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Salamo-type trinuclear and tetranuclear cobalt(II) complexes based on a new asymmetry Salamo-type ligand: syntheses, crystal structures, and fluorescence properties

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ABSTRACT

Two multinuclear Co(II) complexes, [{Co(L)(i-PrOH)}₂Co(H₂O)]·2CH₃CN (1) and [{Co(L)(μ -OAc)Co(MeOH),}]·2CH,COCH, (**2**), have been synthesized with a new asymmetric Salamo-type ligand ($H_{L} = 6$ -hydroxy-6'-ethoxy-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol). The Co(II) complexes were obtained by different solvents, and the structures are completely different. In the Co(II) complex 1, the ratio of the ligand H₂L to Co(II) atom is 2 : 3 and the Co(II) ions are all five-coordinate with trigonal bipyramidal geometries. In the Co(II) complex 2, the ratio of the ligand H₂L to Co(II) atom is 2 : 4. Two central Co(II) ions are six coordinate with distorted octahedral geometries and two terminal Co(II) ions are five coordinate with distorted trigonal bipyramidal geometries. Self-assembling of an infinite 1-D supramolecular chain is formed by C–H $\cdots\pi$ interactions in **1**. Interestingly, an infinite 2-D-layer plane structure is formed by the self-assembling array of **2** linked by C–H··· π interactions. **1** and **2** exhibit blue emissions with the maximum emission wavelengths λ_{max} = 403 and 395 nm when excited at 330 nm.

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Salamo-type ligand; Co(II) complex; synthesis; structure; fluorescence property



1. Introduction

Transition metal complexes with Salen-type ligands have been frequently studied [1, 2] for their catalytic activity [3, 4], especially in the area of asymmetric catalysis [5, 6], biological activity, such as anticancer [7] and fluorescence characteristics [8, 9]. Photoluminescence in Salen-type compounds may have application in luminescent devices [10–14]. Hence, structural characteristics of transition metal complexes bearing Salen-type ligands may be a valuable source of information. Co(II) and Cu(II) complexes with Salen-type ligands receive attention for their photoluminescent characteristics [15–17]. Work has been devoted to synthesize and characterize mononuclear, homo-, or heterodinuclear transition metal complexes bearing symmetric Salen-type bisoxime or its derivatives [18].

This work stems from our interest in syntheses of asymmetric Salamo-type bisoximes. Compared with symmetric Salamo-type bisoxime ligands, the composition $(R^1-CH=N-O-(CH)_n-O-N=CH-R^2)$ is rather unusual. Selective synthesis of asymmetrical Salamo-type ligands is important because electronic and steric effect of the ligand on Salen-metal-assisted catalysis may be controlled by the introduction of different substituents on the ring [19]. The asymmetric configuration with Salamo-type ligands would afford opportunities for greater structural variation and infinite coordination polymers [20], and would be expected to have interesting characteristics [21].

In order to study, the structures and fluorescence characteristics of the transition metal complexes with asymmetric Salamo-type ligands; herein, we report the syntheses, characterizations, and crystal structures of [{Co(L)(i-PrOH)}₂Co(H₂O)]·2CH₃CN (**1**) and [{Co(L)(μ -OAc)Co(MeOH)₂}₂]·2CH₃COCH₃ (**2**) with H₃L (6-ethoxy-6'-hydroxy-2,2'[ethylenediyldioxybis(nitrilomethylidyne)]diphenol) in different solvent systems.

2. Experimental

2.1. Materials and methods

3-Ethoxy-2-hydroxybenzaldehyde and 2,3-dihydroxybenzaldehyde from Aldrich were used without purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory.

Elemental analysis for Co was carried out by an IRIS ER/S·WP-1 ICP atomic emission spectrometer, C, H, and N analyses with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra were recorded on a Vertex70 FT-IR spectrophotometer, with samples prepared as KBr (500–4000 cm⁻¹) and Csl (100–500 cm⁻¹) pellets. UV–vis absorption and fluorescence spectra were recorded on a Shimadzu UV-2550 spectrometer and on a Perkin-Elmer LS-55 spectrometer, respectively. DSC-TG analyses were carried out at a heating rate of 10 °C min⁻¹ on a NETZSCH STA 449 F3 thermoanalyzer. X-ray single-crystal structures were determined on a Bruker Smart APEX CCD area detector. Melting points were measured using a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

2.2. Synthesis

The synthetic route of the ligand is shown in scheme 1.

2.2.1. Synthesis and characterization of H₂L

1,2-Bis(aminooxy)ethane was synthesized by a similar method [17, 20]. Yield, 56.8%. Anal. Calcd for C₂H₈N₂O₂ (%): C, 26.08; H, 8.76; N, 30.42. Found (%): C, 25.98; H, 8.69; N, 30.50.

3-Ethoxysalicylaldehyde-O-(1-ethyloxyamide)oxime: A solution of 3-ethoxy-2hydroxybenzaldehyde (2.5 mmol) in ethanol (50 mL) was added to a solution of 1,2-bis(aminooxy)ethane (5 mmol) in ethanol (100 mL) and the mixture was heated at 50–55 °C for 6 h. The solution was concentrated in vacuo and the residue was purified by column chromatography (SiO₃, chloroform/ethyl acetate,



Scheme 1. The synthetic route of the Salamo-type ligand.

25 : 1) to afford crystals of 3-ethoxysalicylaldehyde-O-(1-ethyloxyamide)oxime. Yield, 80.5%. m.p. 67–68 °C. Anal. Calcd for $C_9H_{11}CIN_2O_3$ (%): C, 54.99; H, 6.71; N, 11.66. Found (%): C, 55.06; H, 6.65; N, 11.73.

6-Hydroxy-6'-ethoxy-2,2'-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol (H₃L): A solution of 3-ethoxysalicylaldehyde-O-(1-ethyloxyamide)oxime (1.32 mmol) in ethanol (10 mL) was added to a solution of 2,3-dihydroxybenzaldehyde (1.35 mmol) in ethanol (20 mL) and the mixture was heated at 50–55 °C for 6 h. After cooling to room temperature, white precipitates were collected. Yield, 80.7%. m.p. 132–133 °C. Anal. Calcd for C₁₈H₂₀N₂O₆ (%): C, 59.99; H, 5.59; N, 7.77. Found: C, 59.87; H, 5.66; N, 7.85.

2.2.2. Synthesis of 1

A solution of cobalt(II) acetate dihydrate (3.08 mg, 0.01 mmol) in isopropanol (3 mL) was added dropwise to a solution of H_{3L} (3.57 mg, 0.01 mmol) in acetonitrile (2 mL) at room temperature. The color of the solution turned to bright brown immediately, the mixture was filtered and the filtrate was allowed to stand at room temperature for about two weeks. The solvent was partially evaporated and several brown needle-like single crystals suitable for X-ray crystallographic analysis were obtained. Yield, 28.07%. Anal. Calcd for $C_{46}H_{58}Co_{3}N_{6}O_{15}$ (%): C, 49.69; H, 5.26; N, 7.56; Co, 15.90. Found: C, 49.66; H, 5.21; N, 7.57; Co, 15.81.

2.2.3. Synthesis of 2

A solution of cobalt(II) acetate hydrate (3.82 mg, 0.015 mmol) in methanol (3 mL) was added dropwise to a solution of H_3L (5.29 mg, 0.1 mmol) in acetone/ethanol (1:2) (15 mL) at room temperature. The color of the mixing solution turned to brown immediately, the mixture was filtered and the filtrate was allowed to stand at room temperature for about two weeks. The solvent was partially evaporated and several brown needle-like single crystals suitable for X-ray crystallographic analysis were obtained. Yield, 34.52%. Anal. Calcd for $C_{25}H_{34}Co_2N_2O_{11}$ (%): C, 45.74; H, 5.22; N, 4.27; Co, 17.96. Found: C, 45.77; H, 5.19; N, 4.31; Co, 17.89.

2.3. X-ray crystallography of the Co(II) complexes

Single crystals of the Co(II) complexes with approximate dimensions of $0.12 \times 0.05 \times 0.03$ mm and $0.32 \times 0.26 \times 0.25$ mm were placed on a Bruker Smart Apex CCD area detector, respectively. The diffraction data were collected using graphite monochromated MoKa radiation ($\lambda = 0.71073$ Å) at 294.68(10) K and 294.58(10) K. The structures were solved by using SHELXL-97 and Fourier difference techniques, and refined by full-matrix least-squares method on F^2 . All hydrogens were added theoretically. The crystal and experimental data are shown in table 1.

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	Table 1. (Crystal data	and structure	refinements	for 1	and 2.
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Compound code	1	2
Empirical formula	C46H58C03N6O15	C ₂₅ H ₃₄ Co ₂ N ₂ O ₁₁
Formula weight	1111.77	656.40
Temperature (K)	294.68(10)	294.58(10)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	c2/c	P-1
Unit cell dimensions		
a (Å)	21.966(4)	9.8007(9)
b (Å)	10.1801(8)	12.2530(7)
<i>c</i> (Å)	23.081(3)	12.5487(9)
α (°)	90.00	73.575(6)
β (°)	97.023(10)	87.115(6)
γ (°)	90.00	85.465(6)
Volume (ų)	5122.6(11)	1440.30(18)
Ζ	4	2
Dc (Mg m ⁻³)	1.442	1.514
μ (mm ⁻¹)	1.031	1.212
F(0 0 0)	2308.0	680.0
Crystal size (mm)	0.12×0.05×0.03	0.32×0.26×0.25
heta Range (°)	3.37 to 26.02	3.36 to 26.02
Index ranges	$-26 \le h \le 27$	$-12 \le h \le 12$
	$-7 \le k \le 12$	$-15 \le k \le 15$
	-28 ≤ <i>l</i> ≤ 22	−15 ≤ <i>l</i> ≤ 15
Reflections collected	10,229	10,648
Independent reflections	5036	5679
R(int)	0.0871	0.0459
Completeness to $\theta = 26.32$	99.71%	99.76%
Data/restraints/parameters	5025/4/325	5666/6/373
GOF	0.989	1.035
Final <i>R</i> indices $[l>2\sigma(l)]$	$R_1 = 0.0679,$	$R_1 = 0.0586,$
	$w\dot{R}_2 = 0.0747$	$w\dot{R}_2 = 0.1084$
R indices (all data)	$R_1 = 0.1651,$	$R_1 = 0.1005,$
	$w\dot{R}_2 = 0.1026$	$w\dot{R}_2 = 0.1350$
Δho max, min (e Å ⁻³)	0.344 and -0.244	0.357 and -0.387

3. Results and discussion

3.1. X-ray crystal structures

The crystal structures of **1** and **2** are shown in figure 1(a) and (b), respectively. The crystal data and experimental details are given in table 1. The selected bond lengths and angles of **1** and **2** are listed in table 2.

Complex **1** crystallizes in the monoclinic system, space group c2/c, the assembly of three Co(II) ions, two (L)^{3–} units and two isopropanol molecules result in a trinuclear Co(II) complex. The coordination sphere of the terminal Co1 or Co1[#] is completed by four N₂O₂ donors and O1 from isopropanol. Meanwhile, the sphere of central Co2 is completed by four oxygens of two (L)^{3–} units and O1 of coordinated H₂O. The terminal Co1 adopts a trigonal bipyramidal geometry, the apical positions occupied by O1 and N2 from one (L)^{3–} unit (τ = 0.827) [22]. One axial bond length of Co1–N2 is 2.114(5) Å, which is longer than the bond length of Co1–N1 (2.041(4) Å). Another axial bond length Co1–O1 (2.028(3) Å) is also longer by 0.105(3) Å than the Co1–O5 bond length (1.923(3) Å) and by 0.006(3) Å than the Co1–O7 bond length (2.022(3) Å). The central Co2 also has trigonal bipyramidal geometry with axial donors of O1 and O1[#] (τ = 0.711). The bond length of Co2–O1 is 2.089(3) Å, which is longer than the bond length of Co2–O3 (2.005(4) Å). Thus, the same coordination geometries (trigonal bipyramid) are formed in **1** (figure 2(a)).

The special interest of **1** is self-assembling array linked by intermolecular hydrogen bonds. In **1**, the hydrogen bond data are summarized in table 3 [23]. Monomers of **1** are linked by intermolecular C17–H17A… $C_{g(C1-C6)}$ hydrogen bond interactions into an infinite 1-D supramolecular chain along the *b*-axis (figure 2(b)).



Figure 1. Molecular structures of 1 and 2 with the atom numbering. Thermal ellipsoids are plotted at the 30% probability level. Hydrogens and solvent CH_3CN or CH_3COCH_3 molecules are omitted for clarity. (a) Molecular structure of 1; (b) Molecular structure 2.

Complex **2** crystallizes in the triclinic system, space group *P*-1, the assembly of four Co(II) ions, two (L)³⁻ units, two acetates and four coordinated methanol molecules result in a tetranuclear Co(II) complex. The structure can be described as two [Co(L)(μ -OAc)Co(MeOH)₂] units connected with diphenoxy bridges. The coordination sphere of terminal Co1 or Co1[#] is completed by N₂O₂ donors and O7 of the acetate ion. Meanwhile, the sphere of Co2 or Co2[#] is completed by three μ -phenolic oxygens, O8 of the acetate and two oxygens (O9 and O4AA) of the two methanol molecules. The acetate coordinates to two Co(II) ions via a Co1–O–C–O–Co2 bridge. The terminal Co1 adopts trigonal bipyramidal geometry with axial donors of O2 and N2 (τ = 0.882) [22]. The bond length of Co1–N2 between Co1 and the apical nitrogen (N2) is 2.109(4) Å, which is about 0.055(3) Å longer than the Co1–N1 bond length (2.054(4) Å) between Co1 and the basal nitrogen (N1). The axial bond length Co1–O2 (2.026(3) Å) is also longer by

Complex 1					
Co1-01	2.028(3)	Co1–N1	2.040(4)	Co2-01	2.089(3)
Co1-05	1.923(3)	Co1–N2	2.114(5)	Co2-08	2.005(4)
Co1-07	2.022(3)	Co2-01	2.089(3)	Co2-O2	1.948(3)
01-Co1-N1	86.42(18)	07-Co1-N2	93.03(16)	C2-02-Co2	113.0(3)
01–Co1–N2	175.60(17)	N1-Co1-N2	89.8(2)	C1-01-Co2	109.6(3)
05-Co1-O1	95.46(14)	02-Co2-01	82.23(14)	C19-07-Co1	128.3(3)
05-Co1-07	112.89(15)	02-Co2-08	115.43(10)	03-N1-Co1	120.3(4)
05-Co1-N1	121.15(16)	08-Co2-O1	94.10(8)	C7-N1-Co1	127.0(4)
05-Co1-N2	88.39(17)	Co1-O1-Co2	120.16(15)	04-N2-Co1	123.9(3)
07-Co1-O1	87.44(14)	02-Co2-01	94.23(14)	C10-N2-Co1	126.2(5)
07-Co1-N1	125.94(16)	C16-O5-Co1	131.2(4)	C1-01-Co1	127.6(3)
Complex 2					
Co1-O2	2.026(3)	Co1–N1	2.054(4)	Co2-O2	2.049(3)
Co1-05	1.945(3)	Co1–N2	2.109(4)	Co2-08	2.035(4)
Co1-07	2.001(3)	Co2-01	2.072(3)	Co2-09	2.204(3)
Co2–O4AA	2.217(3)	Co2-01	2.040(3)		
02-Co2-01	79.14(12)	C2-Co2-O1	79.14(12)	05-Co1-O2	94.95(13)
02–Co2–O4AA	99.30(13)	01-Co2-01	79.43(13)	05-Co1-07	117.66(14)
02-Co2-O9	86.97(11)	01-Co2-O2	157.43(13)	O5-Co1-N1	119.49(14)
08-Co2-O2	97.21(13)	01-Co2-O4AA	85.01(13)	05-Co1-N2	88.35(15)
02-Co1-N1	86.38(15)	01-Co2-09	95.06(13)	07-Co1-O2	92.21(13)
02-Co1-N2	175.67(14)	08-Co2-O1	104.96(13)	07-Co1-N1	122.74(15)
08-Co2-01	171.38(13)	08-Co2-O4AA	90.01(14)	N1-Co1-N2	89.55(17)
09–Co2–O4AA	172.90(13)				





Figure 2. (a) Coordination geometries of [{Co(L)(i-PrOH)}₂Co(H₂O)]·2CH₃CN (1); (b) View of the 1-D chain motif within 1 along the *b* axis.

0.081(3) Å than the bond length Co1–O5 (1.945(3) Å) and by 0.025(3) Å longer than the bond length Co1–O7 (2.001(3) Å). This significant enlargement indicates the (L)^{3–} unit has serious distortion, probably as a result of the asymmetry. Interestingly, the geometry of the central Co2 is different from the Co1. Co2 has octahedral geometry ($\tau = 0.02$) in which the axial positions are occupied by O4AA and O9 from two ethanol molecules and the four donors (O1, O1, O2 and O8) in a relative plane. The bond length of Co2–O9 between the Co2 and the apical oxygen (O9) is 2.204(3) Å, shorter than the bond lengths Co2–O1 and Co2–O2 (2.072(3) Å and 2.049(3) Å) are longer than bond lengths Co2–O1 and Co2–O8 (2.040(3) Å and 2.035(4) Å). Thus, two kinds of coordination geometries (trigonal bipyramid and slightly deformed octahedral) are contained in **2**.

The special interest of **2** is its self-assembling array linked by intermolecular hydrogen bonds. The hydrogen bond data are summarized in table 3. Complex **2** monomers are linked by one C9–H9B····C_{g(C1-C6)} hydrogen bond interaction into an infinite 2-D-layer structure along the *bc* plane (figure 3) [24].

Table 3. Hydrogen bonding distances (Å) and angles (°) for 1 and 2.

D–H…A	d(D–H)	d(H···A)	d(D…A)	∠D–H…A
Complex 1 C17–H17A…Cg Complex 2	0.97(8)	2.99(2)	3.82(7)	144.2(4)
C9–H9B···Cg	0.97(2)	2.95(4)	3.845	154.35(5)

For 1 or 2, Cg is the centroids of atoms C1-C6.



Figure 3. (a) Coordination geometries of $[{Co(L)(\mu-OAc)Co(MeOH)_2}_2] \cdot 2CH_3COCH_3;$ (b) View of the 2-D-layer structure within **2** along the *bc* plane.

3.2. IR spectra

IR spectra of H_3L , **1** and **2** exhibit various bands from 500–4000 cm⁻¹ (figure 4). The free ligand exhibits characteristic C=N stretches at 1612 cm⁻¹, while $v_{C=N}$ of **1** and **2** are observed at 1587 and 1591 cm⁻¹, respectively. In **1**, the C=N stretching frequency shifts to higher frequency by *ca*. 38 cm⁻¹, but in **2**, the C=N stretching frequency shifts to lower frequency by *ca*. 21 cm⁻¹ upon complexation, indicating coordination of the oxime nitrogen lone pair [25].

The Ar–O stretch is a strong band at 1263–1213 cm⁻¹ as reported for similar Salen-type ligands [26–28]. This band is at 1259 cm⁻¹ for H_3L , and at 1249 and 1267 cm⁻¹ for **1** and **2**, respectively. The Ar-O stretching frequency shifts to different frequency, indicating that Co–O bonds are formed between Co(II) and oxygen of the phenolic groups [25]. Infrared spectrum of **1** shows the expected strong absorption band due to v(O–H) at *ca*. 3442 cm⁻¹, evidence for isopropanol molecules. The expected strong absorption bands in **2** were observed at 3445, indicating the presence of coordinated methanol [29]. The characteristic absorption bands at 3442, 1656, and 561 cm⁻¹ in **1** are assigned to coordinated water, substantiated by the crystal structure.

The far-infrared spectra of **1** and **2** were obtained from 500–100 cm⁻¹ to identify frequencies due to the Co–O and Co–N bonds. The IR spectrum of **1** shows $v_{(Co-N)}$ and $v_{(Co-O)}$ frequencies at 522 and 461 cm⁻¹, respectively [29], and **2** shows $v_{(Co-N)}$ and $v_{(Co-O)}$ at 511 and 453 cm⁻¹, respectively [30]. As pointed out by Percy and Thornton [31], the metal–oxygen and metal–nitrogen frequency assignments are at times very difficult.

3.3. UV-vis absorption spectra

The UV–vis absorption spectra of H_3L , **1** and **2** were determined in 5.0×10^{-5} mol L⁻¹ ethanol solution (figure 5). Absorption peaks of **1** and **2** are obviously different from those of the ligand upon complexation. The electronic absorption spectrum of the Salen-type bisoxime H_3L consists of two relatively intense bands centered at 272 and 319 nm, assigned to the π – π * transitions of the benzene ring of salicylaldehyde and the oxime group, respectively [32]. Upon coordination of the ligand, the absorption band at 319 nm disappears from the UV–vis spectra, which indicates that the oxime nitrogens are involved in coordination [33]. The intraligand π – π * transition of the benzene ring of salicylaldehyde is slightly shifted in the corresponding complexes to 278 and 281 nm for **1** and **2**, respectively. Moreover,





Figure 5. UV–vis absorption spectra of H_3L , 1 and 2. H_3L (---), 1 (---) in ethanol (5 × 10⁻⁵ mol L^{-1}), 2 (----) in ethanol (5 × 10⁻⁵ mol L^{-1}).



Figure 6. Emission spectra of **1** and **2.1** (—) and **2** (---) ($C = 5 \times 10^{-5}$ mol L⁻¹, $\lambda_{ex} = 330$, $\lambda_{em} = 395$ and 403 nm).

the new bands observed at 381 and 368 nm for **1** and **2** are assigned to those of L \rightarrow M charge-transfer transitions which are characteristic of the transition metal complexes with N₂O₂ coordination spheres [34].

3.4. Fluorescence properties

The fluorescent properties of H_3L , **1** and **2** were investigated at room temperature (figure 6). The ligand exhibits an intense emission at 403 nm upon excitation at 330 nm, which should be assigned to the intraligand π - π * transition [35]. Complex **2** shows an intense broad photoluminescence with maximum emission at *ca*. 395 nm upon excitation at 330 nm, which is slightly red-shifted to that of H_3L . The emission peak in the spectra of **1** and **2** may also arise from the intraligand transition. The emission observed in **1** is tentatively assigned to the (π - π *) intraligand fluorescence.



Figure 7. Five mg monocrystalline 1 and 2 with heating rate of 10 °C min⁻¹ in N₂; 1 (a) and 2 (b) analyzed by TG and DSC curves.

3.5. Thermal properties

Thermal decomposition process of **1** can be divided into three phases. The first phase of DSC curves with an endothermic peak between 30-170 °C involves 6.8% weight loss roughly equal to two CH₃CN molecules (theoretical value of 7.3%). The second phase is an endothermic peak between 170-240 °C, losing

11.2%, for loss of two isopropanol molecules (theoretical of 10.8%). **1** is temperature more thermally stable than H_3L , because deprotonated (L)^{3–} enhances the thermal stability of free H_3L . Heating was continued; the decomposition of **1** is 240–600 °C (figure 7(a)).

Single-crystal sample of **2** lost acetone with thermal drying at 100 °C. Thermal decomposition of **2** has two phases, an endothermic peak between 100–240 °C, losing 10.2%, from four methanol molecules (theoretical value of 10.7%). The decomposition temperature of **2** is 240–600 °C (figure 7(b)).

4. Conclusion

[{Co(L)(i-PrOH)}₂Co(H₂O)]·2CH₃CN (1) and [{Co(L)(μ -OAc)Co(MeOH)₂}₂]·2CH₃COCH₃ (2), with an asymmetric Salamo-type ligand, have been synthesized and structurally characterized. In FTIR spectra of 1 and 2, v_{Co-O} and v_{Co-N} are observed. 1 and 2 were obtained by different solvent and their structures are different. In 1, the ratio of the ligand H₃L to Co(II) is 2 : 3, with five coordinate Co(II) with trigonal bipyramidal geometries. In 2, the ratio of H₃L to Co(II) is 2 : 4. Two central Co(II) ions are six coordinate with distorted octahedral geometries, and two terminal Co(II) ions are five coordinate with distorted trigonal bipyramidal geometries. 1 and 2 exhibit blue emissions with the maximum emission wavelengths $\lambda_{max} = 403$ and 395 nm when excited at 330 nm.

Supplementary material

Further details of the crystal structure investigation(s) may be obtained from the Cambridge Crystallographic Data Center, Postal Address: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk) on quoting the depository number CCDC Nos. 1424952 and 1424952 for 1 and 2, respectively.

Disclosure statement

No potential conflict of interest was reported by the authors.

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