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Self-assembly properties of Salamo-type trinuclear Cu(II) and Co(II) complexes based on the regulation of H^+/OH^-

Xiu-Yan Dong | Bao-Jun Wang | Quan-Peng Kang | Wen-Kui Dong 🗈

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, Gansu, China

Correspondence

Wen-Kui Dong, School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China. Email: dongwk@126.com

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National Natural Science Foundation of China, Grant/Award Number: 21761018; Program for Excellent Team of Scientific Research in Lanzhou Jiaotong University, Grant/Award Number: 201706 A novel naphthalenediol-based bis(salamo)-type tetraoxime compound (H₄L) was designed and synthesized. Two new supramolecular complexes, [Cu₃(L) $(\mu$ -OAc)₂ and $[Co_3(L)(\mu$ -OAc)₂(MeOH)₂]·4CHCl₃ were synthesized by the reaction of H₄L with Cu(II) acetate dihydrate and Co(II) acetate dihydrate, respectively, and were characterized by elemental analyses and X-ray crystallography. In the Cu(II) complex, Cu1 and Cu2 atoms located in the N₂O₂ sites, and are both penta-coordinated, and Cu3 atom is also penta-coordinated by five oxygen atoms. All the three Cu(II) atoms have geometries of slightly distorted tetragonal pyramid. In the Co(II) complex, Co1 and Co3 atoms located in the N2O2 sites, and are both penta-coordinated with geometries of slightly distorted triangular bipyramid and distorted tetragonal pyramid, respectively, while Co2 atom is hexa-coordinated by six oxygen atoms with a geometry of slightly distorted octahedron. These self-assembling complexes form different dimensional supramolecular structures through inter- and intra-molecular hydrogen bonds. The coordination bond cleavages of the two complexes have occurred upon the addition of the H⁺, and have reformed again via the neutralization effect of the OH-. The changes of the two complexes response to the H⁺/OH⁻ have observed in the UV-Vis and ¹H NMR spectra.

KEYWORDS

crystal structure, Cu(II) and Co(II) complex, response to H⁺/OH⁻, synthesis

1 | INTRODUCTION

According to the relevant reports, the Salen-type ligands and their corresponding analogues are multifunctional and important compounds,^[1–7] mainly because they are capable of catalyzing various reactions. Its attractive properties are used to catalyze,^[8–12] luminescence properties,^[13–20] nonlinear optical materials^[21] and magnetic materials,^[22–27] supramolecular structures,^[28–42] electrochemical behaviors^[43,44] and biological fields.^[45–49] Transition metal Salen-type complexes were extensively used in the application researches of daily life and industrial fields, especially in the exploring of molecular antibacterial $^{[50,51]}$ and antitumor medicines. $^{[52]}$

Recently, a preferred type of Salen-type bisoxime compounds (Salamo and its derivatives) having N_2O_2 coordination spheres have been reported,^[53] which makes the compounds more stable. The study of salamo-type compounds has been well applied.^[54–58] In this article, we have designed and synthesized a naphthalenediol-based bis(salamo)-type tetraoxime compound (H₄L) containing two arms of *O*-alkyloxime unit R–CH=N–O–(CH₂)_n–O–N=CH–R,^[59–63] which can form homotrinuclear transition metal complexes,









FIGURE 2 (a) View of the molecular structure of the Co(II) complex (b) Coordination polyhedra for Co(II) atoms of the Co(II) complex

 $[Cu_3(L)(\mu$ -OAc)₂] and $[Co_3(L)(\mu$ -OAc)₂(MeOH)₂]·4CHCl₃. Further we studied the response of the two complexes to H⁺/OH⁻ in UV-Vis and ¹H NMR spectra, respectively.

2 | RESULTS AND DISCUSSION

2.1 | Crystal structures of the Cu(II) and Co(II) complexes.

From a 1:3 mixture of H_4L and Cu(II) or Co(II) acetate, a clear dark blue crystalline Cu(II) complex or a clear dark reddish brown crystalline Co(II) complex was isolated. The crystal structures were determined by X-ray single crystal diffractions. The crystal structures and atom numberings of the Cu(II) and Co(II) complexes are shown in Figure 1 and Figure 2, selected bond lengths and angles of the Cu(II) and Co(II) complexes are listed in Table S1 and Table S2, respectively.

Both the two complexes crystallize in the monoclinic system, space group P-1. In the Cu(II) complex, Cu1 and Cu2 atoms located in the N₂O₂ sites, and are both penta-coordinated with geometries of slightly distorted tetragonal pyramid, and Cu3 atom is also penta-coordinated by five oxygen atoms with a geometry of slightly distorted tetragonal pyramid, which were deduced by calculating the values of $\tau_1 = 0.3033$, $\tau_2 = 0.186$ and $\tau_3 = 0.025$, respectively. The two μ -OAc⁻ groups have connected Cu1 and Cu2 atoms with Cu3 atom act as 'bridges'. The coordination effect between the $(L)^{4-}$ unit and the Cu(II) atoms forms a stable chelating complex $[Cu_3(L)(\mu - OAc)_2]$, results in the enhancement of the inflexibility and the formation of two perpendicularly crossing planes. In the Co(II) complex, Co1 and Co3 atoms located in the N2O2 sites, and are both pentacoordinated with geometries of slightly distorted triangular bipyramid and distorted tetragonal pyramid, respectively. While Co2 atom is hexa-coordinated by six oxygen atoms, and has a slightly distorted octahedral



FIGURE 3 (a) View of intra-molecular hydrogen bond and $\pi \cdots \pi$ interactions; (b) 2D view of inter-molecular hydrogen bonds

geometry. Which were deduced by calculating the values of $\tau_1 = 0.822$, $\tau_2 = 0.147$ and $\tau_3 = 0.247$, respectively. The two μ -OAc⁻ groups have connected Co1 and Co2 atoms with Co3 atom act as 'bridges'. The coordination effect between the (L)⁴⁻ unit and the Co(II) atoms forms a stable chelating complex [Co₃(L)(μ -OAc)₂(MeOH)₂]·4CHCl₃, while two methanol molecules bond to the Co3 atom, which results in the



FIGURE 4 (a) View of intra-molecular hydrogen bond interactions; (b) View of 1D inter-molecular hydrogen bond interactions; (c) 3D supramolecular structure; (d) 3D model of structure

enhancement of the inflexibility and the formation of two perpendicularly crossing planes.

We studied the inter- and intra-molecular interactions of the two complexes, the Cu(II) complex is linked by two pairs of inter-molecular hydrogen bonding interactions form an infinite 2D supramolecular chain. However, an infinite 1D supramolecular chain of the Co(II) complex is formed through five pairs of inte-rmolecular hydrogen bonding interactions. Hydrogen bonding interactions [Å °] for the Cu(II) and Co(II) complexes are shown in Table S3. The details of the supramolecular interactions in the Cu(II) complex are shown in Figure 3. One intra-molecular hydrogen bond and $\pi \cdots \pi$ interactions exist between the two aromatic rings (Cg1 (C1-C6) and Cg2 (C25-C30)) of the salicylaldehyde in the Cu(II) complex are shown in Figure 3a.^[64] In addition, two inter-molecular hydrogen bonds connect two adjacent molecules (Figure 3b). A long chain has formed by the Cu(II) complex molecules via inter-molecular hydrogen bond interactions, while adjacent chains stack



FIGURE 5 Spectroscopic titrations of H_4L towards (a) Cu^{2+} and (b) Co^{2+}

in an interlaced way via Vander Waals force, and result in a regular array structure. It has a possible application in the research of molecular wires.

The details of the supramolecular interactions in the Co(II) complex are shown in Figure 4. Intra- and intermolecular hydrogen bonds connect two adjacent molecules in the Co(II) complex (Figure 4a and 4b), resulting in the packing of molecules performs as hollow tubular materials along a particular direction (Figure 4c), and its 3D model is drawn as Figure 4d by a simulation software. The diagonal length of the cavity shaped by the molecular chains is 19.39(4) Å, so the metal complex materials are considered as a mesoporous, and the solvent molecules in the cavities are easily replaced by other material, which makes it possible to store materials of suitable size.

2.2 | Response to H⁺/OH⁻

2.2.1 | Spectroscopic titrations.

In order to study the binding properties of H₄L toward Cu²⁺ and Co²⁺ in an organic solvent (Chloroform/methanol: 3:2), UV-vis spectral changes of H₄L toward various concentrations of Cu²⁺ and Co²⁺ were carried out. The results of the spectroscopic titrations are shown in Figure 5. At 340, 360 and 378 nm, three absorption peaks of H₄L were observed, which can be assigned to $n-\pi^*$ type transition. Upon increasing concentration of Cu²⁺, the absorption peak of H₄L changed at 340, 360 and 378 nm, with the enhancement of the new wide peak at 380 nm, which can be assigned to the ligand-to-metal charge-transfer transition (LMCT).^[65] The coordination of Cu^{2+} to the binding sites of N₂O₂ and hydroxyl oxygen of the naphthalene ring breaks the intra-molecular hydrogen-bonding interactions of H₄L, and increases the coplanarity of the conjugated system which causes change in the UV-vis spectra. In addition, upon the addition of Cu^{2+} , the absorbance at 425 nm shows a linear enhancement when the ratio of Cu^{2+}/H_4L is below 3:1, and no longer change when the ratio reaches 3:1. Above this proportion, the absorption peak at 378 nm has shifted to 372 nm, assuming 3:1 stoichiometry between Cu^{2+} and H_4L (Figure 5a). The analogous phenomenon happens to the spectroscopic titrations of H₄L towards Co²⁺. But different from the addition of Cu^{2+} , the peaks of H₄L at 340, 360 and 378 nm also decreased while two new wide peaks at 365 and 416 nm appeared, also the absorption peak at 378 nm has shifted to 396 nm upon the addition of Co^{2+} (Figure 5b).

To sum up, the coordination ratio of the ligand to the Cu(II) or Co(II) ions is 1:3. With the gradual addition of the Cu(II) or Co(II) ions, the Cu(II) or Co(II) complex with different absorption peaks has formed. The absorption peaks of the ligand have changed, and new coordination

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bonds between the ligand and the Cu(II) or Co(II) ions have formed. The original hydrogen bonding interactions of the ligand have been destroyed, which leads to the change of UV–Vis spectra.

Further we studied the response of the two complexes to H^+/OH^- . As is shown in Figure 6a, with the addition of 1.0 equiv H⁺, the UV-vis spectra of the L-Cu²⁺ solution changed. The characteristic peak at 380 nm have decreased gradually while three new peaks appear at 340, 360 and 378 nm, which are overlapped with the characteristic peaks of the H₄L, and in the back titration experiment, with the addition of 1.0 equiv OH⁻, the UV-vis spectra of the mixed solution have changed and almost are overlapped with the initial $L-Cu^{2+}$ solution. In the response of the Co(II) complex towards H⁺/OH⁻, we have observed the analogous experiment result. The results mentioned above probably have demonstrated that the coordination bonds in the two complexes are destroyed by the addition of H⁺, while the coordination bonds have regenerated owning to the acid-base neutralization (Figure 6b).



FIGURE 6 Responses of the (a) Cu(II) and (b) Co(II) complexes to $\rm H^+/OH^-$



FIGURE 7 1 H NMR spectrums of H₄L before and after the addition of 1.0 equiv H⁺.



FIGURE 8 ¹H NMR spectrums of L-Cu²⁺ before and after the addition of 1.0 equiv H⁺.

 $\label{eq:table_$

Complex	Cu(II) complex	Co(II) complex
Empirical formula	$C_{34}H_{26}Cl_4N_4O_{12}Cu_3\\$	$C_{40}H_{38}Cl_{16}N_4O_{14}Co_3$
Molecular weight	1015.01	1542.73
Temperature (K)	293.60 (10)	291.10 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	⁻ P1	⁻ P1
a (Å)	11.8888 (9)	14.5530 (10)
b (Å)	12.4643 (12)	14.7576 (10)
c (Å)	14.4606 (13)	17.2629 (14)
α	82.664 (8)	66.329 (7)
β	72.637 (8)	89.893 (6)
γ	84.036 (7)	70.110 (6)
$V(\text{\AA}^3)$	2023.6 (3)	3153.7 (5)
Ζ	2	2

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TABLE 1 (Continued)

Complex	Cu(II) complex	Co(II) complex
D _{calc} (g/cm ³)	1.666	1.625
Absorption coefficient (mm ⁻¹)	1.890	1.515
F (000)	1018.0	1542.0
Crystal size (mm)	$0.24 \times 0.22 \times 0.21$	$0.26 \times 0.24 \times 0.22$
θ range for data collection(°)	3.474 to 26.022	1.507 to 26.999
Index ranges	$-15 \le h \le 14$ $-16 \le k \le 16$ $-19 \le l \le 19$	$-18 \le h \le 17$ $-18 \le k \le 18$ $-21 \le l \le 21$
Reflections collected/ unique	16832 / 79590 $\rm R_{int}=0.0651$	24781 /13531 $R_{int} = 0.0076$
Completeness(%) (θ)	99.7 (25.24)	99.7 (25.24)
Data / restraints/ Parameters	7959/0/516	13531/8/810
Final R_1 / wR_2 indices $I > 2\sigma(I)^a$	0.0699/0.1563	0.0476/ 0.1556
$R_1 / w R_2$ indices (all data) ^b	0.1336/0.1921	0.0589/0.1600
GOF	0.992	1.054

^a $R_1 = ||F_o| - |F_c||/|F_o|$. ^b $wR_2 = w (F_o^2 - F_c^2)^2/w(F_o^2)^{21/2}$.



SCHEME 1 The synthetic route to H₄L

2.2.2 | ¹H NMR spectroscopy

In order to study the influence of the acidification by 1.0 equiv H⁺, the ¹H NMR spectroscopy experiments were carried. By comparing the ¹H NMR spectra of H_4L before and after the addition of 1.0 equiv H⁺, two

new proton peaks were observed at 10.69 and 10.85 ppm (Figure 7) and we have inferred that the addition of H^+ forms the conjugated acid of the ligand H_4L , which leads to the probable generation of the inter-molecular hydrogen bonds. In addition, by comparing the ¹H NMR spectra of the Cu(II) complex before

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and after the addition of 1.0 equiv H^+ , the experimental results are obviously different from the ligand H_4L , the new proton peak appears at 10.71 ppm in the ¹H NMR spectra, which indicates the dissociation has occurred in L-Cu²⁺ part after the addition of 1.0 equiv H^+ (Figure 8). The addition of H^+ leads to the obvious hydroxyl peaks observed in L-Cu²⁺, which further indicates that the structure of the Cu(II) complex could be regulated by H^+ , the experimental results are in agreement with the UV titration spectra and the crystal structure.

3 | CONCLUSIONS

We have designed and synthesized a naphthalenediolbased bis(salamo)-type tetraoxime H₄L, and the structures of the two transition metal(II) complexes have been determined by X-ray crystallographic analyses. The Cu(II) complex investigates a regular 2D array structure via inter-molecular hydrogen bond interactions and Vander Waals force. In the Co(II) complex, the diagonal length of the cavity shaped by the molecular chains is 19.39(4) Å, so the metal complex materials are considered as a mesoporous, which makes it possible to store materials of suitable size. The experiment results in spectroscopic titrations have demonstrated that the stoichiometry between the two transition metal(II) ions and H₄L are 3:1. The coordination bond cleavages of the two complexes have occurred upon the addition of H⁺, and have reformed again via the neutralization effect of the OH-, the changes of the two complexes response to the H⁺/OH⁻ are observed in the UV-Vis and ¹H NMR spectra, as a result, the two complexes investigate disaggregation and self-aggregation behavior via the addition of H^+/OH^- .

4 | EXPERIMENTAL SECTION

4.1 | Materials and methods

3,5-Dichlorosalicylaldehyde of 98% purity was purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. All the metal salts used were acetates of general formula $M(CH_3COO)_n \cdot xH_2O$. Melting points were obtained by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected. Elemental analyses were performed by using a GmbH VarioEL V3.00 automatic elemental analysis instrument. ¹H NMR spectra were determined by German Bruker AVANCE DRX-400 spectrometer. UV–Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. X-ray single crystal structure determinations were carried out on a SuperNova Dual Eos (Cu at zero) four-circle diffractometer.

4.2 | X-ray Crystallographic Analyses

The crystallographic data for the Cu(II) and Co(II) complexes are summarized in Table 1. The single crystals of the Cu(II) and Co(II) complexes were placed on a SuperNova, Dual (Cu at zero) Eos. diffractometer. The diffraction data were collected using a graphite monochromated Mo K α radiation ($\lambda = 0.71073$ A) at 294.10(10) and 291.60(10) K, respectively. The two crystal structures were solved by direct methods using SHELXS-2014 and refinements were done against F^2 using SHELXL-2014^[66]. The H atoms were included at the calculated positions and constrained to ride on their parent atoms.

4.3 | Synthesis of the ligand H₄L

The ligand H₄L has been synthesized by 2-O-(1ethyloxyamide)oxime-4,6-dichlorophenol and 2,3dihydroxyn- aphthalene-1,4-dicarbaldehyde according to the reported papers earlier.^[67–70] The method used in the process named "One-Pot", the detail steps and conditions were submitted in the Scheme 1. A light yellow powder was obtained after the purification process. Yield, (62.7%) M.p. 183–185 °C. ¹H NMR (400 MHz, CDCl₃): 10.57 (s, 2H), 9.08 (s, 2H), 8.46–8.49 (m, 3H), 8.30 (s, 1H), 7.58 (s, 2H), 7.52–7.53 (s, 2H), 7.35–7.38 (s, 4H), 4.54 (s, 8H). Anal. calc. For $C_{30}H_{24}Cl_4N_4O_8$ (%): C, 50.72; H, 3.41; N, 7.89. Found (%): C, 50.89; H, 3.29; N, 7.79.

4.4 | Synthesis of the Cu(II) complex

A methanol solution (3 ml) of $Cu(OAc)_2 \cdot 2H_2O$ (6.56 mg, 0.03 mmol) was added dropwise to a chloroform solution (3 ml) of the ligand H₄L (7.06 mg, 0.01 mmol) at room temperature. The color of the mixed solution immediately turned blue. The mixture was filtered and the filtrate was allowed to stand at room temperature for about two weeks. The solvent was partially evaporated and clear dark blue prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Yield, (42.7%) Anal. calc. For $C_{34}H_{26}Cl_4N_4O_{12}Cu_3$ (%): C, 40.38; H, 2.60; N, 5.31. Found (%): C, 40.23; H, 2.58; N, 5.52.

4.5 | Synthesis of the Co(II) complex

A methanol solution (3 ml) of $Co(OAc)_2 \cdot 2H_2O$ (6.48 mg, 0.03 mmol) was added dropwise to a chloroform solution

(3 ml) of the ligand H₄L (7.06 mg, 0.01 mmol) at room temperature. The color of the mixed solution immediately turned reddish brown. The mixture was filtered and the filtrate was allowed to stand at room temperature for about two weeks. The solvent was partially evaporated and clear dark reddish brown prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Yield, (45.7%) Anal. calc. For $C_{40}H_{38}Cl_{16}N_4O_{14}Co_3$ (%): C, 40.19; H, 3.24; N, 5.03. Found (%): C, 40.06; H, 3.18; N, 5.19.

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ORCID

Wen-Kui Dong D http://orcid.org/0000-0003-1249-5808

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, No. CCDC 1549320 and 1549321 for the Cu(II) and Co(II) complexes. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Telephone: (44) 01223 762910; Fax: +44–1223-336033; E-mail: deposit@ccdc.cam.ac.uk). These data can be also obtained free of charge at www.ccdc.cam.Ac.uk/conts/ retrieving.html.

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