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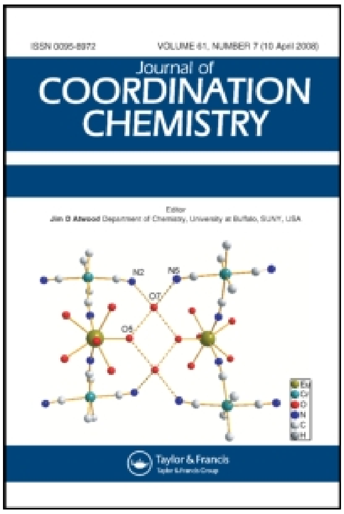

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Synthesis, characterization and crystal structures of two alkaline-earth metal complexes of olsalazine

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Two one-dimensional linear coordination polymers, $[Mg(L)\cdot 4(H_2O)]$ (H_2L = olsalazine) and **2** $[Ca(L)\cdot 4(H_2O)]$ were obtained from self-assembly of $CaCl_2$ or $MgSO_4$ with olsalazine and their structures determined by single crystal X-ray diffraction. Both complexes are one-dimensional polymers, for complex **1** with crystal data: $P2(1)/c$, $a = 9.5224(18)$, $b = 11.309(2)$, $c = 16.211(3)$ Å, $\beta = 106.648(3)^\circ$, $V = 1672.6(6)$ Å^3, $Z = 4$, $R_1 = 0.0695$, $wR_2 = 0.2183$, for complex **2** with crystal data: $P4(3)2(1)2$, $a = 10.4006(2)$, $b = 10.4006(2)$, $c = 32.0746(10)$ Å, $V = 3469.59(14)$ Å^3, $Z = 8$, $R_1 = 0.0332$, $wR_2 = 0.1015$. In the complexes, Mg and Ca adopt totally different coordination modes. Alkaline-earth Mg is six-coordinate octahedronal geometry, however, in **2**, the local coordination geometry around calcium atom can be best described as a slightly distorted pentagonal bipyramid crystallizing in a homo-chiral space group. Olsalazine in both compounds also adopts dissimilar coordination modes.

Keywords: Olsalazine; Crystal structure; Calcium complex; Magnesium complex

1. Introduction

Studies on the interaction between drugs and metal ions have special applications in medicine [1–4]. Metal complexes can improve the solubility of drugs in water [5] and increase their curative effect; olsalazine sodium can be more effectively absorbed than olsalazine [6]. Studying metal complexes of drugs, aids in understanding the coordination behavior of medicines, useful in pharmacology and in the search for better medicine. Olsalazine (3, 3-azo-bis (6-hydroxybenzoic acid), has been widely used to prevent and treat inflammatory bowel diseases, such as ulcerative colitis [7–9]. Although the sodium, potassium [10], calcium [11] and copper [12] complexes of

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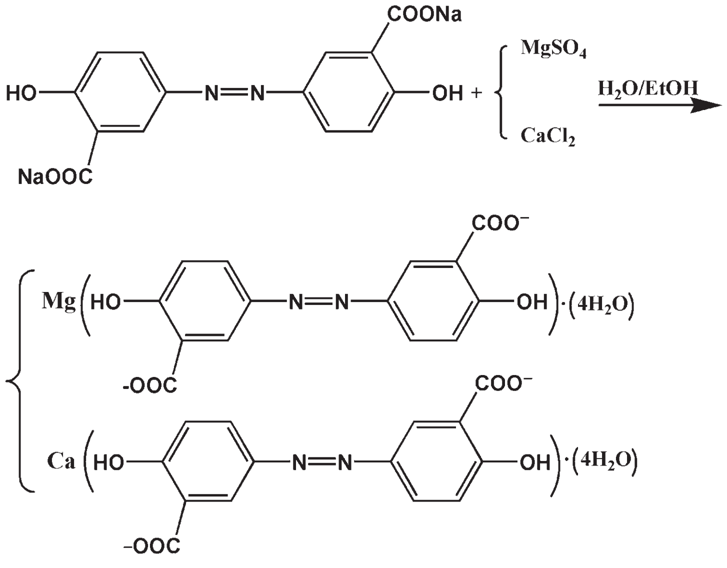
olsalazine have been reported, other complexes with this molecule have not been reported. In previous work, we have reported a series of Cd, Co and Zn complexes [13] of osalazine with the auxiliary ligand 1,10-phenanthroline. Variation of ligands for bridging and conformational preference as well as the metal ions has a profound influence on the polymeric structures obtained [14]. Herein we report the self-assembly of olsalazine with different alkaline-earth metal salts, which yields two different one-dimensional coordination polymers **1** [Mg(L) · 4(H2O)] (H2L = olsalazine) and **2** [Ca(L) · 4(H2O)], their solid state structures and thermal stabilities.

2. Experimental

Olsalazine sodium was purchased locally; other chemicals and solvents were purchased from Aldrich and used as received. The FT-IR spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on a Nicolet Inpact 170S FT-IR spectrometer. Elemental analysis was performed on Perkin-Elmer 240C elemental analyzer.

2.1. *Synthesis of [Mg(L) • 4(H_2O)] and 2 [Ca(L) • 4(H_2O)]*

Title compounds were prepared as shown in scheme 1. A mixture of MgSO4 (or CaCl2) and olsalazine sodium with molar ratio 1 : 1 ethanol and water (V : V = 2 : 1) was stirred at room temperature for eight hours, then filtered. Beautiful golden block-like crystals were obtained from the filtrate about two weeks later. For **1**, yield: 0.544 g (89%) on the basis of olsalazine sodium. Calc. for $C_{14}H_{16}N_2O_{10}Mg$ (%): C, 42.36; H, 4.03. Found (%): C, 42.50; H, 4.01. IR (KBr, cm^{-1}) 3438(m), 2922(w), 2361(m),



Scheme 1. The preparation of **1** and **2**.

1927(w), 1588(s), 1484(s), 1445(vs), 1370(w), 1314(s), 1284(vs), 1005(m), 836(m), 796(w), 685(w), 497 (s), 466(w). For **2**, yield: 0.423g (76%) on the basis of olsalazine sodium. Calc. for C_{14} H_{16} N_2 O_{10} Ca (%): C, 40.74; H, 3.88. Found (%): C, 41.32; H, 3.59. IR (KBr, cm^{-1}) 3438(m), 1589(s), 1480(s), 1441(vs), 1370(m), 1314(s), 1284(vs), 1136(m), 1005(m), 836(m), 796(w), 685(w), 497(s), 466(w).

2.2. *Single crystal structure determination*

A golden block-like crystal of **1** with dimensions 0.408 mm × 0.192 mm × 0.117 mm was selected on a Bruker P4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 292 K using the θ–2θ scan technique. The data were corrected for Lp and absorption effects. The crystal structure was solved using direct methods with the SHELXS-97 program [15]. Subsequent difference Fourier syntheses enabled all heavier atoms to be located. All hydrogen atoms were located from the successive difference Fourier syntheses. The non-hydrogen atoms were finally refined with anisotropic displacement parameters by full-matrix least-squares techniques [16]. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The same manipulation for **2** was conducted as described above. Detailed information about the crystal data and structure determination for both compounds are summarized in table 1.

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	2
Empirical formula	$C_{14}H_{16}MgN_2O_{10}$	$C_{14}H_{16}CaN_2O_{10}$
F_w	396.6	412.37
T/K	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P4(3)2(1)2$
a (Å)	9.5224(18)	10.4006 (2)
b (Å)	11.309(2)	10.4006 (2)
c (Å)	16.211(3)	32.0746 (10)
β (°)	106.648(10)	90
V (Å^3)	1672.6(6)	4.6974(9)
Z	4	8
ρ (Calcd.) (Mg m^{-3})	1.575	1.579
μ (Mo-Kα) (mm^{-1})	0.167	0.421
F(000)	824	1712
Crystal size (mm^3)	0.104 × 0.134 × 0.202	0.211 × 0.219 × 0.251
θ range for data collection (°)	2.23–25.99	2.06–27.80
Index ranges	$-11 \le h \le 11$, $-13 \le k \le 10$, $-19 \le l \le 18$	$-13 \le h \le 13$, $-10 \le k \le 13$, $-33 \le l \le 41$
Completeness to theta	99.3%	97.0%
Reflections collected	8857	20376
Independent reflections	3260 [R (int) = 0.0279]	3909 [R (int) = 0.0217]
Data/restraints/parameters	3260/6/276	3909/6/276
Goodness-of-fit on F^2	1.131	0.908
Final R indices [$I > 2\sigma$ (I)] (6699)	$R_1 = 0.0695$, $wR_2 = 0.2120$	$R_1 = 0.0332$, $wR_2 = 0.0974$
R indices (all data)	$R_1 = 0.0827$, $wR_2 = 0.21837$	$R_1 = 0.0391$, $wR_2 = 0.1015$
Min., max. ρ (e Å^{-3})	0.360, −0.432	0.433, −0.633

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

Mg(1)–O(3W)	2.035(4)	Mg(1)–O(1W)	2.049(4)
Mg(1)–O(4W)	2.054(3)	Mg(1)–O(4)	2.083(3)
Mg(1)–O(2W)	2.083(4)	Mg(1)–O(3A)	2.091(3)
Ca(1)–O(2W)	2.3060(19)	Ca(1)–O(3W)	2.3164
Ca(1)–O(3A)	2.3625(14)	Ca(1)–O(3W)	2.3689(18)
Ca(1)–O(1W)	2.3784(18)	Ca(1)–O(5)	2.4282(15)
Ca(1)–O(5)	2.5322(14)		
O(3W)–Mg(1)–O(1W)	176.32(16)	O(3W)–Mg(1)–O(4W)	92.56(15)
O(1W)–Mg(1)–O(4W)	90.79(15)	O(3W)–Mg(1)–O(4)	88.34(14)
O(4W)–Mg(1)–O(4)	178.49(14)	O(3W)–Mg(1)–O(2W)	89.690(16)
O(3W)–Mg(1)–O(2W)	92.04(18)	O(4W)–Mg(1)–O(2W)	86.36(15)
O(1W)–Mg(1)–O(4)	88.35(14)	O(3W)–Mg(1)–O(3A)	88.57(15)
O(1W)–Mg(1)–O(3A)	89.71(17)	O(4W)–Mg(1)–O(3A)	93.33(14)
O(4)–Mg(1)–O(3A)	87.90(12)		
O(2W)–Ca(1)–O(3W)	172.53(9)	O(2W)–Ca(1)–O(3A)	96.17(9)
O(3W)–Ca(1)–O(3A)	91.26(8)	O(2W)–Ca(1)–O(4W)	95.99(8)
O(3W)–Ca(1)–O(4W)	86.43(8)	O(3A)–Ca(1)–O(4W)	75.96(6)
O(2W)–Ca(1)–O(1W)	90.49(8)	O(3W)–Ca(1)–O(1W)	83.18(8)
O(3A)–Ca(1)–O(1W)	152.42(7)	O(4W)–Ca(1)–O(1W)	76.74(8)
O(2W)–Ca(1)–O(5)	92.87(7)	O(3W)–Ca(1)–O(5)	88.63(7)
(O(3A)–Ca(1)–O(5)	73.25(5)	O4W)–Ca(1)–O(5)	148.68(6)
O(1W)–Ca(1)–O(5)	133.26(7)	O(2W)–Ca(1)–O(6)	8.70(7)
O(3W)–Ca(1)–O(6)	87.46(7)	O(3A)–Ca(1)–O(6)	125.38(5)
O(4W)–Ca(1)–O(6)	157.94(6)	O(1W)–Ca(1)–O(6)	81.49(6)
O(5)–Ca(1)–O(6)	52.13(4)		

Their selected interatomic distances and bond angles are given in table 2. CCDC NO.: 633035 (**1**), 633034 (**2**).

3. Results and discussion

The IR spectra of both compounds display three strong absorptions at 1588(s), 1484(s), 1445(vs) cm^{-1} for **1** and 1589(s), 1480(s), 1441(vs), cm^{-1} for **2**, due to the characteristic υ_{as} (COO) and υ_s (COO) stretching modes of carboxylate groups [17]. There are broad bands around 3438 cm^{-1} observed in **1** and **2**, suggesting water persists in both compounds.

The one-dimensional structure of **1** was revealed by X-ray single-crystal structure analysis. Crystallographic data of **1** (as shown in table 1) indicates that [Mg(L)($4H_2O$)]n **1** belongs to a monoclinic system, space group $P2(1)/c$ and $Z=4$. Figure 1 presents the local coordination environment around magnesium as six-coordinate with two monodentate carboxylate groups of different olsalazine ligands and four water molecules. The coordination geometry can be best described as a distorted octahedron with a plane constructed by O(3A), O1W, O2W and O3W and apical sites occupied by O(4) and O4W with angle (O(4)–Mg(1)–O4W) 178.5°. Each olsalazine in **1** is a double monodentate ligand linking two Mg atoms resulting in a 1 D zig–zag linear structure. All magnesium atoms stand in the vertex of the catenarian structure (as shown in figure 2).

Totally different from **1**, the crystal of [Ca(L) $\cdot$ 4(H_2O)] **2** belongs to a tetragonal crystal system, chiral space group $P4(3)2(1)2$ and $Z=8$. The calciums in **2** adopt

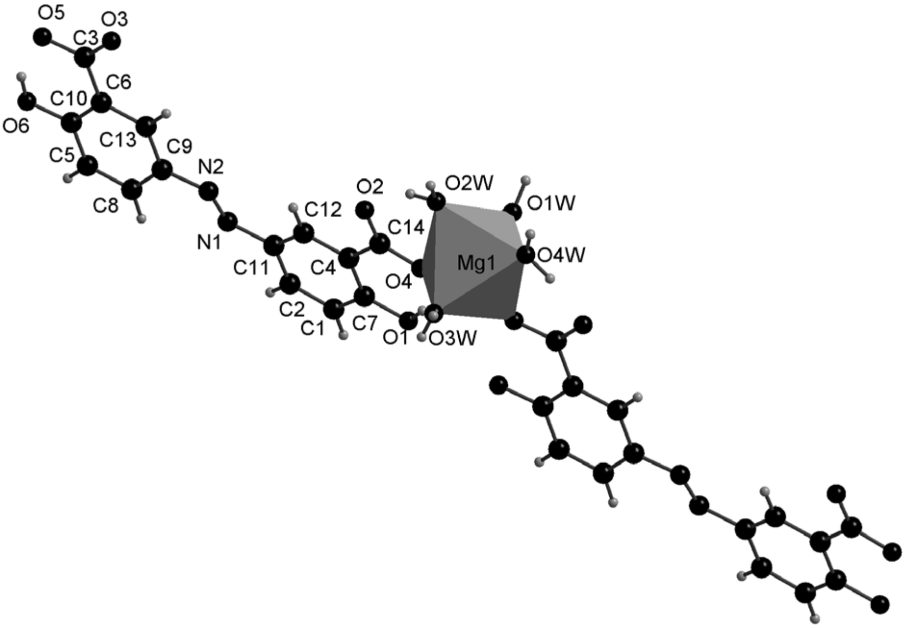


Figure 1. Polyhedral representation of **1** showing the local coordination geometry around Mg as a slightly distorted octahedron.

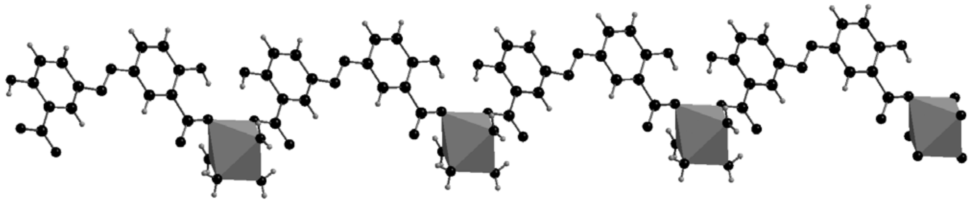


Figure 2. One-dimensional zigzag infinite linear structure of **1** with the octahedron representing Mg.

pentagonal bipyramid coordination mode with one monodentate carboxylate (O3A), one bidentate carboxylate (O5 and O6) of different olsalazine ligands and four water molecules (as shown in figure 3). Olsalazine in **1** was a bidentate bridge, but in **2** is a tridentate bridge linking two calcium atoms in a 1 D zig–zag linear structure (as shown in figure 4).

The distance of chelating oxygen atoms Ca(1)–O(6) (2.532(14) Å) is longer than that of Ca(1)–O(5) (2.428(14) Å) suggesting that the Ca center in **2** is highly unsymmetrical. All other Ca–O bond distances in **2** (2.306–2.5322 Å) are similar to those found in other Ca(II)[19] complexes and within the range for normal Ca–O distances. Similarly, the Mg–O (2.035–2.091 Å) bond distances are normal [20].

Strong H-bonds (O–H $\cdots$ O) exist between uncoordinated oxygen atoms from carboxylate groups and hydrogen atoms of water such as O1W–H4A $\cdots$ O4, O2W–H2WB $\cdots$ O2A (figure 5). Simultaneously, between the phenyl rings there exist

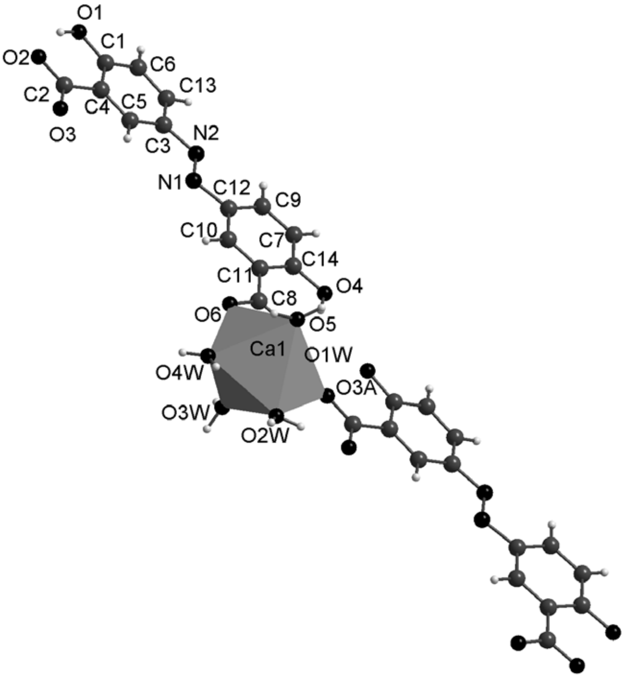


Figure 3. Polyhedral representation of **2** showing the local coordination geometry around Ca as a slightly distorted pentagonal bipyramid.

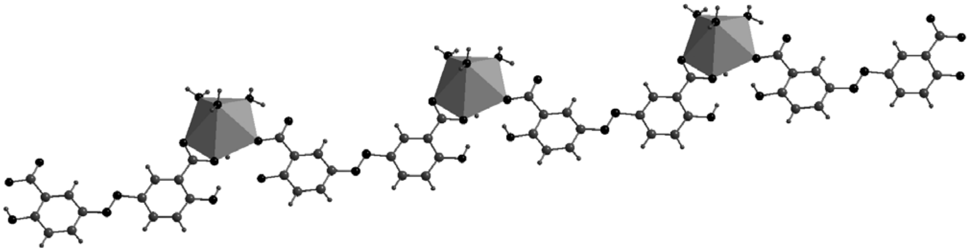


Figure 4. One-dimensional zigzag infinite linear structure of **2** with the pentagonal bipyramid representing the Ca.

weak supramolecular π–π stacking interactions (figure 5), an important factor in the supramolecular assembly and stabilization of the lattice [18].

To study the thermal stability of **1** and **2**, thermo-gravimetric analysis (TGA) was performed on polycrystalline samples (as shown in figures 6 and 7). For **1**, there are three distinct weight loss steps for the removal of coordinated water. Firstly, one strikingly clean weight loss step occurred at ca. 69 ~ 92°C (4.45% loss) corresponding to the removal of one water per formula unit (4.51% calculated). Then, another obvious weight loss (4.53%) happened at ca. 117°C corresponding to loss of a second coordinated water. Lastly, a clear weight loss (9.3%) between 175°C and 205°C suggests

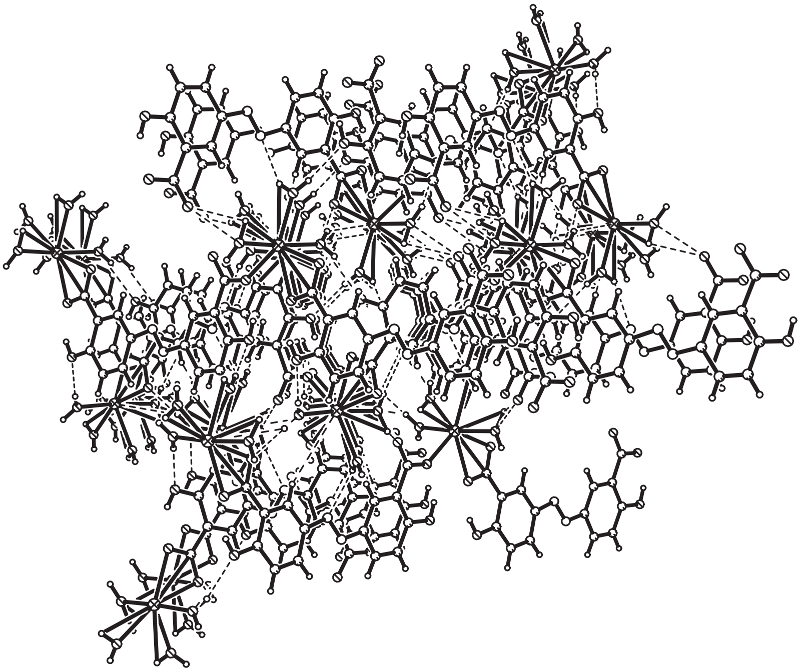


Figure 5. A simple hydrogen-bonding network of **2**.

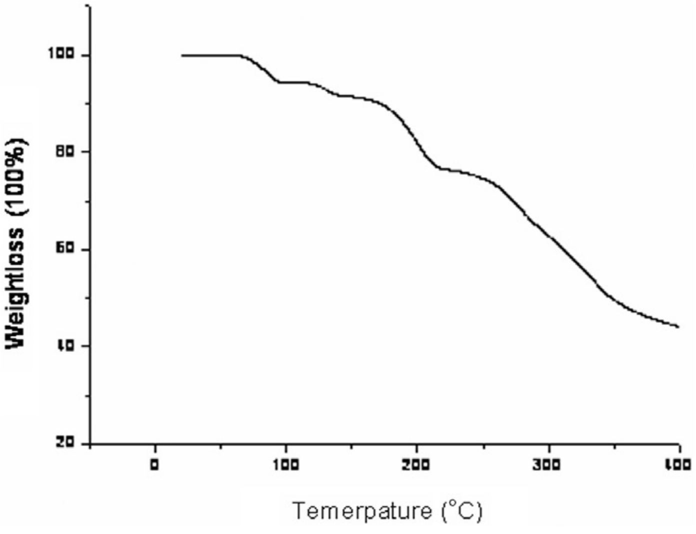


Figure 6. The thermo-gravimetric analysis (TGA) curve for **1**.

two water molecules removed. Compound **2** is stable up to 122°C. Clean weight loss at ca. 122 ~ 187°C (17.35% loss) corresponds to removal of four water molecules per formula unit (17.46% calculated). Another obvious weight loss happened at 201°C. Beyond 530°C, the decomposition was apparent.

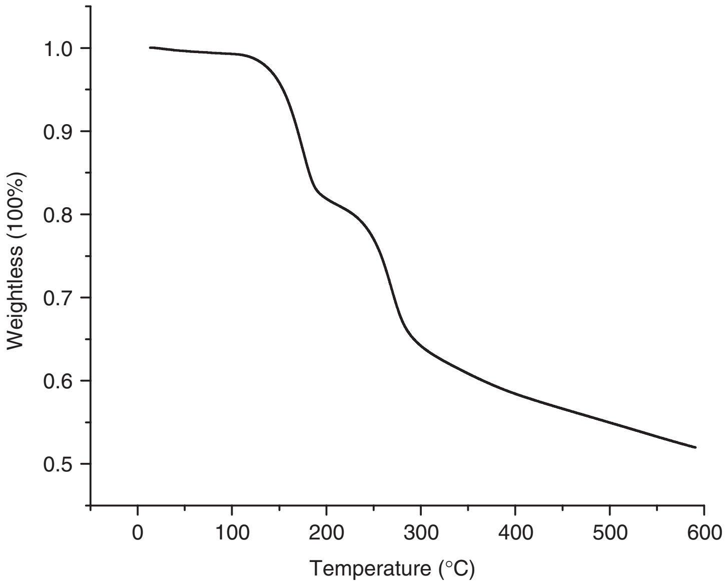


Figure 7. The thermo-gravimetric analysis (TGA) curve for **2**.

In conclusion, we have synthesized the first $\mathrm{Mg^{II}}$ and $\mathrm{Ca^{II}}$ coordination polymers based on the medicine olsalazine as a building block. The complexes exhibit dissimilar coordination behavior. Such studies impact understanding of the pharmacology of olsalazine and the search for better medicine.

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