

The Crystal Structure of RbNiCl_3 and RbNiBr_3

The Weiss Constant in Relation to the Crystal Structure of some Double Halides of the Type ANiX_3

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RbNiCl_3 crystallizes in the hexagonal system with 2 formula units per unit cell. Space group $P6_3/mmc$, $a_0 = 6.955(1)$ Å, $c_0 = 5.906(1)$ Å. The crystal structure based on 83 independent reflexions (Weissenberg and precession) was refined to $R_w = 0.046$ by isotropic least squares procedures. The structure is approximately a hexagonal close packing of layers of the composition RbCl_3 with the Ni^{2+} ions situated in 1/4 of the octahedral holes. Infinite, linear poly-ions, $(\text{NiCl}_3)_n^{n-}$, are formed by the slightly irregular NiCl_6 -octahedra sharing faces. RbNiBr_3 has the same structure, $a = 7.268(8)$ Å, $c = 6.208(8)$ Å. The relation between the crystal structure and the magnetic susceptibility of several Ni double-halides of the same structural type is discussed.

Several X-ray structure investigations of Ni double-halides of the type SABX_3 have been reported in the literature. These compounds, having a very simple crystal structure, are suited for a study of the relation between crystal structure and magnetism.

PREPARATIONS

RbNiCl}_3. 0.06 moles of NiCO_3 and 0.03 moles of RbCl were dissolved in a minimum of hot concentrated hydrochloric acid. The solvent was slowly evaporated by boiling the solution gently in the apparatus shown in Fig. 1. When a reasonable amount of yellow-orange crystals of RbNiCl_3 had separated the apparatus was turned upside down, and the mother liquor was removed by suction. The crystals were washed 10 times with mixtures of concentrated hydrochloric acid and acetone containing an increasing amount of acetone; pure acetone was eventually applied. The very hygroscopic substance was finally dried *in vacuo* over P_2O_5 . Analysis: Cl calc. 42.46, found 42.45; Ni calc. 23.43, found 23.46.

RbNiBr}_3 was prepared from NiCO_3 , RbCO_3 , and concentrated HBr in the same way as RbNiCl_3 . The dark brown crystals decompose in moist air. Analysis: Br calc. 62.45, found 62.04; Ni calc. 15.28, found 15.14.

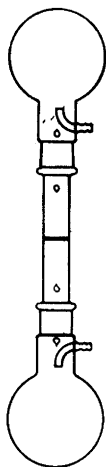


Fig. 1. Apparatus for preparation of RbNiCl_3 .

CRYSTAL STRUCTURES

RbNiCl_3 . Preliminary cell dimensions and symmetry information were obtained from Weissenberg photographs using Zr-filtered Mo-radiation. More precise cell dimensions were derived from a powder-photograph taken with Ni-filtered Cu-radiation using a 114 mm Debye-Scherrer camera, with a Straumanis mount of the film. The graphically extrapolated values of the hexagonal cell constants are $a_0 = 6.955(1)$ Å and $c_0 = 5.906(1)$ Å. The estimated standard deviations are in parenthesis throughout.

The observed density $3.353 \text{ g}\cdot\text{cm}^{-3}$ corresponds with 1.994 formula units per unit cell of volume 247.4 Å^3 .

The Friedel symmetry $6/mmm$ and the systematic extinctions, hkl absent for $l = 2n + 1$, are in keeping with the space groups $P6_3/mmc$, $P6_2c$ and $P\bar{6}_3mc$.

Intensity data were collected from two hexagonal crystal-needles with very nearly the same mean cross section 0.115 mm. ($\mu_l = 157 \text{ cm}^{-1}$, for $\text{MoK}\alpha$ -radiation). Integrated Weissenberg and precession photographs were produced and photometered as described in a previous paper.¹ The processing of data, including L_p and (cylindrical) absorption corrections, relative scaling, and assignment of an estimated standard deviation for each reflexion has been described in detail in that paper.

A Patterson projection $P(u,v)$ calculated by means of the von Eller photosommateur² was interpreted unequivocally in terms of 3 sets of special positions in space group $P6_3/mmc$:

- 2 Ni in pos. a : 0,0,0 etc.
- 2 Rb in pos. d : $1/3, 2/3, 3/4$ etc.
- 6 Cl in pos. h : $x, \bar{x}, 1/4$ etc., $x \sim 0.157$.

Isotropic least squares refinement was undertaken by means of the ORFLS-program, written by Busing, Martin and Levy.³ The atomic form factors used for Ni^{2+} , Rb^+ , and Cl^- are those given by Cromer and Waber⁴ plus the real part of the correction for anomalous dispersion (Cromer⁵). The

Table 1. Observed and calculated structure factors for RbNiCl₃

<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c
0 1 0	46.7	41.1	2 7 1	*	- 2.9
0 2 0	26.9	-21.8	3 3 1	0.0	0.0
0 3 0	64.8	66.3	3 4 1	*	- 4.7
0 4 0	14.1	-10.2	3 5 1	13.0	13.7
0 5 0	*	3.9	3 6 1	*	-10.6
0 6 0	74.4	76.6	3 7 1	*	- 7.2
0 7 0	31.9	26.9	4 4 1	0.0	0.0
1 1 0	71.2	80.0	4 5 1	16.0	-12.3
1 2 0	23.3	17.6	4 6 1	19.6	23.3
1 3 0	32.3	26.0	4 7 1	*	10.7
1 4 0	51.8	50.3	5 5 1	0.0	0.0
1 5 0	10.2	9.1	5 6 1	*	1.6
1 6 0	27.5	20.3			
1 7 0	30.6	27.5	0 0 2	90.7	-90.1
2 2 0	126.8	133.7	0 1 2	54.2	54.2
2 3 0	36.4	33.6	0 2 2	92.4	97.0
2 4 0	*	- 7.1	0 3 2	17.4	11.8
2 5 0	35.4	31.6	0 4 2	67.8	69.0
2 6 0	*	- 4.9	0 5 2	45.7	45.5
2 7 0	*	- 1.5	0 6 2	32.5	-31.7
2 8 0	34.3	34.1	0 7 2	*	6.3
3 3 0	50.3	46.6	0 8 2	27.4	27.7
3 4 0	*	2.6	1 1 2	23.7	12.2
3 5 0	17.1	11.4	1 2 2	58.9	58.7
3 6 0	24.3	22.0	1 3 2	41.5	40.6
3 7 0	*	3.7	1 4 2	14.0	7.6
4 4 0	61.8	61.7	1 5 2	33.2	35.1
4 5 0	23.4	22.2	1 6 2	18.4	16.0
4 6 0	*	- 1.7	1 7 2	*	2.7
4 7 0	13.3	11.7	1 8 2	19.8	21.5
5 5 0	28.3	22.7	2 2 2	52.6	-53.5
5 6 0	*	- 0.6	2 3 2	28.1	24.7
			2 4 2	50.3	53.0
0 0 1	0.0	0.0	2 5 2	15.5	8.7
0 1 1	37.4	-32.2	2 6 2	33.3	35.1
0 2 1	106.9	111.6	2 7 2	23.9	25.9
0 3 1	16.8	14.8	3 3 2	13.7	4.5
0 4 1	73.2	-72.4	3 4 2	35.8	36.7
0 5 1	*	5.5	3 5 2	20.1	21.0
0 6 1	*	- 0.6	3 6 2	*	5.5
0 7 1	14.5	-14.6	3 7 2	19.8	17.4
0 8 1	24.6	28.9	4 4 2	25.8	-25.3
1 1 1	0.0	0.0	4 5 2	*	5.5
1 2 1	22.5	-19.3	4 6 2	25.8	23.4
1 3 1	24.5	24.7			
1 4 1	11.2	-10.5	0 1 3	29.2	25.1
1 5 1	13.2	-13.0	0 2 3	84.0	-82.1
1 6 1	16.0	16.4	0 4 3	64.2	60.6
1 7 1	*	- 5.6	0 0 4	115.9	120.2
2 2 1	0.0	0.0	0 1 4	40.5	24.5
2 3 1	25.6	-24.4	0 3 4	42.4	43.2
2 4 1	53.4	55.3	0 2 5	54.4	57.3
2 5 1	16.3	15.6	0 4 5	45.2	-45.5
2 6 1	33.3	-34.8			

* Reflexion not observable.

results of the final refinement are $R_w=0.046$, $x(\text{Cl})=0.1566(3)$, $B(\text{Cl})=1.02(8)$, $B(\text{Ni})=0.98$, $B(\text{Rb})=1.59(9)$. In the investigated part of the reciprocal space 21 reflexions were too weak to be observed. The observed and calculated structure factors are listed in Table 1.

A projection of the structure on the xy -plane is shown in Fig. 2. The structure may be described as derived from a deformed hexagonal packing of layers of the composition RbCl_3 by introduction of Ni^{2+} -ions in $1/4$

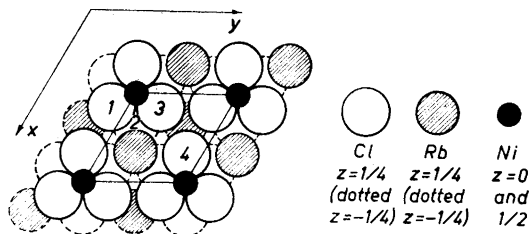


Fig. 2. RbNiCl_3 , projection on the xy -plane.

of the octahedral holes. The principal feature of the structure is the existence of discrete polyions $(\text{NiCl}_3)_n^{n-}$, formed by (NiCl_6) -octahedra sharing faces. RbNiCl_3 is isostructural with CsNiCl_3 ⁶ and several other double halides of the same formula type.

Interatomic distances and bond angles are listed in Table 2. The NiCl_6 -octahedra are trigonally deformed by stretching in the direction of the crystallographic c -axis due to the mutual repulsion of the Ni^{2+} ions. The $\text{Ni}-\text{Cl}$ bond length is $2.396(3)$ Å and the angle $\text{Cl}(1)-\text{Ni}-\text{Cl}(3)$ is $85.99(8)^\circ$. The Rb^+ -ion is 12-coordinated. The 6 coplanar $\text{Rb}-\text{Cl}$ bonds are $3.480(6)$ Å, while the 3+3 bonds "out of plane" are $3.640(5)$ Å. Almost the same bond lengths are found in the isostructural RbCoCl_3 ,¹² viz. $3.504(1)$ Å and $3.655(14)$ Å.

Table 2. Interatomic distances (Å) and bond angles ($^\circ$).

Ni — Cl(3)	2.396 (3)	Ni — Ni	$2.9530 (5) = \frac{1}{2}c_0$
Rb — Cl(3)	3.480 (6)	Ni — Ni	$6.955 (1) = a_0$
Rb — Cl(2)	3.640 (5)	Cl(1) — Ni — Cl(2)	94.01 (8)
Cl(1) — Cl(3)	3.267 (5)	Cl(1) — Ni — Cl(3)	85.99 (8)
Cl(1) — Cl(2)	3.504 (5)	Cl(1) — Rb — Cl(2)	58.91 (6)
Cl(3) — Cl(4)	3.688 (5)	Cl(1) — Rb — Cl(3)	55.98 (6)

RbNiBr_3 . The cell constants were determined from several precession photographs and averaged. $a=7.268(8)$ Å, $c=6.208(8)$ Å. The volume of the unit cell is 283.3 Å³. The reflexions hhl are systematically absent for $l=2n+1$, and the general pattern of intensities is similar to that of RbNiCl_3 . It is therefore considered safe to conclude that the bromide is isostructural with the chloride. An $\text{Ni}-\text{Br}$ bond length = 3.51 Å was calculated tentatively by putting $x(\text{Br})=0.157(1)$.

DISCUSSION

The crystal structures of the several known ANiX₃ compounds all display the infinite, linear poly-ions (NiX₃)_nⁿ⁻. In most cases the Ni—Ni distance within the poly-ion is remarkably short. Anomalous magnetic behavior, particularly at very low temperatures, is therefore expected. Magnetic investigations at helium temperatures have not been reported as yet, but measurements of the magnetic (powder) susceptibility⁷ in the temperature range 80°K to 300°K warrant these expectations.

The results of the magnetic investigation can be expressed by the formula $\chi = C/(T + \theta)$. The data collected in Table 3 show that the compounds investigated may be arranged in a series of bromides and a series of chlorides. A monotonous decrease of θ with increasing Ni—Ni distance is obvious in either series.

Table 3. Ni—Ni distances, Ni—Cl bond lengths in Å and the Weiss constants, θ , in °K, for some ANiX₃ compounds.

Compound	X = Cl				X = Br			
	Ni—Ni	Ni—Cl	θ	Ref.	Ni—Ni	Ni—Br	θ	Ref.
RbNiX ₃	2.953(1)	2.40	112	7	3.104(4)	2.51	156	7
CsNiX ₃	2.968(1) ^a	2.44	76	6,7	3.120(1) ^a	2.56	101	11,7
CH ₃ NH ₃ NiX ₃	2.975(5)	{2.35 2.41	60	10,7	
C ₆ H ₅ NHNiX ₃	36	7	32	
(CH ₃) ₄ NNiX ₃	3.055(1)	2.41	0	8,9	3.175(5)	{2.67 2.45	...	11

^a The preliminary c_H value quoted in Ref. 7 is twice the correct value.

At least in case of the Rb and Cs compounds θ is much larger for the bromides than for the chlorides. That is, the magnetic exchange strongly depends on the nature of the bridging halogen atoms.

The Ni—halogen bond length and the symmetry of the coordination polyhedron are important also. The large decrease in θ when passing from RbNiX₃ to CsNiX₃ is rather attributed to the longer Ni—X bond in the latter than to the very moderate increase in the Ni—Ni distance.

The Ni—Ni distance in CH₃NH₃NiCl₃ is virtually the same as in CsNiCl₃ while the average Ni—Cl bond length is considerably shorter. The effect of this, however, is opposed by the reduced symmetry of the coordination polyhedron, so the net result is a significant decrease in the θ value.

A crystal structure analysis of C₆H₅NHNiCl₃ has not been accomplished as yet. A preliminary investigation seems to indicate that this compound also contains the characteristic poly-ion and that the Ni—Ni distance is 3.03 Å. Thus C₆H₅NHNiCl₃ fits into the scheme at the expected place between CH₃NH₃NiCl₃ and (CH₃)₄NNiCl₃.

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