Synthesis and Characterisation of Na₅[CoO₂]CO₃

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Dedicated to Professor Albrecht Mewis on the occasion of his 60th birthday

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Na₅[CoO₂]CO₃ was prepared via the azide/nitrate route. Stoichiometric mixtures of the precursors (Co₃O₄, NaN₃, NaNO₃ and Na₂CO₃) were heated in a special regime up to 500 °C and annealed at this temperature for 50 h in silver crucibles. Single crystals have been grown by subsequent annealing of the powder at 500 °C for 2000 h in silver crucibles, which were sealed in glass ampoules under dry Ar. According to the X-ray analysis of the crystal structure (*P4/mmm*, *Z* = 1, *a* = 4.6467(4), *c* = 8.2577(6) Å). Na₅[CoO₂]CO₃ is isostructural with Na₅[NiO₂]CO₃ and contains Co¹⁺, which is coordinated by two oxygen atoms forming a dumb-bell. Na₅CoCO₅ decomposes at 600 °C to Na₃CoO₂ and Na₂CO₃.

Key words: Cobalt(I), Crystal Structure, Azide/ Nitrate Route

Introduction

At exploring the synthetic potential of the azide/ nitrate route [1] for the preparation of alkalioxometalates we have tried to prepare representatives containing two different types of complex anions. As the first case we have selected Na₅[CoO₂]CO₃, since recently the corresponding nickel compound [2] had been obtained through the conventional solid state reaction involving sodium oxide.

Results and Discussion

 $Na_5[CoO_2]CO_3$ can be readily prepared by the azide/nitrate route [1] as a micro-crystalline powder. The ruby-red products are very sensitive to air and moisture. The DTA/TG analysis has shown that no chemical reactions or phase transitions occur during heating of the substance up to ~ 600 °C. At this temperature Na_5CoCO_5 begins to decompose into Na_3CoO_2 and Na_2CO_3 .

The crystal structure of the novel sodium cobaltate carbonate (Fig. 1) was determined from single crystal data. Details of the refinement and crystallographic data are given in Tables 1 and 2. The characteristic feature of the structure is the linear CoO_2^{3-} -anion. The Co-O bond length is 1.755 Å and the O-Co-O angle is 180°. The structural features related to the cobaltate(I) anion are in a good agreement for all known alkali metals compounds [3-6]. According to the structure obtained from single crystal data (Table 2), the carbonate unit is orientationally disordered. The situation has been addressed appropriately by applying a split atom model. To confirm the presence of the carbonate ion, an IR spectrum of $Na_5[CoO_2]CO_5$ has been recorded (Fig. 2, Table 3).



Fig. 1 Crystal structure of $Na_5[CoO_2]CO_3$. The octahedron in the central section of the picture corresponds to the orientationally disordered carbonate unit.

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Table 1. X-ray and crystallographic data for Na₅[CoO₂]CO₃ (293 K).

Crystal data	
Crystal system	tetragonal
Space group, Z	P4/mmm (No. 123), 1
Lattice constants (from X-	a = 4.6467(4)
ray powder data) [Å]	c = 8.2577(6)
Calculated density [g/cm ³]	2.474
Crystal shape, color	irregular, red
Crystal size, mm	$0.15 \times 0.1 \times 0.1$
Structure refinement	
Method of refinement	Full-matrix least-squares on F^2
Parameters refined	25
$R1 \ (F_0 > 4 \text{sig} F_0^2 / \text{all})$	0.0436/0.0548
wR2	0.1107
weight	$w = 1/(\sigma^2(F_0^2) + (0.0476 \cdot P)^2 + 0.44 \cdot P),$
- -	where $P = (\max(F_0^2, 0) + 2 \cdot F_c^2)/3$
$\Delta \varrho_{\min}, \varrho_{\max} \left[e^{-/\hat{A}^3} \right]$	- 1.20/1.14
Data collection	
Diffractometer	Bruker AXS, APEX SMART-CCD
Monochromator	Graphite
Mo-K _{α} Radiation, [λ]	0.71073 Å
20 Range for data collection	$2\theta < 75.0^{\circ}$
Range of <i>h</i> , <i>k</i> , <i>l</i>	-6 < h < 6, -7 < k < 6, -11 < l < 10
Total no. reflection	1635
Unique reflections	225
Observed reflections	1635
Absorption coefficient, μ [mm ⁻¹]	2.67
F(000)	122

Table 2. Atomic coordinates and anisotropic displacement parameters (in Å²·10⁴) for Na₅[CoO₂]CO₃.

Atom	Position	x	у	z	U ₁₁	U ₂₂	U ₃₃
Co1 Na1 Na2 O1 O2 O3 C1	1a 1b 4i 2 g 2h ^a 40 ^a 1d ^b	$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{array}$	001/201/20.195(3)1/2	0 0.5 0.2403(3) 0.2125(6) 0.345(2) 0.5	174(6)362(16)678(20)183(15)670(79)503(84)614(78)	174(6)362(16)142(11)183(15)670(79)435(76)614(78)	149(7) 182(19) 384(13) 179(21) 723(125) 530(79) 452(92)

 $U_{12} = U_{13} = U_{23} = 0$ for all atoms;

^a site occupation factor: 0.5;

^b disordered, average site position.

Experimental Section

Starting materials for the preparation of Na₅-[CoO₂]CO₃ were sodium azide (Aldrich, 99.5%), sodium nitrate (Aldrich, 99%), sodium carbonate (Merck, 99.9%) and cobalt oxide Co₃O₄. Cobalt oxide Co₃O₄ was prepared by heating Co(C₂O₄) \cdot 2H₂O in a flow of oxygen at 375 °C for 40 h. The starting materials (NaN₃, NaNO₃, Na₂CO₃ and Co₃O₄) were mixed in the ratio required according to the equation

¹ 25 NaN₃ + 2 NaNO₃ + 9 Na₂CO₃ + 3 Co₃O₄ = 9 Na₅[CoO₂]CO₃ + 38.5 N₂, milled in a planet ball mill, pressed in pellets under 10^5 N, dried under

vacuum (10^{-3} mBar) at 150 °C for 12 h and placed under argon in a tightly closed steel vessel provided with a silver inlay [1]. In a flow of dry argon the following temperature profile was applied: $25 \rightarrow 260$ °C (100 K/h); $260 \rightarrow 380$ °C (5 K/h), $380 \rightarrow 500$ °C (10 K/h) and subsequent annealing for 50 h at 500 °C. The red powder obtained is extremely sensitive to air. It was sealed in glass ampoules under argon atmosphere. All following manipulations with this substance were also performed in inert atmospheres of purified argon or nitrogen. The X-ray investigation on powder



Fig. 2 IR spectrum of Na₅[CoO₂]CO₃ (in KBr).

Table 3. Vibrational data (in cm^{-1}) and assignment for $Na_5[COO_2]CO_3$ at 293 K.

modes	Wawenumber		
$\frac{1}{2\nu_3}$	2875		
$v_1 + v_2$	2499		
$2\nu_1$	2121		
$\nu_1 + \nu_4$	1779/1750		
ν_3	1427		
ν_1	1043		
ν_2	881		
$\nu_{\rm as}({\rm CoO_2^{3-}})$	736		
ν_4	685		
ν (Na-O)	523		

was performed on a STOE Stadi P diffractometer with Co-K_{a1} radiation ($\lambda = 1.78896$ Å) at room temperature using a position sensitive detector and a curved germanium monochromator. The powder diffraction data are given in Table 4. Single crystals have been grown by subsequent annealing of the as prepared powder at 500 °C for 2000 h in silver crucibles, which were sealed in glass ampoules under dry Ar. Single crystals for X-ray diffraction have been selected in Ar atmosphere using a microscope attached to a glove-box.

Table 4. Powder diffraction data of $Na_5[CoO_2]CO_3$ (d > 1.4 Å).

	/			
h	k	l	d [Å]	<i>I</i> / <i>I</i> ₀ [%]
0	0	1	8.2721	3.7
1	0	0	4.6495	54.4
1	0	1	4.0515	100.0
1	1	0	3.2866	9.7
1	0	2	3.0874	8.0
1	1	1	3.0538	3.1
0	0	3	2.7535	1.3
1	1	2	2.5716	77.8
1	0	3	2.3673	0.9
2	0	0	2.3238	81.4
2	0	1	2.2371	1.9
1	1	3	2.1104	2.7
2	1	0	2.0785	22.1
0	0	4	2.0648	21.4
2	0	2	2.0252	2.1
2	1	1	2.0156	7.0
1	0	4	1.8869	12.4
2	1	2	1.8564	7.1
1	1	4	1.7480	1.2
0	0	5	1.6517	0.8
2	2	0	1.6430	13.3
2	2	1	1.6116	1.5
1	0	5	1.5563	3.4
3	0	0	1.5496	0.4
2	0	4	1.5433	18.9
2	2	2	1.5266	1.0
3	0	1	1.5224	2.6
3	1	Ō	1.4691	1.2
2	1	4	1.4647	11.5
3	Ō	2	1.4501	1.4
3	1	1	1.4465	0.6
-	-	-		0.0

The crystal structure of the sodium carbonate oxocobaltate was determined from X-ray single crystal data. The lattice constants were refined from powder data. Details of structural refinement and crystallographic data are given in Table 1. Infrared experiments were carried out on powder samples in KBr discs (handled under Ar) on a Bruker IFS 113v spectrometer. Thermal analyses were carried out using a DTA/TG device (STA 409, Netzsch) coupled with a quadrupole mass spectrometer (QMG 421, Balzers, Wetzlar). The probe (m = 26.5 mg) was heated at a rate of 10 K/min in a corundum crucible under dry argon.

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