

Structural analysis of water-soluble citrates and peroxocitrates complexes available only in the powder crystalline form

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Introduction

Development of convenient, non-toxic d-transition metals' compounds useful as precursors for solution-based synthesis of inorganic materials is an exciting challenge in materials chemistry. We achieved a considerable progress in the synthesis and structural characterizations of water-soluble titanium (IV) compounds [1-3]. For those complexes single crystals could be obtained and used for structure solution by conventional approach. Meanwhile a series of titanium, tantalum and cobalt compounds could be obtained only in the form of crystalline powder. At the same time resolution of the conventional powder X-ray diffractometer and the intensities of the patterns did not allow choice of the space group and structure solution.

In this work, we attempted to collect high-resolution powder patterns for three new complexes $\text{Sr}[\text{Ti}(\text{C}_6\text{H}_4\text{O}_7)_2] \cdot 2\text{H}_2\text{O}$, $\text{Ba}[\text{Ti}(\text{C}_6\text{H}_4\text{O}_7)_2] \cdot 2\text{H}_2\text{O}$ and $\text{H}_4[\text{Co}(\text{C}_6\text{H}_5\text{O}_7)_2]$ using BL-4B2 powder diffraction facility and use the data for structure solution.

Experiment

Powder diffraction data were collected at room temperature in the flat plate geometry using Multi Detector System at BL-4B2 beam station for three metal complexes: $\text{H}_4[\text{Co}(\text{C}_6\text{H}_5\text{O}_7)_2]$, $\text{Sr}[\text{Ti}(\text{C}_6\text{H}_4\text{O}_7)_2] \cdot 2\text{H}_2\text{O}$, $\text{Ba}[\text{Ti}(\text{C}_6\text{H}_4\text{O}_7)_2] \cdot 2\text{H}_2\text{O}$. The wavelength was 1.20525 Å. To find optimal resolution, intensity and sample exposure time to the X-ray beam several data sets were collected in the 2θ range from -5° till 154.98° using $\Delta 2\theta = 0.005-0.01^\circ$ and sampling time of 2-8s/step. The intensities of reflections were extracted by LeBail procedure in the RIETICA program and used in structure solution program EXPO [4]. Direct method was used and the structure was expanded using Fourier technique.

Results

Due to the instrument design, data should be collected in the whole 2θ range from -5° till 154.98° . However the intensities of reflections decline rapidly at $2\theta > 60^\circ$ and can not be used. The indexing of the diffraction patterns of peroxo-citrato complexes $\text{M}[\text{Ti}(\text{C}_6\text{H}_4\text{O}_7)_2] \cdot 2\text{H}_2\text{O}$ (where M = Sr and Ba) failed. In addition, samples changed their color from light-orange into pale yellow, which indicates that peroxo group is decomposed due to

the exposure to the X-ray beam. Probably low temperature data collection should be attempted.

Diffraction pattern of cobalt citrate complex $\text{H}_4[\text{Co}(\text{C}_6\text{H}_5\text{O}_7)_2]$ could be indexed as orthorhombic lattice with $a=5.9122(2)\text{Å}$, $b=10.4129(3)\text{Å}$, $c=13.44282(15)\text{Å}$ and reflection conditions corresponding to $\text{P}2_12_1$ (no. 19) space group. The intensities of first 830 reflections were extracted by LeBail procedure with final $\text{Rwp}=9.57\%$. They were used for structure solution. Cobalt and four oxygen atoms were located by direct method. After the refinement cycle, two more oxygen atoms were found in the nearest coordination of cobalt. Co has slightly distorted octahedral environment with Co-O distance of 1.950-2.197 Å. The shortest Co-Co distance of 3.689 Å suggests that two cobalt ions should be coordinated by one citric acid molecule in the bi-dentate manner. Examination of difference Fourier map gave three more carbon atoms that allows a construction of partial structure in Fig. 1. Fig. 1 shows that Co atoms coordinated by citric acid are arranged into stripes along **a** axis, and probably such stripes are kept together by hydrogen bonds between protonated groups of citric acids. Unfortunately, further expansion of the structure by Fourier technique is difficult. However, this framework can be used for structure expansion by molecular mechanics optimization. This work is currently under way.

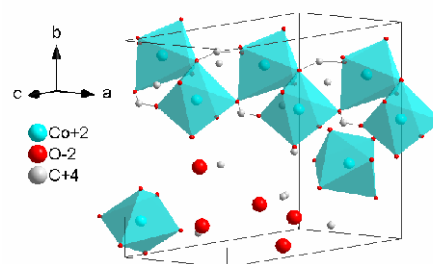


Fig. 1. Part of the Co-citrate crystal structure, solved *ab initio* using powder diffraction data.

References

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