COORDINATION POLYMER OF STRONTIUM (II) BASED ON PHTHALIC ACID AND PYRAZINE ADDUCT


M.Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan
*ASOIU, Research Institute “Geotechnological Problems of Oil, Gas, and Chemistry"

*qudrataliyeva@gmail.com

Received 18.01.2022
Accepted 22.02.2022

The coordination polymer of Sr (II), with the chemical formula of [SrL₂(H₂O)₉]n (L = phthalic acid anion and L₂ = pyrazine), have been synthesized by the interaction of sodium phthalate with a water-soluble strontium salt and pyrazine in the aqueous medium with further evaporation of an aqueous solution and characterized by IR spectroscopic, elemental, single-crystal X-ray diffraction and thermal analysis. The results of XRD analysis showed that the synthesis product has a single-phase and is well-identified by means: 12.73; 11.41; 9.04 showing that the unit cell parameters of this compound are approximately equal to a = 12.74, b = 11.41, and c = 9.04 Å. IR spectroscopic studies showed that phthalate anion in polymer acts as a chelate and bridging ligand. Thermographic analysis showed that the polymer is stable up to a temperature of ~200°C.

Keywords: polymer, phthalic acid, adduct, IR-spectrum, thermogram, structure, X-ray diffraction pattern.
doi.org/10.32737/0005-2531-2022-3-57-62

Introduction

Coordination polymers include a large family of compounds formed by central metal ions linked to a variety of ligands by coordination bonds. They have attracted much attention over the last decade due to their remarkable structures and, more importantly, their potential applications in catalysis, gas storage, luminescence, and sensing, among others [1–4]. Their final solid-state structure is driven by a self-assembly process where mono-, bi-, or three-dimensional structures are formed depending on the selected building blocks. The building blocks of the coordination polymers determine their physical and chemical properties [5–8].

Interestingly, one- or two-dimensional coordination polymers can organize their three-dimensional architecture by means of supramolecular interactions, frequently hydrogen bonding, or less directional Van der Waals forces. Nevertheless, the formation of self-assembled large supramolecular aggregates is also regulated by supramolecular interactions involving aromatic rings. In this regard, C–H⋯π [9], π⋯π stacking [10–12], cation⋯π [13], anion⋯π [14–17], and lone pair⋯π [18–20] interactions are prominent binding forces [21] that have been successfully used for building solid-state networks [22]. The proper understanding of these forces is important not only for rationalizing the existing solid-state architectures of these compounds but also to design and predict new supramolecular formations based on one-dimensional coordination polymers.

Based on the above, we have synthesized and investigated by X-ray, IR spectroscopic, and differential thermal analyzes the pyrazine adduct of the new coordination polymer Sr (II) with phthalic acid.

Materials and Methods

Materials

The reagents were purchased from commercial sources and used without further purification. Freshly boiled, bidistilled water was used throughout the synthesis of the compound.

Instruments

The radiograph was obtained on a Com- mander Sample ID (coupled two thet/theta) WL/1.54060 radiograph. Elemental analysis was performed on a Peckin-Elmer elemental analyzer.
Thermogravimetric analysis (TGA) data were obtained under nitrogen atmosphere in the temperature range from 20°C up to 850°C at a heating rate of 10°C/min with a DTG-60 N thermal analyzer NETZCH STA 449F3STA449F3A-0836-M (range 24/10.0 (k/min/800). IR spectra (KBr disk) were obtained on a SPECORD-MBO in 4000-400 cm\(^{-1}\) area.

Preparations

General Procedure

The compound was prepared by interacting with stoichiometric amounts of metal and ligand in an aqueous solution. To obtain a coordination polymer, we took 0.001 mol phthalic acid and 100 ml of distilled water and then added a portion of 0.002 mol sodium bicarbonate powder by heating. After complete dissolution of the phthalic acid, a solution of 0.001 mol Sr(NO\(_3\))\(_2\) (GOST 542950) and 0.001 mol of pyrazine were added. The resulting solution was allowed to cool to room temperature, filtered, and kept undisturbed for crystallization. Transparent single crystals were obtained after a week. The crystals were collected by filtration, washed with cold distilled water, and dried in the air. Product yield was 70%. The chemical formula of the obtained compound was established based on X-ray phase, elemental, differential thermal (DTA), and IR spectroscopic analyses.

X-ray diffraction analysis

The X-ray diffraction pattern of the synthesized compound is shown in Figure 1.

As can be seen from the figure, the obtained compound is highly crystalline, and most intense peaks are located at the range of 0-600. To determine the unit cell parameters, the Pawley method of the Topas 4.2 program was used. The refined unit cell parameters are as follows*:

- R-Bragg: 0.514
- Spacegroup: P2
- Cell Volume (Å\(^3\)): 1132.28(68)
- Lattice parameters:
  - a (Å): 16.745(5)
  - b (Å): 5.356(2)
  - c (Å): 13.071(4)
  - beta (°): 105.03(3)

* These parameters agree well with the diffractogram. However, taking into account the rather large values of the cell parameters, it is desirable to determine the parameters from single crystals.

IR spectroscopic analysis

The IR spectra of the complex compound are shown in Figure 2.

As seen from the figure, in the spectrum range of 1700-1310 cm\(^{-1}\), in particular, at 1586 and 1548 cm\(^{-1}\) absorption bands are referred to asymmetric stretching vibrations of carboxyl groups (C = O) and bands at 1455 and 1377 cm\(^{-1}\) to symmetric vibrations (C-O) of the phthalic acid anion. The absorption band values indicate that carboxyl groups are differently linked with the central atom.

Fig. 1. X-ray diffraction pattern of the coordination polymer Sr (o-C\(_6\)H\(_4\) (COO)\(_2\))·(C\(_4\)H\(_4\)N\(_2\))\(_{0.5}\) (H\(_2\)O)\(_{0.36}\).
A difference of values $\Delta [\nu_a (\text{CO}_2) – \nu_c (\text{CO}_2)]$ is 170 and 130 cm$^{-1}$, respectively. These values are in good agreement with the values of bidentate bridging complexes. So, we can confidently say that in this complex, in the same molecule, the carboxyl groups of the phthalic acid anion with the central atom are linked by chelate-bridging ($\Delta = 170$ cm$^{-1}$) and chelate-bidentate bonds ($\Delta = 130$ cm$^{-1}$).

As seen from the spectra, in the 3600–3200 cm$^{-1}$, a broad absorption band is also observed, referred to as asymmetric and symmetric vibrations of OH groups of water molecules [20]. This is evidence that water molecules of crystallization are present in the complex. In this spectrum region, two distinct bands are observed at 3246.78 and 3612.36 cm$^{-1}$, which clearly refer to pyrazine, more precisely, to M-N bonds. Usually, high-frequency bands are not sensitive to metal substitution, as they are associated with the vibrations of the aromatic rings of the ligand. In this case, the primary attention is paid to the low-frequency regions where the bands of $\nu$ (M-N) and other vibrations with the participation of a metal atom lie. However, it was not easy to attribute $\nu$ (M-N) empirically since some ligand vibrations are located in the same frequency range. Despite the above, a comparison of the complex compound’s IR spectra with the pyrazine’s IR spectra showed that the absorption band at 3080 and 4469 cm$^{-1}$ in pyrazine noticeably increased 3246.78; 3612.36 cm$^{-1}$ in the complex. This proves that both nitrogen atoms in pyrazine are linked with metal.

**Thermogravimetric Analysis**

The thermogram of the complex compound is shown in Figure 3.

The complex compound is stable up to a temperature of 90$^\circ$C. In the temperature range of 90-125$^\circ$C with a maximum of 109$^\circ$C, a clear, shallow, wide endothermic effect is observed in the DTG curve, which corresponds to the removal of 0.36 mol H$_2$O. At this stage, the experimental weight loss is 1.96% (calculated 2.17%). The low-temperature removal and a small amount of mass force us to assume that this is the loss of water molecules of crystallization located in crystallographic pores of the complex compound. After removing water, the complex compound is stable up to a temperature of 200$^\circ$C. In the temperature range of 200-250$^\circ$C, the process of pyrazine removal occurs, which is accompanied by a clear endothermic effect with a maximum of 216$^\circ$C. In this case, the experimental weight loss is 12.5% (calculated 13.42%) and corresponds to the removal of 0.5 mol pyrazine. In a wide temperature range of 250–900$^\circ$C, decomposition of the non-adduct complex occurs by autocatalytic mechanism, and the organic part of the molecule burns out, which is experimentally 41.18% (calculated 43.74%). These processes are accompanied by an exothermic effect with a maximum of 435; 548; 715; 745 and 849$^\circ$C.

![Fig. 2. IR spectra of the coordination polymer Sr (o-C$_4$H$_4$(COO)$_2$)(C$_4$H$_4$N$_2$)$_{0.5}$(H$_2$O)$_{0.36}$.](image-url)
It should be noted that during the decomposition of the complex compound in a wide temperature range of 534–591°C, a stable phase is formed, which could not be accurately identified, but we assume that it is strontium carbonate. After 591°C, the assumed strontium carbonate decomposes into SrO and CO2. It should also be noted that the percentage weight of the released CO2 (8.0% (mass) is much less than its theoretical value (14.75% (mass). Thus, the final thermolysis product is SrO.

Studies show that the chemical formula resulting from differential thermal analysis, Sr(o-C6H4(COO)2)·0.5C4H4N2·0.36H2O, agrees with the chemical formula obtained from the results of elemental analysis. The scheme of solid-phase transformation of a complex compound can be represented in the following form:

\[
\begin{align*}
\text{Sr}(o-C_6H_4(COO)_2) & \xrightarrow{105^\circ C(90-125^\circ C)} \text{Sr}(o-C_6H_4(COO)_2) \cdot 0.5C_4H_4N_2 \cdot 0.36H_2O \\
& \xrightarrow{216^\circ C(200-250^\circ C)} \text{Sr}(o-C_6H_4(COO)_2) \\
& \xrightarrow{200-250^\circ C(435;517^\circ C)} \text{SrCO}_3 \xrightarrow{>591^\circ C} \text{SrO}
\end{align*}
\]

The results of physicochemical studies have shown that the low temperature of water removal and its small amount indicates that it is the water of crystallization and should be located in crystallographic pores and distributed non-statistically.

Pyrazine behaves like pyridine, as in other metal carboxylates [21, 22]. It can completely displace not only coordination but also crystallization water molecules from the crystal lattices.

The general arrangement of strontium and oxygen atoms in the polymer chain is shown in Figure 4.

It should be noted that such an arrangement of strontium and oxygen atoms in the chain is quite characteristic for strontium complexes and other alkaline earth metals [23, 24].

As seen from Figure 4, the coordination polyhedron of the strontium atom is formed by six oxygen atoms of two carboxylate groups of the phthalic acid anion, of which one forms a chelate ring with strontium, and the other forms a chelate ring with the same atom and a bridge with neighboring strontium atoms. It should be noted that seven-vertex is a rare coordination polyhedron for strontium (2+) ions. Apparently, this is due to the coordination of pyrazine, which binds parallel polymeric chains and leads the one-dimensional chains into a two-dimensional layered assembly (Figure 5).
Fig. 4. One-dimensional polymer chain of a complex compound Sr(о-C₆Н₄(COO)₂)(C₆Н₄N₂)₀.₅(H₂O)₀.₃₆

Fig. 5. Two-dimensional polymer chain of a complex compound Sr(о-C₆Н₄(COO)₂)(C₆Н₄N₂)₀.₅(H₂O)₀.₃₆

References

FTAL TÜRŞUSU VƏ PİRAZİNLƏ Sr (II) KOORDİNASİON POLİMERİ


Ftal turşusunun natrium duzu suda hall ollan stronsium duzu və pirazinin suda məhlulunun qarşılıqlı təsirindən buxarlarıması ilə gənən reaksiyasında koordinasiya polimer olan Sr(II) \{Sr_{n}(L_{2})_{m}(H_{2}O)_{n}a\}a (L_{1}=fтал turşusu anionu, L_{2}=pirazin) sintez olunmuşdur. Alınan monokrystal IQ spектral, element analizi, rentgenfaza analizi (RFA) və termiki analiz (DTA) metodları ilə tədiq olunmuşdur. Rentgenfaza analizi göstərir ki, sintez olunan məhsul bir fəzdədir və piklər 12.73; 11.41; 9.04 maksimumları altında xas identifikasiya \şərərə. Bu onu göstərir ki, elementar qafəsin parametrləri təqribən a=12.74, b=11.41 və c=9.04 Ǻ-də barədədir. IQ-spektər analizindən görünür ki, polimerdə lişən kimi ftal turşusu xelat, xelat-kürlü rolunu oynayır. Termiki analiz nəticəsindən görünür ki, bu polimer 200°C-cə qədər davamlıdır.

Açar sözlər: polimer, fthal turşusu, addukt, IQ spектр, termoqramma, quruluş, rentgenoqramma.

КООРДИНАЦИОННЫЙ ПОЛИМЕР СТРОНЦИЯ (II) НА ОСНОВЕ ФТАЛЕВОЙ КИСЛОТЫ И ПИРАЗИНОВОГО АДДУКТА

Б.Т.Усубалиев, Д.Б.Тагиев, Г.М.Алиева, М.К.Муншива, С.Я.Рахманова, А.Н.Азизова, Н.А.Маммадова, Г.Ф.Маммадова, К.А.Мансурова, Ф.Б.Алиева, С.Р.Алиева

Координационный полимер Sr(II) \{SrL_{n}(L_{2})_{m}(H_{2}O)_{n}a\}a (L_{1}=анион фталевой кислоты и L_{2}=пиразин), был синтезирован взаимодействием натриевой соли фталевой кислоты с водорастворимой солью стронция и пиразином в водной среде с дальнейшим испарением водного раствора и охарактеризован методами ИК-спектроскопии, элементарного анализа, дифракции рентгеновских лучей (РФА) на монокристаллах и термического анализа (ДТА). Результаты РФА показали что продукт синтеза состоит из одной фазы и хорошо идентифицируется под максимумами 12.73; 11.41; 9.04 показывающими, что параметры элементарной ячейки данного соединения приблизительно равны a=12.74, b=11.41 и c=9.04 Å. ИК-спектроскопическое исследование показало, что в полимере фталат действует как хелат и хелат-мостиковый лиганд. Термографический анализ показал, что полимер устойчив до температуры +200°C.

Ключевые слова: полимер, фталевая кислота, аддукт, ИК-спектр, термограмма, структура, рентгенограмма.