Preparation and Characterization of 1,2,3,4- Butane four Carboxylate Transition Metal Complexes

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Abstract. 1,2,3,4- butane four carboxylic acids ( Na₄C₆H₇O₈ ) is mainly used to prepare photosensitive materials, medical polymer materials and functional polymer membrane materials. As a permanent finishing agent, 1,2,3,4- butane four carboxylic acid plays an irreplaceable role. In this paper, the preparation of metal complexes by the reaction of 1,2,3,4-butanetetra-carboxylic acid tetrasodium salt ( Na₄C₆H₇O₈ ) with transition metals is described. The composition and structure of the prepared metal complexes were characterized by infrared spectroscopy, thermogravimetric analysis and elemental analysis. At the same time, through the analysis of thermogravimetric curves, the order of thermal stability of metal complexes is (from large to small): Co₂C₆H₈O₈·2H₂O > Cd₂C₆H₈O₈·2H₂O > Mn₃C₆H₈O₈·2H₂O > Ni₃C₆H₈O₈·2H₂O > Zn₃C₆H₈O₈·2H₂O > Cd₂C₆H₈O₈·2H₂O > Cu₂C₆H₈O₈·2H₂O.

Keywords: Transition metal complexes; thermogravimetric analysis; 1,2,3,4- butane four carboxylic acid; IR spectra

1,2,3,4-butanetetra-carboxylic acid ( Na₄C₆H₇O₈ ) is mainly used to prepare photosensitive materials, medical polymer materials and functional polymer membrane materials. As a permanent calendering agent, 1,2,3,4-butanetetra-carboxylic acid has no formaldehyde in itself. Cotton and silk articles treated by it can obtain wrinkle-resistance, solid shape and ironing-free properties. At present, the synthesis methods of 1,2,3,4-butanetetra-carboxylic acid have been reported in China, but the literature on transition metal complexes of 1,2,3,4-butanetetra-carboxylic acid is less. Therefore, this paper will further study and prepare metal complexes [1] Co, Cu, Ni, Mn, Zn, Cd and so on.

1 Experiment

1.1 Major reagents

(1) 1,2,3,4- butane four carboxylic acid ( Na₄C₆H₇O₈ ).
(2) Two times distilled water.
(3) NaOH, Cd(NO₃)₂·4H₂O (the transition metal chlorides are all analytically pure).

1.2 Preparation of transition metal complexes of 1,2,3,4- butane four carboxylic acid with Cu as an example

In the preparation of copper, the first step is to weigh the amount of H₂C₆H₈O₈ molten water, add 30% NaOH water solution while stirring, cool it, adjust the acidity and alkalinity to PH5-6, and concentrate the reaction solution. After cooling, the crystallization of 1,2,3,4- butane four carboxylic acid will be obtained. The white powder of Na₄C₆H₇O₈ was obtained by drying it at 90 °C for 12 hours, and then it was put into a dryer for use. At this time, the quantitative Na₄C₆H₇O₈ is weighed and dissolved in water. After stirring and adding CuCl₂ to the aqueous solution, it should be noted that the mass ratio of CuCl₂ to Na₄C₆H₇O₈ is 2. It can be observed that a large number of blue precipitates are precipitated in the reaction solution, which is heated to 60-70 °C and stirred for 1 hour, and then cooled and filtered. Wash the precipitates with hot water for 3 times and remove the F in the precipitates. The blue precipitate Cu₃C₆H₈O₈·2H₂O was then dried at 75 °C for 12 hours. The preparation of other metal complexes is basically the same as that of Cu complexes, but Cd complexes are made by Cd(NO₃)₂·4H₂O and Na₄C₆H₇O₈ [2].

1.3 Using thermogravimetric analysis

In the analysis phase, the thermogravimetric analyzer (Pyris 1 TGA) produced by Perkin-Elmer is used. Use M₅C₆H₈O₈·nH₂O, Co₅C₆H₈O₈·nH₂O, Ni₅C₆H₈O₈·nH₂O, Cu₅C₆H₈O₈·nH₂O, Zn₅C₆H₈O₈·nH₂O, Cd₅C₆H₈O₈·nH₂O to analyze and analyze the data. It can be observed that when the heating rate reaches 20°C per minute and the number of samples is 6 mg, when the temperature is between 30°C and 850°C, the flow rate of dry air is 20 ml per minute as the atmosphere.
1.4 Elemental analysis by infrared spectroscopy

In element analysis, the Fourier transform infrared spectrometer (Spectrum GX) produced by Perkin-Elmer Company and the DITGS detector are still used. After preparing the relevant testing instruments, we use KBr pressing method to test. At the same time, he found that the weight loss rate of crystalline water is when the temperature range was 30°C to 650°C.

The acquisition of Mn₃Cr₂O₄ can be achieved by reacting M²⁺ with (Cr₂O₃). At the same time, according to the derivative thermogravimetric curves and thermogravimetric curves (as shown in Fig. 1 and Fig. 2), it is determined that the molecular formula of the final product is Mn₃Cr₂O₄·nH₂O.

2 Experimental result

2.1 Determine the composition of 1,2,3,4-butane tetracarboxylic acid over metal complexes

Thermogravimetric analysis and elemental analysis can be used to verify the molecular formula of Mn₃Cr₂O₄. The acquisition of Mn₃Cr₂O₄ can be achieved by reacting M²⁺ with (Cr₂O₃). At the same time, according to the derivative thermogravimetric curves and thermogravimetric curves (as shown in Fig. 1 and Fig. 2), it is determined that the molecular formula of the final product is Mn₃Cr₂O₄·nH₂O.

![Figure 1. Derivative thermogravimetric curves.](image1)

![Figure 2. Thermogravimetric curves.](image2)

(1) The sample quality was 6302 mg, the experimental temperature range was 30°C to 850°C.
(2) The sample quality was 2028 mg, the experimental temperature range was 30°C to 650°C.

Through the observation of the icon, it can be found that the weight loss rate of crystalline water is when the thermogravimetric curve rises to the first stage. At the same time, the value of N can be further obtained based on this data. Under general experimental conditions, the products of thermal decomposition of the transition metal complexes are Cdo, CuO, ZnO, NiO, Co₂O₄, Mn₂O₃ and so on, in the range of temperature between 30°C and 850°C. At the same time, by analyzing the thermogravimetric data in the experiment (as shown in Table 1), it can be found that the mass fraction values of various complexes after thermal decomposition are basically consistent with the theoretical values, which further illustrates the correctness of the original formulation. Therefore, we can get the theoretical values of H% and C% according to the formulated chemical formula. After calculating the values, we can put the corresponding data into Table 2. Through the analysis of Table 2, we can conclude that the composition of the two elements (C and H) is basically the same as the formulated data. From this, we can see that the chemical formula of the complex is Mn₃Cr₂O₄·nH₂O, and the analysis results can thus be determined. Molecular formula for over metal complexes.

| Complex     | Crystalized water | Residual mass fraction/% | Thermogravimetric data of complex in dynamic air atmosphere |
|-------------|-------------------|--------------------------|------------------------------------------------------------|
| Mn₃Cr₂O₄·2H₂O | 9.11              | 2                        | Mn₂O₃                                                      |
| Cu₃Cr₂O₄·2H₂O | 9.20              | 2                        | CuO                                                        |
| Ni₃Cr₂O₄·2H₂O | 16.84             | 4                        | NiO                                                        |
| Cu₃Cr₂O₄·4H₂O | 6.02              | 1                        | CuO                                                        |
| Zn₃Cr₂O₄·2H₂O | 9.26              | 2                        | ZnO                                                        |
| Cd₃Cr₂O₄·2H₂O | 7.67              | 2                        | CdO                                                        |

| Complex | Colour              | Elemental analysis, measured values (calculated values)/% |
|---------|---------------------|----------------------------------------------------------|
| Mn₃Cr₂O₄·2H₂O | White              | 25 (24/25 53) | 2.7 (2.68) |
| Cu₃Cr₂O₄·2H₂O | Violet             | 24 (24/25 60) | 2.6 (2.63) |
| Ni₃Cr₂O₄·4H₂O | Yellowish green     | 22 (22/25 38) | 3.4 (3.36) |
| Cu₃Cr₂O₄·H₂O  | Blue               | 25 (25/25 59) | 2.3 (2.15) |
| Zn₃Cr₂O₄·2H₂O | White              | 24 (24/25 37) | 2.6 (2.54) |
| Cd₃Cr₂O₄·2H₂O | White              | 19 (19/19 33) | 2.3 (2.05) |

2.2 Data analysis using infrared spectroscopy

Infrared spectra of 1,2,3,4-butane tetracarboxylic acid, 1,2,3,4-butane tetracarboxylic acid tetrasodium salt and their transition metal complexes were determined by infrared spectroscopy. The spectra of these three elements are shown in Table 2 (for transition metals, manganese is taken as an example, and the main characteristic peaks of A infrared spectra are shown in Table 3).

![Figure 3. Infrared spectra comparison of 1,2,3,4- butane four carboxylic acid and four sodium salt and manganese complex.](image3)
In the infrared spectra of 1,2,3,4-butane tetracarboxylic acid (Na₄Cd₄O₈), the C=O bond strong absorption peaks of -COOH are at 1701 cm⁻¹, and a pair of vibration coupling absorption peaks are at 926 cm⁻¹ and 1416 cm⁻¹, respectively. At the same time, it can be further found that the out-of-plane angular vibration of the dimer carboxylic acid OH group causes wide peaks at 920 cm⁻¹, this broad absorption peak is due to ∆vcoo, the C=O bond strong absorption peak of -COOH. This indicates that -COOH does not exist in the experiment of 1,2,3,4-butane tetracarboxylic acid, CoO is oxidized to form CoO₂. At the same time, we can further observe that there are two stages in the diagram of copper, Cd, Mn, Ni and Zn metal complexes: 1,2,3,4-butane tetracarboxylic acid (Na₄Cd₄O₈). During the weightlessness stage, Cu metal complexes began to gain weight in the third stage. Through experiments, we can know that CoO is produced during the thermal decomposition of CuO₂Cd₂O₄·2H₂O at a specific temperature, and CoO is oxidized to form CoO₂. At the same time, we can further find that there is a big difference between the predicted and measured values of CoO, which is due to the partial overlap between CoO and CoO₂ or CoO₄. From this we can speculate that in the whole thermal decomposition reaction, the changes experienced by the experimental substance are:

\[
\begin{align*}
\text{Mn}_2\text{Cd}_4\text{O}_8 \cdot 2\text{H}_2\text{O} & \rightarrow \text{Mn}_2\text{Cd}_4\text{O}_8 \cdot \text{Mn}_2\text{O}_3 \\
\text{Co}_2\text{Cd}_4\text{O}_8 \cdot 2\text{H}_2\text{O} & \rightarrow \text{Co}_2\text{Cd}_4\text{O}_8 \rightarrow \text{Co}_2\text{O}_4 \\
\text{Ni}_2\text{Cd}_4\text{O}_8 \cdot 2\text{H}_2\text{O} & \rightarrow \text{Ni}_2\text{Cd}_4\text{O}_8 \rightarrow \text{NiO} \\
\text{Cu}_2\text{Cd}_4\text{O}_8 \cdot 2\text{H}_2\text{O} & \rightarrow \text{Cu}_2\text{Cd}_4\text{O}_8 \rightarrow \text{CuO} \\
\text{Zn}_2\text{Cd}_4\text{O}_8 \cdot 2\text{H}_2\text{O} & \rightarrow \text{Zn}_2\text{Cd}_4\text{O}_8 \rightarrow \text{ZnO} \\
\text{Cd}_2\text{Cd}_4\text{O}_8 \cdot 2\text{H}_2\text{O} & \rightarrow \text{Cd}_2\text{Cd}_4\text{O}_8 \rightarrow \text{CdO}
\end{align*}
\]

At the same time, through the analysis of thermogravimetric curves, the order of thermal stability of metal complexes from large to small is obtained as follows: Co₂Cd₄O₈·2H₂O > Cd₂Cd₄O₈·2H₂O > Mn₂Cd₄O₈·2H₂O > Ni₂Cd₄O₈·2H₂O > Zn₂Cd₄O₈·2H₂O > Cu₂Cd₄O₈·2H₂O

3 Concluding remarks

In the experimental process, 1,2,3,4-butane tetracarboxylic acid tetrasodium salt (Na₄Cd₄O₈) was prepared by reaction with excess metal salts. The composition and structure of the prepared metal complexes were characterized by infrared spectroscopy,
thermogravimetric analysis and elemental analysis. At the same time, the thermal stability of the complex was studied by thermogravimetric analysis, and the order of thermal stability was obtained as follows:

\[
\text{Co}_2\text{C}_8\text{H}_6\text{O}_8\cdot2\text{H}_2\text{O} > \text{Cd}_2\text{C}_8\text{H}_6\text{O}_8\cdot2\text{H}_2\text{O} > \text{Mn}_2\text{C}_8\text{H}_6\text{O}_8\cdot2\text{H}_2\text{O} > \text{Ni}_2\text{C}_8\text{H}_6\text{O}_8\cdot2\text{H}_2\text{O} > \text{Zn}_2\text{C}_8\text{H}_6\text{O}_8\cdot2\text{H}_2\text{O} > \text{Zn}_2\text{C}_8\text{H}_6\text{O}_8\cdot2\text{H}_2\text{O} > \text{Cu}_2\text{C}_8\text{H}_6\text{O}_8\cdot2\text{H}_2\text{O}
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