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# Tansition Metal Complexes with 2-(1-(Carboxymethyl)-2-Methyl-1*H*-Benzimidazol-3-ium-3-yl)acetate (HL): Synthesis and Crystal Structure of $[Co(L)_2(H_2O)_4] \cdot 6H_2O$ and $[Cu(L)_2(H_2O)_2] \cdot 4H_2O$[1]

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**Abstract**—Transition metal complexes of 2-(1-(carboxymethyl)-2-methyl-1*H*-benzimidazol-3-ium-3-yl)acetate (HL), namely $[Co(L)_2(H_2O)_4] \cdot 6H_2O$ (**I**) and $[Cu(L)_2(H_2O)_2] \cdot 4H_2O$ (**II**), have been synthesized by a hydrothermal procedure and characterized by X-ray crystallography, CIF files CCDC nos. 1007524 (**I**), 1007525 (**II**). Both **I** and **II** are mononuclear molecules. In **I**, the $Co^{2+}$ ion is in octahedral coordiantion environment and surrounded by four O atoms from water molecules and two carboxylate O atoms of two deprotonated ligand ($L^-$) occupied six culmination. While in **II**, the $Cu^{2+}$ ion is located in a square-planar geometry, bounded to two aqua O atoms and two carboxylate O atoms from $L^-$.

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## INTRODUCTION

*N*-Heterocyclic amino acids have been receiving a lot of attention in academia and industry area [1, 2]. These compounds exhibit useful characteristic in biological activity, spectral property, catalysis activity and coordination behaviour. The zwitterion based on benzimidazole or imidazole represents a new member of this family. However, the systematic studies of these ligands are still comparatively minor. Recently, a celebrated ligand of bis(1,3-carboxymethyl)imidazole caused wide public concern in the field. The deprotonated monoanion of bis(1,3-carboxymethyl)imidazole possesses two $-CH_2CO_2-$ moieties that can ligate to a metal [3] and form coordination and hydrogen-bond-based polymeric frameworks [4–6]. In the resultant complexes, one $Sr^{2+}$ hydrate exhibits an interesting feature that a set of water are linked by hydrogen bonds into a hexagon sheets separating the layers of the coordinating polymer [4]; another $Zn^{2+}$ hydrate shows unusual helical tube of nanodimesions occupied by water that can mimic aquaporin [5].

Using the background gived above, we studied a series of alkaline earth metal complexes with 1,3-bis(carboxymethyl)benzimidazolium, aimed at expositing their spectroscopic and chemical behavior. X-ray crystallography revealed that Mg(II), Ca(II) complexes are neutral monomers, while Ba(II) complex is a polymeric species based on the carboxymethyl bridge between metal ions. On the other hand, the studies about their spectroscopic properties and mechanism were gained rationalistic understanding through density functional theory (DFT) and time-dependent density functional theory (TD DFT) calculations [7]. These first results encouraged us to probe into the complexes of these zwitterion ligands. In this paper, we report our present work describing the synthesis, crystal structure of transition metal complexes prepared from 2-(1-(carboxymethyl)-2-methyl-1*H*-benzimidazol-3-ium-3-yl)acetate (HL), namely $[Co(L)_2(H_2O)_4] \cdot 6H_2O$ (**I**) and $[Cu(L)_2(H_2O)_2] \cdot 4H_2O$ (**II**).

## EXPERIMENTAL

**Materials and methods.** Except for 2-(1-(carboxymethyl)-2-methyl-1*H*-benzimidazol-3-ium-3-yl)acetate (HL), which was synthevsized in the laboratory, all chemicals and solvents used in the preparation of the complexes were of analytical grade and were used as received. IR spectra were recorded between 4000–400 $cm^{-1}$ on a PerkinElmer FTIR-8400 spectrophotometer, and KBr pellets were used to analyze solid materials. Elemental analyses were performed on a PerkinElmer 2400/II automatic analyzer.

**Syntheses of complex I.** $CoCl_2 \cdot 6H_2O$ (0.4759 g, 2 mmol), HL (0.2480 g, 1 mmol) and 15 mL of $H_2O$ were stirred at room temperature for 10 min. Triethylamine was added dropwise to adjust the pH to 7–8. The result mixture was sealed in a Parr Teflon-lined stainless steel vessel (25 mL) and heated to 130°C for 3 days. The solution was filtered, and the filtrate was allowed to stand in air. Pink crystals suitable for X-ray

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**Table 1.** Crystallographic data and refinement parameters for **I** and **II**

| Parameter | Value | |
|---|---|---|
| | **I** | **II** |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| $a$, Å | 11.332(9) | 7.1915(9) |
| $b$, Å | 9.279(8) | 20.699(3) |
| $c$, Å | 16.197(13) | 9.7764(12) |
| β, deg | 109.667(10) | 103.505(2) |
| $V$, Å$^3$ | 1604(2) | 1415.0(3) |
| $Z$ | 2 | 2 |
| $\rho_{calcd}$, g/cm$^3$ | 1.519 | 1.563 |
| μ, mm$^{-1}$ | 0.620 | 0.850 |
| $F$(000) | 770 | 694 |
| Crystal size, mm | 0.50 × 0.45 × 0.40 | 0.30 × 0.35 × 0.45 |
| θ Range, deg | 1.91 to 27.71 | 2.36 to 26.50 |
| Reflections collected | 13794 | 12915 |
| Independent reflections ($R_{int}$) | 3735 (0.0389) | 3511 (0.0447) |
| Reflections with, $I > 2\sigma(I)$ | 2909 | 2594 |
| Parameters | 231 | 197 |
| Goodness-of-fit on $F^2$ | 1.078 | 1.009 |
| Final $R$ indices, $I > 2\sigma(I)$ | $R_1 = 0.0369$, $wR_2 = 0.0971$ | $R_1 = 0.0356$, $wR_2 = 0.0817$ |
| $R$ indices (all data) | $R_1 = 0.0516$, $wR_2 = 0.1041$ | $R_1 = 0.0594$, $wR_2 = 0.0914$ |
| Residual electronic density (max/min), $e$ Å$^{-3}$ | 0.520/–0.262 | 0.382/–0.381 |

analysis were obtained (the yield was 22% based on Co).

For $C_{24}H_{42}N_4O_{18}Co$ ($M$ = 733.55)

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 39.29; | H, 5.78; | N, 7.63. |
| Found, %: | C, 39.34; | H, 5.73; | N, 7.66. |

IR (KBr; ν, cm$^{-1}$): 3201.6 s, 2961.6 m, 1626.8 s, 1543.9 m, 1472.5 m, 1442.7 s, 1362.6 s, 1280.6 s, 876.6 m, 756.0 m, 700.1 m, 656.7 m, 578.6 w.

**Syntheses of complex II.** A mixture of $CuCl_2 \cdot 2H_2O$ (0.3410 g, 2 mmol), HL (0.2342 g, 1 mmol), NaOH (0.0040 g, 1 mmol) and 12 mL of EtOH (50%) was sealed in a Parr Teflon-lined stainless steel vessel (25 mL) and heated to 130°C for 6 days. After cooled to room temperature, blue-green crystals suitable for X-ray analysis were obtained (the yield was 20% based on Cu).

For $C_{24}H_{34}N_4O_{14}Cu$ ($M$ = 666.09)

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 43.27; | H, 5.16; | N, 8.41. |
| Found, %: | C, 43.31; | H, 5.06; | N, 8.46. |

**Table 2.** Selected bonds (Å) and angles (deg) for **I** and **II**

| Bond | | Bond | |
|---|---|---|---|
| | **I** | | |
| Co(1)–O(6) | 2.064(2) | Co(1)–O(1) | 2.120(2) |
| Co(1)–O(5) | 2.093(2) | C(1)–C(6) | 1.383(3) |
| C(6)–N(2) | 1.386(3) | C(7)–N(2) | 1.331(3) |
| C(7)–N(1) | 1.332(3) | C(1)–N(1) | 1.386(2) |
| | **II** | | |
| Cu(1)–O(5) | 1.9352(14) | Cu(1)–O(3) | 1.9687(14) |
| C(3)–N(2) | 1.401(3) | C(1)–N(1) | 1.342(2) |
| C(1)–N(2) | 1.344(3) | C(2)–N(1) | 1.401(3) |
| C(2)–C(3) | 1.390(3) | | |
| Angle | | Angle | |
| | **I** | | |
| O(6)Co(1)O(5) | 90.91(6) | O(6)Co(1)O(1) | 86.79(7) |
| O(5)Co(1)O(1) | 90.20(6) | | |
| | **II** | | |
| O(5)Cu(1)O(3) | 89.09(6) | | |

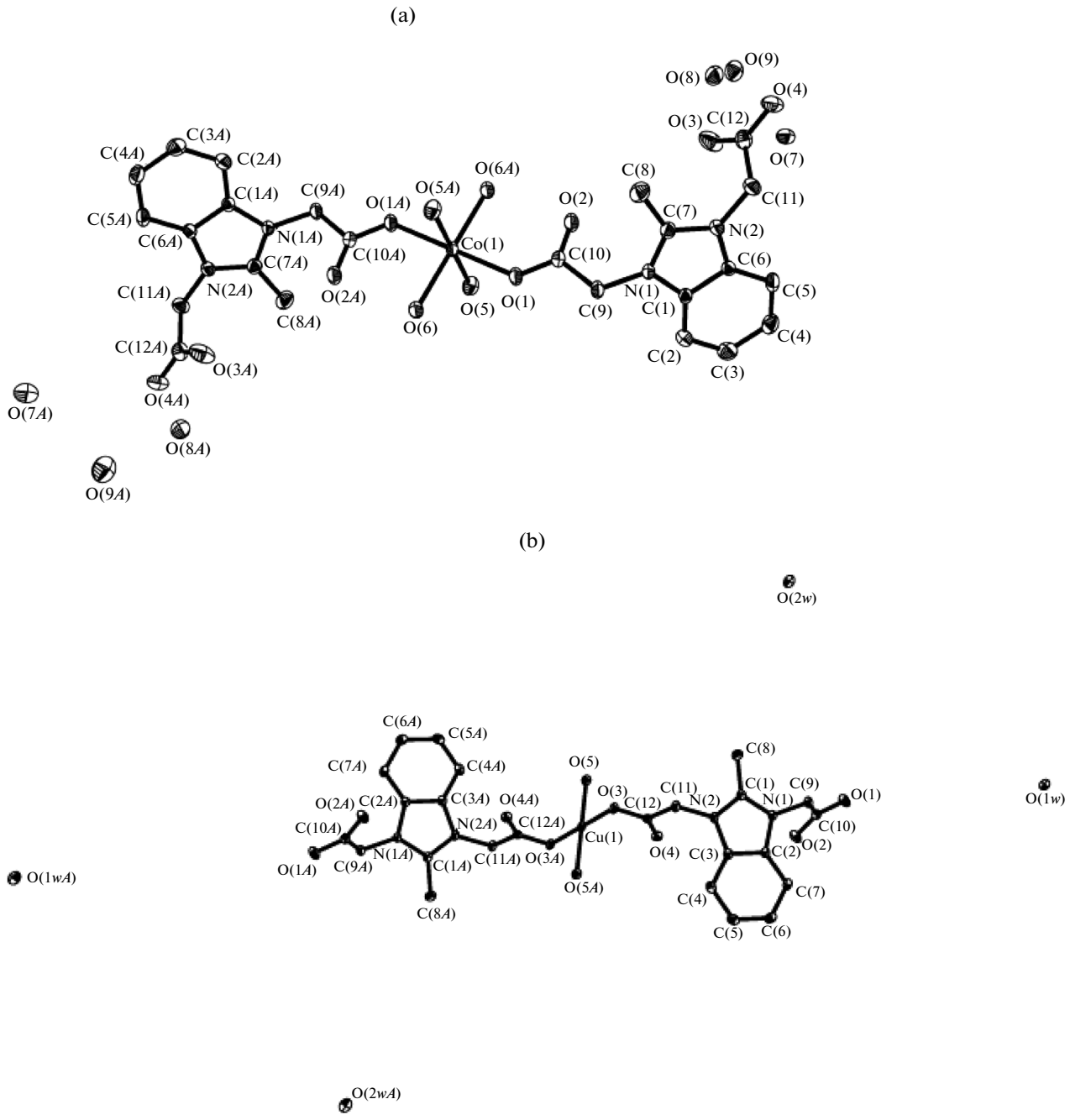


**Fig. 1.** Perspective view of coordination structure in **I** (a) and **II** (b). The thermal ellipsoids are plotted at the 30% probability level and all H atoms were omitted for clarified. Atoms labeled with the suffix A are related by the symmetry codes: $-x, -y + 2, -z$ for **I** and $-x + 1, -y, -z$ for **II**.

IR (KBr; ν, $cm^{-1}$): 3417.6 s, 3334.7 s, 3064.7 s, 2947.0 s, 1651.0 v.s, 1625.9 v.s, 1523.7 m, 1475.4 s, 1384.8 v.s, 1319.2 s, 1292.2 s, 1201.6 w, 1139.9 w, 1068.5 w, 1033.8 w, 918.1 w, 883.3 w, 815.8 w, 773.4 m, 700.1 m, 665.4 w, 617.2 w, 576.7 w, 547.7 w, 489.9 w, 434.0 w.

**X-ray crystallography.** All X-ray crystallographic data were collected on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromated Mo$K_\alpha$ ($\lambda$ = 0.71073 Å) radiation by employing the φ–ω scan technique. The structures were solved by a direct method and refined by a full-

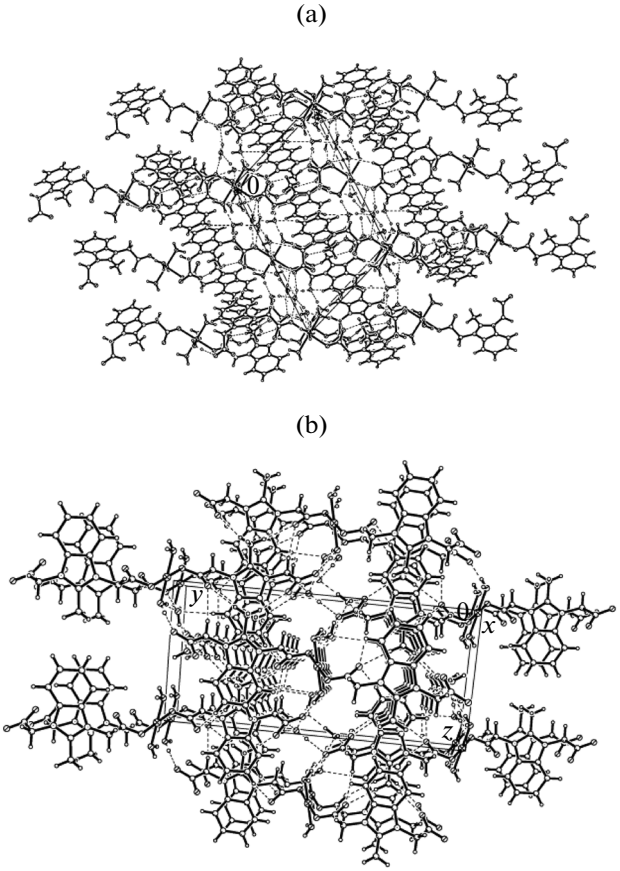


**Fig. 2.** The packing diagram of **I**, viewed down the *y* axis (a) and **II**, viewed down the *x* axis (b). Dashed lines indicate hydrogen bonds.

matrix least-squares procedure based on $F^2$ using SHELXTL software [8–10]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. All hydrogen atoms in **I** and **II** were generated geometrically. Crystallographic data and experimental details of the structures are provided in Table 1.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 1007524 (I), 1007525 (II); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

As shown in Fig. 1a, the mononuclear molecule in **I** consists of octahedral geometry around the $Co^{2+}$ ion with four O atoms from different aqua ligands coordinating four positions, leaving two trans-positions for the two carboxylate O atoms (O(1) and O(1*A*)) of two deprotonated ligand ($L^-$). In the $[CoO_2O_4]$ octahedron is slightly distorted, and the $Co-O_{aqua}$ bond lengths are shorter than the $Co-O_{carboxylate}$ bonds (Table 2). The observed deviation from 90° is indicative of a slightly distorted octahedral configuration. The Co–O bond distances in **I** agree with the values found in octahedral Co complexes containing monodentate carboxylic acid and aqua ligands [11, 12]. In the ligand system, the bond lengths of the imidazolium ring range from 1.331(3) to 1.398(4) Å, which is comparable to a conjugated double bond [13], indicating that the zwitterionic structure of the ligand remained intact [14]. This phenomenon was also found in the free HL ligand.

As shown in Fig. 2a, the lattice water molecules are clathrated in the interspace and are involved in hydrogen bonds via O(7)···O(4), O(7)···O(1), O(8)···O(3), O(8)···O(7), O(9)···O(4), and O(9)···O(7). Moreover, the aqua ligands act as intermolecular hydrogen-bond donors to carboxylate O atoms via O(5)···O(4) and O(6)···O(2) (Table 3). The benzimidazolium rings between adjacent ligands are separated with a face-to-face distance of ~3.502 Å, suggesting the presence of π–π stacking interactions. These supramolecular interactions extend the molecules into a three-dimensional network and play a critical role in the stability of the crystal lattice.

**Table 3.** Geometric parameters of hydrogen bonds in **I** and **II***

| D–H···A | Distance, Å | | | Angle D–H···A, deg |
|---|---|---|---|---|
| | D–H | H···A | D···A | |
| | | **I** | | |
| O(5)–H(5*A*)O(4)$^{ii}$ | 0.88 | 1.86 | 2.726(3) | 169 |
| O(5)–H(5*B*)O(9)$^{iii}$ | 0.91 | 1.93 | 2.824(3) | 167 |
| O(6)–H(6*A*)O(2)$^{i}$ | 0.92 | 1.86 | 2.696(3) | 151 |
| O(6)–H(6*B*)O(8)$^{iv}$ | 0.92 | 1.78 | 2.686(3) | 169 |
| O(7)–H(7*A*)O(4)$^{v}$ | 0.86 | 1.89 | 2.711(3) | 159 |
| O(7)–H(7*B*)O(1)$^{vi}$ | 0.88 | 2.03 | 2.871(3) | 160 |
| O(8)–H(8*D*)O(3) | 0.853(17) | 1.848(17) | 2.689(3) | 168(3) |
| O(8)–H(8*E*)O(7)$^{vii}$ | 0.851(17) | 2.03(2) | 2.845(3) | 161(3) |
| O(9)–H(9*C*)O(4)$^{viii}$ | 0.861(18) | 2.044(19) | 2.902(3) | 175(3) |
| O(9)–H(9*D*)O(7) | 0.857(17) | 1.902(18) | 2.752(3) | 171(3) |
| | | **II** | | |
| O(5)–H(5*A*)···O(1*w*)$^{ii}$ | 0.87 | 1.81 | 2.667(2) | 170 |
| O(5)–H(5*B*)···O(1)$^{iii}$ | 0.83 | 1.79 | 2.610(2) | 174 |
| O(1*w*)–H(1*A*)···O(3)$^{iv}$ | 0.80 | 2.02 | 2.796(2) | 163 |
| O(1*w*)–H(1*B*)···O(2*w*)$^{v}$ | 0.88 | 1.86 | 2.723(2) | 166 |
| O(2*w*)–H(2*A*)···O(1)$^{vi}$ | 0.92 | 1.82 | 2.718(2) | 168 |
| O(2*w*)–H(2*B*)···O(2)$^{vii}$ | 0.81 | 1.94 | 2.731(2) | 165 |

* Symmetry codes: $^{i}$ $-x, -y+2, -z$; $^{ii}$ $-x+1, y-1/2, -z+1/2$; $^{iii}$ $-x+1, -y+1, -z$; $^{iv}$ $x-1, y, z$; $^{v}$ $x, y-1, z$; $^{vi}$ $x+1, y-1, z$; $^{vii}$ $-x+2, y+1/2, -z+1/2$; $^{viii}$ $-x+2, y-1/2, -z+1/2$ for **I**; $^{ii}$ $x, y-1, z$; $^{iii}$ $-x+3/2, y-1/2, -z+1/2$; $^{iv}$ $x-1, y+1, z$; $^{v}$ $-x+1/2, y+1/2, -z+3/2$; $^{vi}$ $-x+1, -y+1, -z+1$; $^{vii}$ $x, y, z+1$ for **II**.

An ORTEP view of the coordination environment at **II** (Fig. 1b) shows $Cu^{2+}$ ion is located on a twofold axis, and coordinated by two carboxylate O atoms from two different deprotonated ligand ($L^-$) and two aqua O atoms, thus completing a square-planar geometry. The bond angles of O(5)Cu(1)O(3) 90.91(6)°, O(5)Cu(1)O(3) 89.09(6)° deviate from 90° by 0.91°, implying that the molecule is slightly distorted from an ideal square. The Cu–$O_{carboxylate}$ bonds (1.9687(14) Å) are longer than the Cu–$O_{aqua}$ bonds (1.9352(14) Å), that are in accordance with the typical bond lengths (1.835 to 1.983 Å) documented previously [15–18]. The C(12)–O(4) bond length of 1.225(2) Å indicates double-bond character.

The lattice water molecules clathrated among the layers are hydrogen-bonded to each other, to coordinated water and to the uncoordinated carboxylate oxygen atoms (O···O 2.610(2)–2.796(2) Å). Moreover, the C–H···O hydrogen bonds between the methyl carbon atoms with the uncoordinated carboxylate oxygen atoms are observed (Table 3). These hydrogen bonding played an important role in the formation of a three-dimensional supramolecule (Fig. 2b).

In summary, we have synthesized and X-ray structurally analysized two novel complexes **I** and **II** by benzimidazole carboxylic acids ligand. Based on lots of hydrogen bonds a three-dimensional supramolecular framework has been created.

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