

Article

Two Supramolecular Cobalt(II) Complexes: Syntheses, Crystal Structures, Spectroscopic Behaviors, and Counter Anion Effects

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Academic Editor: Shujun Zhang

Received: 5 July 2017; Accepted: 30 July 2017; Published: 9 August 2017

Abstract: Two new Co(II) complexes, $[\{\text{Co}(\text{L})\}_2\{\text{Co}(\text{Pic})_2(\text{CH}_3\text{OH})_2\}]$ (**1**) and $[\{\text{CoL}(\mu\text{-OAc})\}_2\text{Co}]$ (**2**), where $\text{H}_2\text{L} = 2,2'$ -[Ethylenedioxybis(nitrilomethylidyne)]dinaphthol, were designed, synthesized and characterized by elemental analysis, FT-IR spectra, UV-Vis spectra, and X-ray crystallography. Complex **1** consists of two $[\text{CoL}]$ and one $[\text{Co}(\text{Pic})_2(\text{CH}_3\text{OH})_2]$ (Pic = picrate) units and in the $[\text{CoL}]$ unit, the Co(II) atom is tetra-coordinated with a slightly distorted square-planar geometry. In the $[\text{Co}(\text{Pic})_2(\text{CH}_3\text{OH})_2]$ unit, the Co(II) atom is hexa-coordinated with a slightly distorted octahedral geometry. Meanwhile in complex **2**, two acetate ions coordinate to three Co(II) atoms through Co-O-C-O-Co bridges and four μ -naphthoxo oxygen atoms from two $[\text{CoL}]$ units also coordinated to the central Co(II) atom. Thus, complex **2** has two distorted square pyramidal coordination geometries around the terminal Co(II) atom and an octahedral geometry around the central Co(II) atom. The supramolecular structures of complex **1** is a 3D-network supramolecular structure linked by C-H \cdots O hydrogen bonds and $\pi\cdots\pi$ stacking interaction, but complex **2** possesses a self-assembled 2D-layer supramolecular structure linked by C-H $\cdots\pi$ and $\pi\cdots\pi$ stacking interactions. The structure determinations show that the coordination anions are important factors influencing the crystalline array.

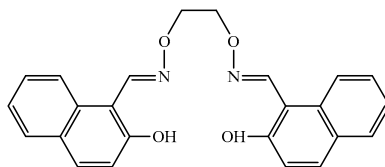
Keywords: Co(II) complex; Salamo-type ligand; synthesis; crystal structure; supramolecular interaction; anion effects

1. Introduction

Salen-type compounds or their derivatives have received much attention not only because of their versatile architectures and topologies tuned by metal ions and organic ligands [1–5], but also due to their properties for potential applications in various areas, such as catalysis [6], bioscience [7–10], host-guest chemistry [11–14], electrochemistry [15,16], magnetism [17–21], optical properties [22–28], and molecular recognition [22,23,29,30]. More and more research programs have focused on the syntheses of Salamo-type complexes by the structural motifs of substituent groups in recent years [31–33], because the Salamo compounds are more stable than the Salen compounds [34]. The Salamo-type N_2O_2 ligands can easily coordinate with several different types of transition metal ions in a tetradentate fashion to obtain stable mononuclear, multinuclear and hetero-polynuclear complexes which have novel structures and excellent capabilities [35–37], such as, recognition of metal cations, used as stereochemical catalysts, and to serve as optoelectronic materials.

There are many important factors, such as the metal ions, ligands, counter anions or coordination anions, temperatures, pH values, and solvents [38–45], which always have a major influence on the

construction of the coordination compounds. Among the groups that can be coordinated with metal ions, apart from ligands, the coordination anion is one of the direct and obvious factors. In order to further study the influencing factors on complex structures in the process of constructing metal complexes with the Salamo ligands, we designed and synthesized a Salamo ligands H_2L (Scheme 1) and its two novel Co(II) complexes. The structures and spectral properties were studied. The results presented herein indicate that the coordination anions have a significant influence on the structures of the resulting complexes.



Scheme 1. Chemical structure of the ligand H_2L .

2. Experimental

2.1. Reagents and Physical Measurements

Commercially available 2-hydroxynaphthaldehyde was purchased from Aladdin Chemistry (Aladdin, Shanghai, China), and other solvents from Tianjin Chemical Reagent Factory (Tianjin, China) were analytical grade, which were used without further purification. C, H, and N analyses were performed with a GmbH VariuoEL V3.00 automatic elemental analyzer. 1H NMR spectra were measured at room temperature in $CDCl_3$ solution on a Bruker 400 instrument recording at 400 MHz frequency. FT-IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr ($400\text{--}4000\text{ cm}^{-1}$) and CsI ($100\text{--}500\text{ cm}^{-1}$) pellets. UV-Vis absorption spectra were determined on a Shimadzu UV-2550 spectrometer (Shimadzu, Tokyo, Japan). X-ray single crystal structures were obtained on a Rapid Auto Version 3.0 Rigaku RAXIS-RAPID detector. The melting points were determined by a micromelting point apparatus produced by BEIJING TAIKE INSTRUMENT CO., LTD. (Beijing, China).

2.2. Synthesis of H_2L

The compound 1,2-bis(aminooxy)ethane was synthesized by a similar method to that reported previously [46,47] and 2,2'-(ethylenedioxybis(nitrilo-methylidyne)]dinaphthol (H_2L) was synthesized according to an analogous method reported previously in the literature [48,49]. A methanolic solution (20 mL) of 1,2-bis(aminooxy)ethane (92.1 mg, 1.0 mmol) was added to a solution of 2-hydroxynaphthaldehyde (349.5 mg, 2.02 mmol) in ethanol (20 mL) and the mixture was stirred at $55\text{ }^\circ\text{C}$ for 4 h. Then the solvent was removed under reduced pressure and the residue was recrystallized from ethanol to give the ligand H_2L (897.5 mg, 56.5%). M.p. $157\text{--}158\text{ }^\circ\text{C}$. Anal. Calcd for $C_{24}H_{20}N_2O_4$ (%): C, 71.99; H, 5.03; N, 7.00. Found: C, 71.81; H, 5.02; N, 6.85. 1H NMR (400 MHz, $CDCl_3$, ppm) δ = 4.59 (s, 4H, $CH_2\text{-O}$, $CH_2\text{-O}$), 7.19 (d, J = 8.8 Hz, 2H, Ar-H), 7.25 (s, 2H, Ar-H), 7.35 (t, J = 3.6 Hz, 2H, Ar-H), 7.50 (t, J = 4.2 Hz, 2H, Ar-H), 7.78 (d, J = 8.8 Hz, 2H, Ar-H), 7.94 (d, J = 8.4 Hz 2H, Ar-H), 9.22 (s, 2H, $N\text{=CH}$), 10.93 (s, 2H, ArO-H).

2.3. Synthesis of Complex 1

A pale-pink methanol solution (2 mL) of cobalt(II) picrate hexahydrate (6.14 mg, 0.01 mmol) was added dropwise to a colorless methanol solution (2 mL) of H_2L (4.00 mg, 0.010 mmol) at room temperature. The mixing solution turned yellow immediately and the filtrate was allowed to stand at room temperature for about three weeks. Brown prismatic single crystals suitable for X-ray structural determination were obtained by slow evaporation from ethanol solution. (Yield: 39% based on $Co(Pic)_2\cdot 6H_2O$). Anal. calcd. for $C_{62}H_{48}Co_3N_{10}O_{24}$ (%): C, 49.85; H, 3.24; N, 9.38. Found: C, 49.97; H, 3.52; N, 9.21.

2.4. Synthesis of Complex 2

Complex **2** was prepared by a similar procedure as complex **1** except for replacing cobalt(II) picrate hexahydrate with cobalt(II) acetate tetrahydrate. (Yield: 32% based on $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$). Anal. calcd. for $\text{C}_{52}\text{H}_{42}\text{Co}_3\text{N}_4\text{O}_{12}$ (%): C, 57.21; H, 3.88; N, 5.13. Found: C, 57.34; H, 3.93; N, 5.17.

2.5. Crystal Structure Determinations of Complexes 1 and 2

The single crystals of complexes **1** and **2** with dimensions of $0.27 \times 0.25 \times 0.22$ mm and $0.17 \times 0.09 \times 0.07$ mm were placed on a Bruker Smart 1000 diffractometer equipped with an Apex CCD area detector. The diffraction data were collected using a graphite monochromatic Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) and Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), respectively. Empirical absorption correction was applied to the data using the SADABS program. The structure was solved by direct methods and refined by the full-matrix least squares method on F^2 using the SHELXL program. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. Details of the crystal parameters, data collection and refinements for complexes **1** and **2** are summarized in Table 1. The complete crystallographic data was deposited as a CIF file in the Cambridge Structural Database (CCDC Nos. 1522381 and 1522382 for complexes **1** and **2**) and are available freely upon request citing the deposition number from the web site: www.ccdc.cam.ac.uk/data_request/cif.

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

Complex	1	2
CCDC	1522381	1522382
Molecular formula	$\text{C}_{62}\text{H}_{48}\text{Co}_3\text{N}_{10}\text{O}_{24}$	$\text{C}_{52}\text{H}_{42}\text{Co}_3\text{N}_4\text{O}_{12}$
Molecular weight	1493.89	1091.69
T/K	296(2)	293(2)
Wavelength (Å)	1.54178	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/n$	$P-1$
$a/\text{Å}$	15.0756(5)	8.9123(7)
$b/\text{Å}$	10.7672(3)	11.9798(9)
$c/\text{Å}$	18.6410(7)	12.2170(7)
$\alpha/^\circ$	90	111.581(6)
$\beta/^\circ$	96.886(2)	97.655(6)
$\gamma/^\circ$	90	92.885(6)
$V/\text{Å}^3$	3004.02(17)	1195.13(14)
Z	2	1
$D_c/(\text{gcm}^{-3})$	1.652	1.517
$\mu/(\text{mm}^{-1})$	7.246	1.098
$F(000)$	1526	559
Crystal size (mm)	$0.27 \times 0.25 \times 0.22$	$0.17 \times 0.09 \times 0.07$
θ range for data collection ($^\circ$)	3.57 to 64.96	3.6740 to 28.4740
$h/k/l$ (max, min)	−17, 17/−11, 12/−21, 21	−11, 11/−16, 13/−14, 15
Reflections collected	18107	9426
Independent reflections	5095/0.0569	4687/0.0305
Completeness to θ (%)	99.7	99.7
Data/restraints/parameters	5095/0/389	4687/0/323
GOF on F^2	1.032	0.908
Final R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0593, wR_2 = 0.1043$	$R_1 = 0.0446, wR_2 = 0.1326$
R_1, wR_2 indices (all data)	$R_1 = 0.0904, wR_2 = 0.1331$	$R_1 = 0.0579, wR_2 = 0.1435$
Largest differences peak and hole/ eÅ^{-3}	−0.793, 0.740	−0.334 and 0.410

3. Results and Discussion

The complexes **1** and **2** were prepared by reaction of ligand H_2L with cobalt(II) picrate hexahydrate and cobalt(II) acetate tetrahydrate in ethanol, respectively. All compounds are stable in air. They are soluble in polar aprotic solvents such as DMF, DMSO, and MeCN, slightly soluble in water, ethanol, ethylacetate, and chloroform, and insoluble in Et_2O and petroleum ether. The elemental analyses show their different compositions.

3.1. IR Spectra

The IR spectra of H_2L and its corresponding complexes **1** and **2** exhibit various bands in the 400–4000 cm^{-1} region (Figure 1). The most important IR bands are listed in Table 2. In general, the O–H stretching frequency of most compounds is usually expected in the 3300–3800 cm^{-1} region, but this frequency of the free ligand H_2L is displaced to 3437 cm^{-1} because of the intramolecular hydrogen bond O–H \cdots N=C interaction. The free ligand exhibits characteristic C=N stretching bands at 1631 cm^{-1} , while those of complexes **1** and **2** were observed at 1603 and 1611 cm^{-1} , respectively. The C=N stretching frequencies are all shifted to lower frequencies by 28 cm^{-1} and 20 cm^{-1} upon complexation, indicating a decrease in the C=N bond order due to the coordinated bond of the Co(II) atom with the imino nitrogen lone pair [50]. The Ar–O stretching frequency appears as a strong band at 1284 cm^{-1} for H_2L and at 1234 cm^{-1} for complex **2**. Meanwhile, a bending vibration of phenolic alcohol in H_2L at 1182 cm^{-1} , which disappears in the complexes, indicated the phenol hydroxy groups of H_2L were protonated and the oxygen atom coordinated to the Co(II) ions [13,15]. The Ar–O stretching frequency was shifted to a lower frequency, indicating that a Co–O bond had been formed between the Co(II) ion and phenolic oxygen atom of the ligand.

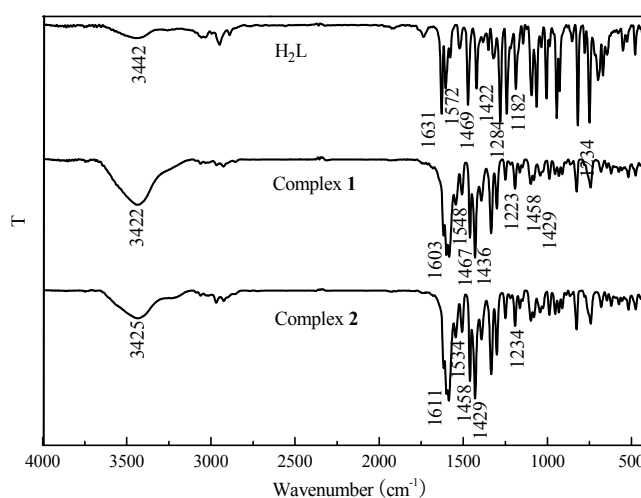


Figure 1. IR spectra of H_2L and the Co(II) complexes **1** and **2**.

Table 2. The most important IR bands of the ligand H_2L and complexes **1** and **2** (cm^{-1}).

Compound	$\nu(O-H)$	$\nu(C=N)$	$\nu(Ar-O)$	$\nu(Co-N)$	$\nu(Co-O)$	$\nu(C=C)$	Benzene Ring Skeleton	
H_2L	3442	1631	1284	—	—	1572	1472	1422
Complex 1	3422	1603	1223	452	431	1548	1467	1436
Complex 2	3425	1611	1234	446	422	1534	1458	1429

The far-infrared spectra of complexes **1** and **2** were also obtained in the region 500–100 cm^{-1} in order to identify frequencies due to the Co–O and Co–N bonds. The FT-IR spectra of the complexes **1** and **2** showed $\nu(Co-N)$ and $\nu(Co-O)$ vibration absorption frequencies possibly at 452, 446 cm^{-1} and

431, 422 cm^{-1} , respectively. But as pointed out by Percy and Thornton [51], the metal–oxygen and metal–nitrogen frequency assignments are at times very difficult.

3.2. UV-Vis Spectra

The UV-Vis absorption spectra of H_2L and its corresponding complexes **1** and **2** in $5.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ DMF solution are shown in Figure 2. The electronic absorption spectrum of the free ligand H_2L consists of two relatively intense bands at 230 nm, 316 nm and one weak band at 357 nm, the first absorptions observed at 230 nm and 316 nm can be signed to the $\pi\text{--}\pi^*$ transition of the benzene rings, while the absorption peak at 357 nm was attributed to the intra-ligand $\pi\text{--}\pi^*$ transition of the oxime group [52]. The complexes **1** and **2** show almost identical UV-Vis absorption spectra. The absorption bands around 313 nm are only marginally red-shifted (4–6 nm) in the spectra of the complexes. Upon coordination of the ligands, the absorption bands at about 357 nm disappeared and the new bands at 256 nm appeared in the UV-Vis spectra of the complexes **1** and **2**, which indicates that the oxime nitrogen atoms are involved in coordination to Co(II) atoms [53]. In addition, the other new absorption peak is observed at ca. 391 nm in Co(II) complexes, which is attributed to the M \rightarrow L charge-transfer transition. This is characteristic of the transition metal complexes with Salen-type ligands [54,55].

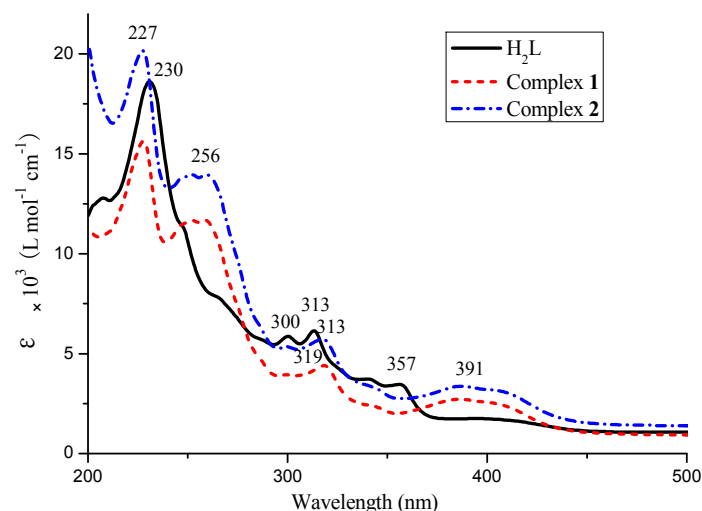


Figure 2. UV-Vis absorption spectra of H_2L and the Co(II) complexes **1** and **2** in dilute DMF solution at room temperature ($c = 5 \times 10^{-5} \text{ mol/L}$).

3.3. Crystal Structure of Complexes 1 and 2

The crystal structures of complexes **1** and **2** with an atom numbering scheme is exhibited in Figures 3 and 4. The selected bond lengths and angles of complexes **1** and **2** are in Table 3. The complex **1** crystallizes in the monoclinic system and $P2(1)/n$ space group and $Z = 1$. The complex **1** consist of two $[\text{CoL}]$ and one $[\text{Co}(\text{Pic})_2(\text{CH}_3\text{OH})_2]$ molecules, and in $[\text{CoL}]$ molecule, the Co1 atom is tetra-coordinated by two phenoxy O and two oxime N atoms from one ligand anion L^{2-} . The O1, O2, N1, N2 atoms from the same ligand anion consist of the square plane with the dihedral angle of N1–N2–O1 and O1–O2–N1 of 2.30° , and the Co(II) atom deviates from the plane 0.069 Å. The Co–O/N bond distances in the square plane are in the range of 1.917(2) to 2.013(2) Å. Therefore, the local coordination geometry around the Co1 center can be described as a distorted square-planar as shown in Figure 3b.

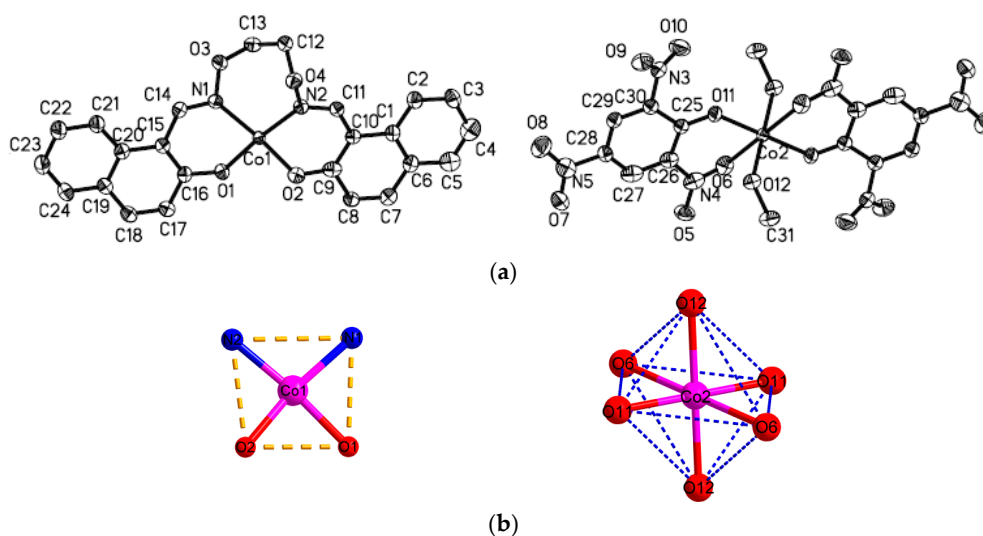


Figure 3. (a) View of the coordination environment of Co(II) center with thermal ellipsoids at 30% probability in **1** with a labelling scheme (all H atoms have been omitted for clarity); (b) The coordination polyhedron of Co(II) in **1**.

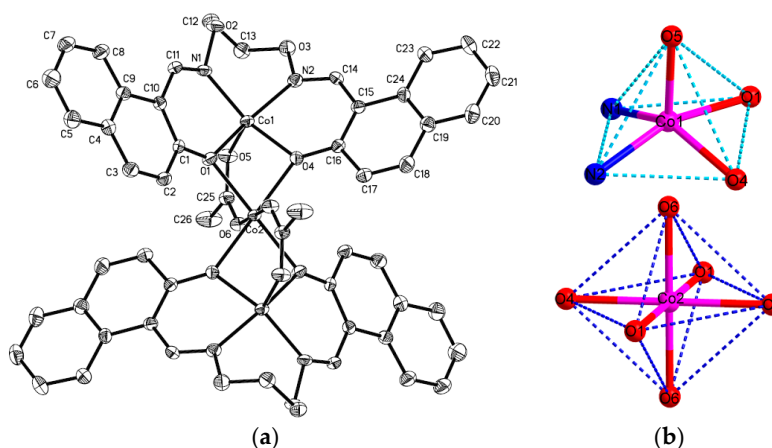


Figure 4. (a) View of the coordination environment of Co(II) center with thermal ellipsoids at 30% probability in **2** with a labelling scheme (all H atoms have been omitted for clarity); (b) The coordination polyhedron of Co(II) in **2**.

The $[\text{Co}(\text{Pic})_2(\text{CH}_3\text{OH})_2]$ molecule is rigorously centrosymmetric, and contains one Co(II) center, two Pic^- and two coordinated methanol molecules. The Co(II) atom is hexa-coordinated by two phenoxy O and two nitro O atoms from two Pic^- , and the other two O atoms from two coordinated methanol molecules to form an octahedral geometry as shown in Figure 3b. The O6, O11, O6ⁱ, and O11ⁱ atoms constitute the equatorial plane with the dihedral angle of O6-O6ⁱ-O11 and O11-O11ⁱ-O6 of 0.00°, and the Co(II) atom strays from the plane 0.00 Å. The Co-O/N bond distances in the equatorial plane are in the range of 1.904(2) to 2.335(2) Å. The axial positions are occupied by O12 and O12ⁱ from methanol molecules with bond lengths of 1.993 Å. The *trans*-coordination angles of O12-Co2-O12ⁱ, O6ⁱ-Co2-O6, O11ⁱ-Co2-O11 are all 180.0°, whereas the *cis*-coordination angles of O12-Co2-O6, O11-Co2-O6, O12-Co2-O11 are 82.92(6)°, 81.33(7)°, 89.82(7)°, respectively. Therefore, the local coordination geometry around the Co2 center can be described as a slightly distorted octahedron.

According to the above, this complex is very interesting from the structural point of view. First, complex **1** with the picrate anion contains in the crystal structure the tetracoordinate molecule $[\text{Co}(\text{L})]$ with a distorted square planar coordination geometry. This geometry is rather rare for the

Co(II) complexes, especially when the abundance of this topology is compared with the tetrahedral and distorted tetrahedral geometries. Second, in the CSD only five other examples of Co(II) complexes with coordinated picrate anions can be found. Two of them, the nitro oxygen atoms of the picrate anion were not involved in coordination with Co(II) ions and in the other three Co(II) complexes [56–58], the coordination mode of picric anions is consistent with the coordination pattern reported in this paper. The Co–O(NO₂) bond lengths in complex **1** is 2.335 Å, which is within the range of previously published Co(II) complexes involving coordinated picrate anion with that of 2.459 Å, 2.190 Å, 2.110 Å, and 2.149 Å [57–59], respectively.

Table 3. Selected bond distances (Å) and angles (°) for complexes **1** and **2**.

1					
Co1–O1	1.917(2)	Co1–O2	1.936(2)	Co1–N1	2.013(2)
Co1–N2	1.933(2)	Co2–O11	1.904(2)	Co2–O12	1.993(2)
Co2–O6	2.335(2)	Co2–O11 ⁱ	1.904(2)	Co2–O12 ⁱ	1.993(2)
Co2–O6 ⁱ	2.335(2)				
O1–Co1–N2	172.74(7)	O1–Co1–O2	85.48(7)	N2–Co1–O2	87.76(7)
O1–Co1–N1	86.78(7)	N2–Co1–N1	99.72(8)	O2–Co1–N1	170.84(8)
O11 ⁱ –Co2–O11	180.0	O11 ⁱ –Co2–O12 ⁱ	89.82(7)	O11–Co2–O12 ⁱ	90.18(7)
O11 ⁱ –Co2–O12	90.18(7)	O11–Co2–O12	89.82(7)	O12 ⁱ –Co2–O12	180.0
O11 ⁱ –Co2–O6 ⁱ	81.33(7)	O11–Co2–O6 ⁱ	98.67(7)	O12 ⁱ –Co2–O6 ⁱ	82.92(6)
O12–Co2–O6 ⁱ	97.08(6)	O11 ⁱ –Co2–O6	98.67(7)	O11–Co2–O6	81.33(7)
O12 ⁱ –Co2–O6	97.08(6)	O12–Co2–O6	82.92(6)	O6 ⁱ –Co2–O6	180.0
2					
Co2–O6	2.037(2)	Co2–O4	2.170(2)	Co2–O1	2.143(2)
Co2–O6 ⁱ	2.037(2)	Co2–O4 ⁱ	2.170(2)	Co2–O1 ⁱ	2.143(2)
Co1–O4	1.977(2)	Co1–O5	1.980(2)	Co1–O1	2.060(2)
Co1–N1	2.020(3)	Co1–N2	2.045(3)		
O4–Co1–O5	103.11(1)	O4–Co1–O1	82.05(8)	O4–Co1–N1	144.54(1)
O4–Co1–N2	87.49(9)	O5–Co1–O1	94.72(10)	O5–Co1–N1	111.18(1)
O5–Co1–N2	101.21(1)	N1–Co1–O1	86.34(9)	N1–Co1–N2	94.33(1)
N2–Co1–O1	162.59(1)	O6–Co2–O4	90.42(9)	O6–Co2–O1	89.82(9)
O6–Co2–O6 ⁱ	180.0	O6–Co2–O4 ⁱ	89.58(9)	O6–Co2–O1 ⁱ	90.18(9)
O6 ⁱ –Co2–O1	90.18(9)	O6 ⁱ –Co2–O4	89.58(9)	O6 ⁱ –Co2–O4 ⁱ	90.42(9)
O6 ⁱ –Co2–O1 ⁱ	89.82(9)	O4 ⁱ –Co2–O4	180.0	O1–Co2–O4 ⁱ	104.19(8)
O1 ⁱ –Co2–O4 ⁱ	75.81(8)	O1–Co2–O4	75.82(8)	O1 ⁱ –Co2–O4	104.19(8)
O1–Co2–O1 ⁱ	180.0				

Symmetry code: ⁱ 1 – x, 1 – y, –z.

The complex **2** crystallizes in the triclinic system and *P*-1 space group, *Z* = 2. The symmetric [$\text{CoL}(\mu\text{-OAc})_2\text{Co}$] unit consists of three Co(II) atoms, two ligand anion L^{2-} units, and two coordinated acetate ions. The terminal Co(II) atom (Co1 and Co1ⁱ) is penta-coordinated by two nitrogen atoms (N1 and N2), two oxygen atoms (O1 and O4) in the N_2O_2 moiety of the L^{2-} unit, and one oxygen atom (O5) from the bridging acetate anion. Crystallographic data $\tau = 0.13$ suggests a slightly distorted tetragonal pyramid coordination arrangement for the complex **2** [59]. However, the coordination geometry of the hexa-coordinated central Co2 atom deviates slightly from an ideal octahedron. The Co2 atom has an O_2O_2 donor set from four μ -phenoxo oxygen atoms (O1, O4, O1ⁱ, O4ⁱ) from two [CoL] chelates. Meanwhile, each of the two acetate anions bridges the terminal Co1 and central Co2 atoms in a *syn-syn* fashion. Hence the central Co2 atom finally has an $\text{O}_2\text{O}_2\text{O}_2$ donor set, in which the coordination sphere is completed by μ -phenoxo oxygen atoms (O1, O4, O1ⁱ, O4ⁱ) from two [CoL] chelates, and both of oxygen atoms O6 and O6ⁱ from the ligating acetate ions which adopt a familiar $\mu\text{-O-C-O}$ fashion, and constitute a slightly distorted octahedral geometry. The Co2–O bond distances are in the range of 2.037(2) to 2.170(2) Å, the coordinated angles of O1–Co2–O1ⁱ, O4–Co2–O4ⁱ, and O6–Co2–O6ⁱ are all 180°. Therefore, the local coordination geometry around the central Co2 atom can be described as deviating

slightly from the ideal octahedron as shown in Figure 4b. The trinuclear structure is stabilized by the two μ -acetato ligands bridging Co2-Co1 and Co2-Co1¹ with shorter separations of Co \cdots Co (3.065 Å), which neutralize the whole charge of complex 2.

3.4. Supramolecular Interaction of Complexes 1 and 2

It should be noted that important intermolecular hydrogen bonding interactions exist between the molecules in complex 1 as listed in Table 4. Firstly, intermolecular hydrogen bonds between the coordinated methanol molecules of [Co(Pic)₂(CH₃OH)₂] unit and oxygen atoms of the μ -naphthoxo group in the ligand anion L²⁻ of [CoL] unit, O12-H12C \cdots O1, are formed between the [CoL] and [Co(Pic)₂(CH₃OH)₂] units which link the neighboring one [Co(Pic)₂(CH₃OH)₂] unit and two [CoL] units into a tri-polymer as shown in Figure 5. In addition, every tri-polymer further links eight other adjacent tri-polymer units into an infinite 3D-network supramolecular structure by four pairs of intermolecular C11-H11 \cdots O7 and C21-H21 \cdots O10 hydrogen bonds (Figure 6) between the two -CH groups of the ligand anion L²⁻ in [CoL] units and the oxygen atoms of the picric acid anion Pic⁻ in [Co(Pic)₂(CH₃OH)₂] units, respectively. Furthermore, this linkage is further stabilized by the $\pi\cdots\pi$ stacking between the benzene ring (Table 5 and Figure 7) of the adjacent [CoL] and [Co(Pic)₂(CH₃OH)₂] units. Consequently, with the help of O-H \cdots O and C-H \cdots O hydrogen bonds, $\pi\cdots\pi$ stacking interactions, the crystal structure of 1 shows an assembly 3D supramolecular network structure (Figure 8) introduced by a coordinated picrate.

Table 4. The main hydrogen bonds [Å, °] for complex 1.

D-H \cdots A	d(D-H)	d(H \cdots A)	d(D \cdots A)	\angle D-H \cdots A	Symmetry Code
O12-H12C \cdots O1	0.85	1.78	2.554(2)	150	x, y, -1 + z
C11-H11 \cdots O7	0.93	2.48	3.383(4)	165	1/2 + x, 1/2 - y, 1/2 + z
C21-H21 \cdots O10	0.93	2.57	3.463(2)	161	3/2 - x, -1/2 + y, 3/2 - z

Table 5. Putative π - π stacking interactions [Å] for complex 1.

Ring (I)	Ring (J)	d(Cg-Cg)	d(Cg(I)-perp)	d(Cg(J)-perp)	Slippage
Cg5	Cg1	3.6242(13)	3.4264(9)	3.5081(9)	0.910
Cg1	Cg6	3.6684(13)	-3.5593(9)	3.6439(9)	0.4232
Cg6	Cg4	3.6866(14)	-3.3947(9)	3.5010(11)	1.155
Cg4	Cg7	3.7938(16)	-3.4919(11)	-3.6100(12)	1.167
Cg5	Cg6	3.6941(13)	-3.2919(9)	-3.3612(9)	1.533

Cg1, Cg4, Cg5, Cg6, and Cg7 are the centroids of benzene ring C25-C30, C1-C6, C1-C6-C10, C15-C20, and C19-C24 of complex 1, respectively.

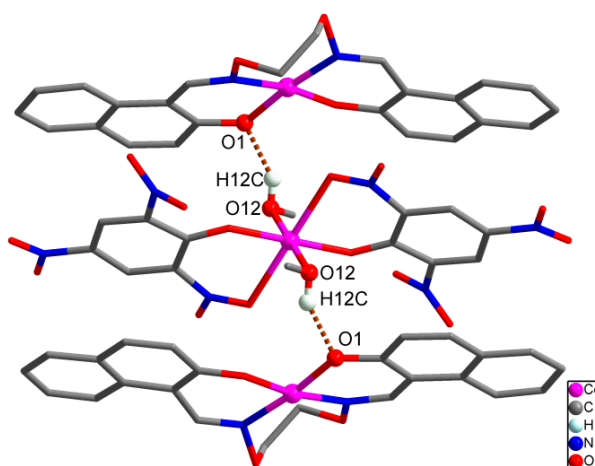


Figure 5. The tri-polymer constructed by intermolecular O-H \cdots O hydrogen bonds in 1.

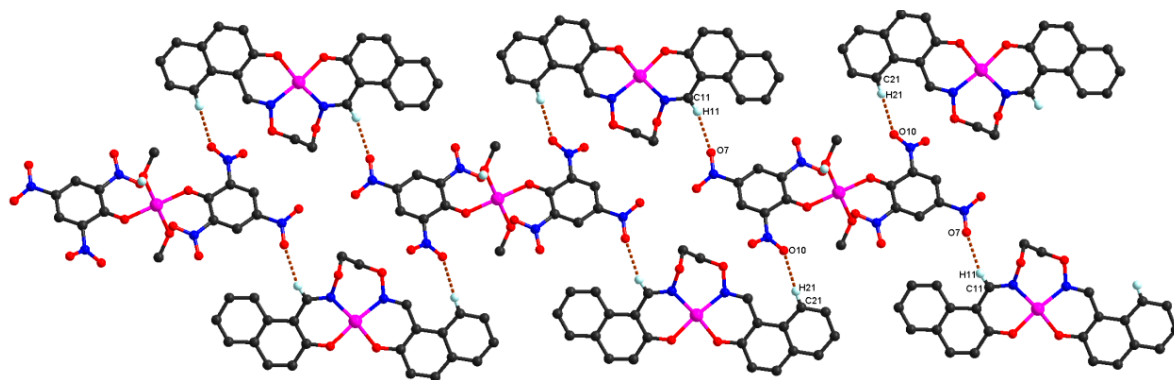


Figure 6. Part of intermolecular C-H...O hydrogen-bonding interactions in **1**.

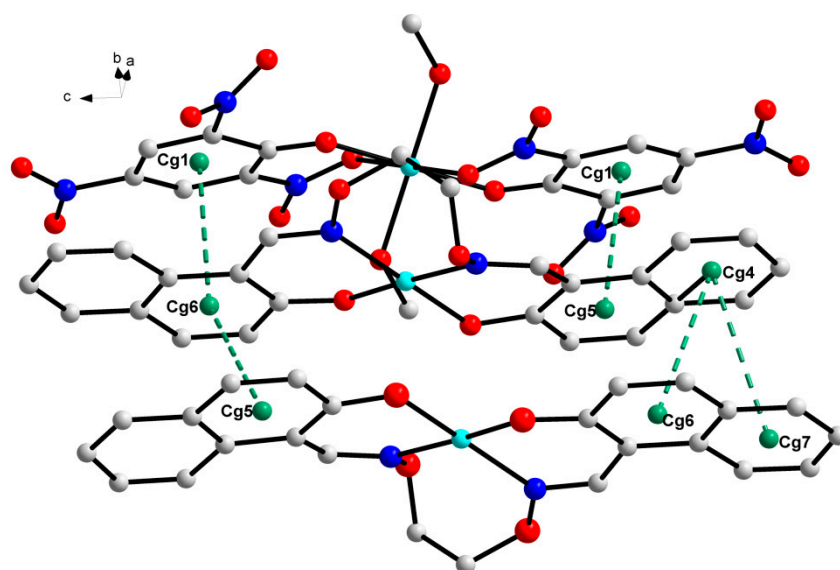


Figure 7. View of supramolecular structure of complex **1** showing the formation five $\pi\cdots\pi$ stacking interaction.

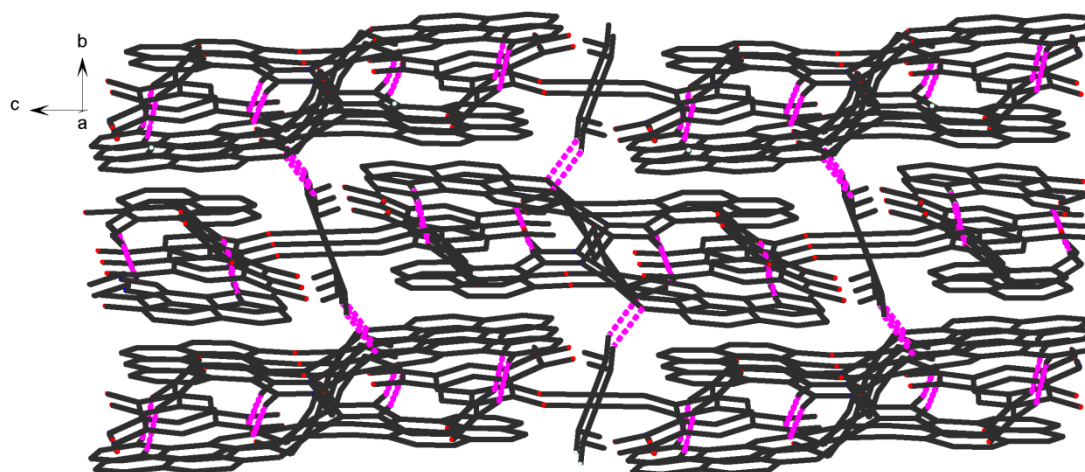


Figure 8. Part of 3D supramolecular network structure in **1**.

In the crystal structure of **2**, a pair of intramolecular C13-H13A...O5 hydrogen bonds are formed between the oxygen (O5) atom of the coordinated acetate anion and the –C13H13A group of the

O-alkyl chain of L^{2-} unit as shown in Figure 9. The hydrogen bond data are given in Table 6. Complex **2** is stabilized by intermolecular $C6-H6 \cdots \pi_{\text{centroid}(C19-C24)}$ interactions between the -CH group of the benzene ring and the aromatic rings of L^{2-} unit linking the neighboring molecules into a 1D infinite chain parallel to the c axis (Figure 10). Synchronously, this linkage is further stabilized by a pair of intermolecular $\pi_{\text{centroid}(C15-C19,C24)}-\pi_{\text{centroid}(C19-C24)}$ stacking interactions between the aromatic rings to form the other 1D infinite chain along b axis (Figure 11 and Table 7). Then these two 1D chains interlink with each other resulting in the crystal packing of **2** showing a 2D-layer supramolecular structure parallel to the bc -planes (Figure 12).

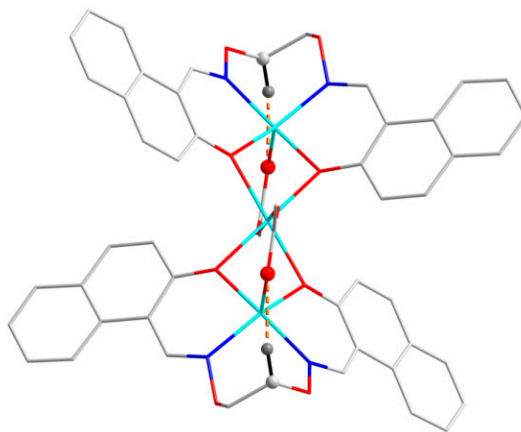


Figure 9. Intramolecular hydrogen bonds in complex **2** (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

Table 6. The main hydrogen bonds [$\text{\AA},^\circ$] for complex **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle\text{D-H}\cdots\text{A}$	Symmetry Operation
C13-H13A...O5	0.97	2.31	3.233(4)	160	x, y, z
C6-H6...Cg2	3.753	3.119	2.93(2)	167	$1 + x, y, 1 + z$

Cg2 is the centroid of benzene ring C19-C24 of complex **2**.

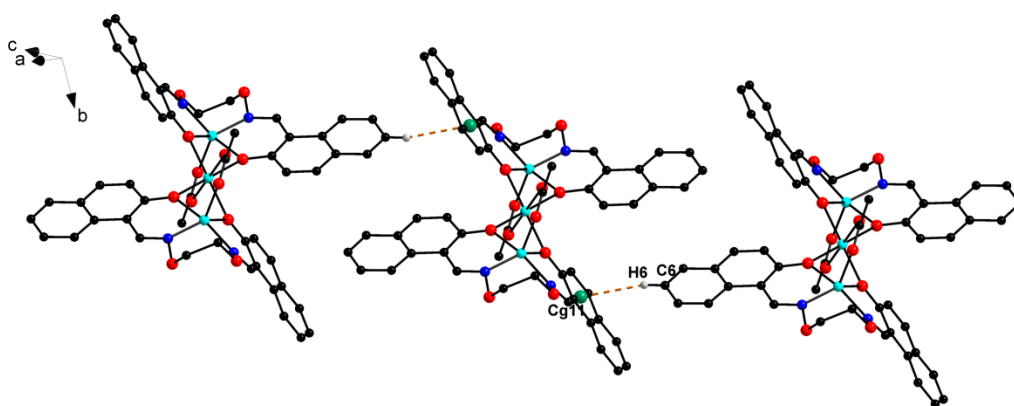


Figure 10. View of 1D supramolecular structure of the complex **2** showing the formation C-H... π stacking interaction.

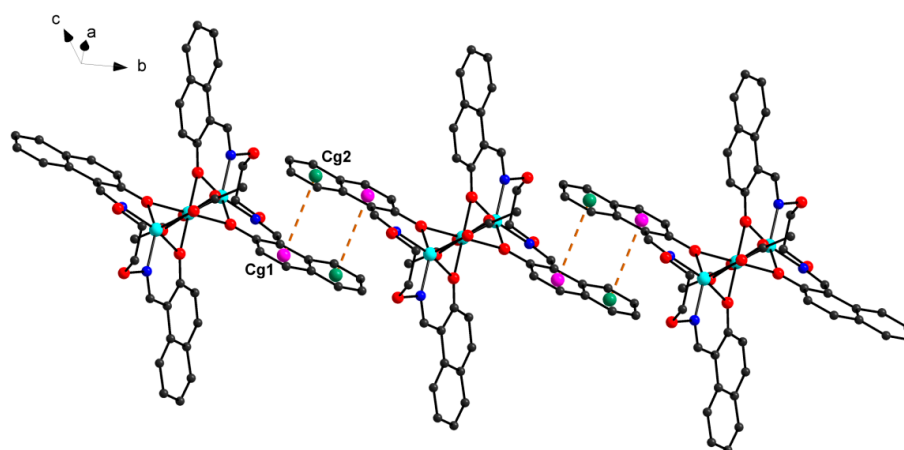


Figure 11. View of 1D supramolecular structure of the complex **2** showing the formation $\pi\cdots\pi$ stacking interaction.

Table 7. Putative $\pi\cdots\pi$ stacking interactions [\AA] for complex **2**.

Ring (I)	Ring (J)	Cg-Cg	Cg(I)-perp	Cg(J)-perp	Slippage
Cg1	Cg2	3.703(2)	3.4883(14)	3.5153(16)	1.163

Cg1 and Cg2 are the centroids of benzene ring C15–C19, C24, and C19–C24 of complex **2**, respectively.

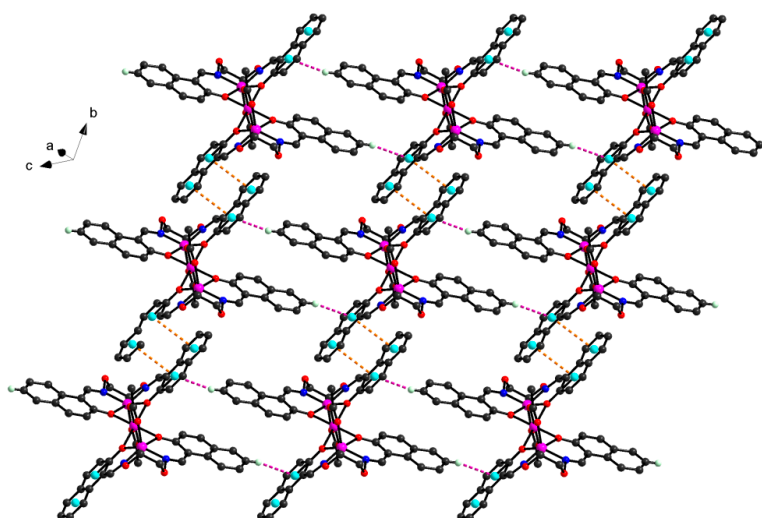


Figure 12. View of the 2D layered motif within **2** (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

3.5. Anion Effects

Obviously, coordination anions play an important part in the formation of the above different structures of Co(II) complexes. From the structure description, the free ligand H_2L presents very different coordination modes when different anions are involved in the coordination with Co(II) atoms. Complexes **1** and **2** were prepared in exactly the same way from a mixture of ligand H_2L with $\text{Co}(\text{Pic})_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in methanol solution, respectively, but the big structural differences in **1** and **2** suggest that the coordination anions indeed affect the ultimate structures of the assemblies: when the Pic^- is involved in the coordination with Co(II) atoms, the mononuclear $[\text{CoL}]$ unit, and the $[\text{Co}(\text{Pic})_2(\text{CH}_3\text{OH})_2]$ unit in the Co(II) complex **1** with distorted square-planar and

slightly distorted octahedron coordination polyhedron formed, respectively. Meanwhile, the OAc^- involved in the coordination with Co(II) atoms resulted in a trinuclear structure with the acetate ions coordinated to three Co(II) atoms through Co-O-C-O-Co bridges, possessing two distorted square pyramidal and an octahedral geometry around the central Co(II) atom. As a unique structure of the tetradentate coordination environment of N_2O_2 , Salamo-type ligands have very good coordination ability. However, for some of the transition metals, the coordination still has some limitations, thus counter anions can easily coordinate with metal ions. In this article, the Pic^- in complex **1** has a larger volume which has a hard coordination with metal ions. While, the OAc^- in **2** has less steric hindrance than **1**, it can easily coordinate to metal ions acting as a second ligand.

4. Conclusions

In summary, we successfully assembled and well characterized two novel Co(II) complexes of Salamo-type ligands. The results presented herein indicate that the coordination anions have a remarkable influence on the structures, coordination geometries, and supramolecular structures of the resulting complexes: when the Pic^- is involved in the coordination with Co(II) atoms, a stable Co(II) complex contains the mononuclear $[\text{CoL}]$ unit and the $[\text{Co}(\text{Pic})_2(\text{CH}_3\text{OH})_2]$ unit with a 3D supramolecular network structure linked by $\text{C-H}\cdots\text{O}$ hydrogen bonds and $\pi\cdots\pi$ stacking interaction. Meanwhile OAc^- involved in the Co(II) complex resulted in a trinuclear structure with a 2D-layer supramolecular structure linked by $\text{C-H}\cdots\pi$ and $\pi\cdots\pi$ stacking interactions. These results may provide us with an interesting insight into how the assembly of Co(II) coordination compounds is affected by the coordination anions.

Acknowledgments: This work was supported by the National Natural Science Foundation of China (21361015) and the Outstanding Research Platform (Team) of Lanzhou Jiaotong University, which is gratefully acknowledged.

Author Contributions: All authors contributed to the writing and production of this manuscript.

Conflicts of Interest: The authors declare no competing financial interests.

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