



Syntheses and structure of hydrothermally prepared CsNiX₃ (X=Cl, Br, I)

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ABSTRACT

During reinvestigation of the hydrothermal synthesis reported earlier of the compound cesium nickel phosphide, “CsNiP”, we arrived at a new route to the synthesis of the cesium nickel halide compounds CsNiX₃ (X=Cl, Br, I). The method has also been shown to extend to cobalt and iron compounds. Single crystals of these compounds were synthesized in phosphoric acid in sealed autoclaves. Their structures were determined by single-crystal X-ray diffraction methods. The compounds crystallize in the hexagonal space group *P6₃/mmc* in the BaNiO₃ structure type. The synthetic method and the resultant crystallographic details for CsNiCl₃ are essentially identical with those reported earlier for the synthesis and structure of “CsNiP”.

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1. Introduction

The hydrothermal synthesis and crystal structure of “CsNiP” were reported earlier [1,2]. The synthesis of a phosphide was very interesting because the source of phosphorus was described as phosphoric acid, which was postulated to reduce to a phosphide during the reaction. The stability of the phosphates in water and the high reduction potential necessary to convert P 5+ to P 3−, a species that exists in a narrow part of the low-pH and high reduction potential region of the Pourbaix diagram [3], suggested a truly unique reaction system. The crystal structure of “CsNiP” was equally remarkable with Ni being octahedrally coordinated by six P atoms, the P atoms being two-coordinate. However, instead of confirming the expected products of the synthesis we found it to represent a novel route to crystal growth of the cesium nickel halides.

The perovskite ABX₃ structure type holds particular interest in solid-state chemistry because of its ubiquity and flexibility. Perovskites have been shown to crystallize in a variety of forms and occur for almost every element thus allowing for a wide range of properties and applications. Whereas oxide perovskites are the most common and well studied there has also been significant research on perovskite structures containing other anions [4–7]. In particular, the hexagonal halide perovskites have drawn interest because of their pseudo one-dimensional structures and predicted magnetic anisotropy and luminescence [8–11]. Although there have been many studies of the electronic

and optical properties of such compounds comparatively little attention has been paid to their structure. Previously such halide perovskites had been synthesized by a wide variety of methods, most of which required relatively harsh conditions [7,8,12]. Here we present a comparatively low-temperature route to the synthesis of CsNiX₃ compounds.

2. Experimental

2.1. Syntheses

All reactions were conducted in a 23 mL Teflon liner inside a sealed Parr pressure vessel. CsOH·XH₂O (99.9%, Alfa Aesar), NiCl₂·6H₂O (98%, Aldrich), NiBr₂ (98%, Aldrich), and NiI₂ (Alfa) were dried in a vacuum oven before weighing. o-H₃PO₄ (85%, Fischer) was used as received. In all syntheses 3.3 mmol (0.5 g) CsOH, and 1.9 mmol (0.247/0.416/0.636 g) NiX₂ (X=Cl, Br, I) were placed in the Teflon liner to which 0.85 mL (12.9 mmol) of o-H₃PO₄ were added. The reaction began immediately upon the combination of the starting materials with phosphoric acid so care was taken to seal the vessels as quickly as possible. In order to produce the best yield of crystalline products the pressure vessels were then heated to 523 K at a rate of 6 K/h, held there for 66 h, and then cooled to 293 K at a rate of 6 K/h. The crystalline products, approximate yield 70% based on the halide, were separated mechanically from a pale green amorphous substrate. CsNiCl₃ crystallized as thin pink/orange hexagonal prisms, CsNiBr₃ crystallized as thick orange/brown hexagonal blocks, and CsNiI₃ crystallized as dark purple/black needles.

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Elemental composition was determined by EDX analysis on a Hitachi S-3400 scanning electron microscope. The crystals showed a composition of cesium, nickel and the corresponding halide. Oxygen is below the detection limit of the instrument and so could not be adequately measured by this method but phosphorus was not detected in any of the samples.

2.2. Structure determinations

Crystals of CsNiX_3 ($X=\text{Cl, Br, I}$) were sensitive to moisture. The stability decreased in the expected order $\text{CsNiCl}_3 > \text{CsNiBr}_3 > \text{CsNiI}_3$ although the degree of stability was also dependent on surface area and morphology. To prevent decomposition the crystalline products were immediately placed under mineral oil and stored under vacuum. Single crystals for X-ray diffraction

Table 1
Crystallographic details of the compounds CsNiX_3 ($X=\text{Cl, Br, I}$)a.

	CsNiCl_3	CsNiBr_3	CsNiI_3
a (Å)	7.1185(2)	7.4312(1)	7.9469(2)
c (Å)	5.9085(1)	6.2023(1)	6.6575(2)
V (Å ³)	259.29(1)	296.620(7)	364.114(17)
ρ (g/cm ³)	3.817	4.830	5.220
μ (mm ⁻¹)	12.021	29.364	20.181
q	0.0106	0.0185	0.0077
R (F) ^b	0.0111	0.0167	0.0106
R_w (F ²) ^c	0.0267	0.0435	0.0358

^a For all compounds $T=100$ K, $Z=2$, $\lambda=0.71073$ Å.

^b $R_1(F) = \frac{\sum \|F_o\| - \sum \|F_c\|}{\sum \|F_o\|}$ for $F_o^2 > 2\sigma(F_o^2)$.

^c $R_w(F_o^2) = \frac{[\sum w(F_o^2 - F_c^2)^2]^{1/2}}{[\sum wF_o^4]^{1/2}}$. For $F_o^2 < 0$, $w^{-1} = c^2(F_o^2)$; for $F_o^2 \geq 0$, $w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$.

Table 2
Selected interatomic distances in (Å).

Distance	CsNiCl_3	CsNiBr_3	CsNiI_3
Ni-X (x6)	2.4088(3)	2.5524(3)	2.7548(2)
Cs-X (x6)	3.5625(1)	3.7175(1)	3.9747(1)
Cs-X (x6)	3.6877(2)	3.8390(2)	4.0997(2)

were placed under heavy oil or epoxy to limit exposure to air during the collection. The structures of these isostructural compounds were determined from single-crystal X-ray diffraction data collected on a Bruker SMART APEX CCD diffractometer [13,14]. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program SADABS [15]. The structures were solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL [16]. The program STRUCTURE TIDY was used to standardize the positional parameters [17]. Additional details of the refinements can be found in Table 1 and in the Supporting material. Selected metrical data may be found in Table 2.

3. Results and discussion

3.1. Syntheses

Previous methods for the synthesis of CsNiX_3 ($X=\text{Cl, Br, I}$) crystals have relied either on high-temperature reactions in evacuated fused-silica tubes and recrystallization with a salt flux, or on precipitation by evaporation of a concentrated solution of the corresponding halide acid [7,10,18]. By comparison the current hydrothermal syntheses, which involve CsOH , NiX_2 , and $o\text{-H}_3\text{PO}_4$, require relatively mild conditions and produce little waste. Owing to the low volume of solvent in the original reaction, all resulting products were solids, requiring phases beyond the halide perovskites for mass balance. The CsNiX_3 phases, however, represented the only crystalline phases and could be separated mechanically or by simple washing. The procedure is general for other transition metals, for example brown crystals of CsFeCl_3 and blue crystals of CsCoCl_3 were prepared with FeCl_2 and CoCl_2 , respectively.

3.2. Structures

The isostructural compounds CsNiX_3 ($X=\text{Cl, Br, I}$) crystallize with two formula units in the hexagonal space group $P6_3/mmc$ in the BaNiO_3 structure type. The structure consists of chains of face-sharing NiX_6 octahedra separated by CsX_{12} cuboctahedra (Fig. 1). The Ni-X distances seen in Table 2 are close to the distances of 2.50, 2.65, and 2.89 Å for 6-coordinate nickel(II) surrounded by

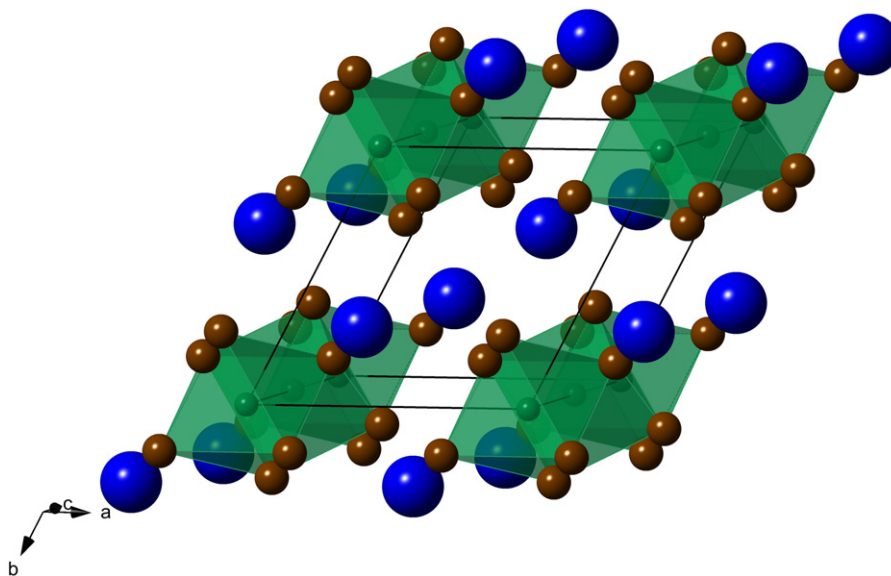


Fig. 1. The CsNiX_3 ($X=\text{Cl, Br, I}$) structure. Cesium is blue, nickel is in dark green polyhedra, halide is brown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

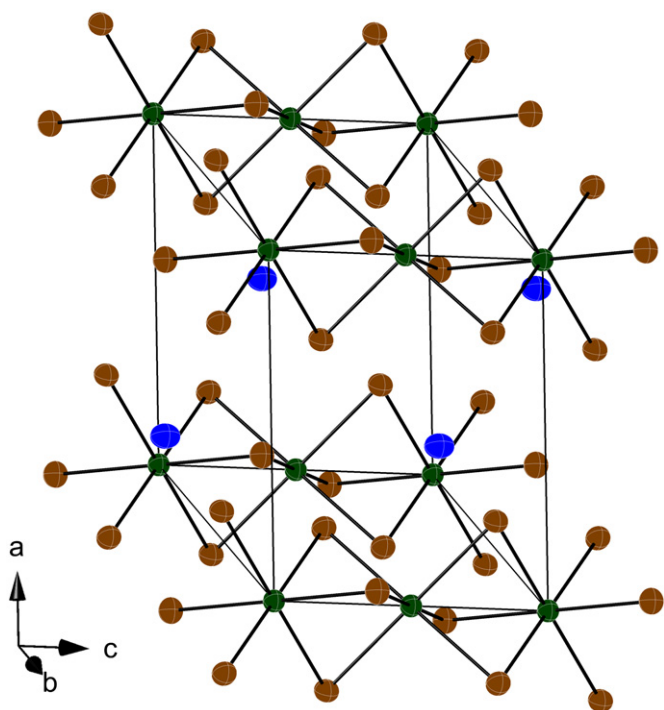


Fig. 2. The CsNiCl_3 unit cell with displacement ellipsoids drawn at the 95% probability level. Cesium is blue, nickel is dark green, chlorine is brown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Comparison of structural results for two determinations of CsNiCl_3 and for “ CsNiP ”.

Item	CsNiCl_3^a	CsNiCl_3^b	“ CsNiP ” ^c
a (Å)	7.1185(2)	7.171(1)	7.173(2)
c (Å)	5.9085(1)	5.944(3)	5.944(9)
V (Å ³)	259.29(1)	264.71	264.87(7)
T (K)	100	293	293
Ni–Cl or NiP (x6) (Å)	2.4088(3)	2.4169(6)	2.4164(1)
Cs–Cl or CsP (x6) (Å)	3.5625(1)	3.5893(5)	3.5904(4)
Cs–Cl or CsP (x6) (Å)	3.6877(2)	3.7181(12)	3.7191(1)

^a This work.

^b Ref. [18].

^c Ref. [1].

six chlorine, bromine or iodine atoms, respectively according to the radii of the ions [19]. Likewise the average Cs–X distances remain close to the predicted values of 3.69, 3.85, and 4.08 Å for cesium coordinated by 12 bromine, bromine, or iodine [19]. The slight decrease in bond lengths is most likely due to the collection temperature of 100 K. The unit cell of CsNiCl_3 with displacement ellipsoids at 95% probability can be seen in Fig. 2.

Table 3 compares some crystallographic results for the present CsNiCl_3 , the previously determined structure [18], and the structure of “ CsNiP ” [1]. The cell constants and interatomic distances among the three structures are in excellent agreement. The small differences result from the different temperatures for data collection between 100 K for the current structure and room temperature for previous reports.

Turning now to the structure of “ CsNiP ” we find that the crystallographic data presented [1] lead to a structure composed of unlikely 2-coordinate phosphorus. The resultant structure comprised of NiP_6 partially occupied octahedra lacks reasonable

coordination environments for both nickel and phosphorus. Given that the difference in X-ray scattering power of P and Cl is not large, and the absence of compositional data in the original report of CsNiP , it is reasonable to presume that the compound actually synthesized and characterized structurally was CsNiCl_3 , rather than “ CsNiP ”. The results presented in Table 3 clearly support this presumption.

4. Conclusions

The structure of “ CsNiP ” had been previously reported [1,2] as a unique example of a hydrothermally prepared phosphide. Repetition of the reported synthesis has resulted in the compound CsNiCl_3 . As a further confirmation, the synthetic procedure repeated with NiBr_2 and NiI_2 resulted in the products CsNiBr_3 and CsNiI_3 . The compositions of the resulting compounds were confirmed crystallographically and by EDX analysis. This hydrothermal synthetic method to produce single crystals of cesium nickel halides is more energy efficient and less waste intensive than those previously reported. It is presumed that the original synthesis [1] of “ CsNiP ” actually produced CsNiCl_3 .

Supporting material

The crystallographic data for CsNiCl_3 , CsNiBr_3 , and CsNiI_3 have been deposited with FIZ Karlsruhe as CSD numbers 423828, 423829, and 423830 respectively. These data may be obtained free of charge by contacting FIZ Karlsruhe at +497247808666 (fax) or crysdata@fiz-karlsruhe.de (email).

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2012.03.037.

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