Synthesis and Fluorescence Properties of Structurally Characterized Heterobimetallic Cu(II)–Na(I) Bis(salamo)-Based Complex Bearing Square Planar, Square Pyramid and Triangular Prism Geometries of Metal Centers

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Abstract: A novel heterotrinuclear complex \([\text{Cu}_2(\text{L})\text{Na}(\mu-\text{NO}_3)] \cdot \text{CH}_3\text{OH-CHCl}_3\) derived from a symmetric bis(salamo)-type tetraoxime \(\text{H}_4\text{L}\) having a naphthalenediol unit, was prepared and structurally characterized via means of elemental analyses, UV-Vis, FT-IR, fluorescent spectra and single-crystal X-ray diffraction. The heterobimetallic Cu(II)–Na(I) complex was acquired via the reaction of \(\text{H}_4\text{L}\) with 2 equivalents of \(\text{Cu(NO}_3\text{)}_2 \cdot 2\text{H}_2\text{O}\) and 1 equivalent of NaOAc. Clearly, the heterotrinuclear Cu(II)–Na(I) complex has a 1:2:1 ligand-to-metal (Cu(II) and Na(I)) ratio. X-ray diffraction results exhibited the different geometric behaviors of the Na(I) and Cu(II) atoms in the heterotrinuclear complex; the both Cu(II) atoms are sited in the \(\text{N}_2\text{O}_2\)-coordination environments of fully deprotonated \((\text{L})^4\) unit. One Cu(II) atom (Cu1) is five-coordinated and possesses a geometry of slightly distorted square pyramid, while another Cu(II) atom (Cu2) is four-coordination possessing a square planar coordination geometry. Moreover, the Na(I) atom is in the \(\text{O}_6\) cavity and adopts seven-coordination with a geometry of slightly distorted single triangular prism. In addition, there are abundant supramolecular interactions in the Cu(II)–Na(I) complex. The fluorescence spectra showed the Cu(II)–Na(I) complex possesses a significant fluorescent quenching and exhibited a hypsochromic-shift compared with the ligand \(\text{H}_4\text{L}\).

Keywords: symmetric bis(salamo)-type tetraoxime; heterobimetallic complex; synthesis; crystal structure; spectroscopic study

1. Introduction

A wide variety of \(\text{N}_2\text{O}_2\)-donor chelate ligands have been proverbially used to prepare alkaline earth, rare earth, and transition metal complexes for several decades. More recently, modified salen-type ligands having imine groups (–C=N–) [1–8], bear the potentially tetradentate \(\text{N}_2\text{O}_2\)-donor and can form relatively stable complexes with different metal ions. Salen and its derivatives are extremely attractive and commonly versatile ligands because their metal complexes have been studied in potential application in catalyses [9,10], supramolecular architectures [11–19], luminescence properties [20–26], electrochemical conducts [27,28], biological systems [29–37], optical sensor [38,39], magnetic materials [40–45] and nonlinear optical materials [46], and so forth. A lot of researches have been fulfilled to design and synthesize mono-nuclear and homo- or hetero-polynuclear metal complexes possessing salen-type or salamo-type ligand or its analogues. Compared to salen,
salamo-type ligand [47–56] has a –CH=N–O–(CH)n–O–N=CH– configuration and its corresponding complexes are more stable relatively.

The bis(salamo)-type ligand H4L containing O6 coordination sphere was already prepared earlier to obtain a series of Zn(II)–M(II), Co(II)–M(II) (M = Ca, Sr and Ba) and Zn(II)–RE(III) (RE = La, Ce and Dy) complexes. Therefore, these compounds are considered to be heterotrinuclear bis(salamo)-type complexes. Meanwhile, the crystal structures and properties of the obtained complexes have been studied in detail [28,57–59]. Owing to the bis(salamo)-type ligand H4L, we have designed and prepared a novel heterobimetallic complex containing an O6 coordination sphere, it can form homotrinuclear bis(salamo)-type complexes. The transition metal atom located in O6 coordination sphere can be replaced by alkali metal atoms with a larger atomic radius. To study the structural characteristics and fluorescent behaviors of heterobimetallic complexes of bis(salamo)-type ligand, herein we have designed and prepared a novel heterobimetallic complex [Cu2(L)Na(μ-NO3)] CH3OH·CHCl3 derived from the bis(salamo)-type tetraoxime H4L containing a naphthalenedioli unit. The structural representation of H4L is shown in Figure 1. Most importantly, the spectroscopic studies of the Cu(II)–Na(I) complex were investigated.

![Figure 1. Structural representation of H4L.](image)

2. Results and Discussion

2.1. IR Spectra

The main FT-IR absorption bands characteristic for H4L and its Cu(II)–Na(I) complex from 500 to 4000 cm⁻¹ regions are shown in Table 1.

| Compound   | ν(O–H) | ν(C=O) | ν(Ar–O) | ν(M–N) |
|------------|--------|--------|---------|--------|
| H4L        | 3172   | 1634   | 1241    | –      |
| Complex    | –      | 1618   | 1232    | 565    |

Generally, the typical O–H stretching band is usually observed at the 3500–3100 cm⁻¹ region. A broad band of medium intensity was found around 3172 cm⁻¹ in the free ligand H4L, this is an evidence for the stretching vibration of the O–H groups. However, this band disappeared in the Cu(II)–Na(I) complex. H4L showed a typical C=N stretching band occurring at 1634 cm⁻¹, while the Cu(II)–Na(I) complex showed this band at 1618 cm⁻¹. In contrast to the free ligand H4L it is moved to a lower wavenumber by 16 cm⁻¹ due to coordination of the N atoms of the C≡N groups to the Cu(II) atoms [57]. This fact is also approved by the appearance of new bands within the wavenumber at 565 cm⁻¹ due to ν(Cu(II)-N) vibrations. The characteristic absorption band of the Ar–O group occurred at 1241 cm⁻¹ in H4L. However, the Ar–O stretching band in the Cu(II)–Na(I) complex was moved to a lower wavenumber at ca. 9 cm⁻¹, exhibiting that the M–O bonds are formed between the metal atoms.
and the methoxy and phenolic O atoms of H₄L [60]. The facts mentioned above fare in agreement with the results of X ray diffraction.

### 2.2. UV-Vis Spectra

In this study, UV-Vis spectra of H₄L in CHCl₃:CH₃OH (1:1) (c = 2.5 × 10⁻⁵ mol L⁻¹) with its Cu(II)–Na(I) complex in CH₃OH:H₂O (10:1) (c = 1 × 10⁻³ mol L⁻¹) in freshly prepared solution are obtained in the range of 250–600 nm.

It can be seen from the absorption spectrum of H₄L, there are four continuous absorption peaks at about 269, 342, 360 and 378 nm [57]. The peak at 269 nm can be attributed to the π-π* transition of the benzene rings while the other three peaks can be assigned to the π-π* transition of the oxime groups [57,61].

In the titration experiment of the Cu(II)–Na(I) complex, the gradual addition of Cu(NO₃)₂ solution aroused the changes of absorption peaks. Compared to H₄L, the peaks are bathochromically shifted [62]. This fact mentioned above is owing to the coordination of the Cu(II) ion with H₄L. When 3 equiv of the Cu(II) ions were added to the solution of H₄L, the absorbance of the solution no longer changed. The spectral titration obviously revealed the formation of a 1:3 (ligand-to-Cu(II) ratio) Cu(II) complex (Figure 2a).

![Figure 2](image_url)

**Figure 2.** (a) UV-Vis spectral changes of H₄L (2.5 × 10⁻⁵ M) on addition of Cu(II) ions (1.0 × 10⁻³ M); (b) UV-Vis spectral changes of the [LCu₃]²⁺ on addition of Na(I) ions (1.0 × 10⁻³ M).

What is more, the gradual additions of NaOAc solution were continuously added the above solution. Upon addition of 1 equiv of Na(I) ions, the solution absorbance basically remains stable. Clearly, the
spectral titration obviously indicated that the ratio of the replacement reaction stoichiometry is 1:1 and is depicted in Figure 2b.

2.3. Crystal Structure Description

The structure of the Cu(II)–Na(I) complex was characterized by X-ray crystallography, and is depicted in Figure 3.

![Figure 3](image_url)

**Figure 3.** (a) Molecular structure of the Cu(II)–Na(I) complex (H atoms, crystallizing methanol and chloroform molecules are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level); (b) Coordination polyhedrons for Cu(II) and Na(I) atoms.

It is shown that the Cu(II)–Na(I) complex crystallizes in the monoclinic system with space group $P 2_1/n$. (Attempting to set the space group to $P2_1/c$, the structure of the complex was not determined, which is determined by the different orientations chosen when determining the crystal cell. The structure of expected complex is obtained when the space group is set to $P2_1/n$, and the bond lengths and angles are all within the expected ranges.) [63] and contains two Cu(II) atoms, one Na(I) atom, one completely deprotonated (L)$_2$ moiety, one μ-NO$_3$ ion, one crystallizing methanol and chloroform molecules, possessing a hetero-trinuclear structure. According to our design, the bis(salamo)-type ligand H$_4$L has an O$_6$ coordination sphere which is usually occupied by a larger radius metal ion [64]. Therefore, we consider the complex obtained to be a heterotrinuclear Cu(II)–Na(I) complex and not sodium salt of the Cu(II) complex [65]. At the same time, it is shown that the ligand-to-metal (Cu(II) and Na(I)) ratio is 1:2:1. This structure in this paper is different from the structure reported earlier, in which the two Cu(II) atoms are located in N$_2$O$_2$ sites, and one Cu(II) atom is still bonded to a methanol molecule, while the other Cu(II) atom is bonded to one O atom of a μ-NO$_3$ ion. Finally, both Cu(II) atoms adopt five-coordinated and possess geometries of slightly distorted
square pyramid. The capped site is occupied by Br3 with the bond length (Na1–Br3, 2.765(3) Å) and the Na-O bond length is in the ranges of 2.324(2)–3.025(3) Å [17].

As shown in Figure 3, the N2O2 compartments of the fully deprotonated (L)4− moiety are occupied by two Cu(II) atoms (Cu1 and Cu2), while the central Na(I) atom is located at O6 cavity. The Cu1 atom is bonded to two N atoms (Cu1–N1, 2.002(3) and Cu1-N2, 1.950(3)) and two O atoms (Cu1–O2, 1.907(2) Å and Cu1-O5, 1.903(2) Å) of the ligand (L)4− moiety forming the square base. Meantime, the Cu1 atom is also coordinated with one O atom (Cu1–O12, 2.462(3) Å) of a bisdentate µ3-NO3 ion. The Cu1 atom is five-coordinated with geometry of a slightly distorted square pyramid, which was deduced by calculating the value of \( \tau = 0.0058 \) [66]. Interestingly, the Cu2 atom is coordinated to the N atoms (Cu2–N3, 1.944(3) Å and Cu2–N4, 1.981(3) Å) and O atoms (Cu2–O6, 1.909(2) Å and Cu2-O9, 1.907(3) Å) of the N2O2 site. Therefore, the Cu2 atom is four-coordinated and possesses a geometry of slightly distorted square planar. The Na(I) atom occupies central O6 site (Na1–O1, 2.546(3) Å; Na1-O2, 2.388(3) Å; Na1-O5, 2.355(3) Å; Na1-O6, 2.454(3) Å; Na1-O9, 2.429(3) Å and Na1-O10, 2.475(3) Å) from four phenolic O and two methoxy O atoms of the ligand (L)4− moiety [17]. Meanwhile, the Na(I) atom is still coordinated to one O atom (Na1-O11, 2.490(4)) of µ3-NO3 ion. In a word, the Na-O bond length is in the range of 2.355(3)–2.546(3) Å, which is in the regular range compared with previously reported data [17]. Therefore, according to our previous report, the Na-O bonds mentioned above could be regarded as coordination bonds. Finally, the Na(I) atom adopts seven-coordinated and possesses a geometry of slightly distorted single triangular prism. The crystallographic data and structure refinement parameters are summed in Table 2. Selected bond lengths and angles are summed in Table 3.

Table 2. Crystal and structure refinement data for the Cu(II)–Na(I) complex.

| Parameter                              | Value                  |
|----------------------------------------|------------------------|
| Empirical Formula                      | C34H33Cl3Cu2Na5O14     |
| Formula weight                         | 992.07                 |
| T (K)                                  | 154.89(10)             |
| Radiation (Å)                          | Mo Kα, 0.71073         |
| Crystal system                         | Monoclinic             |
| Space group                            | P 2₁/n                 |
| a (Å)                                  | 15.8326(3)             |
| b (Å)                                  | 11.4630(2)             |
| c (Å)                                  | 21.7834(4)             |
| α (°)                                  | 90                     |
| β (°)                                  | 98.135(2)              |
| γ (°)                                  | 90                     |
| Volume (Å³)                            | 3913.68(14)            |
| Z                                      | 4                      |
| Dc (g·cm⁻³)                            | 1.684                  |
| Absorption coefficient (mm⁻¹)          | 1.377                  |
| Θ range for data collection (°)        | 3.281 to 26.021        |
| F (000)                                | 2016                   |
| h/k/l (min, max)                       | −19,19/−14,14/−26,26   |
| Crystal size (mm)                      | 0.15 × 0.21 × 0.24     |
| Reflections collected                  | 16726/7694             |
| [Rint = 0.035]                         |                        |
| Independent reflection                | 7694                   |
| S                                      | 1.033                  |
| Data/restraints/parameters             | 5555/54/581            |
| Final R indices [I > 2σ(I)] a          | \( R_1 = 0.0478 \)     |
| R indices (all data) b                 | \( wR_2 = 0.0738 \)    |
2.4. Supramolecular Interactions

Single crystal determination showed that the Cu(II)–Na(I) complex forms a self-assembling infinite supra-molecular structure by C-H⋯π and hydrogen bond interactions. The hydrogen bonds and C-H⋯π stacking interactions are listed in Table 4.

**Table 4.** Hydrogen bondings (Å, deg) and C-H⋯π stacking interactions of Cu(II)–Na(I) complex.

| D-H⋯A       | d(D-H) | d(H⋯A) | d(D⋯A) | ∠DHA |
|-------------|--------|--------|--------|------|
| C8-H8A⋯O12  | 0.97   | 2.29   | 3.252(6)| 171  |
| O14-H14A⋯O12 | 0.82  | 2.37   | 3.075(6)| 144  |
| O14-H14A⋯O13 | 0.82  | 2.50   | 3.267(8)| 157  |
| C23-H23B⋯O13 | 0.97  | 2.31   | 2.987(9)| 126  |
| C15-H15⋯Cg1 | 0.96  | 2.79   | 3.473(5)| 131  |

Symmetry codes: ¹x, 1+y, z; ²1−x, 1−y, −z; Cg1 for the Cu(II)–Na(I) complex is the centroid of C1-C6 atoms.

In the Cu(II)–Na(I) complex, there is one intra-molecular C8-H8A⋯O12 hydrogen bond, showing in Figure 4. As illustrated in Figure 5, an infinite 2D supra-molecular structure is interlinked via three pairs of inter-molecular O14-H14A⋯O12, O14-H14A⋯O13 and C23-H23B⋯O13 hydrogen bonds [67–75]. Especially, one significant C15-H15⋯Cg1 (C1-C6) (C-H⋯π) interaction is constructed and shown in Figure 6.
with the H metal ions (Cu(II) and Na(I)), which is attributed to ligand-to-metal charge transfer (LMCT) [68].

Excitation at 330 nm. That hypsochromic-shift phenomenon can explain the complexation of H metal ions (Cu(II) and Na(I)), which is attributed to ligand-to-metal charge transfer (LMCT) [68].

Figure 5. 2D supra-molecular structure by inter-molecular O-H ··· O and C-H ··· O interactions in the Cu(II)–Na(I) complex.

Figure 6. Intermolecular C-H ··· π interactions of the Cu(II)–Na(I) complex.

2.5. Fluorescence Spectra

The emission spectra of H4L in CHCl3:CH3OH (1:1) (c = 2.5 × 10⁻⁵ mol L⁻¹) solution and its Cu(II)–Na(I) complex in CH3OH (c = 1.0 × 10⁻⁵ mol L⁻¹) were determined at room temperature. As shown in Figure 7, the ligand H4L exhibited one relatively strong emission at 440 nm upon excitation at 330 nm, which should be attributed to the intra-ligand π-π* transition [67]. In comparison with the H3L, fluorescent property study of the Cu(II)–Na(I) complex is shown that the fluorescent intensity weakens markedly, exhibiting a broad peak with maximum emission at 429 nm upon excitation at 330 nm. That hypsochromic-shift phenomenon can explain the complexation of H4L and metal ions (Cu(II) and Na(I)), which is attributed to ligand-to-metal charge transfer (LMCT) [68].
3. Experimental Section

3.1. Materials and Methods

2-Hydroxy-3-methoxybenzaldehyde (99%), pyridinium chlorochromate (98%), methyl trioctyl ammonium chloride (90%) and borontribromide (99.9%) were bought from Alfa Aesar (New York, NY, USA). Hydrobromic acid 33 wt % solution in acetic acid was purchased from J&K Scientific Ltd. (Beijing, China). All chemicals and solvents used for the synthesis were of the best available analytical reagent grade, without further purification in the preparation of the free ligand and its complex. Elemental analyses for C, H, and N were carried out using a GmbH Vario EL V3.00 automatic elemental analysis instrument (Elementar, Berlin, Germany). Elemental analyses for Cu and Na atoms were detected with an IRIS ER/S-WP–1 ICP atomic emission spectrometer (IRIS, Elementar, Berlin, Germany). IR spectra were measured on a VERTEX70 FT-IR spectrophotometer (Bruker, Billerica, MA, USA), with samples prepared as KBr (500–4000 cm\(^{-1}\)) pellets. Melting points were recorded on use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected (Beijing, China). UV-Vis absorption spectra were recorded on a Shimadzu UV-3900spectrometer (Hitachi, Shimadzu, Tokyo, Japan). The fluorescence spectra were taken on Hitachi F-7000 spectrometer (Hitachi, Tokyo, Japan). X-ray single crystal structure determinations were carried out on a Super Nova Dual (Cu at zero) Eos four-circle diffractometer (Bruker, Billerica, MA, USA).

3.2. Synthesis of H\(_4\)L

The main reaction steps involved in the synthesis of H\(_4\)L was gained via reacting 2,3-dihydroxynaphthalene-1,4-dicarbaldehyde with 3-methoxysalicylaldehyde. 2,3-Dihydroxynaphthalene-1,4-dicarbaldehyde and 2-[O-(1-ethyloxyamide)]oxime-6-methoxyphenol were prepared according to an analogous method [28,57–59]. The synthesis of H\(_4\)L is given in Scheme 1.
H₂L was prepared according to the previously reported method [28,57–59]. Yield: 60.2%. m.p. 170–171 °C. Anal. Calcd. (%) for C₃₂H₆₂N₄O₁₀ (632.42): C, 60.75; H, 5.10; N, 8.86. Found (%): C, 60.93; H, 5.23; N, 8.74. ¹H-NMR (400 MHz, CDCl₃) δ11.03 (s, 2H), 9.82 (s, 2H), 9.14 (s, 2H), 8.29 (s, 2H), 7.97 (q, J = 3.2 Hz, 2H), 7.41 (q, J = 6.0, 2.9 Hz, 2H), 7.06–6.68 (m, 6H), 4.58 (t, 8H), 3.89 (s, 6H). UV-Vis [in methanol/chloroform (1:1)], λ_max (nm) [2.5 × 10⁻⁵ M]: 269, 342, 360, 378.

3.3. Synthesis of the Cu(II)–Na(I) Complex

A mixture solution of Cu(NO₃)₂·2H₂O (4.82 mg, 0.02 mmol) in methanol (2 mL) and NaOAc (0.82 mg, 0.01 mmol) in methanol (2 mL) was added to a stirring solution of H₂L (6.32 mg, 0.01 mmol) in chloroform (2 mL). The color of the mixing solution immediately turned dark green. The mixture was filtered, and the filtrate was allowed to stay for slow evaporation. After about three weeks, clear light green single-crystals suitable for X-ray diffraction studies were gained. Yield: 40.3%. Anal. Calcd. (%) for C₃₄H₃₅Cl₃Cu₂Na₅O₁₄ (992.07): C, 41.16; H, 3.35; N, 7.06; Cu, 12.81; Na, 2.32. Found (%): C, 41.33; H, 3.49; N, 6.88; Cu, 12.64; Na, 2.17. UV-Vis [in methanol/H₂O (10:1)], λ_max (nm) [1.0 × 10⁻³ M]: 350, 369, 382.

3.4. Crystal Structure Determination and Refinement

Single crystal of dimensions 0.15 × 0.21 × 0.24 mm for the heterotrinuclear Cu(II)–Na(I) complex was mounted on a glass rod. The crystal data were collected with a Super Nova (Dual, Cu at zero, Eos) diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 154.89(10) K. Multiscan absorption corrections were applied. The structure was solved by direct methods and refined anisotropically using full-matrix least-squares methods on F² with the SHELX-2014 program package. Nonhydrogen atoms of the compound were refined with anisotropic temperature parameters. The positions of H atoms were calculated and isotropically fixed in the final refinement.

Supplementary crystallographic data have been deposited at Cambridge Crystallographic Data Centre (CCDC No. 1815945) and can be gained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

4. Conclusions

Overall, we have designed and synthesized a novel heterobimetallic Cu(II)–Na(I) complex derived from a symmetric bis(salamo)-type ligand H₂L. X-ray crystallographic investigation of the heterotrinuclear Cu(II)–Na(I) complex revealed there is a 1:2:1 ligand-to-metal (Cu(II) and Na(I)) ratio. The Cu1 atom is five-coordinated and possesses the geometry of slightly distorted square pyramid and the Cu2 atom is four-coordinated and possesses the geometry of square planar. The Na(I) atom adopts seven-coordinated with a slightly distorted single triangular prism geometry. The UV-Vis titration experiment clearly displayed the coordination ratio between the ligand H₂L and the Cu(II) and Na(I)
ions. The fluorescence spectra showed the complex possesses a significant fluorescent quenching, and exhibited a hypsochromic-shift compared with the ligand $H_4L$.

**Supplementary Materials:** Supplementary materials are available online.

**Author Contributions:** W.-K.D. supervised the project and contributed materials/reagents/analysis tools; X.-Y.D., Z.-L.W., H.-R.M. and H.Z. performed the experiments; W.-K.D. and Q.Z. wrote the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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**Sample Availability:** Samples of the compounds are available from the authors.

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