成了 2 个通过不同的 Salamo 型香豆素类配体 H_2L1 和 H_2L2 构筑的配合物, $[Cu(L1)(H_2O)]$ (**1**)和 $[Co_3(L2)_2(\mu_2-OAc)_2(MeOH)_2] \cdot 3CH_2Cl_2$ (**2**),并通过元素分析、红外光谱、紫外-可见吸收光谱、荧光光谱以及 X 射线单晶衍射法对其进行了表征。配合物 **1** 中配位的铜(II)离子的空间构型是扭曲的四方锥,并且配合物 **1** 通过分子间的氢键作用形成了二聚体。配合物 **2** 中所有配位的钴(II)离子的配位数均为六,并且 3 个钴(II)离子的配位空间构型均为扭曲的八面体。同时,配合物 **2** 通过分子间的氢键作用形成了一维的超分子链状结构。此外,还分别对配体 H_2L1 和 H_2L2 的荧光性质进行了研究,并且通过荧光滴定实验进一步验证了配合物 **1** 和 **2** 的晶体结构。

关键词: 四齿 N_2O_2 配体; 配合物; 合成; 晶体结构; 荧光性质

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Mononuclear Cu(II) and Trinuclear Co(II) Complexes Based on Coumarin-Containing N_2O_2 Ligands: Syntheses, Structures and Fluorescence Properties

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Abstract: Two newly designed complexes, $[Cu(L1)(H_2O)]$ (**1**) and $[Co_3(L2)_2(\mu_2-OAc)_2(MeOH)_2] \cdot 3CH_2Cl_2$ (**2**) derived from tetradentate Salamo-type chelating ligands (H_2L1 and H_2L2) have been synthesized and characterized by elemental analyses, IR and UV-Vis spectra, fluorescence spectra and X-ray crystallography. Complex **1** shows a slightly distorted tetragonal pyramid, forming a dimer supramolecular structure by intermolecular hydrogen bond interactions. While all of the Co(II) ions in complex **2** are hexa-coordinated with slightly distorted octahedral coordination geometries. The supramolecular structure of complex **2** is formed via intermolecular hydrogen bond interactions leading to a self-assembly infinite 1D chain structure. The fluorescent properties of H_2L1 and H_2L2 have been discussed and the crystal structures of complexes **1** and **2** were confirmed by fluorescence titration experiments. CCDC: 1561039, **1**; 1561040, **2**.

Keywords: tetradentate N_2O_2 ligand; complex; synthesis; crystal structure; fluorescence property

0 Introduction

Salen-type ligand ($R-CH=N-(CH_2)_2-N=CH-R$) is a kind of versatile tetradentate N_2O_2 chelating ligand

in modern coordination chemistry^[1-5], and its metal complexes have been widely investigated in biological fields^[6-10], electrochemical systems^[11-12], luminescent^[13-17] and magnetic^[18-22] materials and supramolecular

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buildings^[23-26] and so on. Specially, replacement of partial atoms of Salen or its analogues with else elements often thoroughly alters its structures and properties when an O-alkyl oxime moiety $(-\text{CH}=\text{N}-\text{O}-(\text{CH}_2)_n-\text{O}-\text{N}=\text{CH}-)$ instead of the imine moiety, the bigger electronegativity of the oxygen atoms is estimated to influence strongly the electronic behaviors of the Salamo-type ligand or its derivatives, which may give rise to novel and different structures and properties of the metal(II) complexes^[27-33].

As important raw materials and intermediates in organic chemical, coumarin has a wide range of applications in agriculture, pharmaceutical, photographic materials and other fields. Although these Salamo-type metal complexes have been in the process of development, there is still a lot of room for their supramolecular structures to be studied. The introduction of different substituted group into Salamo-type compounds may give rise to different structures, and asymmetric ligands can also greatly improve the difference of the structures^[34-38]. Herein, we firstly report two new complexes $[\text{Cu}(\text{L1})(\text{H}_2\text{O})]$ (**1**) and $[\text{Co}_3(\text{L2})_2(\mu_2-\text{OAc})_2(\text{MeOH})_2] \cdot 3\text{CH}_2\text{Cl}_2$ (**2**) with coumarin-containing asymmetric and symmetric Salamo-type N_2O_2 bisoxime ligands.

1 Experimental

1.1 Materials and physical measurements

7-Hydroxyl-4-methyl-coumarin and 3-methoxysalicylaldehyde (98%) were purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents

from Tianjin Chemical Reagent Factory.

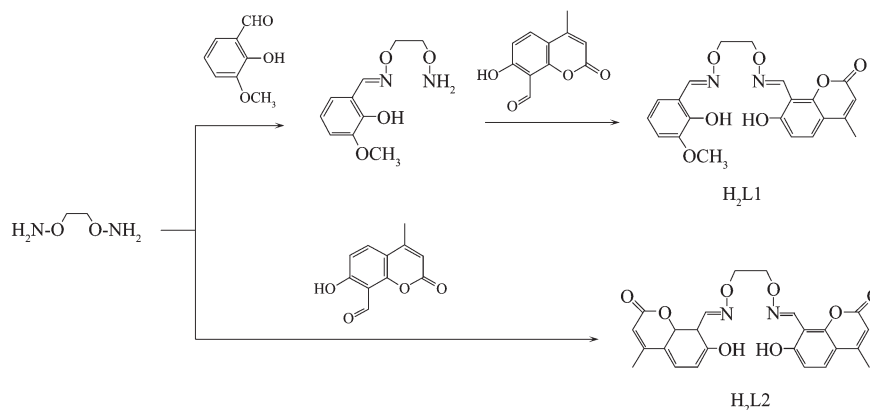
C, H and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analyses for Cu(II) and Co(II) were detected by an IRIS ER/S-WP-1 ICP atomic emission spectrometer. Melting points were measured by the use of a microscopic melting point apparatus made by Beijing Taike Instrument Limited Company and were uncorrected. IR spectra were recorded on a Vertex70 FT-IR spectrophotometer, with samples prepared as KBr ($400\sim 4\,000\text{ cm}^{-1}$) pellets. UV-Vis absorption spectra were recorded on a Shimadzu UV-3900 spectrometer. Luminescence spectra in solution were recorded on a Hitachi F-7000 spectrometer. Luminescence decay curve in the solid state and the quantum yield were recorded on a FLSP920 spectrometer. ^1H NMR spectra were determined by a German Bruker AVANCE DRX-400 spectrometer.

1.2 Syntheses of $\text{H}_2\text{L1}$ and $\text{H}_2\text{L2}$

1,2-Bis (aminoxy)ethane was prepared following the literature^[11]. 8-Formyl-7-hydroxy-4-methylcoumarin was synthesized in the light of reported procedure^[39]. $\text{H}_2\text{L1}$ and $\text{H}_2\text{L2}$ could be obtained by condensation of 1,2-bis(aminoxy)ethane with 3-methoxysalicylaldehyde and 8-formyl-7-hydroxyl-4-methyl-coumarin via a nucleophilic addition (Scheme 1).

1.2.1 Synthesis of $\text{H}_2\text{L1}$

An ethanol solution (50 mL) of 3-methoxysalicylaldehyde (304.30 mg, 2 mmol) was added dropwise to 1,2-bis(aminoxy)ethane (276.30 mg, 3 mmol) in ethanol solution (30 mL). The mixed solution was heated for 3 h in the range of $55\sim 60\text{ }^\circ\text{C}$. After vacuum



Scheme 1 Synthetic routes to $\text{H}_2\text{L1}$ and $\text{H}_2\text{L2}$

concentration of the solution, the residue was purified, and an affordable colorless flocculent crystalline solid of 2-[O-(1-ethoxyamide)]oxime-6-methoxyphenol was obtained. Yield: 42.3% (191.39 mg). Anal. Calcd. for $C_{10}H_{14}N_2O_4$ (%): C 53.09; H 6.24; N 12.38. Found(%): C 53.32; H 6.12; N 12.27.

A solution of 2-[O-(1-ethoxyamide)]oxime-6-methoxyphenol (328.03 mg, 1.45 mmol) in ethanol (20 mL) was added to a solution of 8-formyl-7-hydroxyl-4-methyl-coumarin (296.06 mg, 1.45 mmol) in ethanol (20 mL) and the mixture was subjected to heating at 55 °C for 24 h. After being cooled to room temperature, the resulting yellow solid was collected. 1H NMR (400 MHz, $CDCl_3$): δ 10.73 (s, 1H), 9.70 (s, 1H), 8.94 (s, 1H), 8.27 (s, 1H), 7.50 (d, $J=8.9$ Hz, 1H), 6.93 (s, 1H), 6.91 (s, 1H), 6.87 (s, 1H), 6.85 (s, 1H), 6.14 (s, 1H), 4.51 (s, 4H), 3.91 (s, 3H), 2.40 (s, 3H). Yield: 79.8% (477.18 mg). Anal. Calcd. for $C_{21}H_{20}N_2O_7$ (%): C, 61.16; H, 4.89; N, 6.79. Found(%): C, 61.25; H, 4.71; N, 6.53.

1.2.2 Synthesis of H_2L2

A solution of 8-formyl-7-hydroxyl-4-methyl-coumarin (408.36 mg, 2.0 mmol) in ethanol (30 mL) was added to a solution of 1,2-bis(aminooxy)ethane (92.10 mg, 1.0 mmol) in ethanol (30 mL) and the mixture was subjected to heating at 60 °C for 2 h. After being cooled to room temperature, the resulting white solid was collected. 1H NMR (400 MHz, $CDCl_3$): δ 10.72 (s, 2H), 8.95 (s, 2H), 7.50 (d, $J=8.9$ Hz, 2H), 6.93 (d, $J=8.9$ Hz, 2H), 6.14 (s, 2H), 4.54 (s, 4H), 2.40 (s, 6H). Yield: 79.9% (371.07 mg). Anal. Calcd. for $C_{24}H_{20}N_2O_8$ (%): C, 62.07; H, 4.34; N, 6.03. Found(%): C, 62.46; H, 4.42; N, 5.78.

1.3 Synthesis of complex 1

A dropwise addition of an methanolic solution (2 mL) of copper(II) acetate monohydrate (1.99 mg, 0.01 mmol) to a solution of H_2L1 (4.12 mg, 0.01 mmol) in acetone (3 mL) was carried out at room temperature, and immediately the mixed solution color changed to dark brown. The mixed solution was filtered and the filtrate was kept undisturbed in the dark to avoid decomposition of the coumarin-containing building blocks. Single-crystals suitable for X-ray crystallography were grown up via partial solvent evaporation

after *ca.* two weeks, and collected carefully by filtration, washed gradually with n-hexane, and dried at room temperature. Yield: 45.3% (2.23 mg). Anal. Calcd. for $C_{21}H_{20}CuN_2O_8$ (%): C, 51.27; H, 4.10; N, 5.69; Cu, 19.29. Found (%): C, 51.53; H, 4.28; N, 5.37; Cu, 18.93.

1.4 Synthesis of complex 2

A dropwise addition of an methanolic solution (2 mL) of cobalt(II) acetate tetrahydrate (2.49 mg, 0.01 mmol) to a solution of H_2L2 (4.64 mg, 0.01 mmol) in dichloromethane (5 mL) was carried out at room temperature, and immediately the mixed solution color changed to brown. The mixed solution was filtered and the filtrate was kept undisturbed in the dark to avoid decomposition of the coumarin-containing building blocks. Single-crystals suitable for X-ray crystallography were grown up via partial solvent evaporation after *ca.* two weeks, and collected carefully by filtration, washed gradually with n-hexane, and dried at room temperature. Yield: 70.1% (3.65 mg). Anal. Calcd. for $C_{57}H_{56}Cl_6Co_3N_4O_{22}$ (%): C, 44.50; H, 3.67; N, 3.64; Co, 11.49. Found(%): C, 44.76; H, 3.86; N, 3.43; Co, 11.23.

1.5 Crystal structure determinations of complexes 1 and 2

X-ray single crystal diffraction data of complexes **1** and **2** were recorded using a SuperNova Dual (Cu at zero) and Bruker APEX-II CCD diffractometers with a monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) source at 290.80(10) and 296.15(10) K, respectively. The L_p corrections were applied to the SAINT program^[40] and semi-empirical correction were applied to the SADABS program^[41]. The crystal structures were solved by the direct methods (SHELXS-2014)^[42]. All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. The aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Crystal data and experimental parameters involved in the structure determinations are presented in Table 1.

CCDC: 1561039, **1**; 1561040, **2**.

Table 1 Crystal data and structure refinement parameters for complexes **1** and **2**

Complex	1	2
Empirical formula	C ₂₁ H ₂₀ CuN ₂ O ₈	C ₂₇ H ₂₆ Cl ₆ Co ₃ N ₄ O ₂₂
Formula weight	491.93	1 538.54
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> / nm	0.769 19(9)	1.036 3(4)
<i>b</i> / nm	1.109 66(10)	1.140 7(4)
<i>c</i> / nm	1.203 52(14)	1.436 9(5)
β / (°)	79.991(10)	97.421(5)
<i>V</i> / nm ³	1.006 90(19)	1.589 6(10)
<i>Z</i>	2	1
<i>D_c</i> / (g·cm ⁻³)	1.623	1.607
μ / mm ⁻¹	1.139	1.106
<i>F</i> (000)	506	785
Crystal size / mm	0.24×0.21×0.17	0.27×0.22×0.19
θ range / (°)	3.692~26.885	1.892~ 28.320
Limiting indices	$-8 \leq h \leq 9, -13 \leq k \leq 13, -14 \leq l \leq 14$	$-13 \leq h \leq 13, -15 \leq k \leq 13, -19 \leq l \leq 19$
Independent reflection	3 968	7 712
Completeness to θ / %	99.8	98.2
Data, restraint, parameter	3 968, 0, 292	7 712, 67, 453
GOF on <i>F</i> ²	1.039	1.065
Final <i>R</i> indices [<i>I</i> >2 σ (<i>I</i>)]	<i>R</i> =0.043 4, <i>wR</i> =0.092 5	<i>R</i> =0.068 1, <i>wR</i> =0.202 9
Largest diff. peak and hole / (e·nm ⁻³)	342 and -319	138 and -189.8

2 Results and discussion

2.1 Crystal structure of complex **1**

As presented in Fig.1 and Table 2, the complex **1** crystallizes in the triclinic system, space group $P\bar{1}$, which comprises one Cu(II) ion, one deprotonated (L1)²⁻ unit and one coordinated water molecule.

The Cu(II) ion is penta-coordinated by two oxime nitrogen (N1 and N2) atoms and two deprotonated

phenoxo oxygen (O1 and O5) atoms, the four atoms are all from one deprotonated (L1)²⁻ unit, and one oxygen (O8) atom from the coordinated water molecule (Fig.1a). The coordination sphere around the Cu(II) ion is best described as a distorted tetragonal pyramid since the τ value was estimated to be $\tau=0.060\ 5$ (Fig. 1b)^[43-44]. Note worthily, this 1:1 type of Cu(II) complex is different from the earlier reported structures of 1:2^[35,37,45], 2:2^[28,46-48], 2:3^[49] and 2:4^[49] type in the

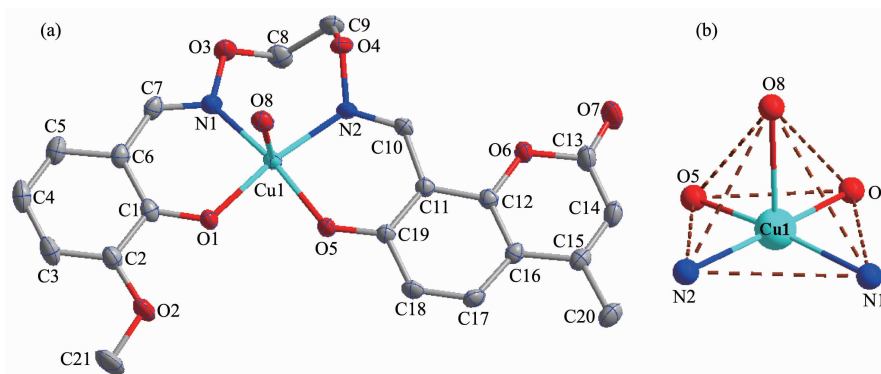


Fig.1 (a) X-ray crystal structure and atom numbering of complex **1** with 30% probability displacement ellipsoids; (b) Coordination polyhedron for Cu(II) ion of complex **1**

Table 2 Selected bond lengths (nm) and angles (°) for complex **1**

Cu1-O1	0.191 5(2)	Cu1-O8	0.228 9(2)	Cu1-N2	0.197 3(2)
Cu1-O5	0.195 3(2)	Cu1-N1	0.201 3(2)		
O1-Cu1-O5	84.18(8)	O5-Cu1-O8	94.76(9)	N2-Cu1-O8	90.83(9)
O1-Cu1-O8	93.66(9)	O5-Cu1-N1	167.45(10)	N2-Cu1-N1	98.21(10)
O1-Cu1-N1	88.98(9)	O5-Cu1-N2	87.77(9)		
O1-Cu1-N2	171.08(9)	N1-Cu1-O8	96.17(9)		

Table 3 Hydrogen bonding parameters for complexes **1** and **2**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠ D-H...A / (°)
1				
O8-H8A...O1#1	0.088	0.255	0.303 6(3)	116
O8-H8A...O2#1	0.088	0.204	0.291 9(3)	175
O8-H8B...O5#1	0.088	0.193	0.278 7(3)	166
2				
O11-H11A...O1#1	0.089	0.182	0.270 8(5)	179

Symmetry codes: #1: 2-*x*, 2-*y*, 1-*z* for **1**; -*x*, 1-*y*, 1-*z* for **2**.

Salamo-type Cu(II) complexes. The bond length of typical Cu-O distance in square pyramidal is 0.236 9(2) nm, which was found in similar complex [Cu(MeO-Salen)(H₂O)]^[47]. In addition, the mean plane (N₂O₂) and Sal(1) (3-methoxysalicylaldehyde) have a dihedral angle of 13.75(3)°, and the dihedral angle of Sal(2) (8-formyl-7-hydroxyl-4-methyl-coumarin) with the mean plane is 13.05(3)°. The reasons for these differences can be attributed to their asymmetric structure^[50-52].

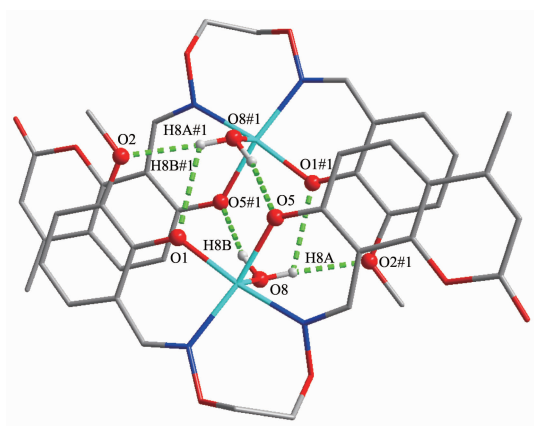
As presented in Table 3 and Fig.2, the supramolecular structure of the complex **1** is linked by intermolecular hydrogen bonding interactions O8-

H8A...O1#1, O8-H8B...O5#1 and O8-H8A...O2#1, which perform a dimer supramolecular structure^[53-56]. Each of the complex **1** molecule is linked to the hydrogen bonds with another complex **1** molecule, leading to a very stable spatial structure^[57-59].

2.2 Crystal structure of complex **2**

X-ray crystallographic analysis reveals complex **2** possesses a symmetric trinuclear structure. It crystallizes in the triclinic system, space group *P* $\bar{1}$, comprises three Co(II) ions, two deprotonated (L2)²⁻ units, two μ_2 -acetate ions, two coordinated methanol molecules and three lattice dichloromethane molecules. Selected bond lengths and angles are listed in Table 4.

As presented in Fig.3, complex **2** is formed with the Co1 ion occupying the center of symmetry and the other two Co(II) ions (Co2 or Co2#1) to be related by this center of symmetry^[60-62]. The two deprotonated (L2)²⁻ units, two μ_2 -acetate ions and the two coordinated methanol molecules are also centrosymmetric related (Fig.3a). All of the six oxygen atoms coordinate to Co1 constituting an octahedral geometry: one μ_2 -acetate ion serves as bridging group for Co1 and Co2 and another coordinates to Co1 and Co2#1, in both cases via Co-O-C-O-Co bridges. The Co...Co distances between central Co(II) ion (Co1) and the terminal Co(II) ions

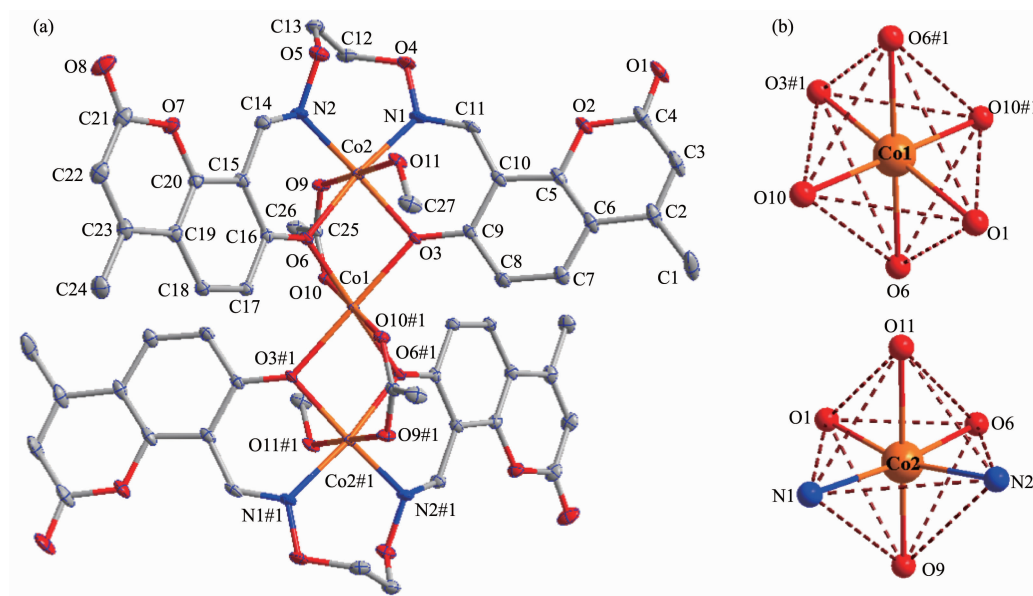
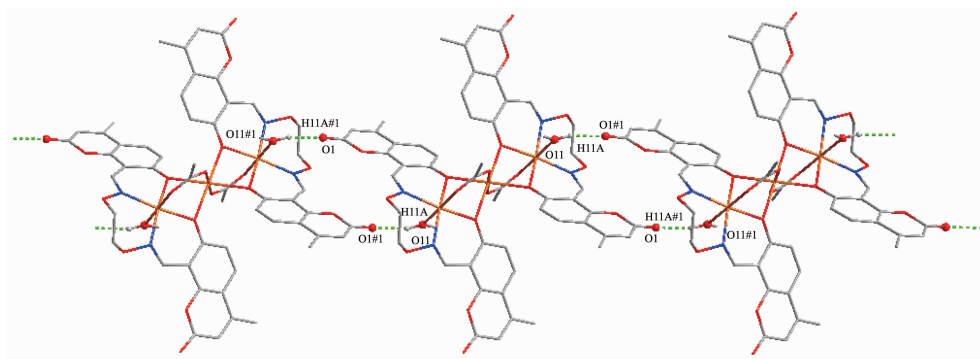


Symmetry codes: #1: 2-*x*, 2-*y*, 1-*z*

Fig.2 View of a dimer formed by complex **1** molecules via the O-H...O hydrogen bonding interactions

Table 4 Selected bond lengths (nm) and angles ($^{\circ}$) for complex **2**

Co1-O3	0.217 4(2)	Co2-O11	0.218 4(3)	Co2-N2	0.207 2(4)
Co1-O6	0.215 8(3)	Co2-O9	0.206 2(3)	Co2-O3	0.203 0(3)
Co1-O10	0.202 8(3)	Co2-N1	0.209 8(3)	Co2-O6	0.205 9(3)
O3#1-Co1-O3	180.0	O10-Co1-O10#1	180.0	O3-Co2-N2	165.36(12)
O6-Co1-O3#1	102.10(10)	O6-Co2-O11	90.08(10)	O3-Co2-O6	83.52(10)
O6-Co1-O3	77.90(10)	O9-Co2-N1	92.25(12)	O3-Co2-O9	94.31(11)
O6#1-Co1-O6	180.0	O9-Co2-N2	98.05(13)	O3-Co2-O11	86.12(11)
O10-Co1-O3#1	93.05(10)	N1-Co2-O11	87.77(12)	O6-Co2-N1	172.03(12)
O10-Co1-O3	86.95(10)	N2-Co2-N1	98.62(13)	O6-Co2-N2	88.65(12)
O10#1-Co1-O6#1	89.58(10)	N2-Co2-O11	81.53(13)	O6-Co2-O9	89.96(11)
O10-Co1-O6#1	90.42(10)	O3-Co2-N1	88.67(12)	O9-Co2-O11	179.57(12)

Symmetry codes : #1: $-x+1, -y+2, -z+1$ Symmetry codes: #1: $-x+1, -y+2, -z+1$ Fig.3 (a) X-ray crystal structure and atom numberings of complex **2** with 30% probability displacement ellipsoids; (b) Coordination polyhedrons for Co1(III) and Co2(III) ions of complex **2**Symmetry codes: #1: $-x, 1-y, 1-z$ Fig.4 View of the 1D supramolecular structure of complex **2** showing the O-H...O hydrogen bondings

(Co2) is 0.313 0(2) nm^[24,46]. Then, all of the hexa-coordinated Co(II) ions of complex **2** have distorted octahedral geometries (Fig.3b)^[63-65].

As shown in Fig.4 and Table 3, the 1D supra-molecular chain of complex **2** is composed by intermolecular O11–H11A \cdots O1#1 hydrogen bonding interactions. The oxygen (O11) atoms of the coordinated methanol molecules as donors form hydrogen bonds with carbonyl oxygen (O1#1) atoms of adjacent complex **2** molecules^[66].

2.3 FT-IR spectra

The FT-IR spectra of H₂L1 and H₂L2 with their corresponding complexes **1** and **2** demonstrate different bands in the 400~4 000 cm⁻¹ region (Table 5). The characteristic C=N stretching bands of the ligands H₂L1 and H₂L2 appear at 1 612 and 1 613 cm⁻¹, and those of complexes **1** and **2** appear at 1 597 and 1 581

cm⁻¹, respectively^[67]. The C=N stretching frequencies are shifted to lower frequencies, indicating that the Cu(II) and Co(II) ions are coordinated by azomethine nitrogen atoms of (L1)²⁻ and (L2)²⁻ moieties. In addition, characteristic C=O stretching bands at 1 733 and 1 731 cm⁻¹ are exhibited by the ligands H₂L1 and H₂L2, and the complexes **1** and **2** at 1 718 and 1 710 cm⁻¹ show the characteristic C=O stretching bands, respectively^[39]. The ligands H₂L1 and H₂L2 exhibit characteristic Ar-O stretching frequencies at 1 261 and 1 282 cm⁻¹, while those of the complexes **1** and **2** appear at 1 221 and 1 220 cm⁻¹, respectively^[68]. The Ar-O stretching frequencies are shifted to lower frequencies, which could be evidence of the Cu-O or Co-O bond formation between Cu(II) or Co(II) ions and oxygen atoms of phenolic groups^[65].

Table 5 FT-IR spectra of the ligands and their complexes **1** and **2**

Compound	$\nu_{C=N}$	ν_{Ar-O}	ν_{M-N}	ν_{M-O}	$\nu_{C=O}$	$\nu_{C=C}$
H ₂ L1	1 612	1 261	—	—	1 733	1 467
H ₂ L2	1 613	1 282	—	—	1 731	1 450
Complex 1	1 597	1 221	561	456	1 718	1 408
Complex 2	1 581	1 220	525	461	1 710	1 400

2.4 UV-Vis absorption spectra

The UV-Vis absorption spectra of the ligands H₂L1 and H₂L2 with their corresponding complexes **1** and **2** in the dichloromethane solutions (10 μ mol·L⁻¹) at 298 K are shown in Fig.5. For the ligand H₂L1, the peak at 273 nm can be assigned to the π - π^* transitions of the phenyl rings, the peak at 281 nm can be assigned to the π - π^* transitions of the phenyl rings of coumarin group, the peak at 330 nm can be assigned to the n - π^* transitions of the oxime group, and the peak at 345 nm can be assigned to the n - π^* transitions of lactone carbonyl group^[69]. Upon coordination of the ligand H₂L1, the π - π^* transitions of the phenyl rings and the phenyl rings of coumarin group in complex **1** are bathochromically shifted to 280 and 290 nm, respectively, indicating the coordination of Cu(II) ion with the (L1)²⁻ units^[70]. Compared with the free ligand H₂L1, the absorption peak at 330 nm disappears from

the UV-Vis spectrum of complex **1**, which indicates that the oxime nitrogen atoms are involved in coordination to the Cu(II) ion. Meanwhile, the n - π^* transitions of the lactone carbonyl group in complex **1** assumes a hypsochromic shift to 340 nm indicating

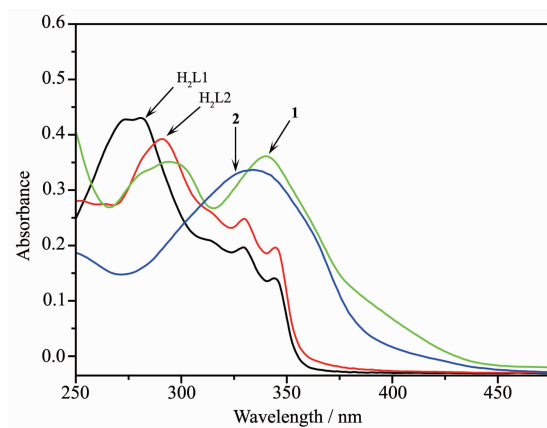


Fig.5 UV-Vis spectra of the ligands and their complexes **1** and **2**

the coordination of the $(L1)^{2-}$ units with $Cu(II)$ ion. For the ligand H_2L2 , the peak at 290 nm can be assigned to the $\pi-\pi^*$ transitions of the phenyl rings of coumarin group, the peak at 330 nm can be assigned to the $n-\pi^*$ transitions of the oxime group, and the peak at 345 nm can be assigned to the $n-\pi^*$ transitions of lactone carbonyl group. Compared with the free ligand H_2L2 , the absorption peak at 330 nm disappears from the UV-Vis spectrum of complex **2**, which indicates that the oxime nitrogen atoms are involved in coordination to the $Co(II)$ ion^[70]. Additionally, two weak broad absorption peaks are observed at 394 and 383 nm for complexes **1** and **2**, these new absorption peaks can be assigned to $L \rightarrow M$ charge-transfer (LMCT) transitions which are characteristic of the transition metal complexes with N_2O_2 coordination sphere^[70].

2.5 Fluorescence properties

The fluorescent spectra of H_2L1 and H_2L2 ($25 \mu\text{mol} \cdot \text{L}^{-1}$) in DMF solution were measured at room temperature (Fig.6). The ligands H_2L1 and H_2L2 exhibit broad emissions at about 432 nm upon excitation at 392 nm, which should be assigned to intraligand $\pi^*-\pi$ transition^[70-72].

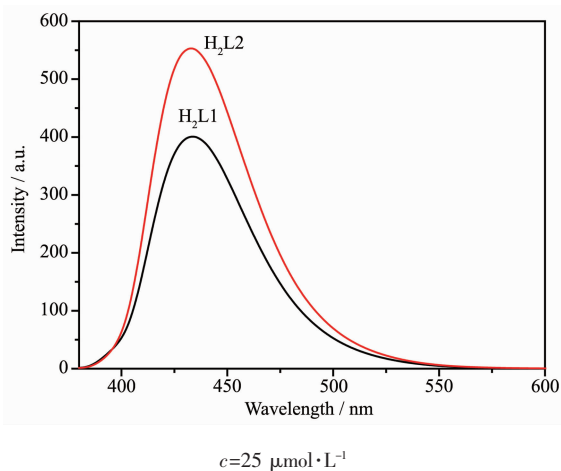


Fig.6 Fluorescent spectra of H_2L1 and H_2L2 in DMF solution

Luminescence decay curves of H_2L1 and H_2L2 in the solid state were measured at room temperature (Fig.7 and Fig.8). The fluorescence lifetimes of ligands H_2L1 and H_2L2 are obtained by fitting 3.01 and 1.47 μs , respectively, and the quantum yield

results of H_2L1 and H_2L2 in the solid state were measured at excitation range of 375 ~415 nm and luminescence range of 480 ~635 nm. The quantum yields of H_2L1 and H_2L2 in the solid state are 2.56% and 0.54%, respectively.

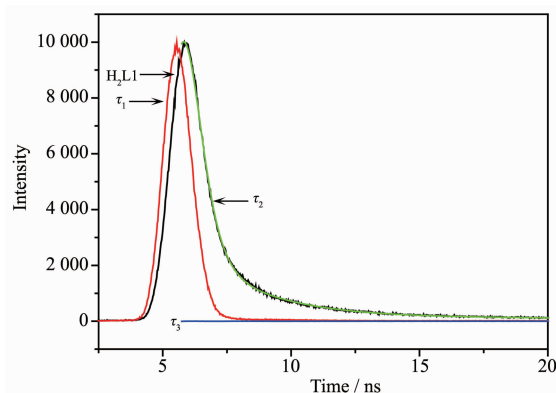


Fig.7 Luminescence decay curves of H_2L1 in the solid state

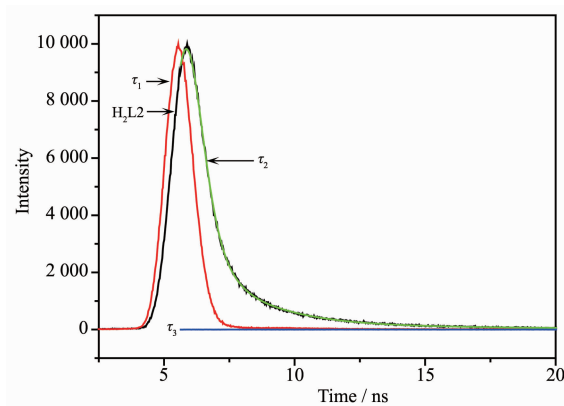
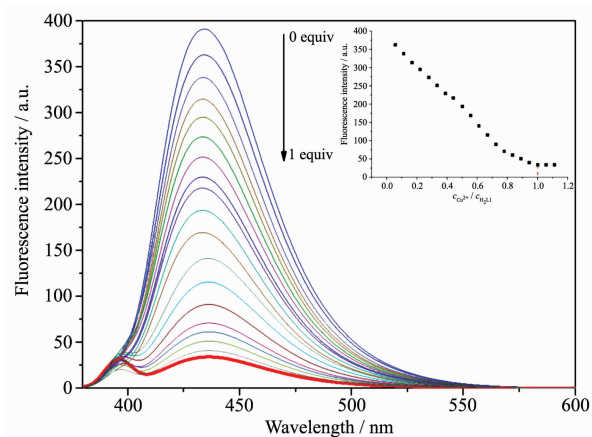


Fig.8 Luminescence decay curves of H_2L2 in the solid state

The fluorescence titration experiments of H_2L1 and H_2L2 were performed in DMF solution ($25 \mu\text{mol} \cdot \text{L}^{-1}$) with $Cu(OAc)_2 \cdot H_2O$ and $Co(OAc)_2 \cdot 4H_2O$ in methanol solution ($1 \text{ mmol} \cdot \text{L}^{-1}$), and the results are shown in Fig.9 and Fig.10, respectively.

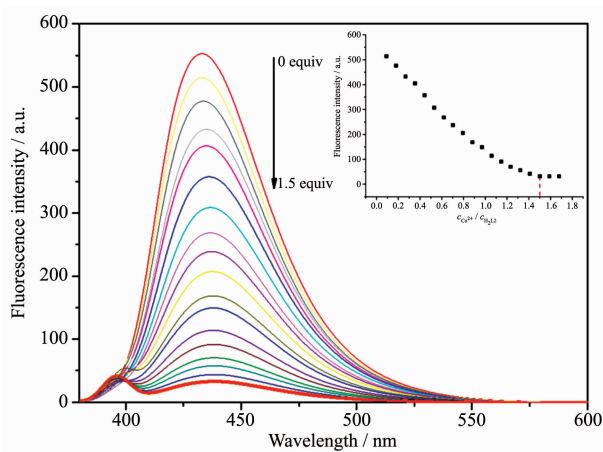
The fluorescence intensity of H_2L1 decreased remarkably upon incremental addition of the Cu^{2+} . When the added amount of the Cu^{2+} reached 1.0 equiv, the fluorescence emission intensity almost complete quenching and became stable (Fig.9), which can provide understanding 1:1 stoichiometry between Cu^{2+} and H_2L1 . Weakening of fluorescence is due to the coordination of metal(II) ion with the ligand^[73-74]. Likewise, complex **2** displays weakened emission

intensities compared to the corresponding ligand (H_2L2) when excited at 432 nm. When the added amount of the Co^{2+} reached 1.5 equiv, the fluorescence emission intensity almost complete quenching (Fig.10). The result is corresponding to the crystal structure of complex **2**.



Inset: linear response as a function of $c_{Cu^{2+}}/c_{H_2L1}$

Fig.9 Fluorescence spectra of H_2L1 in DMF solution upon the addition of Cu^{2+}



Inset: linear response as a function of $c_{Co^{2+}}/c_{H_2L2}$

Fig.10 Fluorescence spectra of H_2L2 in DMF solution upon the addition of Co^{2+}

3 Conclusions

In summary, we have reported the successful syntheses and characterizations of two newly designed complexes, $[Cu(L1)(H_2O)]$ (**1**) and $[Co_3(L2)_2(\mu_2-OAc)_2(MeOH)_2] \cdot 3CH_2Cl_2$ (**2**) derived from Salamo-type N_2O_2 ligands H_2L1 and H_2L2 . Complex **1** shows a slightly distorted tetragonal pyramid, forming a dimer supramolecular structure by intermolecular hydrogen

bond interactions. The supramolecular structure of the complex **2** is formed via intermolecular hydrogen bonds leading to a self-assembly infinite 1D chain structure. The fluorescent properties of H_2L1 and H_2L2 have been discussed and the structures of complexes **1** and **2** were confirmed by fluorescence titration experiments.

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