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Journal Name

ARTICLE

A highly selective colorimetric chemosensor for cobalt(II) ion based on a tripodal amide ligand

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A tripodal amide based ligand, tris{2-carbamoyl-(5-carbomethoxy-pyridine-2)ethyl}amine (**H₃L, 1**), was synthesized and structurally characterized by single crystal X-ray diffraction. The investigation of the cations recognition behavior showed that the ligand has a selective colorimetric sensing property for cobalt (II) ion by an obvious color change from colorless to yellow. To investigate the sensing mechanism of **H₃L** for Co^{2+} ion, the UV-vis absorption spectra and single-crystal structural analysis were performed. The mixture of ligand and cobalt(II) ion displayed a selective colorimetric sensing property for weak acid anions, such as CO_3^{2-}, Ac^-, HCO_3^-, SO_3^{2-}, and PO_4^{3-} anions. The detailed ^{1}H NMR experiments revealed that the basicity of the anions played an important role in the intensity of the interaction between the ligand and anions. The structures of compounds **CoL (2)**, **Co-Ac-HL (3)**, **H₄L-NO₃ (4)**, and **H₄L-ClO₄ (5)** were also determined by single crystal diffraction study.

Introduction

The design and synthesis of efficient artificial receptors for various cations and anions have received much interest in the last decades due to the essential roles that cations and anions played in biology, environment and chemistry.[1] Cobalt is an essential trace element found in rocks, minerals, soils and seawater and plays an important role in various biological systems, such as cobalt is a component of vitamin B_{12},[2] However, exposure to high levels of cobalt can cause toxicological effects, including heart disease and thyroid enlargement.[3] So a high sensitive and selective analytical method to detect cobalt(II) ion is of great importance to avoid these toxic effects.

Up to now, much efforts have been made to detect cobalt(II) ion based on different analytical strategies,[4-7] among which, fluorometric methods have attracted considerable attention.[8-9] For example, Ocak and coworkers have developed a new cryptand compound with $N_2O_2S_2$ donor atoms which can interact with cobalt(II) thus causing fluorescence quench.[10] Recently, a new reaction based fluorescent probe for selective turn-on detection of cobalt(II) ion in aqueous media and in living cells was reported.[11] Although showing high sensitivities toward cobalt(II) ion, fluorometric methods are practically difficult for real time detection because of the fluorescence quenching problem.

Comparing to fluorometric detection, colorimetric sensors have gained more attention for allowing "naked–eye"

detection.[6, 12-14] Actually, colorimetric chemosensors for cobalt(II) ion are still very rare.[6] Besides several carboxyl-functional metal nanoparticles based colorimetric sensors for cobalt(II) were reported,[15-17] one coumarin-conjugated thiocarbanohydrazone-based colorimetric chemosensors was developed recently.[6]
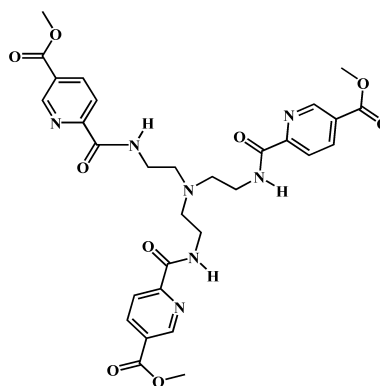

Figure 1. Structure of tris{2-carbamoyl-(5-carbomethoxy-pyridine-2)ethyl} amine (**H₃L, 1**)

As we know, tren (N4) has been used to design multiple artificial receptors for anions, such as halide anion, nitrate anion, and phosphate anion.[18-20] However, it is still rare to use the tren unit to detected cations.[21-24] In this work, we have designed and synthesized one tren-based amide ligand, tris- {2-

carbamoyl-(5-carbomethoxy-pyridine-2)-ethyl}amine (**H₃L, 1,** Figure 1), which showed potential to be a highly selective colorimetric chemosensor for cobalt(II) ion. More encouragingly, it was able to detect cobalt(II) ion at a concentration of 10^{-5} mol/L by "naked-eye". We also found that the ligand is an effective colorimetric sensor for weak acid anions.

Experiment section

Materials and General Methods

All reagents were of analytical reagent grade and were used as received without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV 500 NMR spectrometer. ^{1}H NMR spectra was registered in CDCl₃, and chemical shifts are expressed in parts per million (δ) relative to internal Me₄Si. All coupling constants are absolute values and J values are expressed in Hertz (Hz). The description of signals include: s = singlet, bs = broad singlet, d = doublet, m = multiplet, dd = doublet of doublets. HR-MS spectra were recorded on a Bruker En Apex ultra 7.0T FT-MS apparatus. Elemental analyses were performed on an Elemental Vario EL analyzer. UV-vis spectra were recorded on SHIMADZU UV-2550 spectrometer at room temperature.
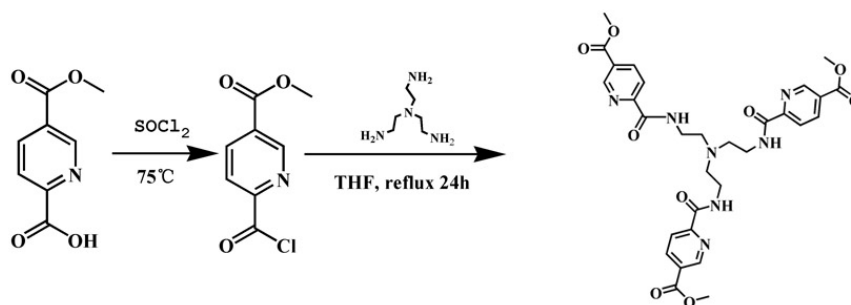

Figure 2. Synthesis of (**H₃L, 1**)

Synthesis of tris{2-carbamoyl-(5-carbomethoxy-pyridine-2)ethyl} amine (H₃L, 1): The ligand **H₃L** can be synthesized through two steps as shown in Figure 2.[25] The first one involves the chloroformylation reation of the 5-(Methoxycarbonyl) picolinic Acid. The second one step starts with the tris(2-aminoethyl)amine and methyl 6-carbonyl chloride nicotinate in THF.[26] The solution was refluxed for 24h under room temperature, then the solvent was removed in vacuo (The detailed synthesis method of **H₃L** are available in the Supporting Information). The crude product was purified by column chromatography on silica gel with ethyl acetate as the eluent to afford **H₃L** as a colorless powder in 40% yield. Anal.Calc for $C_{30}H_{33}N_7O_9$: C, 56.69; N, 15.43; H, 5.20; Found: C, 56.68; N, 15.62; H, 3.71. HR-MS (ESI): 636.26045 ($[M+H]^+$). IR (KBr, cm^{-1}): 3422(m), 3351(m), 2881(w), 1723(s), 1682(s), 1655(s), 1596(m), 1524(s), 1435(m), 1310(s), 1286(s), 1114(s), 1027(s), 870(w), 748(s). ^{1}H NMR (500 MHz, CDCl₃) □ 2.86 (t, 6H, J = 5.5 Hz), 3.51 (q, 6H, J = 5.5 Hz), 3.95 (s, 9H), 8.13 (d, 3H, J = 8 Hz), 8.34 (dd, 3H, J = 2 Hz, J = 8 Hz), 8.60 (s, 3H), 8.80 (d, 3H, J = 2 Hz); ^{13}C NMR (125 MHz, CDCl₃) □ 37.9(3C), 52.5(3C), 53.5(3C), 121.8(3C), 127.7(3C), 138.3(3C), 149.2(3C), 152.9(3C), 163.5(3C), 164.8(3C).

Synthesis of 2 (CoL): The compound **2** was prepared by adding a solution of a cobalt(II) perchlorate (36.6 mg, 0.1 mmol) in the methanol (15 mL) to a warm solution of **H₃L** (63.5 mg, 0.1 mmol) in acetonitrile (5 mL) with Et₃N (42 uL, 0.3 mmol). The solution was left for about a week at room temperature and red crystals were obtained. Yield: 50.1%. Anal.Calcd for $C_{30}H_{30}N_7O_9Co•4.5H_2O$: C, 46.64; N, 12.69; H,

5.09; Found: C, 46.72; N,12.73; H, 4.53. IR (KBr, cm^{-1}): 3422(m), 2827(w), 1732(s), 1619(s), 1607(s), 1572(s), 1435(m), 1298(s), 1122(s), 1057(s), 879(w), 745(s).

Synthesis of 3 (Co-Ac-HL): The compound **3** was prepared by adding a solution of cobalt(II) acetate (24.9 mg, 0.1 mmol) in methanol (15 mL) into a solution of **H₃L** (63.5 mg, 0.5 mmol) in acetonitrile (5 mL). The solution was left for about a week at room temperature and red crystals were obtained. Yield: 20.7%. Anal.Calcd for $C_{32}H_{34}CoN_7O_{11}•5H_2O•CH_3OH$: C, 46.32; N, 12.71; H, 4.58; Found: C, 46.72; N, 12.73, H, 4.07. IR (KBr, cm^{-1}): 3422(m), 2827(w), 1732(s), 1619(s), 1607(s), 1572(s), 1435(m), 1298(s), 1122(s), 1057(s), 879(w), 745(s).

Synthesis of 4 (H₄L-NO₃): The compound **4** was prepared by adding a solution of cobalt(II) nitrate (29.1 mg, 0.1 mmol) in methanol (15 mL) into a solution of **H₃L** (63.5 mg, 0.5 mmol) in acetonitrile (5 mL). The solution was left for about a week at room temperature and colorless crystals were obtained. Yield: 35.3%. Anal.Calcd for $C_{30}H_{34}N_8O_{12}•H_2O$: C, 50.28; N, 15.64; H, 5.06; Found: C, 50.15; N, 15.29; H, 5.44. IR (KBr, cm^{-1}): 3433(m), 3396(m), 3039(m), 1720(s), 1672(s), 1655(s), 1596(m), 1566(m), 1532(s), 1437(m), 1384(s), 1310(s), 1111(s), 1130(s), 879(w), 830(w), 745(s).

Synthesis of 5 (H₄L-ClO₄): The compound **5** was prepared by adding a solution of cobalt(II) perchlorate (36.6 mg, 0.1 mmol) in methanol (15 mL) into a solution of **H₃L** (63.5 mg, 0.5 mmol) in acetonitrile (5 mL). The solution was left for about a week at room temperature and colorless crystals were obtained. Yield: 37.8%. Anal.Calcd for $C_{30}H_{34}ClN_7O_{13}•H_2O•CH_3OH$: C, 47.36; N, 12.47; H, 5.09; Found: C, 47.81; N, 12.57; H, 3.63. IR (KBr, cm^{-1}): 3601(w), 3529(w), 3375(m), 3330(m),

3107(m), 3039(m), 2842(m), 1735(s), 1715(s), 1661(s), 1596(m), 1569(m), 1432(m), 1378(m), 1283(s), 1099(s), 1024(s), 873(w), 825(w), 745(s), 658(s), 636(s).

Crystal structure determination

Data of compounds **1** and **4** were collected by Agilent Supernova Mo-Kα radiation (λ = 0.71073 Å) at 100 K. Data of compound **2** was collected on a Rigaku R-AXIS SPIDER IP CCD area detector with monochromatic Mo Kα radiation (λ = 0.71073 Å) at 173 K. Data of compounds **3** and **5** were collected on an Oxford Gemini S Ultra CCD area detector at 173 K. The absorption corrections were applied by using the multiscan program CrysAlis Red. The structures were solved by direct and Fourier methods and refined by full-matrix least squares based on F_2 using the SHELX software. The non-hydrogen atoms were refined anisotropically. The detailed data of the X-ray measurements and refinements are available in the Supporting Information. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 972309-972313 for **1-5**.

Table 1 Crystal data for **1 – 5**

Compound	1	2	3	4	5
Formula	$C_{30}H_{33}N_7O_9$	$C_{30}H_{39}N_7O_{13.5}Co$	$C_{33}H_{48}N_7O_{17}Co$	$C_{30}H_{36}N_8O_{13}$	$C_{30}H_{40}N_7ClO_{15}$
Mr	635.63	772.61	873.71	716.67	754.11
Crystal colour	yellow	red	red	colorless	colorless
Crystal system	Monoclinic	Hexagonal	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$R\bar{3}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	5.9605(6)	13.1062(16)	16.3575(9)	7.1760(8	7.1623(6)
b/Å	41.573(5)	13.1062(16)	17.3926(9)	14.1252(14)	13.8115(15)
c/Å	12.0127(11)	35.354(7)	14.9132(8)	17.4500(18)	17.8102(13)
α/deg	90	90	90	108.268(9)	107.186(9)
β/deg	102.063 (10)	90	110.956(6)	91.425(9)	92.852(6)
γ/deg	90	120	90	103.228(9)	97.661(8)
V/Å^3	2911.0(5)	5259.2(14)	3962.2(4)	1626.1(3)	1660.7(3)
Dc/g cm^{-3}	1.450	1.464	1.465	1.464	1.508
Z	4	6	4	2	2
T/K	100	173	173	100	173
θ /deg	3.41-26.00	3.11-25.99	3.29-25.00	3.33- 25.00	3.24-25.00
μ(Mo-Kα)/mm^{-1}	0.109	0.565	0.516	0.107	0.197
Data/params	5718/415	2299/157	6965/523	5728/460	5857/488
Obs reflns	2979	1821	5256	3147	4457
R_1 [$I > 2\sigma(I)$]	0.0651	0.0598	0.0647	0.0627	0.0734
wR_2(All data)	0.1367	0.1808	0.1769	0.1547	0.1942

^{a}R$_1$ = $\sum||F_O| - |F_C||/\sum|F_O|$ ^{b}wR$_2$ = $\{\sum[w(F_O{}^2 - F_C{}^2)_2]/\sum[w(F_O{}^2)^2]\}^{1/2}$

Results and discussion

Cobalt(II) ion Sensing. The colorimetric chemosensing behavior of **H₃L** for Co^{2+} was studied in the presence of various competing metal ions in DMSO solutions (10^{-4} mol/L). 1 equiv of Et₃N was added to turn **H₃L** into L^{3-}.[27-28] As shown in Figure 3a, the solutions showed a distinct color change from colorless to yellow upon the addition of 1 equiv of Co^{2+}. Moreover, no visible color change was observed for **H₃L** solution in the presence of 1 equiv of the other metal ions (Na$^+$, K$^+$, Ca^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+}). The competition studies exhibited that the color of **H₃L** solution containing Co^{2+} still turned yellow in the presence of different metal ions (Figure 3b), which suggesting that these metal ions have no significant effect on the selectivity of Co^{2+}. The mixed solution of DMSO and H₂O (50:1) was chosen as the solvent since both the **H₃L** and metal salts could dissolve well in it.[29]

The UV-vis absorption spectra of **H₃L** containing different metal ions were performed. As shown in Figure 4a, the **H₃L** solution showed almost no absorption band upon the addition of Na$^+$, K$^+$, Ca^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, and Mn^{2+}. When addition of Ni^{2+}, Fe^{2+}, and Cu^{2+}, the UV-vis absorption spectrum displayed one band at 310 nm, respectively. In the case of the Co^{2+}, the **H₃L** solution shows two new bands centered at 310nm and 370nm, which was quite different from other metal ion solution (Figure 4). The distinct absorption at 370nm might be ascribed to the distinct yellow color of the **H₃L** solution containing Co^{2+}.
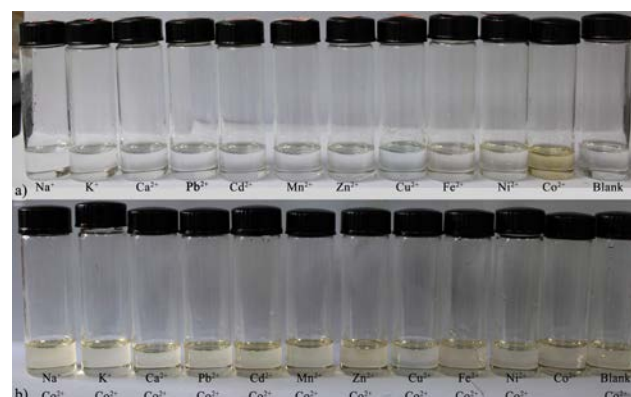

Figure 3. (a) Photograph of H₃L solutions upon the addition of different metal ions in DMSO/H₂O (50/1, v/v) in the presence of 1 equiv of Et₃N. (b) Photograph of H₃L solutions containing Co^{2+} and different metal ions in DMSO/H₂O (50/1, v/v) solutions (all the metal ions were added as their perchlorate salts. The amount of cations were added equvilent to H₃L. The blank means H₃L solution, same as follows)
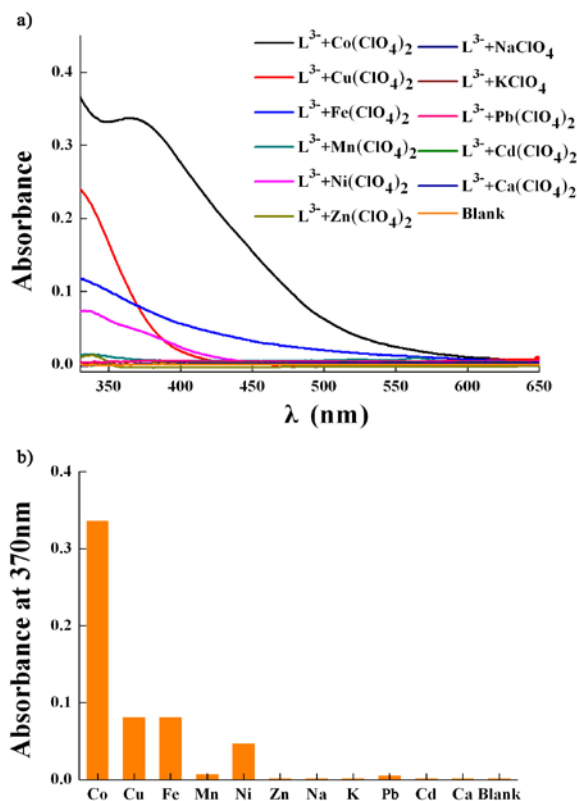
Figure 4. a) The UV-vis absorption spectra and b) column chart of the **H₃L**/cation mixtures in DMSO/H₂O (50/1, v/v) solutions (The absorbance of the **H₃L** solution was defined as 0, all the metal ions were added as their perchlorate salts. The metal ions were added equivalent to the **H₃L**).
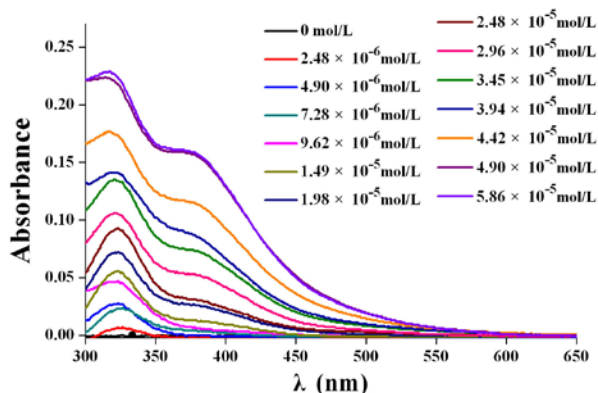

Figure 5. UV-vis absorption spectrum of the **H₃L** solution with different concentrations of Co^{2+} in DMSO/H₂O (50/1, v/v). (The absorbance of the L^{3-} in DMSO solution (5.00×10^{-5} mol/L) was defined as zero, the Co^{2+} was added as perchlorate salt.)

The high selectivity of **H₃L** towards cobalt(II) ion over the other metal ions was also revealed by measuring the UV-vis spectra of **H₃L** with cobalt(II) ions in the presence of other competitive cations at 370nm. As shown in Figure S6, the **H₃L** solution coexisting Co^{2+} and other metal ions had a higher absorbance over the **H₃L** solution only containing other metal ions, which illustrated that the **H₃L** is a high selectivity colorimetric receptor for cobalt(II) ion.

UV-vis absorption titrations of the receptors were carried out systematically with different concentrations of cobalt(II) ion to get a quantitative insight into the Co-L interactions (Figure 5). We picked the absorption of the solution at 370nm to find out the function between the concentration of the Co^{2+} and the absorbance. The results confirmed that even the concentration of the Co^{2+} was only 1.0×10^{-5} mol/L, the absorbance of the solution reached 0.01. When the concentration of the Co^{2+} was 4.9×10^{-5} mol/L, the solution became remarkably yellow with the absorbance reached 0.16. The relationship between the UV-vis absorbance and the Co^{2+} concentrations in the range of 0.8×10^{-5} mol/L to 10^{-4} mol/L in DMSO/H₂O solutions was studied (Figure S8). The absorbance curve reached a platform when one equiv of Co^{2+} was added, which means the **H₃L** has reacted with Co^{2+} completely and the ratio of the reaction is 1:1.
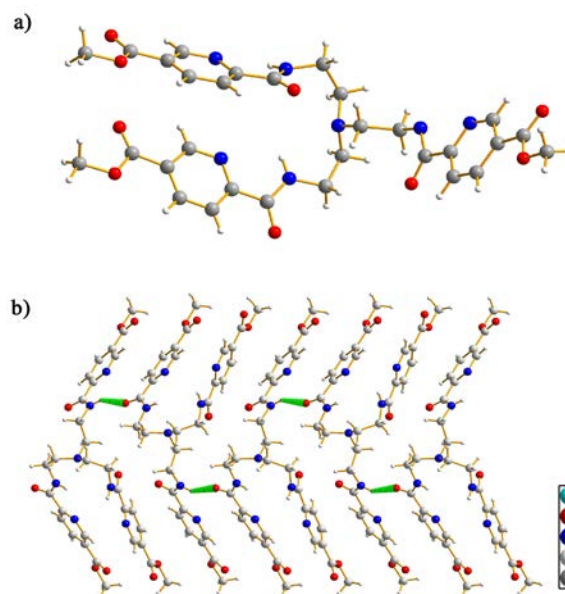

Figure 6. Crystal structures of the **H₃L** ligand (a) and the intermolecular hydrogen-bonding interactions between adjacent **H₃L** ligand (b).

To investigate the sensing mechanism of **H₃L** for Co^{2+} ion, crystal structural analyses were performed. Single crystal X-ray diffraction revealed that **H₃L** was crystallized in the monoclinic system $P2_1/c$ space group (Table 1). The ligand **H₃L** was composed of a tris-ethylamine and three 5-(Methoxycarbonyl)-pyridine carboxamide units (Figure 6a). The tris-ethylamine connected with the 5-(Methoxycarbonyl)-pyridine carboxamide via the C-N bond with the bond length of 1.35 Å, generating the tripodal amide based ligand. There are seven N atoms in this ligand, which could be divided into three groups according to their different coordination environments. The first group was N1 atom, which located at center of the **H₃L** ligand. The second group was composed of three pyridine N atoms, and the other three N atoms were the tren N atoms. Two adjacent **H₃L** ligands connected via the intermolecular hydrogen-bonding interactions with the N-H…O distance of 2.941(3)

Å, forming a 1D chain structure (Figure 6b). Further study showed that the ligand has a selective and strong interaction with Co(III) in aqueous solution by the joint efforts of the N atoms on the pyridyl group, forming compound **2** of **CoL.**

  Compound **2** of **CoL** crystallized in the *R*-3 space group of trigonal system. As shown in Figure 7, three N atoms of the pyridyl group and three N atoms of the tren coordinated with one Co(III), forming a six-coordination Co(III) complex. Interestingly, the screw coordination arrangement of the tripodal ligand around the Co(III) ion decreases the symmetry of the coordination complex, leading to the **CoL** unit with chiral configuration. In compound **2**, one Δ(clockwise) and one Λ(anticlockwise) configurations were arranged with Δ–Λ mode, forming one cage-like structure

with one water molecule residing in the cage. As a result, the final molecule is racemic and crystallize an achiral space group *R*-3, containing both Δ and Λ enantiomers. The bond lengths of Co-N are in the range of 1.923(2)-1.945(2) Å. Bond valence sum analysis indicates that the cobalt center is in the +3 oxidation state. Notably, among various metal cations, only the Co-based single crystal could be obtained from this reaction system, which maybe a proof for specific selectivity of **H3L** towards cobalt ion. The UV-vis spectra of **CoL** single crystal solution also showed the absorption band at 370 nm (Figure S7), revealing that the sensing mechanism of **H3L** for Co^{2+} ion might be attributed to the formation of **CoL** compound.
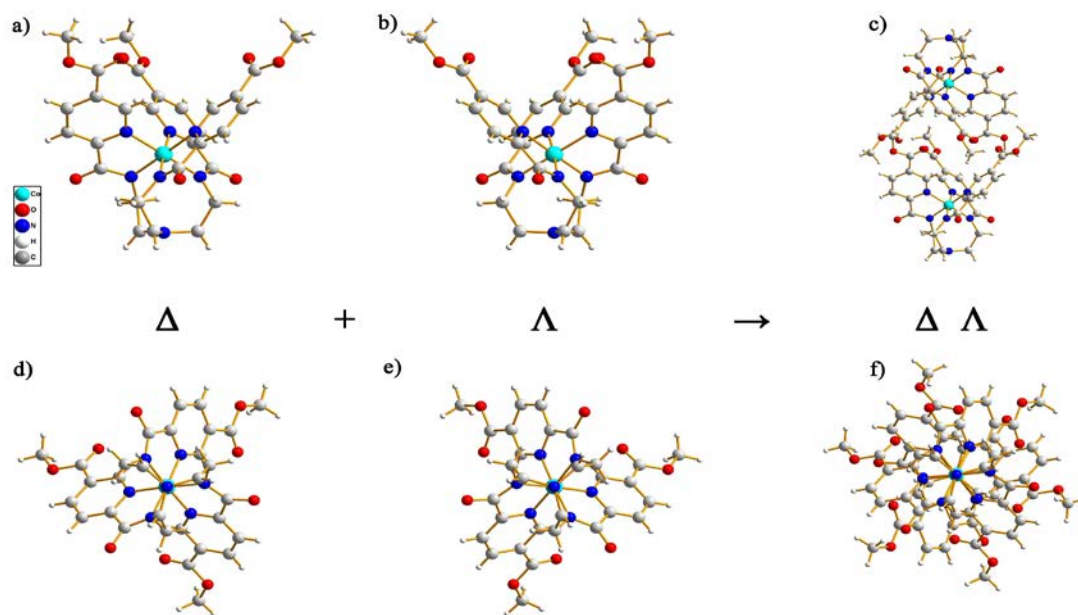

Figure 7. Crystal structures of the Δ and Λ configurations of **CoL**.

Anion Sensing. The mixtures of **H3L** and cobalt(II) perchlorate were checked for anion sensing by monitoring UV-vis absorbance with the existence of different anions (CO_3^{2-}, Ac^-, HCO_3^-, SO_3^{2-}, PO_4^{3-}, $H_2PO_4^-$, Br^-, Cl^-, and ClO_4^- were added as their sodium salts) in the DMSO/H_2O (50/1, v/v) solutions. As shown in Figure 8, the color of the solution turned from colorless to yellow at the presence of weak acid anions (CO_3^{2-}, Ac^-, HCO_3^-, SO_3^{2-}, and PO_4^{3-}), and the absorption band centered at 370 nm, which is consistent with the absorbance of the CoL solutions (Figure 9a). But there were no changes in the UV-vis absorption spectra of the solutions by adding strong acid anions, revealing that weak acid anions have a much stronger interaction with **H3L** than the strong acid anions (Figure 9b).

  The interactions between **H3L** and the anions (I^-, Br^-, Cl^-, HSO_4^-, $H_2PO_4^-$, and Ac^- were added as their TBA salts) were studied by ^1H NMR experiments. Slightly changes in ^1H NMR spectra were observed during the titration of the anions in the **H3L**/DMSO-d_6 solutions. When the anions were added, all the NH signals of the amides experienced

considerable highfield shifts, indicating cooperative interaction of the anions with the carboxamide H.
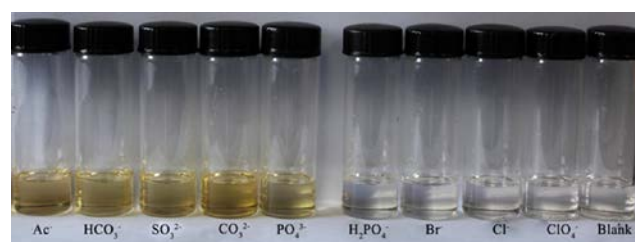

Figure 8. Photograph of the H3L/cobalt(II) perchlorate mixtures with various anions in DMSO/H2O (50/1, v/v) solutions. The anions were added equivalent to **H3L**. The blank means the H3L solution, same as follows.
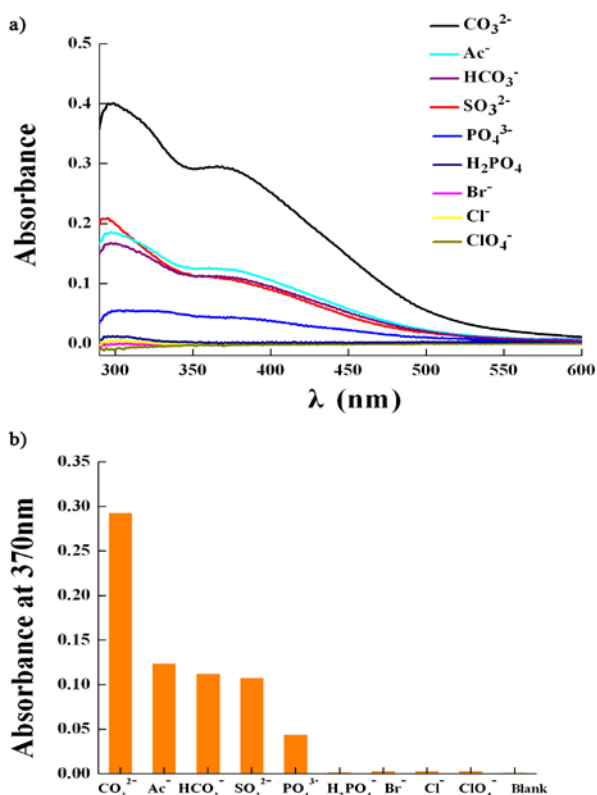
Figure 9. a) UV-vis spectra and b) column chart of the **H₃L**/cobalt(II) perchlorate mixtures with various anions in DMSO/H₂O (50/1, v/v) solutions. (The absorbance of the **H₃L** in DMSO solution was defined as 0. The anions were added equivalent to **H₃L**).

Nevertheless, the shifts were remarkably larger when weaker acid anions were added. These anions could be divided into two groups according to the different interactions with the carboxamide H. The halide ion bonds with the carboxamide H in the form of $X{\cdots}H{-}N$ interactions, while the O-containing acid anions bond with the carboxamide H via the $O{\cdots}H{-}N$ interactions. The general order of the shifts is the following: $I^- < Br^- < Cl^-$ (Figure 10), $HSO_4^- < H_2PO_4^- < Ac^-$ (Figure 11), which exactly coincided with the basicity of acid anion. The results demonstrated that **H₃L**-Co selectively binds weak acid anions over strong acid anions.

We have tried to isolate the single crystal of the **H₃L**/Co/anions, so as to provide the chance to peruse the mechanism of anion sensing. By plenty of experiments, the crystal structure of **H₃L**/Co(III) was successfully obtained with the existence of the Ac⁻ ion. Crystal structural analysis showed that five N atoms of tren unit coordinated with cobalt(III) ions, in addition with the O atom of the Ac⁻ to form a six-coordinated environment of the central cobalt(III) (Figure 12a). No cobalt ions were captured by the **H₃L** ligands when adding the strong acid anions, only the single

crystal containing ClO_4^- and NO_3^- were isolated, however, they all acted as the counter anion of the protonized $[H_4L]^+$ ligand, due to their weaker coordinated ability (Figure 12b, 12c).
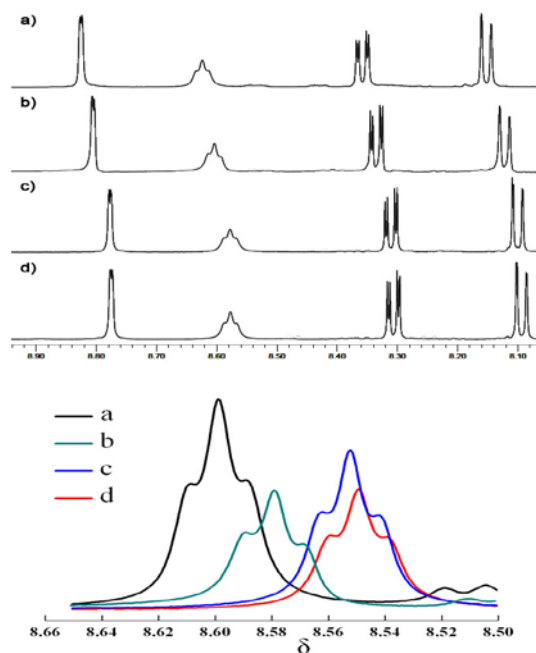

Figure 10. ^1H NMR spectra of the conjugated amide unit of **H₃L** (0.016 mmol/L) in DMSO-d₆ a) in the presence of equivalent b) I⁻, c) Br⁻, d) Cl⁻ (Top). All the anions were added as their TBA salts. The shifts of the carboxamide H were magnified to be clear (Bottom).
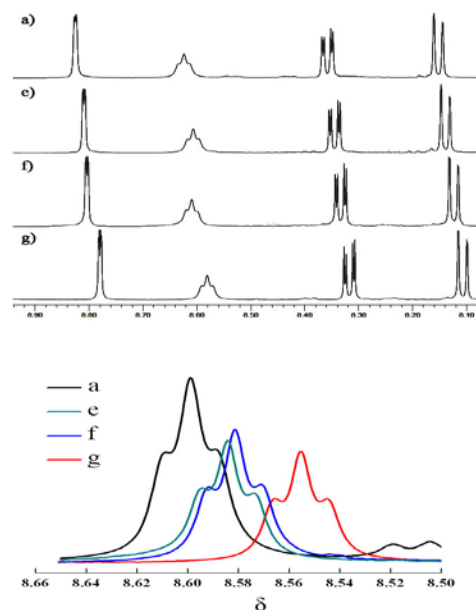

Figure 11. ^1H NMR spectra of the conjugated amide unit of H₃L (0.016 mmol/L) in DMSO-d₆ a) in the presence of equivalent e) HSO₄⁻, f) H₂PO₄⁻, g) Ac⁻ (Top). All the anions were added as their TBA salts. The shifts of the carboxamide H were magnified to be clear (Bottom).
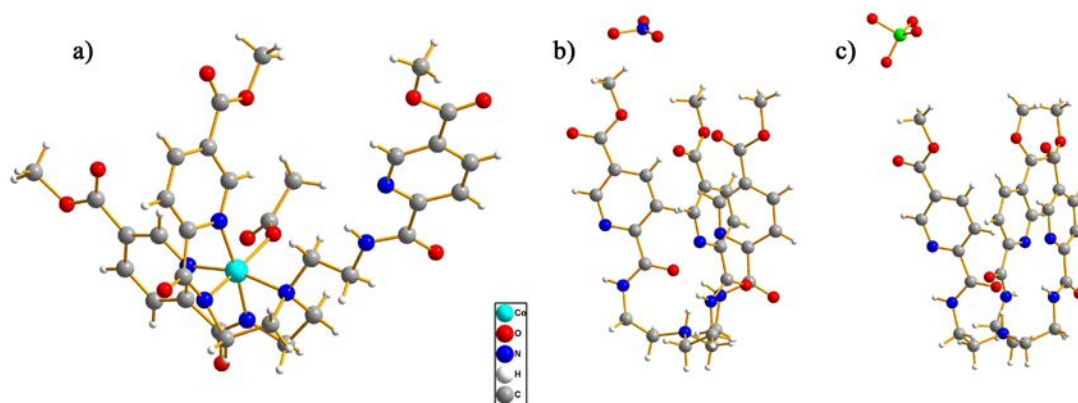
Dalton Transactions

Figure 12. Ball and stick view for crystal structures of **Co-Ac-HL** (a), **H₄L-NO₃** (b) and **H₄L-ClO₄** (c)

Conclusions

In summary, we developed a highly sensitive and specific colorimetric probe **H₃L** for cobalt(II) ion based on a tripodal amide ligand. The colorimetric chemosensing study showed that the **H₃L** can detect cobalt(II) ion at a concentration of 10^{-5} mol/L by "naked-eye" with a visible color change from colorless to yellow. UV-vis spectra and single crystal structural analysis suggested that the sensing mechanism of **H₃L** for Co^{2+} ion was attribute to the formation of a **CoL** compound. The mixture of ligand and Co^{2+} ion showed a selective colorimetric sensing property for weak acid anions, because of the cooperative interaction of the anion with the carboxamide H via $X \cdots H - N$ or $O \cdots H - N$ interactions. The present results provided a facile route to design and synthesize of selective colorimetric sensors for cations and anions.

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Notes and references

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A highly selective colorimetric chemosensor for cobalt(II) ion based on a tripodal amide ligand

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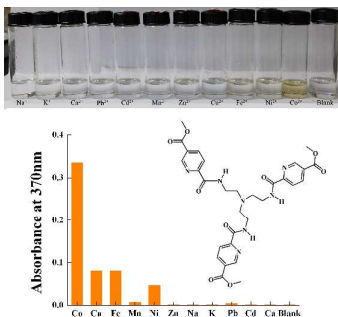
A highly selective colorimetric chemosensor for cobalt(II) ion was synthesized and structurally characterized by single crystal X-ray diffraction. The ligand was able to detect cobalt(II) ion at a concentration of 10^{-5} mol/L by "naked-eye".