

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

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Introduction

Recently we synthesized and characterized a series of water soluble complexes of titanium (IV) and tantalum (V) [1-3]. These compounds are stable, non-toxic and can be used as precursors for solution-based synthesis of inorganic materials. For those complexes single crystals could be obtained and used for structure solution by conventional approach. Nevertheless we identified a series of compounds which can be prepared only in the powder crystalline form and analysis of their structures is not trivial. At the same time resolution of the conventional powder X-ray diffractometer is not sufficient to choose the correct space group and to solve crystal structure.

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 $\Delta 2\theta = 0.005\text{-}0.01^\circ$ and sampling time of 2-8s/step. For cobalt citrate two independent patterns were collected to investigate preferred orientation due to the sample packing in sample holder and possible decay of the compound under X-ray. For solution of crystal structures using powder diffraction data EXPO [4] and FOX [5] programs were used.

Results

Although instrument design requires collecting data in the 2θ range of -5° till 154.98° , the intensities of reflections decline rapidly at $2\theta > 60^\circ$ and can not be used for structure solution. The diffraction patterns of peroxocitrate 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) could not be indexed as belonging to one phase. In addition, samples changed their color from light-orange into pale yellow, which indicated that peroxo group decomposed under the X-ray beam.

Diffraction pattern of cobalt citrate complex $\text{H}_4[\text{Co}(\text{C}_6\text{H}_5\text{O}_7)_2]$ could be indexed assuming orthorhombic lattice with $a = 5.9122(2)\text{Å}$, $b = 10.4129(3)\text{Å}$, $c = 13.44282(15)\text{Å}$. Reflection conditions allowed to

choose $\text{P2}_12_12_1$ (no. 19) space group. At first we attempted to solve the structure by direct method using first 830 reflections extracted by LeBail procedure with final $\text{Rwp} = 9.57\%$. Cobalt atom and four oxygen atoms were located by direct method, then two more oxygen atoms were found by Fourier technique in the nearest coordination of cobalt with Co-O distance of 1.950-2.197 Å and the shortest Co-Co distance of 3.689 Å. It means that two cobalt ions should be coordinated by one citric acid molecule in the bi-dentate manner. However the rest of the citric acid molecule fragments could not be located. It seemed that the main difficulty was related to insufficient number of reflections and limited resolution in the 2θ range of non-overlapping reflections. Therefore we decided to use a Monte Carlo algorithm in FOX program starting from one cobalt atom and two citric acid molecules without hydrogen atoms. After ~150 million trials we were able to identify a group of 71 models with low "cost" parameter. The best configuration is shown in Fig. 1. More careful analysis of the obtained models in combination with spectroscopic data is necessary and this study is currently under way.

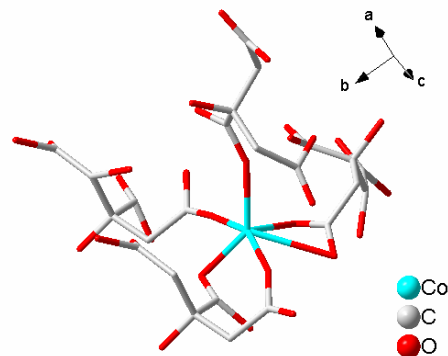


Fig. 1. Coordination of single Co atom by citric acid molecules in the best cost model.

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