

Preparation and Crystal Structures of $M[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ ($M = \text{Mg}, \text{Zn}$)

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The crystals of two isostructural uranyl selenates, $M[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ ($M = \text{Mg}, \text{Zn}$), have been prepared by water evaporation from aqueous solutions. The structures have been solved by direct methods ($M = \text{Mg}$: $P2_1/c$, $a = 8.4666(8)$, $b = 11.6306(14)$, $c = 13.1669(12)$ Å, $\beta = 90.959(7)^\circ$, $V = 1296.4(2)$ Å³, $R_1 = 0.061$; $M = \text{Zn}$: $P2_1/c$, $a = 8.4492(18)$, $b = 11.5860(17)$, $c = 13.240(3)$ Å, $\beta = 92.382(18)^\circ$, $V = 1294.9(4)$ Å³, $R_1 = 0.074$). The structures are based upon $[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})]^{2-}$ chains running parallel to the b axis and consisting of corner-sharing $[\text{UO}_6(\text{H}_2\text{O})]^{6-}$ pentagonal bipyramids and $[\text{SeO}_4]^{2-}$ tetrahedra. The equatorial planes of the uranyl pentagonal bipyramids are oriented approximately parallel to (001). The uranyl selenate chains are linked into sheets parallel to (010) by $[M(\text{H}_2\text{O})_6]^{2+}$ octahedra which share common H_2O molecules with the $[\text{UO}_6(\text{H}_2\text{O})]^{6-}$ pentagonal bipyramids.

Key words: Uranyl Selenate, Magnesium, Zinc, Crystal Structure

Introduction

Uranyl minerals and uranyl compounds have received considerable attention within the last years because of their important role in radioactive waste management and safe disposal of spent nuclear fuel [1–3]. Uranium oxysalts containing selenium are of special interest because ^{79}Se is a long-lived fission product with a half-life of 1.1×10^6 years and is chemically and radiologically toxic [4].

Uranyl selenates of divalent metals were first studied by Serezhkin *et al.* [5]. These authors reported uranyl selenates with general formula $M\text{UO}_2(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ where M is Mg, Co, or Zn. The powder X-ray diffraction patterns for these compounds were indexed on the basis of monoclinic C -centered cells with parameters $a = 19.39 - 19.43$, $b = 10.44 - 10.46$, $c = 17.86 - 17.91$ Å, $\beta = 91.1 - 91.2^\circ$. Later, Serezhkina and Serezhkin [6] re-investigated the Mg phase and demonstrated that its correct formula is $\text{Mg}_2(\text{UO}_2)_3(\text{SeO}_4)_5(\text{H}_2\text{O})_{16}$ and that it is monoclinic, space group $C2/c$, $a = 19.47(2)$, $b = 10.45(1)$, $c = 17.95(2)$ Å, $\beta = 91.1(1)^\circ$, $Z = 4$. Our recent structure determination of this compound [7]

confirmed the formula and the crystallographic parameters given above. Serezhkina and Serezhkin [8] also investigated the $\text{MnSeO}_4 - \text{UO}_2\text{SeO}_4 - \text{H}_2\text{O}$ system at 25°C and reported formation of the phase $\text{MnUO}_2(\text{SeO}_4)_2 \cdot 5\text{H}_2\text{O}$, for which they obtained the orthorhombic space group $Pm2_1n$ with lattice parameters $a = 13.576$, $b = 11.642$, $c = 8.519$ Å, $Z = 4$. However, the structure of $\text{MnUO}_2(\text{SeO}_4)_2 \cdot 5\text{H}_2\text{O}$ has not been determined. Herein we report the crystal structures of the Mg and Zn analogs of this compound.

Experimental Section

Preparation: Single crystals of $\text{Mg}[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ were prepared by water evaporation from aqueous solution. 0.115 g $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.03 g MgO , and 0.3 ml of a 40%-solution of H_2SeO_4 in water were mixed with 2 ml of H_2O . The yellow homogeneous liquid was left to evaporate in a fumehood. The crystals of the compound began to crystallize within ca. 48 hours, together with crystals of α - and β - $\text{Mg}_2[(\text{UO}_2)_3(\text{SeO}_4)_5](\text{H}_2\text{O})_{16}$ [7]. For the preparation of single crystals of $\text{Zn}[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$, 0.170 g of $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.03 g of ZnO , and 0.3 ml of a 40%-solution of H_2SeO_4 were mixed with 2 ml of H_2O . The

Table 1. Crystallographic data and refinement parameters for $M[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ ($M = \text{Mg}, \text{Zn}$).

Compound	Mg	Zn
a [Å]	8.4666(8)	8.4492(18)
b [Å]	11.6306(14)	11.5860(17)
c [Å]	13.1669(12)	13.240(3)
β [°]	90.959(7)	92.382(18)
V [Å ³]	1296.4(2)	1294.9(4)
Space group	$P2_1/c$	$P2_1/c$
μ [mm ⁻¹]	18.260	20.039
Z	4	4
D_{calc} [g/cm ³]	3.435	3.649
Crystal size [mm ³]	$0.07 \times 0.09 \times 0.09$	$0.14 \times 0.16 \times 0.04$
Diffractometer	Stoe IPDS II	Stoe IPDS II
Radiation	Mo- K_{α}	Mo- K_{α}
Total ref.	16226	10813
Unique ref.	2833	3146
2θ Range, °	4.68–54.02	4.68–56.14
Unique $ F_o \geq 4\sigma_F$	2695	2519
R_{int}	0.085	0.125
R_{σ}	0.041	0.085
$R_1(F_o \geq 4\sigma_F)$	0.061	0.074
$wR_2(F_o \geq 4\sigma_F)$	0.135	0.150
R_1 (all data)	0.066	0.095
wR_2 (all data)	0.141	0.159
S	1.088	1.267
$\rho_{\text{min}}, \rho_{\text{max}}, e/\text{\AA}^3$	–3.241, 4.241	–3.272, 2.371

Note: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

Table 2. Atomic coordinates and displacement parameters (Å²) for $\text{Mg}[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$.

Atom	x	y	z	U_{eq}
U	0.61720(8)	0.09313(5)	0.75282(6)	0.0178(2)
Se1	–0.2405(2)	–0.21836(13)	0.75793(14)	0.0175(4)
Se2	0.2628(2)	–0.09969(14)	0.77104(13)	0.0184(4)
Mg	–0.1582(8)	–0.2722(5)	0.0063(5)	0.022(1)
O1	–0.267(2)	–0.0869(11)	0.7956(11)	0.029(3)
O2	0.671(2)	0.1306(12)	0.8794(11)	0.035(4)
O3	0.4191(19)	0.2262(14)	0.7778(11)	0.039(4)
O4	0.250(2)	–0.1029(12)	0.6491(11)	0.035(4)
O5	0.4132(16)	–0.0216(11)	0.8115(11)	0.025(3)
H ₂ O6	0.0878(18)	–0.2715(13)	0.9996(13)	0.032(4)
O7	–0.153(2)	–0.2867(12)	0.8485(10)	0.029(4)
O8	0.5673(19)	0.0559(12)	0.6264(10)	0.027(3)
O9	–0.1276(19)	–0.2202(13)	0.6603(10)	0.028(3)
H ₂ O10	0.8990(18)	0.0749(11)	0.7006(11)	0.029(3)
O11	0.2856(18)	–0.2317(11)	0.8153(11)	0.026(3)
O12	0.1044(19)	–0.0490(12)	0.8219(12)	0.030(3)
H ₂ O13	–0.162(3)	–0.0969(14)	0.0082(13)	0.047(5)
H ₂ O14	–0.168(2)	–0.0522(13)	0.5035(12)	0.037(4)
H ₂ O15	0.4068(19)	0.2728(17)	0.9944(15)	0.046(5)

solution was left to evaporate in a fumehood at room temperature. After *ca.* 24 hours, isometric yellow crystals of $\text{Zn}[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ were formed together with yellow transparent plates of $\text{Zn}_2[(\text{UO}_2)_3(\text{SeO}_4)_5](\text{H}_2\text{O})_{17}$

Table 3. Selected interatomic distances (Å) in the structure of $\text{Mg}[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$.

U–O8	1.77(1)	Se2–O4	1.61(2)
U–O2	1.77(2)	Se2–O12	1.62(2)
U–O3	2.31(1)	Se2–O5	1.65(1)
U–O5	2.33(1)	Se2–O11	1.65(1)
U–O1	2.38(1)	⟨Se2–O⟩	1.63
U–O11	2.38(1)		
U–H ₂ O10	2.50(2)	Mg–H ₂ O13	2.04(2)
⟨U–O _{Ur} ⟩	1.77	Mg–H ₂ O9	2.04(2)
⟨U–O _{eq} ⟩	2.38	Mg–H ₂ O14	2.04(2)
		Mg–H ₂ O7	2.09(2)
Se1–O7	1.61(1)	Mg–H ₂ O6	2.09(2)
Se1–O9	1.62(1)	Mg–H ₂ O15	2.11(2)
Se1–O1	1.62(1)	⟨Mg–H ₂ O⟩	2.07
Se1–O3	1.70(1)		
⟨Se1–O⟩	1.64		

Table 4. Atomic coordinates and displacement parameters (Å²) for $\text{Zn}[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$.

Atom	x	y	z	U_{eq}
U	0.61849(7)	0.09298(5)	0.75439(4)	0.0183(2)
Se1	–0.24199(18)	–0.22026(14)	0.75550(11)	0.0175(3)
Se2	0.26229(19)	–0.09904(15)	0.77192(12)	0.0211(3)
Zn	–0.1614(3)	–0.27224(19)	0.00633(15)	0.0264(4)
O1	–0.2664(14)	–0.0864(10)	0.7950(9)	0.023(2)
O2	0.6815(17)	0.1284(11)	0.8805(10)	0.032(3)
O3	0.4234(17)	0.2302(13)	0.7805(10)	0.035(3)
O4	0.2485(19)	–0.1001(13)	0.6496(9)	0.038(3)
O5	0.4122(15)	–0.0216(11)	0.8138(9)	0.027(3)
H ₂ O6	0.0857(18)	–0.2783(14)	0.9981(11)	0.039(3)
O7	–0.1594(17)	–0.2968(10)	0.8485(9)	0.028(3)
O8	0.5578(17)	0.0570(12)	0.6287(8)	0.031(3)
O9	–0.1213(13)	–0.2247(13)	0.6623(8)	0.027(3)
H ₂ O10	0.8947(17)	0.0725(11)	0.7006(10)	0.031(3)
O11	0.2884(17)	–0.2300(11)	0.8146(10)	0.033(3)
O12	0.1069(16)	–0.0470(13)	0.8234(11)	0.035(3)
H ₂ O13	–0.151(3)	–0.0955(13)	0.0062(11)	0.062(6)
H ₂ O14	–0.172(2)	–0.0497(12)	0.5053(10)	0.043(4)
H ₂ O15	0.412(2)	0.2678(18)	0.9971(13)	0.058(5)

[9], $\text{Zn}_2[(\text{UO}_2)_3(\text{SeO}_4)_5](\text{H}_2\text{O})_{16}$ [10], and colorless crystals of $\text{ZnSeO}_4(\text{H}_2\text{O})_2$ [11].

Structure analysis: The crystals selected for data collection were examined under an optical microscope and mounted on glass fibers. Data were collected by means of a STOE IPDS II diffractometer using monochromated Mo- K_{α} X-radiation and framewidths of 2° in ω . The unit-cell dimensions (Table 1) were refined by least-squares techniques. The data were corrected for Lorentz, polarization, and background effects. For both compounds, an analytical absorption correction based on the indexed faces was applied. The structures were solved and refined by means of the programs SIR-92 [12] and SHELXL-97 [13], respectively. For the structure of $\text{Mg}[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$, a twinning model was introduced at the last stages of the refinement by means of the matrix $[\bar{1}00/010/001]$ (pseudomerohedral twinning of mono-

Table 5. Selected interatomic distances (Å) in the structure of $\text{Zn}[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$.

U–O8	1.77(1)	Se2–O4	1.62(1)
U–O2	1.78(1)	Se2–O12	1.62(1)
U–O3	2.33(2)	Se2–O5	1.63(1)
U–O1	2.35(1)	Se2–O11	1.63(1)
U–O5	2.35(1)	⟨Se2–O⟩	1.63
U–O11	2.39(1)		
U–H ₂ O10	2.48(1)	Zn–H ₂ O13	2.05(2)
⟨U–O _{Ur} ⟩	1.78	Zn–H ₂ O14	2.06(1)
⟨U–O _{eq} ⟩	2.38	Zn–H ₂ O9	2.08(1)
		Zn–H ₂ O6	2.10(2)
Se1–O9	1.63(1)	Zn–H ₂ O7	2.11(1)
Se1–O7	1.65(1)	Zn–H ₂ O15	2.12(2)
Se1–O1	1.65(1)	⟨Zn–H ₂ O⟩	2.09
Se1–O3	1.69(1)		
⟨Se1–O⟩	1.66		

clinic cell with the β angle close to 90°), which improved the refinement significantly. The refined ratio of twin components was found to be close to 1:3. No twinning was observed for the structure of $\text{Zn}[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$. The final models for both structures included anisotropic displacement parameters for all atoms. The hydrogen positions were not localized. The final atomic positional and displacement parameters for the Mg and Zn compounds are listed in Tables 2 and 4, respectively, selected interatomic distances are given in Tables 3 and 5, respectively. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-415060 and 415061, for the Mg and Zn compounds, respectively, the name of the author(s), and citation of the paper.

Results and Discussion

The crystal structures of $M[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ ($M = \text{Mg}, \text{Zn}$) contain one independent U^{6+} cation which is coordinated by two O atoms to form linear uranyl UO_2^{2+} cations (Ur) with short U^{6+} – O_{Ur} bonds of 1.77–1.78 Å. The uranyl cations are equatorially coordinated by four O^{2-} anions and one H_2O molecule each to form $[\text{UO}_6(\text{H}_2\text{O})]^{6-}$ pentagonal bipyramids. The equatorial U^{6+} –O bond lengths are in the range of 2.31–2.39 Å, whereas the U^{6+} – H_2O bond lengths equal to 2.50 and 2.48 Å for $M = \text{Zn}$ and Mg, respectively. There are two independent Se sites in the structure which are coordinated by four O atoms to form tetrahedral $[\text{SeO}_4]^{2-}$ anions. The Se^{6+} –O bond lengths range from 1.61 to 1.70 Å. The M^{2+} cations are octahedrally coordinated by six water molecules.

The structures of the compounds $M[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ ($M = \text{Mg}, \text{Zn}$) are based upon $[(\text{UO}_2)$

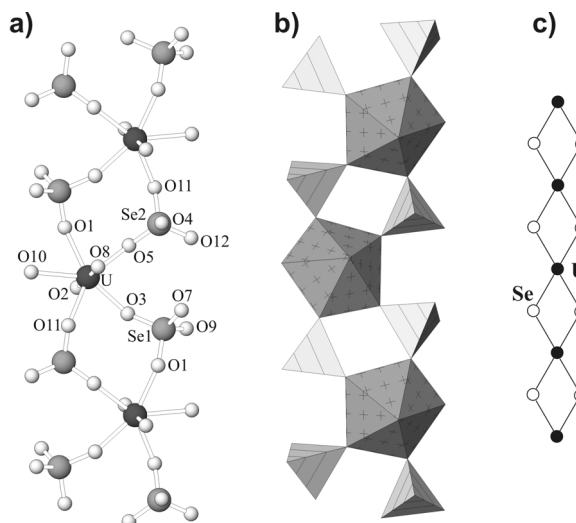


Fig. 1. Ball-and-stick (a), polyhedral (b), and nodal representations of the $[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})]^{2-}$ chain found in the structures of $M[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ ($M = \text{Mg}, \text{Zn}$). (b): $[\text{UO}_6]$ polyhedra = cross-hatched; $[\text{SeO}_4]$ tetrahedra = lined; (c): $[\text{UO}_6]$ polyhedra and $[\text{SeO}_4]$ tetrahedra are symbolized by black and white vertices, respectively.

$(\text{SeO}_4)_2(\text{H}_2\text{O})]^{2-}$ chains shown in Fig. 1a,b. The chains run parallel to the b axis and consist of corner-sharing $[\text{UO}_6(\text{H}_2\text{O})]^{6-}$ pentagonal bipyramids and $[\text{SeO}_4]^{2-}$ tetrahedra. The equatorial planes of the uranyl pentagonal bipyramids are oriented approximately parallel to (001). The uranyl selenate chains are linked into sheets parallel to (010) by $[M(\text{H}_2\text{O})_6]^{2+}$ octahedra that share common water molecules with the $[\text{UO}_6(\text{H}_2\text{O})]^{6-}$ pentagonal bipyramids.

The topology of the interpolyhedral linkage in the structures of $M[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ ($M = \text{Mg}, \text{Zn}$) can be described by means of a nodal representation. Using this approach, each cation coordination polyhedron is associated with a vertex of a graph and the linked vertices correspond to the linked polyhedra [14]. In the structures of the title compounds, there are three types of coordination polyhedra: $[\text{UO}_6(\text{H}_2\text{O})]^{6-}$ pentagonal bipyramids, $[\text{SeO}_4]^{2-}$ tetrahedra, and $[M(\text{H}_2\text{O})]^{2+}$ octahedra. These polyhedra are designated with black, white, and grey vertices, respectively. Thus, the graph of the uranyl selenate chain is shown in Fig. 1c and it consists of black and white vertices. Fig. 2c shows a tricolor graph that corresponds to the topology of the complex sheet consisting of uranyl selenate chains and $[M(\text{H}_2\text{O})]^{2+}$ octahedra (the latter are symbolized by grey vertices).

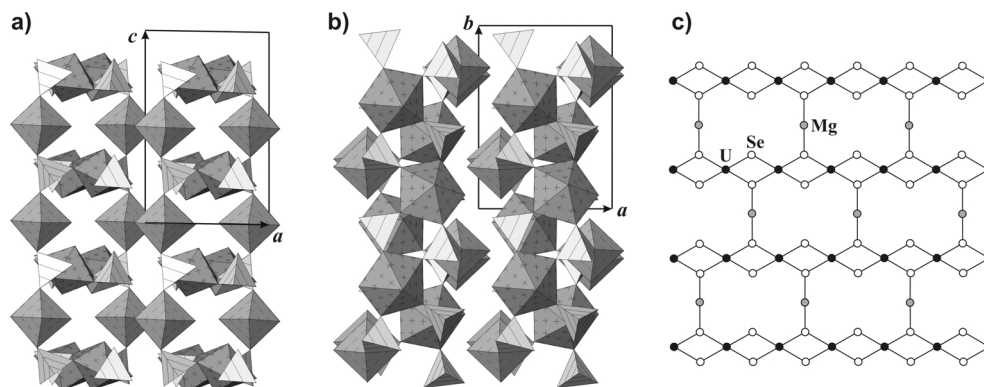


Fig. 2. The structure of $M[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ ($M = \text{Mg}, \text{Zn}$) projected onto the (010) (a) and (001) (b) planes, respectively ([UO_7] polyhedra = cross-hatched; [SeO_4] tetrahedra = lined; [$M(\text{H}_2\text{O})_6$] octahedra = dashed), and black-grey-white graph describing topology of interpolyhedral linkage ([UO_7] polyhedra, [SeO_4] tetrahedra, and [$M(\text{H}_2\text{O})_6$] octahedra are symbolized by black, white, and grey vertices, respectively).

We note that the black-and-white graph shown in Fig. 1c corresponds to the topology of kröhnkite chains that were recently reviewed by Fleck and Kolitsch [15,16]. However, kröhnkite chains usually consist of octahedra and tetrahedra, whereas, in our case, a pentagonal bipyramidal coordination is observed for the U^{6+} cations. The $[(\text{UO}_2)(\text{TO}_4)_2(\text{H}_2\text{O})]^{2-}$ chain found in the structures of $M[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ ($M = \text{Mg}, \text{Zn}$) is common for structures of uranyl compounds with TO_4 tetrahedra ($T = \text{S}, \text{P}, \text{As}$). It has been observed first in the structure of $\text{Mn}[(\text{UO}_2)(\text{SO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_5$ [17] and later in a number of amine-templated uranyl sulfates [18–23]. It is also present in the structures of $[(\text{UO}_2)(\text{H}_2\text{PO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_2$ [24] and $[(\text{UO}_2)(\text{H}_2\text{AsO}_4)_2(\text{H}_2\text{O})]$ [25]. To our knowledge, the

only example of the uranyl selenate chain of this topology was recently observed in the structure of $[\text{C}_5\text{H}_{16}\text{N}_2]_2[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{NO}_3)_2$ [26].

The compounds $M[(\text{UO}_2)(\text{SeO}_4)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_4$ ($M = \text{Mg}, \text{Zn}$) reported here are probably closely related to the compound $\text{MnUO}_2(\text{SeO}_4)_2 \cdot 5\text{H}_2\text{O}$ reported by Serezhkina and Serezhkin [8]. However, for the Mg and Zn compounds we have observed a monoclinic symmetry with the β angle close to 90° , whereas Serezhkin and Serezhkina [8] described the Mn compound as orthorhombic, space group $Pm2_1n$, but did not solve its structure.

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