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Dineptunium Sodium Nonafluoride

BY ALAIN COUSSON, HICHAM ABAZLI, ALAIN TABUTEAU ET MONIQUE PAGÈS

Laboratoire Curie, associé au CNRS, 11 rue Pierre et Marie Curie, 75231 Paris CEDEX 05, France

ET MADELEINE GASPERIN

Laboratoire de Minéralogie–Cristallographie, associé au CNRS, Université Pierre et Marie Curie, 4 place Jussieu, 75230 Paris CEDEX 05, France

Abstract. NaNp$_2$F$_9$, orthorhombic, *Pnma*, $a = 8.617$ (5), $b = 11.274$ (9), $c = 6.955$ (4) Å, $V = 676$ Å^3, $d_{calc} = 6.56$ Mg m^{-3}, $Z = 4$. The Np atoms are surrounded by nine F atoms at distances between 2.260 (5) and 2.371 (5) Å. Na atoms are surrounded by ten F atoms at distances between 2.552 (6) and 3.171 (6) Å. This compound, prepared by hydrothermal synthesis, is isostructural with KU$_2$F$_9$. The crystal structure was refined to $R = 0.030$ for 1816 independent reflexions.

Introduction. NaTh$_2$F$_9$ was reported to be cubic (Zachariasen, 1948). NaU$_2$F$_9$ is orthorhombic and was thought probably to be isomorphous with KU$_2$F$_9$ by Thoma, Insley, Herbert, Friedman & Weaver (1963). Since this type of compound was unknown for Np, we decided to synthesize NaNp$_2$F$_9$ as single crystals in order to establish its crystal structure and to compare it with the existing Th and U compounds.

In our laboratory we recently introduced an apparatus that enables us to prepare single crystals of transuranium fluoride complexes: hydrothermal synthesis under hydrofluoric acid atmosphere. In fact, the flux-growth method, previously used successfully for the preparation of single crystals containing actinide elements, presented some drawbacks which do not appear with this new method. In particular, cation exchange between the chloride flux and the fluoride compound to be synthesized do not occur (Cousson, Tabuteau, Pagès & Gasperin, 1979). A major advantage is that single crystals can be grown using very small quantities of transuranium tetrafluoride.

NaNp$_2$F$_9$ is the first neptunium fluoride obtained as single crystals using hydrothermal synthesis. 20 mg of

a sodium fluoride and neptunium tetrafluoride mixture with a ratio $1NaF/2NpF_4$ were placed in a gold tube. The gold tube, sealed after adding hydrofluoric acid, was then introduced into the autoclave under an initial pressure of about 100 MPa. It was then heated to 800 K and maintained for several hours at a pressure of about 220 MPa. After slow cooling (5 K h^{-1}) to the initial temperature and pressure conditions, the gold tube contained a large number of clear green crystals with complicated morphology and many faces.

All experiments were performed in glove boxes under low vacuum because the isotope used (^{237}Np) is an α emitter with a long period ($2 \cdot 14 \times 10^6$ a).

The single crystal used for the measurement of intensities was nearly spherical (radius $R = 55$ μm). A Philips PW 1100 diffractometer with a graphite monochromator was used. Cell parameters and the space group were determined by a preliminary study of single crystals with Weissenberg and precession photographs and then of powder on a focusing goniometer. Cu $K\bar{\alpha}$ and Mo $K\bar{\alpha}$ radiations were used (Laue group mmm; reflexion conditions: $0kl$, $k + l = 2n$; $hk0$, $k = 2n$; results are consistent with space groups $Pn2_1a$ and $Pnma$). 2881 reflexions were measured; scanning mode: θ–2θ step scan [80 steps ($0 \cdot 02°\theta$ per step)] with a counting time of 2 s per step; background determination: correlation algorithm. Three standard reflexions were measured after every 35 reflexions. Intensities were then treated using a program from the Laboratory of Mineralogy–Crystallography (Rigoult, 1978), deduced from that of Blessing, Coppens & Becker (1974). This program optimizes intensities, corrects with the Lorentz–polarization factor and calculates the structure factors and their relative σ deviation. Spherical absorption corrections were made ($\mu R \simeq 1 \cdot 1$).

A three-dimensional Patterson map enabled us to determine the positions of the heavy atoms in the space group $Pnma$ and to predict the positions of the Na and F atoms. We then made sure that this compound is isostructural with KU_2F_9, the structure of which was established by Brunton (1969) and the crystallographic data of which were previously given by Zachariasen (1948). A series of refinements were made [program AFFINE: a modified version of ORFLS (Busing, Martin & Levy, 1962)]. After omitting the weakest reflexions, we obtained $R = 0 \cdot 030$ and $R_w = 0 \cdot 049$ for the 1816 remaining reflexions.* The scattering factors used were those given in International Tables for X-ray Crystallography (1974). Anomalous-dispersion corrections for the heavy atoms were used in the calculation of the structure factors.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36694 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Atomic parameters are listed in Table 1 and principal interatomic distances in Table 2.

In this structure the Np atom is surrounded by nine F atoms. The coordination polyhedron resembles a tricapped trigonal prism. The Na atom is surrounded by ten F atoms at distances between $2 \cdot 552$ (6) and $3 \cdot 171$ (6) Å. A comparison of $NaNp_2F_9$ and KU_2F_9 shows the expected contraction when K is replaced by Na and U by Np. The F–F distances of KU_2F_9 (given in Table 2) show this contraction of the anionic packing and illustrate that the shortest F–F distances remain unchanged.

Table 1. *Atomic positional parameters* ($\times 10^4$) *and* B_{eq} *values, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij} \, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Np	3260 (<1)	4504 (<1)	3456 (<1)	0·5 (1)
Na	4637 (4)	$\frac{1}{4}$	8581 (6)	0·3 (1)
F(1)	−46 (5)	5995 (5)	759 (7)	1·0 (2)
F(2)	2922 (5)	976 (5)	269 (7)	1·1 (2)
F(3)	2857 (6)	6083 (5)	1422 (7)	1·1 (2)
F(4)	5664 (6)	801 (5)	1984 (7)	1·2 (2)
F(5)	3270 (9)	$\frac{1}{4}$	3375 (10)	1·0 (2)

Table 2. *Principal interatomic distances* (Å)

Np–F(5)	2·260		2× Na–F(2)	2·552
Np–F(4)	2·284		2× Na–F(1)	2·618
Np–F(1)	2·291		2× Na–F(3)	2·686
Np–F(1)	2·292		2× Na–F(3)	3·070
Np–F(3)	2·300		2× Na–F(4)	3·171
Np–F(2)	2·300		Mean standard	0·006
Np–F(2)	2·320		deviation	
Np–F(4)	2·336			
Np–F(3)	2·371			
Mean standard	0·005			
deviation				

	$NaNp_2F_9$	KU_2F_9
F(1)–F(1)	2·48 (1)	2·49 (3)
F(1)–F(3)	2·546 (8)	2·55 (3)
F(1)–F(2)	2·579 (8)	2·60 (3)
F(1)–F(4)	2·634 (8)	2·65 (3)
F(1)–F(3)	2·668 (8)	2·70 (3)
F(1)–F(4)	2·688 (8)	2·71 (3)
F(1)–F(5)	2·823 (8)	2·89 (3)
F(2)–F(3)	2·457 (8)	2·47 (3)
F(2)–F(4)	2·654 (8)	2·66 (3)
F(2)–F(4)	2·734 (8)	2·76 (3)
F(2)–F(3)	2·761 (8)	2·78 (3)
F(2)–F(5)	2·776 (8)	2·82 (3)
F(2)–F(4)	2·820 (8)	2·89 (3)
F(3)–F(4)	2·709 (8)	2·79 (3)
F(3)–F(5)	2·826 (8)	2·86 (3)
F(3)–F(4)	3·052 (8)	
F(4)–F(5)	2·962 (8)	2·99 (3)
F(4)–F(5)	2·977 (8)	

There is no significant difference between the structures of $NaNp_2F_9$ and KU_2F_9. In this case, U and Np have a similar behaviour, different from that of Th. This study confirms that compounds with U and Na at this stoichiometry are isomorphous with compounds containing U and K. The value of the ionic radius for Np^{IV} in nine coordination is not given by Shannon (1976). With regards to the Np—F distances, no great difference should be expected between ionic radii when going from eight ($r_{Np^{IV}} = 0.98$ Å in eight coordination) to nine coordination.

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$La_3Rh_4Ge_4$ of Orthorhombic $U_3Ni_4Si_4$ Type

BY E. HOVESTREYDT, K. KLEPP AND E. PARTHÉ

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

Abstract. Trilanthanum tetrarhenium tetragermanide, $La_3Rh_4Ge_4$, orthorhombic, space group *Immm*, $a = 4.1746$ (3), $b = 4.2412$ (2), $c = 25.234$ (3) Å, $Z = 2$, $D_x = 8.32$ Mg m^{-3}, μ(Mo $K\alpha$) = 35.1 mm^{-1}, $F(000) = 958$, $R = 0.035$ (271 F_o). The structure is of the $U_3Ni_4Si_4$ type. A comparison with the $Gd_3Cu_4Ge_4$ type, reported for the $Sc_3Ni_4Si_4$ compound among others, is given.

Introduction. In the course of a systematic study of equiatomic ternary rare-earth transition-metal gallides, silicides and germanides (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982) the compounds *R*RhGe were investigated. It was found that from CeRhGe to TmRhGe a series of isotypic compounds with the TiNiSi structure type is formed. The powder diffraction diagram of the lanthanum compound was, however, completely different and could not be interpreted with any of the known ternary equiatomic structure types found in similar systems. Therefore it appeared necessary to undertake a single-crystal study.

A sample of nominal composition LaRhGe was prepared by arc melting stoichiometric amounts of high-purity elements (La: 99.9%, Rh: 99.99%, Ge: 99.999%) under purified Ar atmosphere. Microscopic investigation showed that the sample was not single phased. One component, however, was well crystallized. A single crystal of prismatic shape (50 × 60 × 100 μm) was selected and mounted on a computer-controlled single-crystal diffractometer (Philips PW 1100 with graphite-monochromated Mo $K\alpha$ radiation). Preliminary crystallographic investigations indicated an *I*-centered cell of Laue symmetry *mmm*. The only systematic absences were those of the body-centered Bravais lattice leading to *Immm*, *Imm*2, $I2_12_12_1$ or *I*222 as possible space groups. The lattice constants given in the *Abstract* were obtained by least-squares refinement of the 2θ values of 34 reflections measured with Mo $K\alpha_1$ radiation ($\lambda = 0.7093$ Å). Intensity data were collected using ω–2θ scans in one quadrant of reciprocal space ($6 \le 2\theta \le 54°$). Absorption was accounted for by a spherical absorption correction ($\mu R = 1.4$). Averaging of equivalent reflections yielded a unique set of 323 reflections of which 237 with $I > 3\sigma(I)$ were considered as significant.

Comparison of the unit-cell volume with those of the other *R*RhGe compounds assuming similar density led to an estimate of 20–24 atoms for the unit-cell content. Symmetry and the relative cell dimensions indicated a relationship with $U_3Ni_4Si_4$ (*oI*22, *Immm*) (Yarmolyuk, Akselrud, Grin, Fundamenskii & Gladyshevskii, 1979). Hence the atomic positions of this structure were used