NEW DIFFRACTION DATA

The crystal structure of trisodium hexachlororhodate (Na_3RhCl_6)

Martin Etter[a)]
Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, 22607 Hamburg, Germany

(Received 4 April 2017; accepted 2 January 2018)

Commercially available trisodium hexachlororhodate (Na_3RhCl_6) was dehydrated and characterized by laboratory X-ray powder diffraction. The crystal structure is isostructural to the Na_3CrCl_6 structure type with space group $P\bar{3}1c$. Unit-cell parameters are $a = 6.8116(1)$ Å, $c = 11.9196(2)$ Å, $V = 478.95(2)$ Å^3, and $Z = 2$. © *2018 International Centre for Diffraction Data.*
[doi:10.1017/S0885715618000155]

Key words: trisodium hexachlororhodate, Na_3RhCl_6

I. INTRODUCTION

Trisodium hexachlorometalates (Na_3MCl_6, M = metal ion) were reported to crystallize in three crystal structure types namely the Na_3AlF_6 (cryolite) structure type (for M = Dy, Er, Ho, Lu, Sc, Ti, Tm, Y, Yb) (space group $P2_1/n$), the Na_3CrCl_6 structure type (for M = Cr, In, Mo, V) (space group $P\bar{3}1c$), and the Na_3GdCl_6 structure type (M = Eu, Gd, Tb) (space group $R\bar{3}$H) (an overview and related literature can be found in Table I). Interestingly, another trisodium hexachlorometalate, trisodium hexachlororhodate (Na_3RhCl_6) was reported in a diffraction study by Krylov *et al.* (1983) (ICDD PDF4 + ID # 00-036-0754); however, neither the crystal structure nor the indexing of the reported X-ray diffraction (XRD) pattern was given by them.

Here, the crystal structure of Na_3RhCl_6 was examined using laboratory X-ray powder diffraction.

II. EXPERIMENTAL

A. Sample preparation

Commercially available trisodium hexachlororhodate(III) was bought from the Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany). The bright red powder was ground in an agate mortar with an agate pestle to a fine powder and subsequently filled in a quartz capillary of 0.5 mm diameter (Hilgenberg GmbH, Malsfeld, Germany). The dehydration of the sample was done by mounting the capillary on the diffractometer and by heating it for half an hour at a constant temperature of 350 °C with an MRI capillary heater. The heating and the cooling rate from room temperature to 350 °C and back was 0.5 °C/s. After the heat treatment, the color of the powder turned into a darker red.

B. XRD data collection

Room temperature X-ray powder diffraction measurements of the Na_3RhCl_6 specimen were carried out using a Bruker D8 Advance diffractometer in Debye–Scherrer geometry. The diffractometer was equipped with a sealed tube Molybdenum X-ray source (operated at 50 kV and 40 mA) and a Ge(220) primary beam monochromator to obtain pure Mo$K\alpha_1$ radiation at a wavelength of $\lambda = 0.7093$ Å. Detection of diffracted X-rays was done using a Lynxeye detector. The diffractogram was collected from 2 to 45.0° 2θ with a resolution of 0.01° 2θ and a total integration time of 8 h.

C. Data treatment

Crystal structure determination and subsequent Rietveld refinements of the measured powder diffraction pattern of Na_3RhCl_6 were performed using the TOPAS 4.2 software from Bruker AXS Inc. (Cheary *et al.*, 2004). The background of the pattern was modeled by Chebyshev polynomials plus five broad Lorentzian peak shapes, whereas phase peaks where modeled by the fundamental parameter approach.

III. RESULTS AND DISCUSSION

The first indexing attempts (Coelho, 2003) of the measured powder diffraction pattern at room temperature suggested either monoclinic (e.g. $P2$, $P2_1$), trigonal (e.g. $P31c$, $P3$), or orthorhombic (e.g. $Ccc2$, $C222_1$, $Cmc2_1$) space groups for Na_3RhCl_6. From the suggested solutions, the monoclinic ones provided the smallest volume and the best figure of merit (de Wolff, 1968); however, subsequent whole powder pattern decomposition refinements (Le Bail *et al.*, 1988) revealed that not all reflections could be satisfactorily modeled. In contrast to the monoclinic solutions, trigonal and orthorhombic solutions (which had an exactly double unit-cell volume compared with the trigonal ones) did only match under the assumption, that two of the observed reflections have to be classified as impurity lines. Subsequent whole powder pattern decomposition refinements of the trigonal solutions unveiled several possible impurity lines. Therefore, possible by-products, which could emerge because of the heating process, were checked. It was found that ordinary sodium chloride (NaCl) could be reasonably fitted by a Rietveld refinement to the impurity reflections. Interestingly, no other crystalline rhodium containing impurity phase could be identified. As the trigonal solutions and the corresponding lattice parameters suggested a close structural relationship to the Na_3CrCl_6 structure type, Na_3CrCl_6 was used as starting model for a Rietveld refinement

---

[a)]Author to whom correspondence should be addressed. Electronic mail: martin.etter@desy.de

TABLE I. Overview of Na_3MCl_6 (M = metal ion) compounds and related literature.

Compound	Structure type	Space group	Powder diffraction analysis	Single crystal diffraction analysis
Na_3DyCl_6	Na_3AlF_6	$P2_1/n$	Meyer *et al.* (1987)	Schurz *et al.* (2011)
Na_3ErCl_6	Na_3AlF_6	$P2_1/n$	Meyer *et al.* (1987)	Meyer *et al.* (1987)
Na_3HoCl_6	Na_3AlF_6	$P2_1/n$	Meyer *et al.* (1987)	Böcker *et al.* (2001)
Na_3LuCl_6	Na_3AlF_6	$P2_1/n$	Meyer *et al.* (1987)	
Na_3ScCl_6	Na_3AlF_6	$P2_1/n$	Meyer *et al.* (1987)	
Na_3TiCl_6	Na_3AlF_6	$P2_1/n$	Hinz *et al.* (2000)	
Na_3TmCl_6	Na_3AlF_6	$P2_1/n$	Meyer *et al.* (1987)	
Na_3YCl_6	Na_3AlF_6	$P2_1/n$	Meyer *et al.* (1987)	Liao and Dronskowski (2004)
Na_3YbCl_6	Na_3AlF_6	$P2_1/n$	Meyer *et al.* (1987)	
Na_3CrCl_6	Na_3CrCl_6	*P*-31*c*		Friedrich *et al.* (1987)
Na_3InCl_6	Na_3CrCl_6	*P*-31*c*		Yamada *et al.* (2005)
Na_3MoCl_6	Na_3CrCl_6	*P*-31*c*	Friedrich *et al.* (1987)	Beran and Meyer (2011)
Na_3VCl_6	Na_3CrCl_6	*P*-31*c*	Friedrich *et al.* (1987)	
Na_3EuCl_6	Na_3GdCl_6	*R*-3*H*	Meyer *et al.* (1987)	
Na_3GdCl_6	Na_3GdCl_6	*R*-3*H*	Meyer *et al.* (1987)	Meyer (1984)
Na_3TbCl_6	Na_3GdCl_6	*R*-3*H*	Meyer *et al.* (1987)	

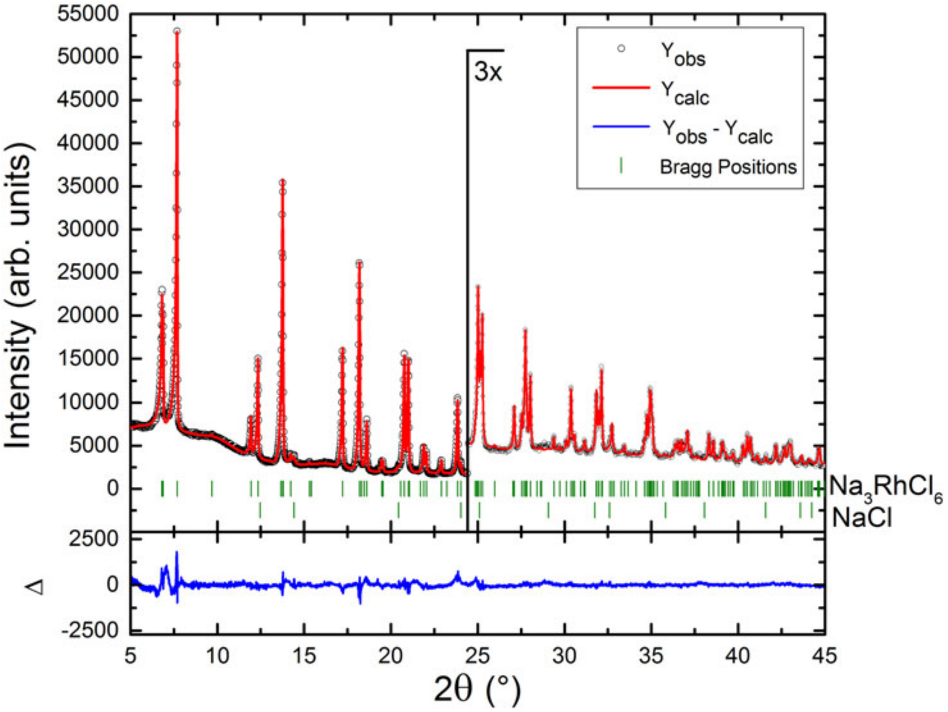

Figure 1. (Color online) Rietveld plot of the measured powder X-ray diffraction data. Two phases, Na_3RhCl_6 [wt% = 96.03(2)] and NaCl [wt% = 3.97(2)] were refined. At low 2Theta values the background is increased because of amorphous scattering of the quartz capillary.

TABLE II. Crystal structure data obtained from the Rietveld refinement for Na_3RhCl_6 at room temperature (303 K).

Formula	Na_3RhCl_6
Crystal system	Trigonal
Space group	*P*-31*c*
a (Å)	6.8116(1)
c (Å)	11.9196(2)
Cell volume (Å^3)	478.95(2)
Formula units *Z*	2
Calculated density (g cm^{-3})	2.6668(1)
Scan range	$2° \leqslant 2\theta \leqslant 45°$
Radiation wavelength Mo$K\alpha_1$ (Å)	0.7093
Zero shift	0.0005(3)
Numbers of refined parameters	48
R_p (%)	2.651
R_{wp} (%)	3.602
R_B (%)	1.309
GOF	2.085

(Rietveld, 1969), exchanging the chromium ion by a rhodium one. Together with the NaCl phase, a successful Rietveld refinement of all reflections could be performed (Figure 1). Intriguingly in this refinement, anisotropic displacement parameters could be utilized for all atoms within the Na_3RhCl_6 phase, as the quality of the collected data was insomuch excellent, that the R_{wp} dropped by a significant value of 0.3% compared with the usage of sole isotropic displacement parameters. The reasonability of the values of the anisotropic displacement parameters was subsequently confirmed by drawing ellipsoidal atomic models of the crystal structure (see Figure S2 in the online Supplementary material). The final agreement factors of this refinement are $R_p = 2.651\%$, $R_{wp} = 3.602\%$, $R_B(Na_3RhCl_6) = 1.309\%$, $R_B(NaCl) = 1.232\%$, and GOF = 2.085 (all agreement factors as defined in TOPAS 4.2). The

TABLE III. Refined atomic coordinates, occupancy, and atomic anisotropic displacement parameters for Na_3RhCl_6 at room temperature (303 K).

Atom	Wyckoff position	Oxidation state	x	Y	z	Occupancy	Anisotropic displacement parameter ($Å^2$)					
							u11	u22	u33	u12	u13	u23
Rh1	2d	+3	2/3	1/3	0.25	1	0.0148 (7)	0.0148 (7)	0.0221 (13)	0.0074 (4)	0	0
Na1	2a	+1	0	0	0.25	1	0.0320 (43)	0.0320 (43)	0.0229 (67)	0.0160 (22)	0	0
Na2	4f	+1	2/3	1/3	0.5476(3)	1	0.0404 (18)	0.0404 (18)	0.0301 (35)	0.0202 (9)	0	0
Cl1	12i	−1	0.9412(3)	0.6157(3)	0.3654(1)	1	0.0356 (16)	0.0321 (19)	0.0237 (18)	0.0108 (13)	−0.0184 (11)	0.0023 (12)

TABLE IV. Selected bond lengths for Na_3RhCl_6.

Bond	Length (Å)
Rh1-Cl1	2.343(2)
Na1-Cl1	2.803(2)
Na2-Cl1(1)	2.884(3)
Na2-Cl1(2)	2.721(2)

TABLE V. Powder X-ray diffraction data for Na_3RhCl_6. Calculated values are from the Rietveld refinement, whereas observed values are determined by single peak fittings. Lines which are uniquely identified as NaCl reflections are omitted here.

h	k	l	$2\theta_{obs}$ (°)	d_{obs} (Å)	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)	I_{obs} (%)
0	0	2	6.821	5.961	6.823	5.960	−0.002	18.0
0	1	0	6.891	5.901	6.893	5.899	−0.002	34.6
0	1	1	7.692	5.287	7.693	5.287	−0.001	100.0
0	1	2			9.705	4.193		
1	1	0	11.953	3.406	11.954	3.406	−0.001	8.6
0	1	3	12.356	3.296	12.356	3.295	0.000	22.0
0	0	4			13.670	2.980		
1	1	2	13.777	2.957	13.777	2.957	0.000	66.4
1	−2	−2			13.777	2.957		
0	2	0			13.812	2.950		
0	2	1			14.231	2.863		
0	1	4			15.325	2.660		
0	2	2			15.420	2.643		
0	2	3	17.224	2.368	17.225	2.368	−0.001	25.3
1	1	4	18.197	2.243	18.198	2.243	−0.001	46.6
1	−2	−4			18.198	2.243		
2	1	0			18.305	2.230		
0	1	5			18.467	2.210		
2	1	1	18.623	2.192	18.625	2.192	−0.002	12.3
1	−3	−1			18.625	2.192		
0	2	4	19.481	2.096	19.480	2.096	0.001	1.7
2	1	2	19.559	2.088	19.556	2.088	0.003	1.6
1	−3	−2			19.556	2.088		
0	0	6			20.567	1.987		
0	3	0	20.781	1.966	20.782	1.966	−0.001	25.5
2	1	3	21.018	1.944	21.019	1.944	−0.001	23.4
1	−3	−3			21.019	1.944		
0	3	1			21.066	1.940		
0	1	6			21.716	1.883		
0	3	2	21.897	1.867	21.897	1.867	0.000	5.6
0	2	5	22.055	1.854	22.055	1.854	0.000	3.8
2	1	4	22.916	1.785	22.917	1.785	−0.001	3.5
1	−3	−4			22.917	1.785		
0	3	3			23.219	1.762		
1	1	6	23.853	1.716	23.855	1.716	−0.002	19.7
1	−2	−6			23.855	1.716		
2	2	0	24.031	1.704	24.041	1.703	−0.010	5.1
0	2	6			24.859	1.648		
0	3	4			24.959	1.641		
2	2	2			25.019	1.637		
2	−4	−2			25.019	1.637		
3	1	0	25.031	1.637	25.038	1.636	−0.007	18.5
0	1	7			25.040	1.636		
2	1	5	25.165	1.628	25.159	1.628	0.006	3.2
1	−3	−5			25.159	1.628		
3	1	1	25.277	1.621	25.277	1.621	0.000	9.0
1	−4	−1			25.277	1.621		
3	1	2			25.981	1.578		
1	−4	−2			25.981	1.578		
0	3	5			27.042	1.517		

Continued

TABLE V. Continued

h	k	l	$2\theta_{obs}$ (°)	d_{obs} (Å)	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)	I_{obs} (%)
3	1	3	27.116	1.513	27.115	1.513	0.001	2.5
1	−4	−3			27.115	1.513		
0	0	8	27.543	1.490	27.540	1.490	0.003	1.8
2	1	6			27.667	1.483		
1	−3	−6			27.667	1.483		
2	2	4	27.758	1.478	27.758	1.479	0.000	11.4
2	−4	−4			27.758	1.479		
0	4	0			27.830	1.475		
0	2	7	27.836	1.474	27.831	1.475	0.005	1.8
0	4	1	28.046	1.464	28.046	1.464	0.000	4.8
0	1	8			28.423	1.445		
3	1	4			28.634	1.434		
1	−4	−4			28.634	1.434		
0	4	2			28.687	1.432		
0	3	6	29.399	1.398	29.402	1.398	−0.003	0.6
0	4	3			29.726	1.383		

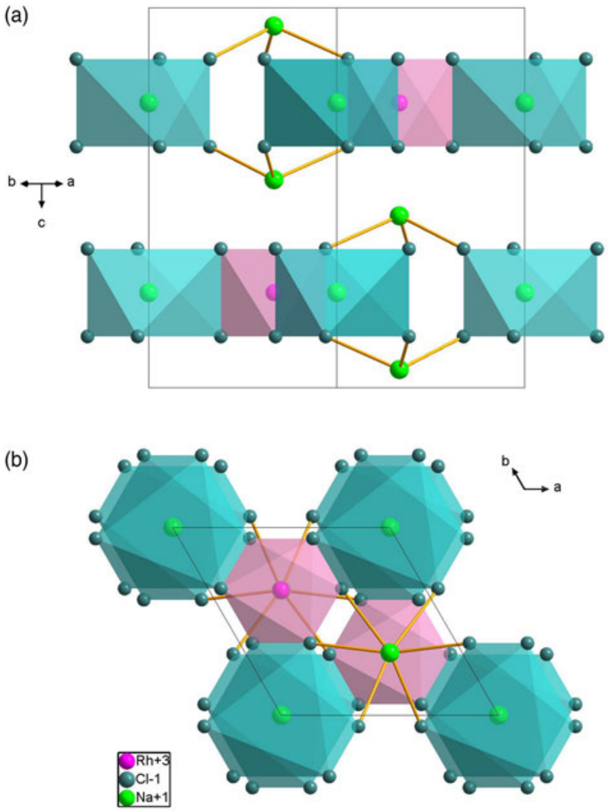

Figure 2. (Color online) Trigonal crystal structure of Na_3RhCl_6. (a) View along the crystallographic (110)-direction, (b) view along the crystallographic c-direction.

calculated weight percentage of the Na_3RhCl_6 phase is wt% = 96.03(24), whereas that of the NaCl impurity could be determined to wt% = 3.97(24). The results of the final Rietveld refinement of the Na_3RhCl_6 phase (lattice parameters, agreement factors, etc.) are summarized in Table II, whereas atomic positions, occupancies, and anisotropic displacement parameters of this phase are listed in Table III. Selected bond lengths are listed in Table IV and the powder diffraction data are given in Table V. The crystal structure of Na_3RhCl_6 is presented in Figure 2.

IV. CONCLUSION

Commercially available trisodium hexachlororhodate (Na_3RhCl_6) was dehydrated and characterized by laboratory X-ray powder diffraction. The crystal structure is isostructural to the Na_3CrCl_6 structure type with space group $P\bar{3}1c$. Unit-cell parameters are $a = 6.8116(1)$ Å, $c = 11.9196(2)$ Å, $V = 478.95(2)$ Å^3, and $Z = 2$.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S0885715618000155

ACKNOWLEDGEMENT

The author acknowledges Christine Stefani, Max Planck Institute for Solid State Research (Stuttgart, Germany) for carrying out the powder X-ray diffraction experiments.

Beran, M. and Meyer, G. (**2011**). "Crystal structure of Na_3MoCl_6," Crystals **1**, 99–103.

Böcker, M., Gerlitzki, N., and Meyer, G. (**2001**). "Crystal structure of trisodium homium(III) hexachloride, Na_3HoCl_6," Z. Kristallogr. **216**, 19.

Cheary, R. W., Coelho, A. A., and Cline, J. P. (**2004**). "Fundamental parameters line profile fitting in laboratory diffractometers," J. Res. Natl. Inst. Stand. Technol. **109**, 1–25.

Coelho, A. A. (**2003**). "Indexing of powder diffraction patterns by iterative use of singular value decomposition," J. Appl. Crystallogr. **36**, 86–95.

de Wolff, P. M. (**1968**). "A simplified criterion for the reliability of a powder pattern indexing," J. Appl. Crystallogr. **1**, 108–113.

Friedrich, G., Fink, H., and Seifert, H. J. (**1987**). "Über Alkali-hexachlorochromate(III): Na_3CrCl_6," Z. Anorg. Allg. Chem. **548**, 141–150.

Hinz, D., Gloger, T., and Meyer, G. (**2000**). "Ternäre Halogenide vom Typ A_3MX_6. Kristallstrukturen von Na_3TiCl_6 und K_3TiCl_6," Z. Anorg. Allg. Chem. **626**, 822–824.

Krylov, V. V., Danilov, M. P., Stepareva, N. N., and Kotlyar, Yu. A. (**1983**). "Phase interactions in the NaCl-$RhCl_3$ system," Russ. J. Inorg. Chem. **28**, 1230–1232.

Le Bail, A., Duroy, H., and Fourquet, J. L. (**1988**). "Ab-initio structure determination of LiSbWO6 by X-ray powder diffraction," Mater. Res. Bull. **23**, 447–452.

Liao, W., and Dronskowski, R. (**2004**). "Trisodium yttrium(III) hexachloride," Acta Crystallogr. **E60**, i72-i73.

Meyer, G. (**1984**). "Na_3gdcl_6: Einkristalle der Tieftemperaturform bei der metallothermischen Reduktion von $GdCl_3$ mit Na," Z. Anorg. Allg. Chem. **517**, 191–197.

Meyer, G., Ax, P., Schleid, T., and Irmler, M. (**1987**). The chlorides Na3MCl6 (M = Eu-Lu, Y, Sc): synthesis, crystal structures, and thermal behaviour," Z. Anorg. Allg. Chem. **554**, 25–33.

Rietveld, H. M. (**1969**). "A profile refinement method for nuclear and magnetic structures," J. Appl. Crystallogr. **2**, 65–71.

Schurz, C. M., Meyer, G., and Schleid, T. (**2011**). "Na_3dycl_6," Acta Crystallogr. **E67**, i33.

Yamada, K., Kumano, K., and Okuda, T. (**2005**). "Conduction path of the sodium ion in Na3InCl6 studied by X-ray diffraction and ^{23}Na and ^{115}In NMR," Solid State Ion. **176**, 823–829.