

Inclusion complexes of sodium perchlorate into $[\text{CuL}^{\text{SS}}]$ and $[\text{CuL}^{\text{rac}}]$; $\text{H}_2\text{L}^{\text{SS}} = \text{bis}(3\text{-methoxy-2-hydroxy-1-benzylidene)-1S,2S-cyclohexanediamine}$, $\text{H}_2\text{L}^{\text{rac}} = \text{its racemic form}$

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Abstract Inclusion complexes of LiClO_4 or NaClO_4 into $[\text{CuL}^{\text{SS}}]$ or $[\text{CuL}^{\text{rac}}]$ are reported, where $[\text{CuL}^{\text{SS}}]$ denotes bis(3-methoxy-2-oxy-1-benzylidene)-1*S*,2*S*-cyclohexanediaminecopper(II) and $[\text{CuL}^{\text{rac}}]$ denotes the racemic complex. The inclusion reaction of LiClO_4 and NaClO_4 into $[\text{CuL}^{\text{SS}}]$ gave the [1 + 1] adduct of $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$ and the [2 + 1] adduct of $[(\text{CuL}^{\text{SS}})_2\text{Na}(\text{H}_2\text{O})_3]\text{ClO}_4$, respectively, while that of NaClO_4 into $[\text{CuL}^{\text{rac}}]$ gave the [2 + 2] adduct of $[\text{CuL}^{\text{rac}}\text{NaClO}_4]_2 \cdot \text{CH}_3\text{CN}$ ($[(\text{CuL}^{\text{SS}}\text{NaClO}_4)(\text{CuL}^{\text{RR}}\text{NaClO}_4)] \cdot \text{CH}_3\text{CN}$).

Keywords Alkali ion · Copper · Chiral coordination complex · Crystal structure · Assembly structure

Introduction

Coordination compounds exhibit well-defined stereochemistry and hence the compounds can be useful building blocks for the construction of supramolecular assembly structures [1, 2]. There are many synthetic strategies for the synthesis of the functional supramolecular materials. There are many examples that alkali ion is included into coordination compound to influence the assembly reaction since the studies by Sinn [3] and Lindoy [4]. We have reported that the alkali ion in a p-d-f molecular system of $\text{M}[(\text{Cu}^{\text{II}}\text{L})_4\text{Gd}^{\text{III}}]$ ($\text{M} = \text{Na}^+$, K^+ , Cs^+ ; $\text{H}_3\text{L} = N$ -(4-methyl-6-oxo-3-azahept-4-enyl) oxamic acid) can affect the assembly structures, in which the alkali cation plays a role of connector between adjacent $[(\text{Cu}^{\text{II}}\text{L})_4\text{Gd}^{\text{III}}]^-$ cores [5]. The sodium and potassium salts take a 1D chain structure bridged by Na^+ or K^+ ion, while the cesium salt takes a cyclic cluster structure bridged by Cs^+ ion. The result demonstrated that the definitely different assembly structures can be generated by the selection of the size of alkali ion.

Chirality often plays a crucial role for the assembly process. Many examples exist where molecular chirality influences on the supramolecular stereochemistry of containers, helical fibers, micelles, bilayers, and crystals [6–10]. The assembly reactions involving chiral coordination compounds have been reported and a number of functional materials have been generated [6–10]. In our previous papers [11, 12], we have examined the selective syntheses of cyclic cluster and one-dimensional chain d-f assembly structures by introduction of chiral moiety, in which a chiral d-component as “*ligand-complex*” and the f-component with vacant coordination sites were used for the assembly reaction. The results demonstrated that the chiral modification is effective to generate the definitely different assembly structures.

Dedicated to Professor Len Lindoy, one of the originators of the field of chemistry concerned in this article, on the occasion of his 75th birthday.

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These two examples described above demonstrate that the alkali ion and chirality can influence the assembly structures. In this study, we have examined a simple molecular system that involves a chiral moiety and suitable site for alkali ion at the same time. In this study, the assembly reaction of LiClO_4 or NaClO_4 and chiral $[\text{CuL}^{\text{SS}}]$ or racemic $[\text{CuL}^{\text{rac}}]$ were examined, in order to see whether or not the assembly reactions give the definitely different supramolecular structures, where $[\text{CuL}^{\text{SS}}]$ denotes bis(3-methoxy-2-oxy-1-benzylidene)-1*S*,2*S*-cyclohexanediaminecopper(II) and $[\text{CuL}^{\text{rac}}]$ denotes the racemic form. The assembly reactions of $[\text{CuL}^{\text{SS}}]$ with LiClO_4 and NaClO_4 gave the [1 + 1] adduct of $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$ and the [2 + 1] adduct of $[(\text{CuL}^{\text{SS}})_2\text{Na}(\text{H}_2\text{O})_3]\text{ClO}_4\cdot\text{CH}_3\text{CN}$, respectively, while that of $[\text{CuL}^{\text{rac}}]$ and NaClO_4 gave the [2 + 2] adduct of $[\text{CuL}^{\text{rac}}\text{NaClO}_4]_2$. We report here the syntheses and crystal structures of the inclusion complexes of LiClO_4 or NaClO_4 into $[\text{CuL}^{\text{SS}}]$ and $[\text{CuL}^{\text{rac}}]$.

Materials and methods

All chemicals and solvents used for the syntheses were reagent grade and were obtained from Tokyo Kasei Co., Ltd. and Wako Co., Ltd. and used without further purification. C, H and N elemental analyses were carried out at the Instrumental Analysis Centre of Kumamoto University.

Synthesis

Ligands $\text{H}_2\text{L}^{\text{SS}}$ and $\text{H}_2\text{L}^{\text{rac}}$

The two tetradentate Schiff-base ligands bis(3-methoxy-2-hydroxy-1-benzylidene)-1*S*,2*S*-cyclohexanediamine ($\text{H}_2\text{L}^{\text{SS}}$) and bis(3-methoxy-2-hydroxy-1-benzylidene)-*trans*-1,2-cyclohexanediamine ($\text{H}_2\text{L}^{\text{rac}}$) were prepared according to the general synthetic methods described in the literature [13]. Both were obtained as yellow crystalline materials by the [2 + 1] condensation reactions of 3-methoxysalicylaldehyde (*o*-vanillin) with either 1*S*,2*S*-cyclohexanediamine or *trans*-1,2-cyclohexanediamine in methanol, respectively. They were collected by suction filtration and used directly for the syntheses of the Cu^{II} complexes.

Cu^{II} complexes, $[\text{CuL}^{\text{SS}}]$ and $[\text{CuL}^{\text{rac}}]$

The Cu^{II} complexes $[\text{CuL}^{\text{SS}}]$ and $[\text{CuL}^{\text{rac}}]$ were prepared by mixing the ligands and copper(II) acetate monohydrate in methanol in 1:1 molar ratio, according to the general literature method [13].

A solution of copper(II) acetate monohydrate (798 mg, 4 mmol) in 20 mL of methanol was added to a solution of $\text{H}_2\text{L}^{\text{SS}}$ (456 mg, 4 mmol) in 50 mL of methanol. The

mixture was stirred for 30 min at 50 °C, and then cooled to room temperature. After several hours, fine crystalline materials precipitated. They were collected by suction filtration, washed with water and small amount of methanol, and then recrystallized from acetonitrile. Anal. Calcd for $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}=\text{C}_{24}\text{H}_{31}\text{N}_3\text{O}_6\text{Cu}$: C, 55.32; H, 6.00; N, 8.06. Found: C, 55.44; H, 5.85; N, 8.04.

The racemic form $[\text{CuL}^{\text{rac}}]$ was prepared by a similar method of $[\text{CuL}^{\text{SS}}]\cdot\text{CH}_3\text{CN}$.

Adducts of $[\text{CuL}^{\text{SS}}]$ and $[\text{CuL}^{\text{rac}}]$ with LiClO_4 or NaClO_4

$[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$ (1:1 adduct). To a suspension of $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}$ (0.111 g, 0.25 mmol) in a mixture of acetonitrile (20 mL) and dichloromethane (10 mL) was added a solution of lithium perchlorate (0.027 g, 0.25 mmol) in acetonitrile (1 mL). The mixture was warmed at 70 °C with stirring for 10 min and filtered. The filtrate was allowed to stand for a few hours, during which time dark red, needle-like crystals precipitated. These were collected by suction filtration, then recrystallized from acetonitrile. Anal. Calcd for $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]=\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_9\text{ClCuLi}$: C, 46.49; H, 4.61; N, 4.93. Found: C, 46.86; H, 4.69; N, 5.00.

$[(\text{CuL}^{\text{SS}})_2\text{Na}(\text{H}_2\text{O})_3]\text{ClO}_4\cdot 3\text{H}_2\text{O}$ ([2 + 1] adduct). This complex was prepared by mixing $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}$ and sodium perchlorate in 1:1 molar ratio in acetonitrile according to the similar procedure of the $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$. Anal. Calcd for $[(\text{CuL}^{\text{SS}})_2\text{Na}(\text{H}_2\text{O})_3]\text{ClO}_4\cdot 3\text{H}_2\text{O}=\text{C}_{44}\text{H}_{54}\text{N}_4\text{O}_{15}\text{ClCu}_2\text{Na}\cdot 3\text{H}_2\text{O}$: C, 47.25; H, 5.41; N, 5.00. Found: C, 46.78; H, 5.05; N, 5.28.

$[\text{CuNa}(\text{L}^{\text{rac}})(\text{ClO}_4)]_2\cdot\text{CH}_3\text{CN}$ ([2 + 2] adduct). This complex was prepared by mixing $[\text{CuL}^{\text{rac}}]$ and sodium perchlorate in 1:1 molar ratio in acetonitrile according to the similar procedure of the $[(\text{CuL}^{\text{SS}})_2\text{Na}(\text{H}_2\text{O})_3]\text{ClO}_4\cdot 3\text{H}_2\text{O}$. $[\text{CuL}^{\text{rac}}\text{NaClO}_4]_2\cdot\text{CH}_3\text{CN}=[\text{Cu}_2\text{Na}_2(\text{L}^{\text{SS}})(\text{L}^{\text{RR}})(\text{ClO}_4)_2]\cdot\text{CH}_3\text{CN}$. Anal. Calcd for $[\text{CuL}^{\text{rac}}\text{NaClO}_4]_2\cdot\text{CH}_3\text{CN}=\text{C}_{46}\text{H}_{51}\text{N}_5\text{O}_{16}\text{Cl}_2\text{Cu}_2\text{Na}_2$: C, 47.06; H, 4.38; N, 5.97. Found: C, 46.86; H, 4.32; N, 5.46.

X-ray crystallography

Single-crystal X-ray structure determinations were performed at ambient temperature for the precursor complex $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}$ as well as the three adducts $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$, $[(\text{CuL}^{\text{SS}})_2\text{Na}(\text{H}_2\text{O})_3]\text{ClO}_4$ and $[\text{Cu}_2\text{Na}_2(\text{L}^{\text{SS}})(\text{L}^{\text{RR}})(\text{ClO}_4)_2]\cdot\text{CH}_3\text{CN}$. The data were collected on a Rigaku RAXIS RAPID imaging plate diffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All calculations were performed using the Crystal Structure crystallographic software package [14]. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilation. Crystal data and structure refinement

details are given in Table 1, and selected bond lengths and angles are presented in Table 2.

Results and discussion

Synthesis of the alkali metal ion adducts

The tetradentate Schiff-base ligands H_2L^{SS} and H_2L^{rac} were easily obtained by the 2:1 condensation reactions of 3-methoxysalicylaldehyde (*o*-vanillin) with either *1S,2S*-cyclohexanediamine or *trans*-1,2-cyclohexanediamine as yellow crystalline materials according to the literature method [13]. The Cu^{II} complexes $[CuL^{SS}]$ and $[CuL^{rac}]$ were synthesized by the reaction of the ligands and copper(II) acetate monohydrate in methanol [13]. The inclusion complexes with $LiClO_4$ or $NaClO_4$ were obtained by the mixed solution of $[CuL^{SS}]$ or $[CuL^{rac}]$ and $LiClO_4$ or $NaClO_4$ with 1:1 molar ratio in methanol. The precipitates were collected and recrystallized from acetonitrile and chloroform. The inclusion complexes, the [1 + 1] adduct of $[CuL^{SS}(H_2O)LiClO_4]$, the [2 + 1] adduct of $[(CuL^{SS})_2Na(H_2O)_3]ClO_4$, and the [2 + 2] adduct of $[CuL^{rac}NaClO_4]_2 \cdot CH_3CN$ were obtained as block crystals suitable for single-crystal X-ray analyses. The inclusion reaction of perchlorate salts of K^+ , Rb^+ and Cs^+ into $[CuL^{SS}]$ gave the fine needle-like crystals exhibiting colors different from that of the precursor complex, but the suitable sized crystals for the X-ray diffraction analyses have not been obtained so far.

Structure of precursor Cu^{II} complex $[CuL^{SS}(H_2O)] \cdot CH_3CN$

The precursor Cu^{II} complex $[CuL^{SS}(H_2O)] \cdot CH_3CN$ crystallizes in the noncentrosymmetric monoclinic space group $P2_1$ (no. 4), the asymmetric unit consisting of a complex $[CuL^{SS}(H_2O)] \cdot CH_3CN$ and one acetonitrile molecule as crystal solvent. The Flack parameter [15] refined to essentially zero for the assumed *S,S* configuration of the ligand. The molecular structure of $[CuL^{SS}(H_2O)] \cdot CH_3CN$ and the one-dimensional structure are shown in Fig. 1a, b, respectively. The complex of $[CuL^{SS}(H_2O)] \cdot CH_3CN$ assumes a square pyramidal N_2O_3 coordination geometry, where the equatorial coordination plane consists of N_2O_2 donor atoms of the tetradentate ligand L^{SS} and the axial coordination site is occupied by a water oxygen atom with $Cu-O(5) = 2.427(7)$ Å. The water molecule at the axial site is hydrogen bonded to two methoxy oxygen atoms of the adjacent unit $[CuL^{SS}(H_2O)] \cdot CH_3CN$ with $O(5) \cdots O(3') = 2.939(9)$ Å and $O(5) \cdots O(4') = 2.932(10)$ Å. The intermolecular hydrogen bonds are repeated to form a one-dimensional structure running along the *a*-axis as shown in Fig. 1b.

Structure of the [1 + 1] adduct with $LiClO_4$, $[CuL^{SS}(H_2O)LiClO_4]$

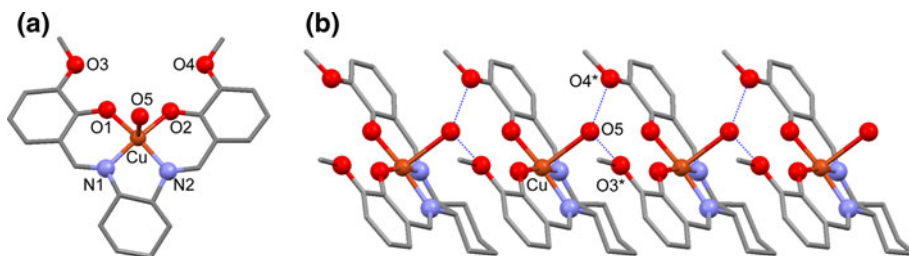
$[CuL^{SS}(H_2O)LiClO_4]$ was obtained as thin plate-like small crystals. Due to the small size of the crystal, the final structural refinement was of less than optimal quality. The complex crystallizes in the noncentrosymmetric

Table 1 Crystallographic data of $[CuL^{SS}(H_2O)] \cdot CH_3CN$, $[CuL^{SS}(H_2O)LiClO_4]$, $[(CuL^{SS})_2Na(H_2O)_3]ClO_4$ and $[CuL^{rac}NaClO_4]_2 \cdot CH_3CN$ at 296 K

Complex	$[CuL^{SS}(H_2O)] \cdot CH_3CN$	$[CuL^{SS}(H_2O)LiClO_4]$	$[(CuL^{SS})_2Na(H_2O)_3]ClO_4$	$[CuL^{rac}NaClO_4]_2 \cdot CH_3CN$
Formula	$C_{24}H_{29}CuN_3O_5$	$C_{22}H_{26}CuClLiN_2O_9$	$C_{44}H_{54}Cu_2ClNaN_4O_{15}$	$C_{46}H_{51}Cu_2Cl_2Na_2N_5O_{16}$
Fw	503.06	568.40	1064.46	1173.90
Crystal System	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1$ (no. 4)	$P1$ (no. 1)	$P2_1$ (no. 4)	$P2_1/n$ (no. 14)
<i>a</i> (Å)	5.5020(12)	5.9618(16)	12.6702(4)	10.9353(3)
<i>b</i> (Å)	20.239(5)	9.849(2)	13.9938(5)	21.3615(6)
<i>c</i> (Å)	10.499(3)	11.399(3)	12.7575(6)	21.5400(7)
α (°)	90.0000	65.545(5)	90.0000	90.0000
β (°)	100.257(6)	81.527(7)	90.165(2)	95.6800(8)
γ (°)	90.0000	76.394(6)	90.0000	90.0000
<i>V</i> (Å ³)	1150.5(5)	591.2(3)	2261.9(2)	5006.9(3)
<i>Z</i>	2	1	2	4
D_{calc} (Mg m ⁻³)	1.452	1.596	1.563	1.530
μ (MoK α) (mm ⁻¹)	9.896	1.0926	1.0838	1.0467
R^a	0.0826	0.0979	0.0383	0.0912
wR^b	0.1766	0.2198	0.0772	0.2558

Table 2 Relevant coordination bond lengths (Å) for $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}$, $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$, $[(\text{CuL}^{\text{SS}})_2\text{Na}(\text{H}_2\text{O})_3]\text{ClO}_4$ and $[\text{CuL}^{\text{rac}}\text{NaClO}_4]_2\cdot\text{CH}_3\text{CN}$

Complex	$[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}$	$[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$	$[(\text{CuL}^{\text{SS}})_2\text{Na}(\text{H}_2\text{O})_3]\text{ClO}_4$	$[\text{CuL}^{\text{rac}}\text{NaClO}_4]_2\cdot\text{CH}_3\text{CN}$
Cu(1)–O(1)	1.922(5)	1.89(2)	1.902(4)	1.895(5)
Cu(1)–O(2)	1.911(6)	1.849(17)	1.900(3)	1.884(6)
Cu(1)–O(5)	2.427(7)	2.702(14)		
Cu(1)–O(15)			2.518(4)	
Cu(1)–N(1)	1.948(7)	1.966(16)	1.927(4)	1.922(7)
Cu(1)–N(2)	1.939(7)	1.94(3)	1.933(4)	1.909(6)
Cu(2)–O(5)			1.894(3)	1.888(5)
Cu(2)–O(6)			1.903(3)	1.926(5)
Cu(2)–N(3)			1.931(4)	1.919(6)
Cu(2)–N(4)			1.935(4)	1.920(7)
Cation(1)–O(1)		2.17(7)	2.343(4)	2.337(7)
Cation(1)–O(2)		2.09(10)	2.334(4)	2.418(6)
Cation(1)–O(3)		2.80(8)	2.753(4)	2.570(6)
Cation(1)–O(4)		2.73(7)	2.733(4)	2.841(7)
Cation(1)–O(6)				2.521(7)
Cation(1)–O(13)			2.294(6)	
Cation(1)–O(14)			2.296(5)	
Cation(2)–O(4)				2.607(6)
Cation(2)–O(5)				2.290(6)
Cation(2)–O(6)				2.426(6)
Cation(2)–O(7)				2.563(7)
Cation(2)–O(8)				2.723(7)

Fig. 1 **a** Molecular structure of precursor complex $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}$ with the selected atom numbering scheme **b** One dimensional structure of $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}$. The crystal solvent CH_3CN is omitted for clarity

triclinic space group $P1$ (no. 1) and the crystallographic unique unit consists of a complex $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$. The Flack parameter is refined nearly to zero [15] and the configuration of the ligand is consistent with L^{SS} . The molecular structure of $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$ and the one-dimensional structure are shown in Fig. 2a, b, respectively. The coordination geometry of $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$ can be described as a square pyramidal N_2O_3 or square planar coordination geometry, where the equatorial coordination plane consists of N_2O_2 donor atoms of the tetradentate ligand L^{SS} and the axial site is occupied by a water oxygen atom with $\text{Cu}-\text{O}(5) = 2.702(14)$ Å. However, the distance of $\text{Cu}-\text{O}(5) = 2.702(14)$ Å is appreciably longer than the normal coordination bond to the axial water oxygen and it can be described that the water molecule $\text{O}(5)$ is kept in the cavity. The water molecule $\text{O}(5)$ is hydrogen-bonded

to two methoxy oxygen atoms $\text{O}(3)$ and $\text{O}(4)$ with the distance of $\text{O}(5)\cdots\text{O}(3) = 2.96(2)$ and $\text{O}(5)\cdots\text{O}(4) = 2.93(2)$ Å. The water molecule $\text{O}(5)$ is coordinated to Li^+ ion of the adjacent unit $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$ with $\text{Li}-\text{O}(5) = 1.83(9)$ Å. The intermolecular $\text{Li}-\text{O}$ coordination bond is repeated to form a one-dimensional structure as shown in Fig. 2b. As shown in Fig. 2a, Li^+ ion is linked by $[\text{CuL}^{\text{SS}}]$ through two $\text{Li}-\text{O}(1)$ and $\text{Li}-\text{O}(2)$ interaction consisting of two oxygen atoms (two phenoxy). The Li^+ ion is further linked by an oxygen atom $\text{O}(9)$ of ClO_4^- ion. Among the four $\text{Li}-\text{O}$ distances, $\text{Li}-\text{O}(5)$ of 1.83(9) is the shortest. The $\text{Li}-\text{O}$ distances are $\text{Li}-\text{O}(1) = 2.17(7)$ Å, $\text{Li}-\text{O}(2) = 2.09(10)$ Å, $\text{Li}-\text{O}(3) = 2.80(8)$ Å, and $\text{Li}-\text{O}(4) = 2.73(7)$ Å. The coordination environment of Li^+ ion is of a distorted tetrahedral form, with $\text{Li}-\text{O}(1) = 2.17(7)$, $\text{Li}-\text{O}(2) = 2.09(10)$, $\text{Li}-\text{O}(5) = 1.89(9)$ and $\text{Li}-\text{O}(9) = 1.83(9)$ Å.

Structure of the [2 + 1] adduct with NaClO₄,
 [(CuL^{SS})₂Na(H₂O)₃]ClO₄

The [2 + 1] adduct of [(CuL^{SS})₂Na(H₂O)₃]ClO₄ crystallizes in a monoclinic noncentrosymmetric space group *P*2₁ (no. 4) and the crystallographic unique unit consists of one Na⁺ cation, two complexes [CuL^{SS}], three water molecules, and one perchlorate anion, in which one Na⁺ cation, two complexes [CuL^{SS}], and three water molecules construct a [2 + 1] inclusion complex of [(CuL^{SS})₂Na(H₂O)₃]⁺ and one perchlorate anion exists as a discrete counter anion. The molecular structure of [(CuL^{SS})₂Na(H₂O)₃]⁺ is shown in Fig. 3a, b. The [2 + 1] complex [(CuL^{SS})₂Na(H₂O)₃]⁺ forms a dimer structure bridged by a water molecule O(15), where two [CuL^{SS}] complexes are stacked to array in the same direction with a stepped structure. The Cu(2) site has a square planar N₂O₂ coordination geometry and Cu(1) site has an elongated tetragonal pyramidal N₂O₃ geometry with the axial coordination of O(15) with Cu(1)–O(15) = 2.518(4) Å. The bridging water molecule O(15) is hydrogen bonded to two phenoxy and two methoxy oxygen atoms of Cu(2) site with O(15)⋯O(5) = 2.989(5) Å, O(15)⋯O(6) = 2.941(5) Å, O(15)⋯O(7) = 2.862(5) Å, and O(15)⋯O(8) = 2.837(5) Å. The Na⁺ ion is coordinated by two phenoxy and two methoxy oxygen atoms of Cu(1) site with Na–O(1) = 2.343(4) Å, Na–O(2) = 2.334(4) Å, Na–O(3) = 2.753(4) Å, and Na–O(4) = 2.733(4) Å, and further by two water molecules with Na–O(13) = 2.294(6) Å and Na–O(14) = 2.296(5) Å. The water molecule O(13) is further hydrogen bonded to the bridging O(15) with O(15)⋯O(13) = 2.794(7) Å to form a closed cyclic structure as shown in Fig. 3b.

Structure of the [2 + 2] adduct,
 [CuL^{rac}NaClO₄]₂·CH₃CN
 [(Cu₂Na₂(L^{SS})(L^{RR})(ClO₄)₂·CH₃CN)

The [2 + 2] adduct [CuL^{rac}NaClO₄]₂·CH₃CN crystallizes in the centrosymmetric monoclinic space group *P*2₁/*n* (no. 14) with *Z* = 4. The crystallographic unique unit consists of two Na⁺ cations, two complexes consisting of [CuL^{SS}] and

[CuL^{RR}], two ClO₄[−] anions, and one acetonitrile molecule as crystal solvent and the unique unit can be described as [Cu₂Na₂(L^{SS})(L^{RR})(ClO₄)₂·CH₃CN. The structure is shown in Fig. 4. Each complex of [CuL^{SS}] and [CuL^{RR}] includes one Na⁺ ion at the O₄ site provided by two phenoxy and two methoxy groups, in which Na–O distances are Na(1)–O(1) = 2.337(7), Na(1)–O(2) = 2.418(6), Na(1)–O(3) = 2.570(6), Na(1)–O(4) = 2.841(7) Å for Cu(1) site and Na(2)–O(5) = 2.290(6), Na(2)–O(6) = 2.426(6), Na(2)–O(7) = 2.563(7), Na(2)–O(8) = 2.723(7) Å for Cu(2) site, respectively. These Na–O distances indicate that the Na⁺ ion is shifted to one side of two 3-methoxysalicylaldehyde moieties. The Na⁺ ion is further coordinated by O₂ atoms of a perchlorate ion as a bidentate chelate ligand. Thus, each complex of [CuL^{SS}] and [CuL^{RR}] gives an inclusion species of [CuL^{SS}NaClO₄] and [CuL^{RR}NaClO₄]. These two species are linked through Na(1)–O(6) = 2.521(7) Å (O(6) is a phenoxy oxygen atom of Cu(1) site) and Na(2)–O(4) = 2.607(6) Å (O(4) is a methoxy oxygen atom of Cu(1) site) to give a dimer structure of [(CuL^{SS}NaClO₄)(CuL^{RR}NaClO₄)], where the equatorial coordination planes of [CuL^{SS}NaClO₄] and [CuL^{RR}NaClO₄] are stacked nearly parallel but the planes are rotated nearly to perpendicular to each other. The dimer structure of [(CuL^{SS}NaClO₄)(CuL^{RR}NaClO₄)] represented by the different colors are shown in Fig. 5.

In summary, we have examined the inclusion reaction of alkali ions into chiral [CuL^{SS}] and racemic [CuL^{rac}] host compounds. The host compounds of [CuL^{SS}] and [CuL^{rac}] have O₄ cavity per component provided by two phenoxy and two methoxy oxygen atoms, which can permit the accommodation of alkali ion. All the inclusion reactions were performed by a similar method, where the alkali ion and the host compound are mixed in 1:1 mol ratio. Reaction of NaClO₄ and [CuL^{SS}] gave the [2 + 1] adduct [(CuL^{SS})₂Na(H₂O)₃]ClO₄, while the reaction of NaClO₄ and the racemic complex [CuL^{rac}] gave the [2 + 2] adduct [CuL^{rac}NaClO₄]₂·CH₃CN. The result demonstrates that the chirality at the part of the ligand framework can produce different assembly structures. The preferable assembly structure may be obtained by the inclusion ratio of alkali ion and host compound, in which the chirality can affect significantly on the assembly structure.

Fig. 2 **a** Molecular structure of [CuL^{SS}(H₂O)LiClO₄] with the selected atom numbering scheme. **b** One dimensional structure of [CuL^{SS}(H₂O)LiClO₄]

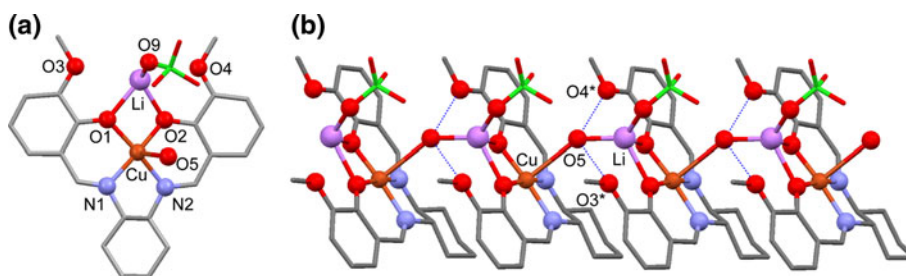


Fig. 3 **a** Molecular structure of the [2 + 1] complex $[(\text{CuL}^{\text{SS}})_2\text{Na}(\text{H}_2\text{O})_3]^+$ projected on the equatorial N_2O_2 coordination plane with the selected atom numbering scheme. **b** Side view of the [2 + 1] complex showing the bridging manner of two $[\text{CuL}^{\text{SS}}]$ species

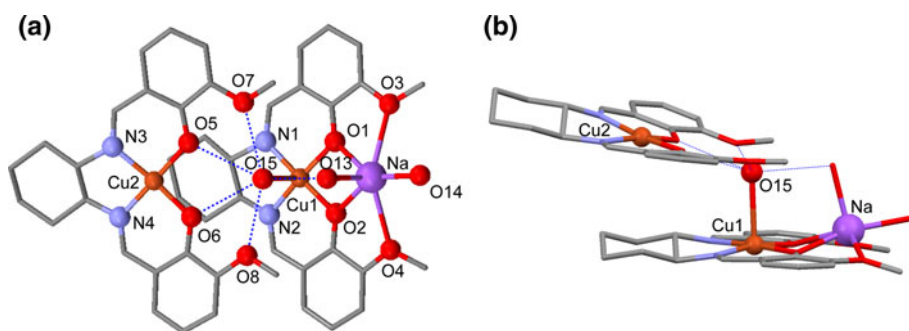


Fig. 4 **a** Molecular structure of the [2 + 2] adduct $[\text{CuL}^{\text{rac}}\text{NaClO}_4]_2$ ($[(\text{Cu}_2\text{Na}_2(\text{L}^{\text{SS}})(\text{L}^{\text{RR}})(\text{ClO}_4)_2])$ projected on the equatorial N_2O_2 coordination plane with the selected atom numbering scheme. **b** Side view of $[\text{Cu}_2\text{Na}_2(\text{L}^{\text{SS}})(\text{L}^{\text{RR}})(\text{ClO}_4)_2]$ showing the bridging manner of two $[\text{CuL}^{\text{SS}}\text{NaClO}_4]$ and $[\text{CuL}^{\text{RR}}\text{NaClO}_4]$

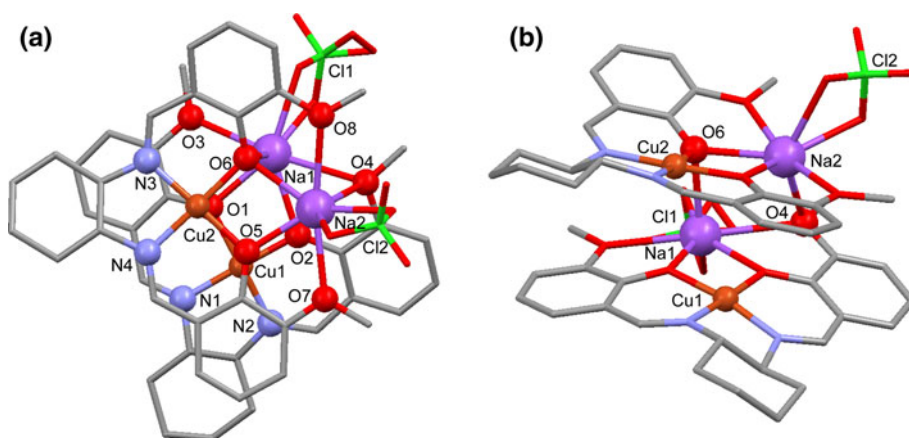
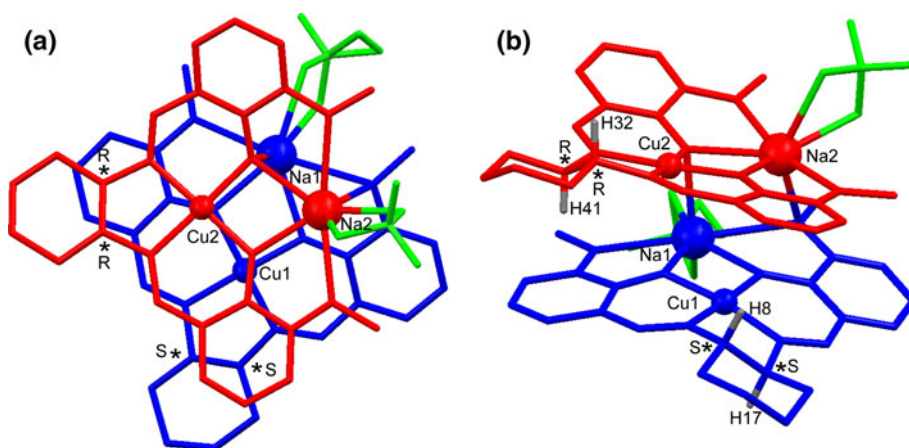


Fig. 5 **a** Structure of the [2 + 2] adduct $[\text{CuL}^{\text{rac}}\text{NaClO}_4]_2$ consisting of $[\text{CuL}^{\text{RR}}\text{NaClO}_4]$ (red) and $[\text{CuL}^{\text{SS}}\text{NaClO}_4]$ (blue). **b** Side view of the [2 + 2] adduct showing the bridging manner of $[\text{CuL}^{\text{RR}}\text{NaClO}_4]$ (red) and $[\text{CuL}^{\text{SS}}\text{NaClO}_4]$ (blue)



Supplementary data

CCDC 818117 - 818120 contain the supplementary crystallographic data for $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CN}$, $[\text{CuL}^{\text{SS}}(\text{H}_2\text{O})\text{LiClO}_4]$, $[(\text{CuL}^{\text{SS}})_2\text{Na}(\text{H}_2\text{O})_3]\text{ClO}_4$, and $[\text{CuL}^{\text{rac}}\text{NaClO}_4]_2\cdot\text{CH}_3\text{CN}$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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