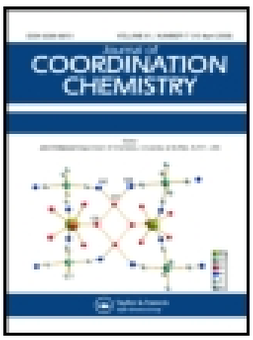

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# Synthesis of a tetrazine-based catecholamide derivative and its evaluation as a chelating agent for removal of Cd(II), Co(II), and Cu(II)

Shan Lei[a], Bo Jin[a,b], Rufang Peng[a,b], Qingchun Zhang[a] and Shijin Chu[a]

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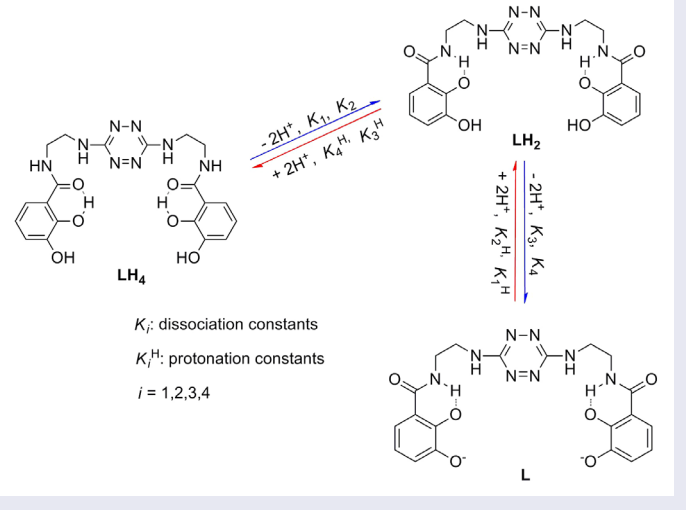
**ABSTRACT**

The synthesis and structural characterization of a tetrazine-based catecholamide (CAM) ligand, *N,N'*-bis(*N"*-(aminoethyl)-2,3-bis(hydroxy) benzamide)-1,2,4,5-tetrazine-3,6-diamine (**5**), were investigated. All compounds were characterized by $^{1}$H NMR spectroscopy, $^{13}$C NMR spectroscopy, and FTIR spectroscopy. The protonation equilibria of **5** and complexation capacities (log $\beta_{pqr}$) of $Cd^{2+}$, $Co^{2+}$, and $Cu^{2+}$ complexes of **5** were evaluated through potentiometric titration and spectrophotometric titration, respectively. Species independent pM value (=–log $[M]_{free}$) was used to compare metal affinities with the final sequence $Cu^{2+} > Cd^{2+} > Co^{2+}$. Results show that **5** has potential for heavy metal removal.

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## 1. Introduction

Heavy metal ions in living systems have received attention because of their potential contamination and diverse uses in many fields, such as cigarettes [1], seafood [2], and cosmetics [3]. Once ingested into the human body, some heavy metals disrupt physiological systems by binding to protein groups even at low concentrations [4]. For example, cadmium can cause cell apoptosis, kidney damage, and cancer [5], and cobalt may be carcinogenic to humans [6]. Copper is an essential trace element in physiological processes; however, excessive copper causes deposition in the brain, jaundice, and liver enlargement [7]. These metals threaten human health.

The use of chelating agents is the most effective heavy metal removal method, forming complexes with these metals. Numerous chelating agents, including catecholamides [8], hydroxylpyridones [9], and azamacrocyclic derivatives [10], have been synthesized and investigated for their complexing capacities with metal ions. Catecholamides are effective chelators because the amide carbonyl at the ortho position relative to one of the chelating oxygens can improve the affinity with metal ions [11].

Chemical characteristics of azacyclic metal complexes of cadmium [12], cobalt [13] and copper [14] have been studied extensively. Azacyclic compounds are an essential part of coordination chemistry, and formation constants of metal complexes are usually greater than ordinary ligands due to the amine scaffold [15]. Tetrazine is one of the azacyclic structures which is used to complex metal ions [16]. Thus, a new tetradentate catecholaminde ligand linked to tetrazine was investigated for its potential as a chelator for heavy metal ions. In this study, *N,N′*-bis(*N″*-(aminoethyl)-2,3-bis(hydroxy)benzamide)-1,2,4,5-tetrazine-3,6-diamine was synthesized and investigated as a chelating agent for Cd(II), Co(II), and Cu(II).

## 2. Experimental

### 2.1. Materials and instrumentation

The organic reagents were commercially available from Aladdin and used without purification. Anhydrous solvents were purchased from Chengdu Kelong Chemical Reagents Co.; $CH_2Cl_2$ was distilled before use. Flash chromatography was carried out on 300–400 mesh silica gel from Qingdao Hailang. NMR spectra were recorded with Bruker AVANCE 600 ($^1$H: 600 MHz, $^{13}$C: 150 MHz) and Bruker AVANCE 300 ($^1$H: 300 MHz, $^{13}$C: 75 MHz) spectrometers in $CDCl_3$ or $CD_3OD$. FTIR spectra were recorded on a Nicolet 380 FTIR spectrophotometer (Thermo Fisher Nicolet, USA) in KBr with a resolution of 4 $cm^{-1}$ from 400 to 4000 $cm^{-1}$. A UV–Vis spectrophotometer (Thermo Scientific Evolution 201, USA) with a double beam light source from 190 to 1100 nm was used.

### 2.2. Potentiometric and spectrophotometric titrations

All titrations were carried out on a ZDJ-4B automatic potentiometric titrator (Shanghai INESA Scientific Instrument Co., Ltd.) at 25 ± 0.1 °C and $I$ = 0.1 M (KCl) under $N_2$, and spectrophotometric titrations were simultaneously performed with a Thermo Scientific Evolution 201 UV–Vis spectrophotometer. Solid reagents were weighed on a Sartorius BT25S analytical balance. Ultrapure water was distilled using a ULUP-IV ultrapure water system (Sichuan ULUPURE Technology Co., Ltd.) and degassed by ultrasonic device. The 0.1 M nitric acid

standard solution and 0.1 M KOH standard solution were commercially available from Aladdin. Stock solutions of 0.01 M metal ions were made from $Cd(NO_3)_2{\cdot}4H_2O$, $CoCl_2{\cdot}6H_2O$, and $Cu(NO_3)_2{\cdot}3H_2O$. The metal ion stock solutions were obtained using certain amounts of respective metal salts which were directly diluted with 0.1 M KCl aqueous solution to 10 mL. The ligand stock solution was $2 \times 10^{-4}$ M. KCl aqueous solution (0.1 M) was prepared to 1 L in volumetric flask. A certain amount of the chelating agent was weighed accurately with a starting ethanol volume of 1%, dissolved, and diluted with 0.1 M KCl aqueous solution to 250 mL in volumetric flask.

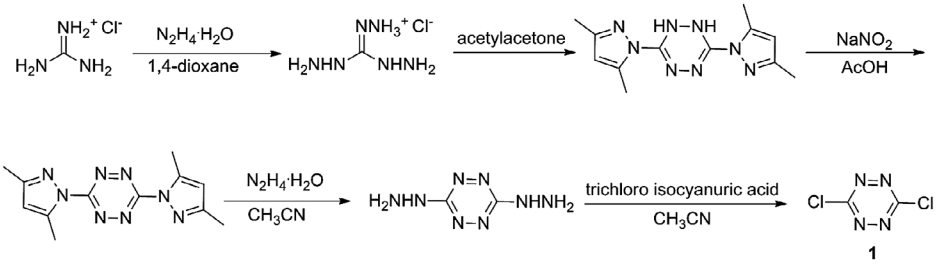
The protonation constants of **5** were investigated with 25 mL ligand stock solution, and 0.01 M diluted KOH standard solution was continuously dropped into the titration vessel. To study the formation constants of $Cd^{2+}$, $Co^{2+}$, and $Cu^{2+}$ complexes, a mixture of 0.5 mL metal ions stock solutions, 1.5 mL nitrate standard solution (reducing pH value of the titration solution), and 25 mL ligand stock solution were added to the titration vessel; the titrations were measured with 0.01 M KOH solution gradually adding into the titration vessel from low to high pH. All titrations were repeated thrice.

### 2.3. Synthesis of N-(aminoethyl)-2,3-bis(hydroxy)benzamide (4)

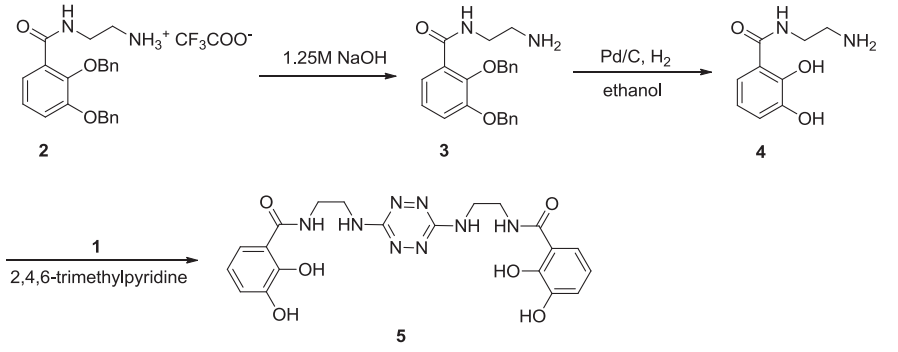
The mixture of *N*-(aminoethyl)-2,3-bis(benzyloxy)benzamido-trifluoroacetate **2** (2 g, 4.08 mmol) and 20 mL 1.25 M NaOH aqueous solution was stirred for 20 min. After extraction by $CH_2Cl_2$ (20 mL × 3), the organic layer was dried over anhydrous $Na_2SO_4$, and then the filtrate was evaporated to dryness to obtain *N*-(aminoethyl)-2,3-bis(benzyloxy)benzamide **3** as clear oil (1.34 g, 87%). A mixture of **3** (1.34 g, 3.55 mmol) and 10% Pd/C (200 mg) was dissolved in 50 mL ethanol and stirred under $H_2$ (130 mL $min^{-1}$) atmosphere for 4 h. The resulting mixture was filtered, and the filtrate was concentrated in vacuo to obtain *N*-(aminoethyl)-2,3-bis(hydroxy)benzamide **4** as yellow solid (0.69 g, 99%). $^1$H NMR (600 MHz, $CD_3OD$, 298.0 K) $\delta$ (ppm): 7.27 (dd, *J* 7.8 and 1.8 Hz, 1H, Ar-H), 6.83 (dd, *J* 7.8 and 1.8 Hz, 1H, Ar-H), 6.50 (t, *J* 7.8 Hz, 1H, Ar-H), 3.56 (t, *J* 6 Hz, 2H, $CH_2$), 2.97 (t, *J* 6 Hz, 2H, $CH_2$); $^{13}$C NMR (150 MHz, $CD_3OD$, 298.0 K) $\delta$ (ppm): 172.48 (C=O), 154.90 (Ar-C), 149.14 (Ar-C), 119.81 (Ar-CH), 117.43 (Ar-CH), 117.25 (Ar-CH), 116.44 (Ar-C), 41.76 ($CH_2$), 40.51 ($CH_2$); FTIR (KBr) *v* ($cm^{-1}$): 3432 (N–H and O–H), 2974, 2926 (C-H from -$CH_2$), 1623 (C=O), 1552 (C–N–H), 1445 (benzene ring), 1049 (C–N), 746.

### 2.4. Synthesis of N,N′-bis(N″-(aminoethyl)-2,3-bis(hydroxy)benzamide)-1,2,4,5tetrazine-3,6-diamines (5)

A mixture of 3,6-dichlorotetrazine **1** (0.08 g, 0.53 mmol), *N*-(aminoethyl)-2,3-bis(hydroxy) benzamide **4** (0.21 g, 1.06 mmol), and 2,4,6-trimethylpyridine (0.13 g, 1.06 mmol) was dissolved in 30 mL distilled $CH_2Cl_2$ and stirred at room temperature for 2 h. The solution was concentrated in vacuo, and the residue was chromatographed on a silica gel column with a mixture of ethanol and $CH_2Cl_2$ as the mobile phase to derive **5** as orange solid (0.25 g, 80%). $R_f$ = 0.5. $^1$H NMR (300 MHz, $CD_3OD$, 298.0 K) $\delta$ (ppm): 7.78 (s, H, CO-NH), 7.46 (s, H, CO-NH), 7.14 (dd, *J* 8.1 and 1.5 Hz, 1H, Ar-H), 6.90 (dd, *J* 7.8 and 1.5 Hz, 1H, Ar-H), 6.69 (t, *J* 7.8 Hz, 1H, Ar-H), 3.74 (m, 2H, $CH_2$), 3.68 (m, 2H, $CH_2$); $^{13}$C NMR (75 MHz, $CD_3OD$, 298.0 K) $\delta$ (ppm): 171.82 (C=O), 163.10 (C–N), 160.67 (C–N), 150.05 (Ar-C), 146.99 (Ar-C), 119.53 (Ar-CH), 119.40 (Ar-CH), 118.42 (Ar-CH), 116.24 (Ar-C), 41.72 ($CH_2$), 38.98 ($CH_2$); FTIR (KBr) *v* ($cm^{-1}$): 3432 (N–H and




**Scheme 1.** Synthetic route to 3,6-dichlorotetrazine **1**.




**Scheme 2.** Synthetic route to **5**.

O–H), 2926 (C–H from $–CH_2$), 1638 (C=O and C=N), 1457 (benzene ring), 1384, 1330 (C–N from tetrazine ring), 794, 741.

## 3. Results and discussion

### 3.1. Synthesis

3,6-Dichlorotetrazine **1** was synthesized according to the reported procedure [17] shown in Scheme 1, and the $^{13}C$ NMR spectrum of **1** matched with that reported previously.

The synthetic route of *N,N′*-bis(*N″*-(aminoethyl)-2,3-bis(hydroxy)benzamide)1,2,4,5-tetrazine-3,6-diamine **5** is presented in Scheme 2. *N*-(aminoethyl)-2,3bis(benzyloxy) benzamido-trifluoroacetate **2** was prepared according to our previous work [18]. After *N*-(aminoethyl)-2,3-bis(benzyloxy)benzamido-trifluoroacetate **2** stirring in 10 wt. % NaOH aqueous solution, **3** was obtained in good yield (87%). The protecting groups were removed by 130 mL·min$^{-1}$ $H_2$ and Pd/C in ethanol at room temperature to produce **4** in a 99% yield. The deprotecting compound **4** was treated with 3,6-dichlorotetrazine **1** in the presence of 2,4,6-trimethylpyridine to obtain the desired tetradentate ligand **5** in a 80% yield.

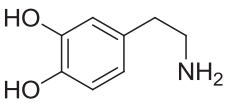
### 3.2. Ligand protonation

The protonation constants of **5** were investigated by potentiometric titration [19] beyond the 5.9–11.0 pH range. The fitting analysis by the Hyperquad 2013 program [20] presented the global protonation constants (log $\beta$) which allowed calculation of the stepwise

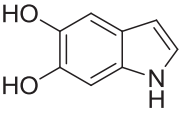
**Table 1.** Stepwise protonation constants (log $K_i^H$)[a] of **5**, dopamine and DHI for comparison.

| Ligand | log $K_1^H$ | log $K_2^H$ | log $K_3^H$ | log $K_4^H$ |
|---|---|---|---|---|
| **5** | 10.50(2) | 9.89(4) | 7.94(2) | 7.06(3) |
| dopamine[b] | 13.11 | 9.59 | – | – |
| DHI[b] | 13.09 | 9.54 | – | – |

[a]$I$ = 0.1 M KCl, 25.0 ± 0.1°C. $K_i^H = [H_iL] / ([H_{i-1}L] [H])$.
[b]Ref. [19b].




dopamine




DHI

**Figure 1.** Molecular structures of dopamine and DHI.

protonation constants (log $K_i^H$, $i$ = 1, 2, 3, 4) presented in Table 1. Ligand **5** has four dissociable protons because of the two dihydroxybenzene cores of catechol, and the first two protonation constants are 10.50 and 9.89, respectively. The gap of 0.61 logarithm units for the first two protonation constants can be explained by the electrostatic repulsion between positive charges in the protonation species [21]. The average log $K_i^H$ values of the first two protonation constants (10.50 and 9.89) and the last two protonation constants (7.94 and 7.06) are 10.20 and 7.50, respectively, and lower than the values of 4-(2-aminoethyl)benzene-1,2-diol (dopamine, Figure 1) and 5,6-dihydroxyindole (DHI, Figure 1) [15(b)], indicating that **5** has more acidic property as a result of the electron-withdrawing effect of the amide carbonyl groups [11]. For this reason, the four protonation constants of **5** can be calculated only by potentiometric titration without the use of spectrophotometric titration.

The concentration distribution curve was obtained with the HySS program [22]. The first two protonation constants correspond to the *meta* hydroxyl groups (high pH) and the last two protonation constants correspond to the *ortho* hydroxyl groups (low pH). At pH < 5, **5** displays the fully protonated form $H_4L$, where L is ligand. As pH increased, the ligand loses its protons from hydroxyl oxygens to form $H_3L^-$, $H_2L^{2-}$, $HL^{3-}$, and $L^{4-}$ species, respectively. Among these species, $H_3L^-$ is the main form at neutral pH as shown in Figure 3(A). The proposed forms of **5** are shown in Figure 2, in agreement to previous research [23].

### 3.3. Metal complexation

Metal affinities of **5** were studied with $Cd^{2+}$, $Co^{2+}$, and $Cu^{2+}$ at a 1 : 1 ratio to form mononuclear complexes. Spectrophotometric titrations [24] were carried out until there were no significant changes on the UV–Vis curves. The raw data were analyzed by HypSpec 2014 program [25] yielding cumulative stability constants (log $\beta_{pqr}$) according to the equilibrium in solution, and spectrophotometric curves are shown in Supporting Information. The concentration distribution curves were determined with the HySS program, as shown in Figure 3.

Figure 3(B–D) show that deprotonations of complexes of **5** with $Cd^{2+}$, $Co^{2+}$, and $Cu^{2+}$ occur stepwise as pH increased. The five species, $[MH_4L]$, $[MH_3L]$, $[MH_2L]$, [MHL], and [ML], are formed in all three systems, but there are some differences between the amount of ligand

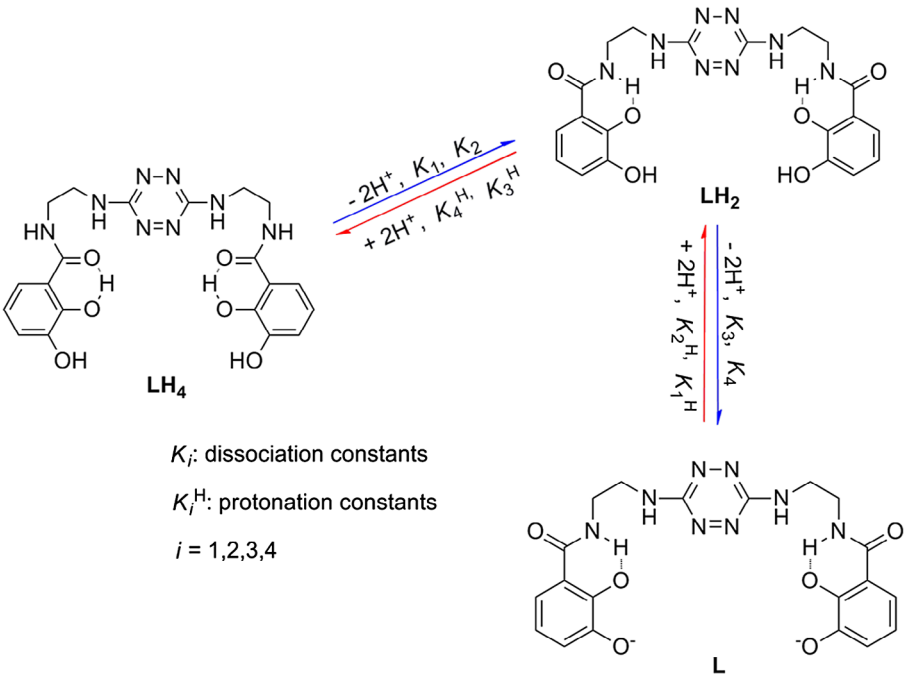



**Figure 2.** Proposed forms of **5** under acidic and basic conditions.

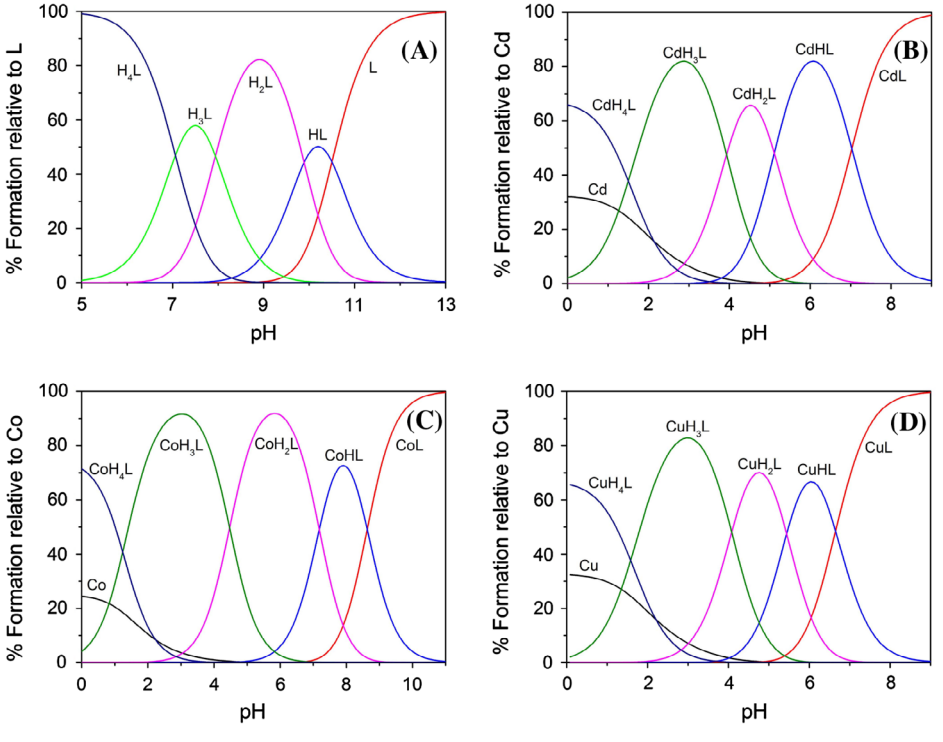



**Figure 3.** Concentration distribution curves of free **5**, $C_L = 2.0 \times 10^{-4}$ M (A) and the complexes formed in the system **5**-metal ions at a 1 : 1 ratio: $Cd^{2+}$ (B), $Co^{2+}$ (C), and $Cu^{2+}$ (D), $C_L = C_M = 1.852 \times 10^{-4}$ M. Conditions: $T = 25.0 \pm 0.1$ °C, $I = 0.1$ M KCl.

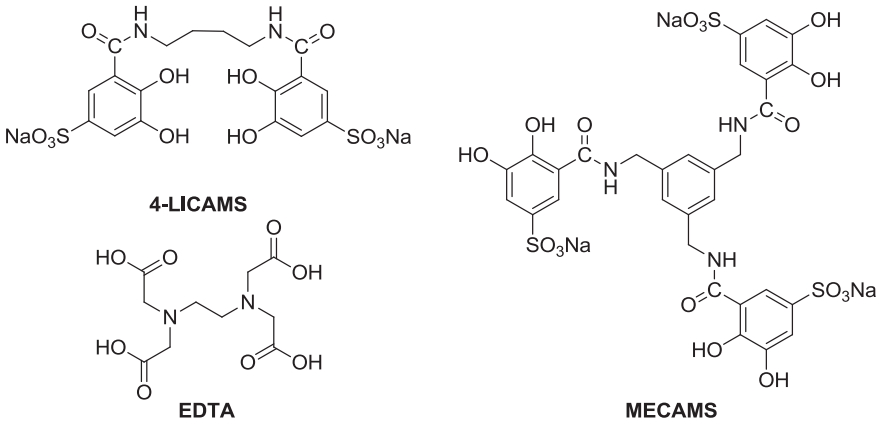



**Figure 4.** Molecular structures of 4-LICAMS, EDTA, and MECAMS.

**Table 2.** Cumulative stability constants (log $\beta_{pqr}$) of complexes of **5** with $Cd^{2+}$, $Co^{2+}$, and $Cu^{2+}$; pM values for **5** and some reported ligands at pH 7.4.[a]

| | | log $\beta_{pqr}$ | | |
|---|---|---|---|---|
| Compound | (p, q, r) | $Cd^{2+}$ | $Co^{2+}$ | $Cu^{2+}$ |
| **5** | (1, 0, 1) | 22.36(4) | 18.68(2) | 22.53(4) |
| | (1, 1, 1) | 29.39(3) | 27.31(4) | 29.09(5) |
| | (1, 2, 1) | 34.50(5) | 34.49(3) | 34.44(2) |
| | (1, 3, 1) | 38.43(4) | 38.96(5) | 38.43(3) |
| | (1, 4, 1) | 39.93(2) | 40.20(2) | 39.92(3) |
| | pM | 17.10 | 14.71 | 17.17 |
| 4-LICAMS[b] | pM | – | 6.5 | 13.6 |
| MECAMS[b] | pM | – | 7.7 | 16.9 |
| EDTA[c] | pM | – | 14.5 | 16.9 |

[a] $I$ = 0.1 M KCl, 25.0 ± 0.1°C. pM = $-\log [M]_{free}$ with $C_L = 10^{-5}$ and $C_M = 10^{-6}$ M. $\beta_{pqr} = [M_pH_qL_r] / ([M]p[H]q[L]r)$.
[b]Ref. [26a].
[c]Ref. [26b].

**5**-$Co^{2+}$ complex and the other two complexes at different pH. At pH 3, $[CoH_3L]$ exists at 90% of the total metal concentration, while $[CdH_3L]$ and $[CuH_3L]$ exist at 80%. Moreover, [CoL] is the main species at pH > 9, and [CdL] and [CuL] at pH > 7, indicating that **5** tends to complex $Cd^{2+}$ and $Cu^{2+}$ if the three metal ions co-exist under neutral condition.

Table 2 lists the cumulative stability constants of complexes of **5** with $Cd^{2+}$, $Co^{2+}$, and $Cu^{2+}$ and pM values for **5** and other reported ligands at pH 7.4. The greater pM value, the stronger binding affinity is. Cumulative stability constants show that the deprotonated ligand is more efficient for metal complexation. The pM values of **5** for $Co^{2+}$ (14.71) are slightly lower than that for $Cd^{2+}$ (17.10) and $Cu^{2+}$ (17.17) at pH 7.4, the values for $Co^{2+}$ and $Cu^{2+}$ are higher than known ligands, such as 1,6-bis(2,3-dihydroxy-5-sulfobenzoyl)-1,6-diazahexa (4-LICAMS), ethylenediaminetetraacetic acid (EDTA), and 1,3,5-tris(2,3-dihydroxy-5sulfobenzoyl)triamino-methyl-benzene (MECAMS) [26], whose structures are shown in Figure 4. There has been no study performed for $Cd^{2+}$ complexes using the spectrophotometric titration method, such that it is hard to compare the pCd value of **5** with other ligands. pCu and pCd values at neutral pH are similar. This indicates that **5** can chelate cadmium effectively.

**Table 3.** pM values of complexes of **5** with $Cd^{2+}$, $Co^{2+}$, and $Cu^{2+}$ at different pH.

| | pM[a] (M = $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$) | | |
|---|---|---|---|
| Metal ion | pH 3.0 | pH 7.4 | pH 9.0 |
| $Cd^{2+}$ | 7.10 | 17.10 | 20.84 |
| $Co^{2+}$ | 7.56 | 14.71 | 17.31 |
| $Cu^{2+}$ | 7.09 | 17.17 | 21.01 |

[a]$pM = -\log [M]_{free}$ with $C_L = 10^{-5}$ and $C_M = 10^{-6}$ M.

The pM values are calculated at pH 7.4, but it is also valuable to study the values under acidic and basic conditions in the treatment of environmental pollution. Therefore, pM values of complexes of **5** with $Cd^{2+}$, $Co^{2+}$, and $Cu^{2+}$ at pH 3.0 and 9.0 are also investigated, as shown in Table 3. The pCo value is generally higher than pCd and pCu at pH 3.0, suggesting that some complexing atoms (N, O) are capable for metal complexation. At pH 7.4 and 9.0, the pM values are similar with the sequence $Cu^{2+} > Cd^{2+} > Co^{2+}$, indicating that the influential moiety for complexation is phenolic hydroxyl.

## 4. Conclusion

A new tetrazine-based catecholamide ligand **5** was prepared and characterized by $^{1}H$, $^{13}C$ NMR, and FTIR spectroscopy. Protonation constants were studied by potentiometric titration showing more acidic property than bidentate dopamine and hexadentate MECAM. Complexation capacities with cadmium(II), cobalt(II), and copper(II) were investigated by spectrophotometric titration. The pM values of the complexes were calculated under acidic, neutral, and basic conditions, and the values indicate that complexation capacities of **5** with these metal ions are in the sequence $Cu^{2+} > Cd^{2+} > Co^{2+}$ at pH 7.4. Results show that **5** can complex the three heavy metal ions effectively and may be used in metal removal.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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