Differential study on the transition from a new polyhalogen-substituted unsymmetric salamo-based ligand to its Cu(II) and Co(II) complexes

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ABSTRACT
Two structurally different Cu(II) and Co(II) complexes, [Cu(L)] (1) and [Co2(L)2]·2CH3OH (2), constructed from a new polyhalogen-substituted unsymmetric salamo-based ligand (H2L, 4-chloro-4′-bromo-6-bromo-6′-tert-butyl-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenol) were synthesized by wet-chemical methods. Complexes 1 and 2 were characterized through elemental analyses, IR and UV-vis spectroscopies and single crystal X-ray crystallography. In addition, the differences of the structures, electronic absorption characteristics and fluorescence property transitions from the ligand to complexes 1 and 2 were studied. The largest difference is that the ligand H2L can react with M(OAc)2 (M = Cu(II) and Co(II)) to give two complexes with distinct structures and behaviors. There are two chemically identical but crystallographically independent structural units (molecules A and B) in 1. Moreover, each Cu(II) ion (Cu1 or Cu2) is four-coordinate and possesses a square planar geometry, but both Co(II) ions of 2 are bridged by phenoxide ions and possess five-coordinate trigonal bipyramidal configurations. At the same time, Hirshfeld surface analyses showed there are short-range interaction features from the ligand to complexes 1 and 2, the O····H−O interactions of the ligand are significantly stronger than those of 1 and 2.
1. Introduction

It is of great significance for material science and coordination chemistry to design and synthesize salen-based ligands. Salen-based ligands [1–3] and their complexes are very extraordinary compounds linked with the rapid development of magnetic materials [4–6], photoluminescence [7–10], catalytic reactions [11–13], sensing and ion recognition [14–18]; the breadth and depth of these research fields [19–23] are expanding. In modern coordination chemistry, salen-based ligands are relatively common and universal compounds synthesized from salicylaldehyde and ethylenediamine [24–26]. Fascinatingly, in order to obtain better ligands with excellent properties, some atoms and groups have been introduced into the salen-based ligands [27, 28]. The salamo-based ligands [29–32] derived from salen-based ligands have added O atoms into the imine part to provide more stable N2O2 coordination cavities to obtain various metal complexes with unique structures [33–35].

Among several new synthetic methods developed so far, the design and exploitation of the salamo-based ligands containing a N2O2 coordination cavity are undoubtedly the most useful methods, because the tailored synthesis of these ligands can be completed through simple procedures [36–38]. The great majority of the complexes are based on symmetrical N2O2-donor ligands. In recent years, wide attention has been focused on functional unsymmetric salamo-based ligands [39–41], all of which is possible due to their unique structures and extensive applications.

As part of our long-term research, a newly designed polyhalogen-substituted unsymmetric salamo-based ligand H2L and its two 3d metal(II) complexes were designed and synthesized. The specificity of the new unsymmetric salamo-ligand is thanks to the introduction of polyhalogen-substituted atoms (bromine and chlorine atoms) [42, 43] and a tert butyl group [44, 45]. It is hoped that the special groups or atoms can influence the construction of the structures and form novel complexes. Herein, the single crystal X-ray diffraction analyses of the unsymmetric ligand H2L and
complexes 1 and 2 were also characterized. Most importantly, the distinct structures of 1 and 2 were formed by adding two different transition metal ions into H2L separately. Complex 1 is a simple mononuclear compound, whereas 2 is a dimer. Moreover, the UV-vis spectra, IR spectra and fluorescence spectra of 1 and 2 were investigated to ascertain their properties.

2. Experimental

2.1. Methods and Materials

All chemicals were analytical grade reagents from Shanghai Merery Chemical Technology Co., Ltd.; solvents were analytical grade reagents from Tianjin Chemical Reagent Factory and were used without purification. 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 with an IRIS ER/S-WP-1 ICP atomic emission spectrometer. The IR spectra (4000-400 cm\(^{-1}\)) of the ligand and complexes were investigated using a Vertex70 FT-IR spectrophotometer and samples were prepared as KBr disks. The UV–vis absorption spectra were recorded by a Shimadzu UV-3900 spectrometer. The \(^1\)H NMR spectra were measured on a Bruker AV 500 MHz spectrometer. The melting points were measured by a micro melting point instrument manufactured by Beijing Tektronix Instrument Co., Ltd. A F-7000 FL spectrophotometer was used to record the fluorescence spectra. The crystal structures were determined on a four-circle diffractometer (H2L) or a Bruker D8 Venture diffractometer (complexes 1 and 2).

2.2. Preparation of H2L

3-Tert-butyl-5-bromosalicylaldehyde: to a dichloromethane solution (100 mL) of 3-tert-butyl-salicylaldehyde (178 mg, 1.00 mmol) was slowly added 3.5 mL of liquid bromine with a syringe. The mixture system was kept stable at 0\(^\circ\)C in ice water for 2.5 h, then the solution was separated with a separatory funnel; bright yellow product 3-tert-butyl-5-bromo-salicylaldehyde was obtained by vacuum distillation. Yield: 89.2% (229 mg). M. p.: 63–64 \(^\circ\)C. Anal. calcd. for C\(_{11}\)H\(_{13}\)O\(_2\)Br (%): C, 51.38; H, 5.10. Found: C, 51.47; H, 5.04. \(^1\)H NMR (Figure S1) (500 MHz, CDCl\(_3\)) \(\delta\) 11.73 (s, 1H), 9.81 (s, 1H), 7.58 (d, \(J = 2.5 \text{ Hz}\), 1H), 7.52 (d, \(J = 2.4 \text{ Hz}\), 1H), 1.41 (s, 9H).

4-Chloro-4’-bromo-6-bromo-6’-tert-butyl-2,2’-[ethylenedioxybis(nitrilemethylidyne)]diphenol (H2L): H2L was synthesized by the reaction of 2-[O-(1-ethyloxyamide)]oxime-3-bromo-5-chlorophenol and 3-tert-butyl-5-bromo-salicylaldehyde. The 2-[O-(1-ethyloxyamide)]oxime-3-bromo-5-chlorophenol (310 mg, 1.00 mmol) was added into a round-bottomed flask with 40 mL dichloromethane/ethanol (1:1, v/v) mixture. Then a solution of 3-tert-butyl-5-bromo-salicylaldehyde (257 mg, 1.00 mmol) in 40 mL dichloromethane/ethanol (1:1, v/v) mixture was dropped into the solution with a constant pressure dropping funnel over 6 h at 56 \(^\circ\)C. The solution was allowed to cool to normal temperature. Colorless needles were obtained by filtration, recrystallization, washing with ethanol and air drying. Yield: 68.1% (374 mg). M. p.:153–155 \(^\circ\)C. Anal. calcd. for C\(_{20}\)H\(_{21}\)Br\(_2\)ClN\(_2\)O\(_4\) (%): C, 43.78; H, 3.86; N, 5.11. Found: C, 43.97; H, 3.68; N,
5.02. $^1$H NMR (Figure S2) (500 MHz, CDCl$_3$) δ 10.49 (s, 1H), 10.25 (s, 1H), 8.15 (d, $J = 1.7$ Hz, 2H), 7.53 (d, $J = 2.4$ Hz, 1H), 7.36 (d, $J = 2.4$ Hz, 1H), 7.14 (d, $J = 2.4$ Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 1H), 4.50 (d, 4H), 1.39 (s, 9H).

2.3. Preparation of 1 and 2

4-Chloro-4′-bromo-6-bromo-6′-tert-butyl-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenolato)copper(II) (1): 0.0100 mmol of copper(II) acetate monohydrate (2.00 mg) was stirred with 4 mL methanol solvent for 10 minutes, which was then added to a clear solution of H$_2$L (5.49 mg, 0.0100 mmol) in acetone (1 mL) with stirring for 15 minutes. The mixed system was filtered and sealed with silver paper for storage. Black block-shaped single crystals of 1 suitable for X-ray crystal analysis were collected through placing it in an undisturbed and quiet environment for 14 days. Yield: 51.1% (3.12 mg). Anal. calcd. for [Cu(L)] (C$_{20}$H$_{19}$Br$_2$ClCuN$_2$O$_4$) (%): C, 39.31; H, 3.10; N, 4.51; Cu, 10.33. Found: C, 39.57; H, 3.24; N, 4.59; Cu, 10.21.

Bis(μ$_2$-2,2′-dioxoxygen-(4-chloro-4′-bromo-6-bromo-6′-tert-butyl-2,2′-[ethylenedi-oxybis (nitrilomethylidyne)]diphenolato)dicobalt(II) monohydrate (2): A solution of cobalt(II) acetate tetrahydrate (2.41 mg, 0.0100 mmol) in methanol (3 mL) was added to a clear solution of H$_2$L (5.49 mg, 0.0100 mmol) in dichloromethane (3 mL) with stirring for 15 minutes. The mixed system was filtered and sealed for storage with silver paper. Some dark red block-shaped single crystals of 2 suitable for X-ray crystal analysis were collected through placing it in an undisturbed and quiet environment for 21 days. Yield: 49.6% (3.16 mg). Anal. calcd. for [Co$_2$(L)$_2$]-2CH$_3$OH (C$_{42}$H$_{46}$Br$_4$Cl$_2$Co$_2$N$_4$O$_{10}$) (%) : C, 39.56; H, 3.64; Co, 9.24; N, 4.39. Found: C, 39.62; H, 3.57; Co, 9.02; N, 4.28.

2.4. Crystal structure analyses of H$_2$L, 1 and 2

The single-crystal data of H$_2$L were collected on a four-circle diffractometer equipped with graphite monochromated Cu-Kα radiation ($λ$ = 1.54184 Å) at 99.99(10) K. The single-crystal data of 1 and 2 were collected on a Bruker D8 Venture diffractometer with graphite monochromated Cu-Kα radiation ($λ$ = 1.54178 Å) at 173(2) K. The data collection and reduction of H$_2$L were performed using the package CrysAlisPro [46]. For 1 and 2, data reduction was performed using the SAINT programs [47]. The data were corrected for absorption correction using the multi-scan method by SADABS software [48]. The crystal structures and integrated space-group were determined by a direct method using the ShelXT [49] in Olex 2 as a graphical interface [50]. The data were merged by SHELXL and the structures were refined using full-matrix least squares on $F^2$ [51]. The positions of Cu (or Co) ions are easily ascertained. The hydrogen atoms were placed on calculated positions and refined with a riding model; the coordinates of the nonhydrogen atoms were refined anisotropically.

Details of crystal data and the refinement parameters are summarized in Table 1. CCDC 2163079, 2163080 and 2163081 contain the supplementary crystallographic data for H$_2$L, 1 and 2, respectively. The complete crystallographic data have been stored in the Cambridge Crystallographic Data Center as CIF files and can be provided free of charge from the website: https://www.ccdc.cam.ac.uk/structures/.
3. Results and discussion

3.1. Preparation of H$_2$L, 1 and 2

The preparation route for the salamo-based ligand (H$_2$L) is shown in Scheme 1.

According to the formerly reported literatures [29, 30], the 1,2-bis(aminooxy)ethane and the 2-[(1-ethyloxyamide)oxime-3-bromo-5-chlorophenol were prepared and collected. 3-Tert-butyl-5-bromosalicylaldehyde was prepared as previously reported [52]. Treatment of 2-[(1-ethyloxyamide)oxime-3-bromo-5-chlorophenol with 3-tert-butyl-5-bromosalicylaldehyde in a 1:1 molar ratio in a dichloromethane/ethanol mixture led to the formation of 4-chloro-4$_0$-bromo-6-bromo-6$_0$-tert-butyl-2,2$_0$-[ethylenedioxybis(nitrilemethylidyne)]diphenol (H$_2$L) (Scheme 1).

The routes to the synthesis of 1 and 2 are depicted in Scheme 2. The single crystals of 1 (or 2) were accessible from the reaction of H$_2$L with copper(II) acetate monohydrate (or cobalt(II) acetate tetrahydrate) in a 1:1 molar ratio in methanol/acetone (or methanol/dichloromethane) mixed solvents (Scheme 2). After stirring for 15 minutes, the mixed system was filtered off and standing with undisturbed for about 14 (or 21) days (see Experimental).

3.2. IR spectra analyses

The IR spectra of H$_2$L, 1 and 2 are shown in the range of 4000–400 cm$^{-1}$ (Figure 1). In H$_2$L, a strong absorption peak observed at 3428 cm$^{-1}$ is due to the stretching vibration of O–H groups [53, 54], and a strong sharp peak appeared at 1615 cm$^{-1}$ can be

| Compounds | H$_2$L | 1 | 2 |
|-----------|--------|---|---|
| Empirical formula | C$_{20}$H$_{21}$Br$_2$ClN$_2$O$_4$ | C$_{20}$H$_{19}$Br$_2$ClCuN$_2$O$_4$ | C$_{42}$H$_{46}$Br$_4$Cl$_2$Co$_2$N$_4$O$_{10}$ |
| Molecular weight | 548.66 | 610.18 | 1275.23 |
| Crystal size (mm) | 0.13 × 0.12 × 0.11 | 0.14 × 0.12 × 0.11 | 0.25 × 0.23 × 0.22 |
| Habit | Block-shaped | Block-shaped | Block-shaped |
| Crystal system | Triclinic | Triclinic | Trigonal |
| Space group | P – 1 | P – 1 | R – 3c |
| a (Å) | 7.0328(2) | 9.0855(2) | 21.1181(3) |
| b (Å) | 9.2380(2) | 13.2107(3) | 21.1181(3) |
| c (Å) | 17.1166(4) | 19.3229(5) | 58.6290(16) |
| α (°) | 74.809(2) | 100.1640(10) | 90 |
| β (°) | 88.883(2) | 92.447(10) | 90 |
| γ (°) | 81.327(2) | 101.908(10) | 120 |
| V (Å$^3$) | 1060.69(5) | 2226.18(9) | 22644.0(9) |
| Z | 2 | 4 | 18 |
| D$_{calc}$ (g·cm$^{-3}$) | 1.718 | 1.821 | 1.683 |
| μ (mm$^{-1}$) | 6.263 | 6.950 | 10.335 |
| F(000) | 548 | 1204 | 11412 |
| θ Range for data collection (°) | 10.036 to 152.048 | 6.964 to 144.05 | 5.696 to 136.656 |
| Index ranges | h 10 to 8 | k 11 to 11 | l 21 to 10 |
| | h 8 to 8 | k 11 to 11 | l 21 to 10 |
| | h 11 to 11 | k 16 to 16 | l 24 to 24 |
| | h 20 to 21 | k 21 to 21 | l 70 to 70 |
| Reflections collected | 9585 | 23048 | 83807 |
| Completeness to θ (%) | 96.0 | 97.6 | 99.9 |
| Data/restraints/parameters | 4260/2/271 | 8557/1/547 | 4622/178/346 |
| Final R1, wR2 indices | 0.0298, 0.0833 | 0.0515, 0.1346 | 0.0452, 0.1036 |
| Final R1, wR2 indices (all data) | 0.0307, 0.0840 | 0.0585, 0.1393 | 0.0658, 0.1148 |
| Largest diff. peak and hole (e.Å$^{-3}$) | –0.70, 0.53 | –1.39, 1.38 | –0.74, 0.87 |
assigned to the typical $\nu(C=\text{N})$ vibration [55]. Moreover, an absorption peak at 1260 cm$^{-1}$ is a typical $\nu(\text{Ar}-\text{O})$ vibration [56]. In the IR spectra of 1 and 2, the absorption peak at 3428 cm$^{-1}$ has completely disappeared, which proves that the phenolic hydroxyl groups of H$_2$L have been deprotonated and have coordinated to the Cu(II) or Co(II) ions. The wide O–H stretching vibration band was found at 3420 cm$^{-1}$ in 2, which is in agreement with the result of elemental analysis. The corresponding O–H stretching vibration band was discovered at 3415 cm$^{-1}$ in 1, which could correspond to the water molecules in the manufacturing process of KBr.

The vibrational peaks of C=\text{N} and Ar–O bonds were discovered at 1590 and 1221 cm$^{-1}$ in 1, respectively [57]. The noteworthy shift to low wavenumber indicates that the coordination has happened. Moreover, the moderate absorption peak which appeared at 546 cm$^{-1}$ is due to the Cu–N stretching vibration, and that at 479 cm$^{-1}$ is due to the stretching vibration of the Cu–O bond, indicating the occurrence of coordination between the Cu(II) ion and the ligand H$_2$L [58]. In 2, the absorption peak which appeared at 515 cm$^{-1}$ is assigned to the Co–N absorption peak, and that at 466 cm$^{-1}$ is owing due to the absorption peak of the Co–O bond, which indicates the coordination of Co(III) ions with the ligand H$_2$L has occurred [59].

**Scheme 1.** The preparation route for H$_2$L.
3.3. UV–vis absorption spectral analyses

The UV–vis absorption spectra of H₂L, 1 and 2 (EtOH, 1 × 10⁻⁵ M) are depicted in figure 2. The UV–vis absorption curve of free H₂L is composed of two intense absorption peaks at 327 and 272 nm, which are due to the n–π* transitions of chromophore C=N groups and the π–π* transitions of benzene rings [60]. Contrasted with the unsymmetric ligand H₂L, the absorption peaks of 1 and 2 at 272 nm decreased in intensity obviously. Unexpectedly,
A new peak of 1 was found at 382 nm (370 nm for 2), which is possibly caused by the ligand to metal charge transition (LMCT) effect [61].

The titration absorption spectra of 1 and 2 were measured (Figure 3a). With the slow addition of Cu(II) ions ($1 \times 10^{-3}$ M), the intensity of the absorption peak at 382 nm increased gradually, and the absorption spectra essentially did not change when adding additional Cu(II) ions (1 equiv.). The titration experiment results and the Job plot (Figure S3a) reveal that the optimum binding ratio of Cu(II) ions to H$_2$L is 1:1. As shown in Figure 3b, with the slow addition of Co(II) ions ($1 \times 10^{-3}$ M), the intensity of the absorption peak at 370 nm increased gradually, and the absorption spectra essentially no longer changed when continuing to add Co(II) ions (beyond 1 equiv.). The titration experiment results and the Job plot (Figure S3b) also indicate that the optimum binding ratio of Co(II) ions to H$_2$L is 1:1.

3.4. Descriptions of crystal structures

The important bond angles (°) and lengths (Å) of H$_2$L, 1 and 2 are summarized in Table 2. The hydrogen bond interactions of H$_2$L, 1 and 2 are shown in Table 3. The X-H⋯π interactions of 1 are shown in Table S1.
As depicted in Figure 4, the molecule is an unsymmetric structure. There are four pairs of important intramolecular hydrogen bonds (C18–s presented in Figure 4 by its asymmetric unit. The molecular formula is C20H21Br2ClN2O4.

### 3.4.1. Crystal structure description of H2L

H2L crystallizes in the triclinic space group P-1 and Z = 2. There is one molecule represented in Figure 4 by its asymmetric unit. The molecular formula is C20H21Br2ClN2O4. As depicted in Figure 4, the molecule is an unsymmetric structure. There are four pairs of important intramolecular hydrogen bonds (C18–H18A...O4, C19–H19C...O4, O1–H1...N1 and O4–H4...N2) in free H2L (figure S4a).
halogen atoms (bromine and chlorine atoms), the presence of one intermolecular halogen bond (Br2…O2 3.049 Å) is of great significance for the structural construction between the two molecules (Figure S4b). Finally, as shown in Figure 5, a three-dimensional supramolecular structure of H2L is generated by different torsion angles and intermolecular hydrogen bonds.

3.4.2. Crystal structure description of 1

The molecular formula of 1 is C20H19Br2ClCuN2O4. It crystallizes in triclinic space group P-1 and Z = 4. There are two molecules within the asymmetric unit (Z’ = 2).

Complex 1 is mononuclear (Figure 6). The unit cell includes two complex 1 molecules (A and B), which are chemically identical but crystallographically independent units. To emphasize the relationship between the two complex 1 molecules, a molecular fit (Platon) is interesting (see Figure S5). The Cu(II) ions in both molecules are four-coordinate by the two O and N atoms of the ligand (L)2– unit, resulting in a distorted square planar geometry. Such geometry is quite common with this kind of salmo-
based ligand. Importantly, the $\tau_4$ parameter values ($\tau_4 = [360 - (\alpha + \beta)/141]$) of Cu1 and Cu2 are both 0.279 [62], indicating that Cu1 (or Cu2) ion forms a distorted square planar geometry. For molecules A and B, the biggest distinction is the variety of the bond lengths and angles, as listed in Table 2.

Furthermore, the hydrogen bond interactions in 1 cannot be ignored. There are four pairs of intramolecular hydrogen bonds (C18–H18C…O4, C19–H19A…O4, C39–H39C…O8 and C40–H40A…O8) (Figure S6a) and two pairs of important intermolecular hydrogen bonds (C9–H9A…O6 and C29–H29B…O2) in 1 (Figure S6b). In addition, a C–H…π interaction (C28–H28A…Cg12) is represented in Figure S6c. Finally, one-dimensional supramolecular structure (Figure 7) of 1 is formed by these abundant intermolecular hydrogen bond interactions. Formation of the above-mentioned intermolecular hydrogen bonds plays a non-negligible role in stabilizing the structure of 1.

3.4.3. Crystal structure description of 2
Complex 2 crystallizes in the trigonal space group $R$-3c with $Z = 18$ with the molecular formula $C_{42}H_{46}Br_4Cl_2Co_2N_4O_{10}$, which means that the asymmetric unit contains half of the dinuclear unit ($Z' = 0.5$).
In Figure 8, the dimeric complex $2$ is comprised of two deprotonated ligand (L)$_2$ units, two Co(II) ions and two crystallized methanol molecules. The C and O atoms of each methanol molecule are disordered over two positions (C21 and C21A, 0.25), (C22 and C22A, 0.25), (O5 and O5A, 0.25) and (O6 and O6A, 0.25), which were allowed for during refinement. Two Co(II) ions (Co1 and Co1#1) are bridged by the phenoxide ions (O1 and O1#1) from the deprotonated (L)$_2$ units forming a four-membered ring (Co1-O1-Co1#1-O1#1). The two Co(II) ions are five-coordinate by N and O atoms of the ligand (L)$_2$ units, with one of the O atoms participating in forming a Co-O-Co bridge. Each Co(II) ion has a distorted trigonal bipyramidal geometry as shown by the $\tau$ parameter value \[ \tau = (\beta - \alpha)/60 \] of 0.771 [63].

Data for $2$ are summarized in Table 3. There are three pairs of important intramolecular hydrogen bonds (C9–H9A···O1, C18–H18A···O4 and C20–H20C···O4) (Figure S7a), and one pair of intermolecular hydrogen bond (C19–H19B···O4) in $2$ (Figure S7b). Finally, a three-dimensional supramolecular structure (Figure 9) of $2$ is formed by these intermolecular hydrogen bond interactions.

### 3.5. Hirshfeld surface analyses

In recent years, Hirshfeld surfaces have been used as a tool for molecular crystal structure analysis [64]. It is a technique for obtaining the information of crystal stacking trend, which provides a convenient and intuitive method for quantitative analysis of the interactions in single crystal structures through the derivation of the Hirshfeld surfaces and the decomposition of two-dimensional fingerprints [65]. Hirshfeld surface analyses of H$_2$L, $1$ and $2$ are shown in Figure 10. The Hirshfeld surfaces are mapped to $d_{in}$, $d_{i}$ and $d_{o}$. The differences between H$_2$L, $1$ and $2$ directly show the level of intermolecular bindings. For H$_2$L, $1$ and $2$, the red region usually represents the interactions of O···H/H···O in the map $d_{in}$. On the surface, the white region is caused by H···H
interactions. Meanwhile, there is no interaction on the blue area, which indicates that the distance between the atoms is large.

To better understand the characteristics of H$_2$L, 1 and 2, the 2D fingerprint plots were investigated. As depicted in Figure 11, the major interactions occur between H···H, O···H/H···O, C···H/H···C. In H$_2$L, the major interactions of C···O/O···C, C···H/H···C, O···H/H···O and H···H account for 1.4%, 9.3%, 36.5% and 36.5%. In 1, the contributions of C···O/O···C, C···H/H···C, O···H/H···O and H···H are 2.7%, 9.9%, 10.5% and 33.6%. In 2, the proportions of C···O/O···C, C···H/H···C, O···H/H···O and H···H are 0.1%, 12.6%, 7.9% and 39.3%. In summary, comparing the ligand H$_2$L with complexes 1 and 2, it was found that the interaction of O···H/H···O in the ligand is significantly stronger than

Figure 9. The three-dimensional supramolecular structure of 2.

Figure 10. Hirshfeld surface analysis of H$_2$L, 1 and 2 mapped with $d_n$, $d_i$ and $d_e$. 
3.6. Fluorescence properties

The fluorescence spectral measurements were carried out at excitation wavelength 373 nm and the solvent used was absolute ethanol. The fluorescence emission spectra of H$_2$L, 1 and 2 (5 × 10$^{-5}$ M) are shown in Figure 12. The unsymmetric ligand H$_2$L has an intense emission peak at 475 nm, which is probably attributed to the π-π* intraligand transition [66]. The emission peaks of 1 and 2 decrease significantly. The reduction of the fluorescence intensity of 1 and 2 is assigned to the interaction of the Cu(II) and Co(II) ions. Impressively, compared with H$_2$L the emission peaks of 1 and 2 also have notable blue shifts compared to 475 nm and appear at 460 and 463 nm, which may be due to the LMCT effect [67].

As depicted in Figure 13, the fluorescence titration experiments of 1 and 2 were carried out in ethanol solution. The fluorescence intensity was monitored and a
gradual decrease was observed (Figure 13a) with the addition of Cu(II) ions \((1 \times 10^{-3} \text{ M})\) at 475 nm. The emission peak decreased to a minimum at 475 nm when \(1\) equivalent Cu(II) ions was added. Thereafter, with continuous addition of the Cu(II) ions, the emission intensity did not change. In all cases, a typical saturation binding curve can be observed when the fluorescence intensity value was plotted against the Cu(II) ions concentration, which demonstrates the optimal coordination ratio of the unsymmetric ligand \(H_2L\) to Cu(II) ions is 1:1. In Figure 13b, a similar phenomenon occurred and the fluorescence intensity decreased gradually with the addition of Co(II) ions \((1 \times 10^{-3} \text{ M})\) until the amount of Co(II) ions reached \(1.0\) equivalent. A typical saturation binding curve can be observed when the fluorescence intensity value was plotted against the Co(II) ions concentration. It shows that the optimal coordination ratio of the unsymmetric ligand \(H_2L\) to Co(II) ions is 1:1, which agrees with the single crystal structure.

**4. Conclusion**

Two new 3d metal(II) complexes, \([\text{Cu}(L)]\) (1) and \([\text{Co}_2(L)_2\cdot2\text{CH}_3\text{OH}]\) (2), were obtained by the reactions of a new polyhalogen-substituted unsymmetrical salamo-based ligand with different metal(II) acetates. The current study was performed using various spectral techniques (\(^1\text{H}\) NMR, IR, fluorescence and UV-vis spectra). Single crystal X-ray diffraction analysis showed that the ligand \(H_2L\) is a simple linear molecule. The Cu(II) ion locates in N2O2 coordination sphere and forms a square planar geometry for 1, while each Co(II) ion is bridged by phenoxide ions (O1 and O1#1), which leads to the formation of a five-coordinate distorted trigonal bipyramidal geometry for 2. The binding ratio between the ligand and metal(II) ions was verified by UV-Vis titration experiments and Job plots. The result of Hishfield surface analysis suggests that the difference of interactions is that the O···H/H···O interaction in the ligand is significantly stronger than those of complexes 1 and 2. Moreover, \(H_2L\) has good fluorescence based on a strong emission band at 475 nm, but 1 and 2 show intense fluorescence quenching behaviors, indicating that the Cu(II) and Co(II) ions have coordinated with the ligand.

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