

# Two new coordination polymers of Co(II) with 1,1'-(1,4-butanediyl)bis(benzimidazole)

Jian-Fang Ma,<sup>\*a</sup> Jing-Fu Liu,<sup>a</sup> Ying-Chun Liu,<sup>a</sup> Yan Xing,<sup>b</sup> Heng-Qing Jia<sup>b</sup> and Yong-Hua Lin<sup>b</sup>

<sup>a</sup> Department of Chemistry, Northeast Normal University, Changchun 130024, China.

E-mail: jfma@public.cc.jl.cn

<sup>b</sup> Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

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Two new compounds,  $[\text{CoL}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$  (**1**) and  $[\text{CoL}(\text{H}_2\text{O})_2(\text{CH}_3\text{CO}_2)_2] \cdot \text{H}_2\text{O}$  (**2**), were obtained from self-assembly of the corresponding metal salts with 1,1'-(1,4-butanediyl)bis(benzimidazole) (L). In **1**, each cobalt ion is coordinated to four nitrogen atoms from four molecules of L, and to two water molecules. Metal ions are bridged by L ligands to form infinite (4, 4) networks that contain 44-membered rings. The (4, 4) networks of **1** stack in a parallel fashion, resulting in the formation of large channels in the material. In **2**, each cobalt ion is coordinated to two N atoms from two L molecules, two water molecules and two carboxylate O atoms from two acetate anions. Each L molecule is coordinated to two cobalt ions, acting as a bridging ligand as in **1**. The bridged cobalt ions form an infinite zigzag chain structure.

Coordination polymers are currently of great interest due to their two and three-dimensional polymeric structures<sup>1</sup> that can endow them with special properties, such as electrical conductivity,<sup>2</sup> magnetism,<sup>3</sup> host–guest chemistry<sup>4</sup> and catalysis.<sup>5</sup> So far most of these materials are formed with rigid ligands, such as 4,4'-bipyridine<sup>6</sup> and pyrazine.<sup>7</sup> Most of these structures have relatively large voids and are of potential interest for guest–host interactions and molecular recognition. The study of flexible ligands is relatively rare,<sup>8</sup> and we are interested in coordination polymers containing flexible ligands. 1,1'-(1,4-Butanediyl)bis(benzimidazole) (L) has been used in the synthesis of polyamides,<sup>9</sup> however, the coordination chemistry of L has not been explored. Based on its structure, L can be used as a flexible divergent ligand to construct coordination polymer materials. Here we report the preparation and crystal structures of two new coordination polymers of L with cobalt salts, namely  $[\text{CoL}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$  (**1**) and  $[\text{CoL}(\text{H}_2\text{O})_2(\text{CH}_3\text{CO}_2)_2] \cdot \text{H}_2\text{O}$  (**2**).

## Experimental

All reagents were commercially available and used as received. The C, H and N microanalyses were carried out with a Carlo Erba 1106 elemental analyzer. The thermogravimetric analyses were carried out on a Perkin–Elmer TGA7 thermal analyzer in flowing nitrogen with a heating rate of 10 °C min<sup>-1</sup>. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm<sup>-1</sup> on a Mattson Alpha-Centauri spectrometer.

## Syntheses

**1,1'-(1,4-Butanediyl)bis(benzimidazole) (L).** Powdered NaOH (1.18 g, 30 mmol) and benzimidazole (3.50 g, 30 mmol) was added to 50 ml of acetone in a flask. After stirring the mixture, giving a clear solution, 1,4-dichlorobutane (1.88 g, 15 mmol) and NaI (0.1 g) were added to the solution, which was then stirred overnight at 50 °C. After the acetone was removed, 50 ml of distilled water was added to give a brown solid. The solid was collected and recrystallized from a

mixture of water and ethanol to give L as a white crystalline solid. Anal. calc. for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>: C, 74.46; H, 6.25; N, 19.30. Found: C, 74.21; H, 6.42; N, 19.81%.

**$[\text{CoL}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$  (**1**).** A solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.073 g, 0.25 mmol) in distilled water (5 ml) was overlaid in a test tube with a solution of L (0.145 g, 0.5 mmol) in MeOH (5 mL). After one week at room temperature, the pink crystals formed were collected, washed with water and methanol and dried in air. The compound is not soluble in water or common organic solvents. Yield 0.122 g (0.13 mmol, 52%). Anal. calc. for C<sub>36</sub>H<sub>56</sub>CoN<sub>10</sub>O<sub>16</sub>: C, 45.81; H, 5.98; N, 14.84. Found: C, 45.45; H, 5.92; N, 14.62%. IR (cm<sup>-1</sup>): 3420 m, 3098 m, 2941 w, 2360 m, 2342 m, 1615 m, 1515 s, 1464 s, 1373 vs, 1292 vs, 1256 s, 1199 s, 1011 w, 924 w, 745 vs, 634 w, 500 w, 427 m.

**$[\text{CoL}(\text{H}_2\text{O})_2(\text{CH}_3\text{CO}_2)_2] \cdot \text{H}_2\text{O}$  (**2**).** **2** was prepared analogously to **1** but with  $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$  (0.062 g, 0.25 mmol) in place of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . **2** does not dissolve in common organic solvents or water. Yield 0.075 g (0.14 mmol, 58%). Anal. calc. for C<sub>22</sub>H<sub>30</sub>CoN<sub>4</sub>O<sub>7</sub>: C, 50.68; H, 5.80; N, 10.74. Found: C, 50.92; H, 5.72; N, 10.92%. IR (cm<sup>-1</sup>): 3423 s, 2360 m, 2342 m, 1576 vs, 1512 s, 1464 vs, 1398 vs, 1338 m, 1292 w, 1259 w, 1231 w, 1197 w, 1011 w, 881 w, 750 s, 659 m, 430 w.

## X-Ray crystallography

Crystals obtained directly from the reaction mixture were suitable for single-crystal X-ray diffraction study. Diffraction intensities for complexes **1** and **2** were collected at 20 °C on a Siemens P4 diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) using the  $\omega - 2\theta$  scan technique. Lorentz polarization and absorption corrections were applied.<sup>10</sup> The structures were solved with the direct method of SHELXS-86<sup>11</sup> and refined with full-matrix least-squares techniques using the SHELXL-93 program.<sup>12</sup> Non-hydrogen atoms were refined anisotropically. Hydrogens on carbon atoms were generated geometrically, while the aqua hydrogen

**Table 1** Crystallographic and experimental data for **1** and **2**

	<b>1</b>	<b>2</b>
Formula	C <sub>36</sub> H <sub>56</sub> CoN <sub>10</sub> O <sub>16</sub>	C <sub>22</sub> H <sub>30</sub> CoN <sub>4</sub> O <sub>7</sub>
FW	943.84	521.43
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> /Å	15.290(3)	9.603(2)
<i>b</i> /Å	9.609(2)	15.914(3)
<i>c</i> /Å	16.956(3)	15.723(3)
$\beta$ /°	97.93(3)	97.17(3)
<i>U</i> /Å <sup>3</sup>	2467.4(9)	2384.0(8)
<i>Z</i>	2	4
<i>T</i> /°C	20(2)	20(2)
$\mu$ /mm <sup>-1</sup>	0.419	0.770
Measured reflections	5204	5572
Independent reflections ( <i>R</i> <sub>int</sub> )	3973 (0.0240)	4192 (0.0284)
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0637	0.0488
<i>wR</i> <sub>2</sub> (all data)	0.244	0.145

**Table 2** Selected bond lengths (Å) and angles (°) for **1** and **2**

[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> · 8H <sub>2</sub> O ( <b>1</b> )			
Co–Ow(1)	2.092(5)	Co–N(1)	2.132(4)
Co–N(3)	2.159(4)	Co–Ow(2)	2.202(6)
Ow(1)–Co–N(1)	92.7(1)	Ow(1)–Co–Ow(2)	180.0(0)
N(1a)–Co–N(1)	174.5(3)	Ow(1)–Co–N(3)	91.3(1)
N(1a)–Co–N(3)	90.4(2)	N(1)–Co–N(3)	89.4(2)
N(3)–Co–N(3a)	177.3(3)	N(3)–Co–Ow(2)	88.7(1)
N(1)–Co–Ow(2)	87.2(1)		
Symmetry code: <i>a</i> = − <i>x</i> + 1.5, <i>y</i> , − <i>z</i> + 1.5			
[CoL(H <sub>2</sub> O) <sub>2</sub> (CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> ] · H <sub>2</sub> O ( <b>2</b> )			
Co–O(1)	2.106(3)	Co–Ow(1)	2.112(3)
Co–O(3)	2.122(3)	Co–N(1)	2.143(3)
Co–N(2a)	2.148(3)	Co–Ow(2)	2.153(3)
O(1)–Co–Ow(1)	92.6(1)	O(1)–Co–O(3)	176.5(1)
Ow(1)–Co–O(3)	90.4(1)	O(1)–Co–N(1)	93.0(1)
Ow(1)–Co–N(1)	92.4(1)	O(3)–Co–N(1)	88.5(1)
O(1)–Co–N(2a)	85.8(1)	Ow(1)–Co–N(2a)	87.0(1)
O(3)–Co–N(2a)	92.8(1)	N(1)–Co–N(2a)	178.5(1)
O(1)–Co–Ow(2)	90.4(1)	Ow(1)–Co–Ow(2)	176.2(1)
O(3)–Co–Ow(2)	86.6(1)	N(1)–Co–Ow(2)	85.1(1)
N(2a)–Co–Ow(2)	95.6(1)		
Symmetry code: <i>a</i> = <i>x</i> − 1, − <i>y</i> + 2.5, <i>z</i> + 0.5			

atoms were not located. Analytical expressions for neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated.<sup>13</sup> The crystallographic data for the complexes are listed in Table 1, while selected interatomic distances and angles are given in Table 2. Drawings were produced with SHELXTL-Plus.<sup>14</sup>

CCDC reference number 440/201. See <http://www.rsc.org/suppdata/nj/b0/b004787m/> for crystallographic files in .cif format.

## Results and discussion

### Syntheses

With a 1 : 2 molar ratio of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O : L, crystals of **1** were isolated. A 1 : 1 product with a one-dimensional polymeric structure would be expected with a 1 : 1 molar ratio of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O : L, however the isolated crystals are also the 1 : 2 complex (**1**). This may be because the solubility of the 1 : 1 complex is too high to crystallize from the solution. When Co(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> · 4H<sub>2</sub>O was used in place of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, only the 1 : 1 complex (**2**) was isolated using either a 1 : 2 or 1 : 1 molar ratio of Co(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> · 4H<sub>2</sub>O : L. This may be caused by the low solubility of the 1 : 1 complex (**2**). Crystals of **2** formed immediately when Co(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> · 4H<sub>2</sub>O was reacted with L, and no further reactions between **2** and L occurred.

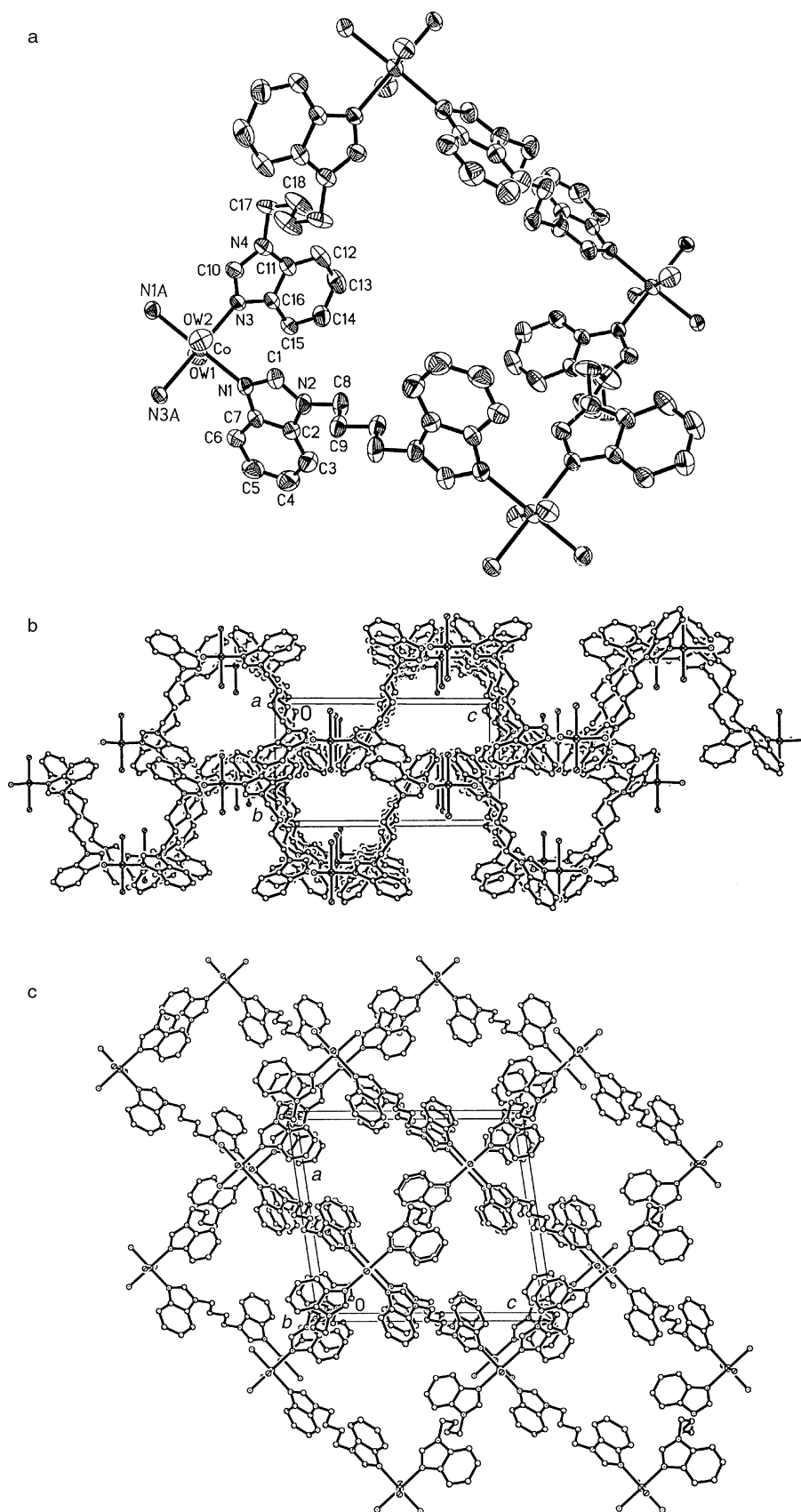
### Crystal structures

Part of the structure of compound **1** is shown in Fig. 1(a). Each cobalt ion is coordinated to four nitrogen atoms from four molecules of L, and to two water molecules that are *trans* to each other, leading to an octahedral coordination polyhedron. The Co–N distances of 2.132 and 2.159 Å are similar to the Co–N distances in other cobalt complexes.<sup>6a,i,8a,15</sup> The Co–O(water) distances of 2.092 and 2.202 Å are also similar to those in other cobalt complexes.<sup>6a,15</sup> The presence of an uncoordinated nitrate group is somewhat unexpected. In the related compounds, [Co(NO<sub>3</sub>)<sub>2</sub>(bpe)<sub>1.5</sub>],<sup>8a</sup> [Co<sub>2</sub>(bpy)<sub>3</sub>(NO<sub>3</sub>)<sub>4</sub>] · xH<sub>2</sub>O<sup>6i</sup> and [Co(NO<sub>3</sub>)<sub>2</sub>(bpee)<sub>1.5</sub> · 3CHCl<sub>3</sub>],<sup>15b</sup> the nitrate ion is coordinated to the cobalt ion. However, as in **1**, the nitrate ion of [Co(H<sub>2</sub>O)<sub>4</sub>(bpee)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> · 8/3H<sub>2</sub>O · 2/3bpee is uncoordinated.<sup>15b</sup> All of the water molecules and nitrate anions are interconnected through hydrogen bonds. There are two crystallographically independent L molecules in **1**. Both of them have an inversion center at the midpoint of two central methylene carbon atoms. Each L molecule is coordinated to two cobalt ions, bridging the metal ions to form infinite (4, 4) networks that contain 44-membered rings with a metal ion at each corner and a molecule of L at each edge [Fig. 1(a)]. The lengths of the opposite edges are equal (the edge lengths are 12.42 and 13.78 Å) and the orthogonal distances are 15.29 and 16.956 Å. The metal ions of the (4, 4) networks do not lie in the same plane, but form a layer having a thickness of 6.5 Å. This results in the intercalation of neighboring sheets [Fig. 1(b)]. The (4, 4) networks of **1** stack in a parallel fashion, resulting in the formation of large channels in the material [Fig. 1(c)]. The framework is positively charged and the channels are filled with nitrate ions and lattice water molecules. It is somewhat unexpected that no interpenetration occurs between the (4, 4) networks of **1**. It has been noted that this type of coordination polymer is highly likely to form interpenetration compounds if the cavity generated in this way is large enough. Many coordination polymers with (4, 4) network structures have been reported,<sup>6a,b,16</sup> but examples containing a flexible ligand are very rare.<sup>8b,17</sup>

Part of the structure of **2** is shown in Fig. 2(a). Each cobalt ion is coordinated to two N atoms from two L molecules, to two water molecules and to two carboxylate O atoms from two acetate anions, with a distorted octahedral geometry. The Co–N distances of 2.143(3) and 2.148(3) Å are similar to those in **1**. The Co–O (water) distances of 2.112(3) and 2.153(3) Å are also similar to those of **1**. The Co–O (acetate) distances are longer than the Co–O (bridging acetate ion) distances but shorter than the Co–O (chelating acetate ion) distances in Co(bipy)(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>.<sup>15a</sup> Each L molecule is coordinated to two cobalt ions, acting as a bridging ligand to form an infinite zigzag chain structure [Fig. 2(b)]. The distance between neighboring cobalt ions is 13.35 Å, which is similar to that in **1**.

### Thermogravimetric analysis

**1** and **2** were heated to 600 °C in N<sub>2</sub>. When the crystals of **1** were removed from the mother liquor, they immediately lost most of their water molecules. TGA of **1** was performed after most of the water molecules had evaporated. Even for the sample containing some water molecules, a weight loss corresponding to the remaining water was observed over the wide temperature range 25–160 °C. The skeleton of the (4, 4) network is stable up to 330 °C; the absence of a phase transition suggests that the integrity of the structure is preserved after liberation of the water. For **2**, the solvate water molecules and aqua ligands were lost in the range 87–194 °C (obs. 10.6%, calc. 10.4% weight loss by TGA). A dramatic weight loss corresponding to L ligands (obs. 56.1%, calc. 55.6% by TGA) was observed at 320 °C.



**Fig. 1** (a) The ring of the (4, 4) networks in **1**. (b) The intercalation between neighboring sheets of **1**. (c) The channels of **1**.

## Conclusion

Two new coordination polymers formed by the flexible bridging ligand 1,1'-(1,4-butanediyl)bis(benzimidazole) with cobalt

nitrate and cobalt acetate have been prepared and characterized.  $[\text{CoL}(\text{H}_2\text{O})_2(\text{CH}_3\text{CO}_2)_2] \cdot \text{H}_2\text{O}$  is composed of infinite polymeric chains while  $[\text{CoL}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$  shows a two-dimensional polymeric structure with a (4, 4) network having large channels.

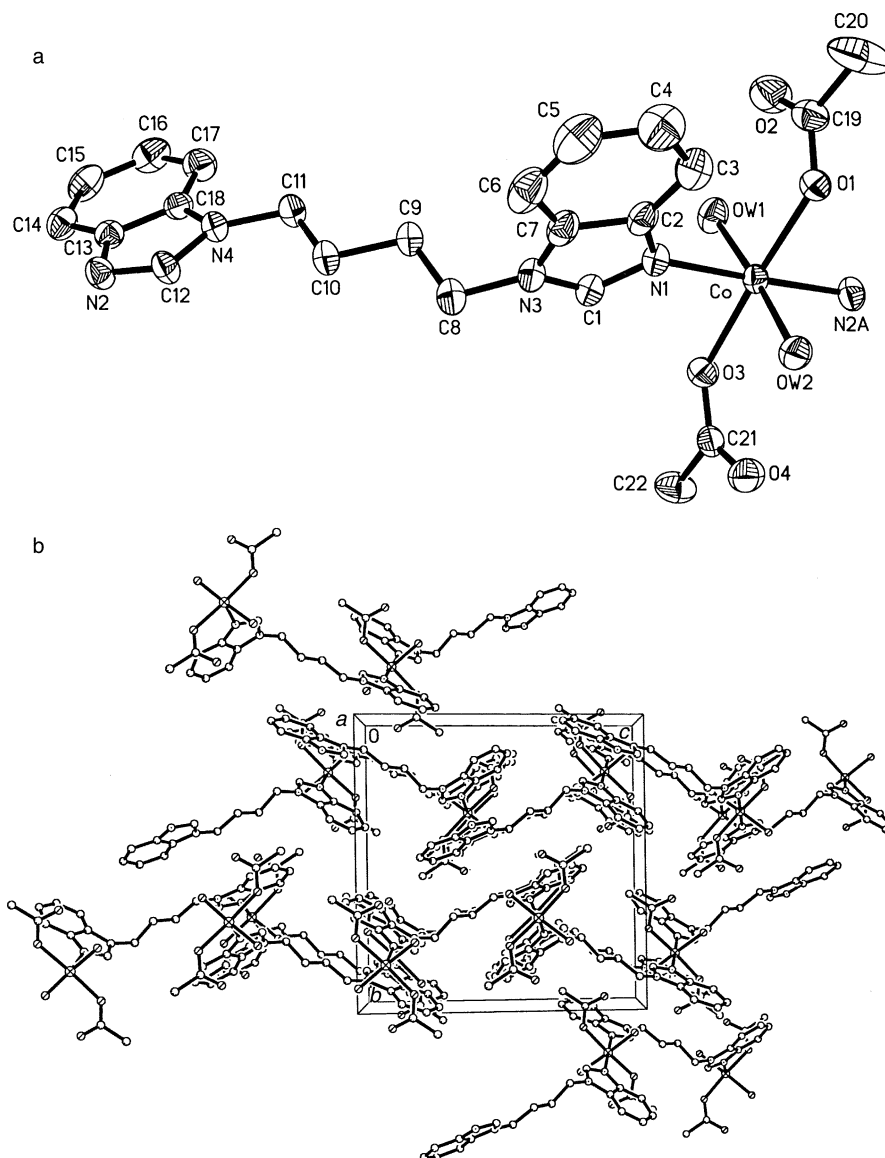


Fig. 2 (a) ORTEP drawing of the local coordination of Co in **2**. (b) The infinite zigzag polymeric chain of **2**.

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