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Synthesis and Crystal Structure of Ternary Sulfides A_3MS_4 with A = Na, Rb and M = Nb, Ta

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The new ternary sulfides Na_3MS_4 and Rb_3MS_4 (M = Nb, Ta) were prepared from tantalum nitride or niobium powder in the respective alkali metal polysulfide melt. Both sodium sulfides crystallize in form of yellow (Nb) or yellow-orange (Ta) needles in the orthorhombic space group *Fdd*2 with $Z = 32$ and a = 27.3034(4) Å, b = 28.4662(1) Å, and c = 7.9642(1) Å, R/R_w = 0.024/0.048 for M = Nb and a = 27.2322(2) Å, b = 28.4264(2) Å, and c = 7.9634(6) Å, R/R_w = 0.066/0.177 for M = Ta. The rubidium sulfides were obtained as yellow (Nb) and orange (Ta) crystals with irregular shape. They crystallize in the orthorhombic space group *Pnma* with $Z = 4$ and a = 9.6109(6) Å, b = 11.1013(7) Å, and c = 9.6390(6) Å, R/R_w = 0.030/0.072 for M = Nb and a = 9.6084(5) Å, b = 11.1067(6) Å, and c = 9.6426(5) Å, R/R_w = 0.031/0.070 for M = Ta. The structures of all four compounds are built by stacking isolated MS_4^{3-} units with the alkali metal ions. © 1998 Academic Press

INTRODUCTION

Ternary sulfides are a fairly well-explored class of compounds. Still, recent years led to a number of new ternary and quaternary alkali metal sulfides and polysulfides of niobium and tantalum (e.g. Refs. (1–8)). The polysulfides were typically prepared from alkali metal polysulfide melts (reactive flux method) at fairly low temperatures of 300–400°C, whereas higher temperatures led to sulfides without sulfur–sulfur bonds.

To our surprise some simple compositions have not yet been investigated. The preparation and the structure of K_3NbS_4 were reported; K_3TaS_4 crystallizes with an isotypic structure according to its X-ray powder pattern (2). $CsTaS_3$ is formed from sulfur and tantalum powders in excess Cs_2S_5 melt at 650°C (3). Its crystal structure consists of rods of face-sharing octahedra $^1_\infty[TaS^-_{6/2}]$ stacked together in hexagonal rod packing.

Here we report the preparation from polysulfide melts of Na_3MS_4 and Rb_3MS_4 (M = Nb, Ta) and their structures. The tantalum compounds were initially discovered in syntheses designed to explore the existence of compounds containing both nitrogen and sulfur. Although we did not identify any of these mixed anion compounds, the title ternaries were discovered.

EXPERIMENTAL DETAILS

Synthesis

As many of the reagents and products in this study are moisture-sensitive, the work was carried out in an argon-filled glovebox.

Ta_3N_5 was obtained from $TaCl_5$ powder (Alpha Aesar, 99.99%) by heating in a flow of ammonia (Matheson Gas Products, further dried and stored over sodium) to 750°C. The product is a dark red powder, characterized as single-phase Ta_3N_5 (9) by powder X-ray diffraction. The yield is typically quantitative.

TaN can be prepared from Ta_3N_5 in a molybdenum crucible when heated inductively (Ameritherm Model Sp-2.5) in nitrogen atmosphere ($P(N_2)$ = 1 atm) to approximately 1000°C for 20 min. Optical pyrometry was used to monitor the reaction temperature. The resulting black powder was found to be TaN (10) by X-ray diffraction.

Na_2S_2 and Rb_2S_3 were made from the respective alkali metal (Na, Cerac, 99.95%; Rb, Cerac, 99.8%) and sulfur (Cominco American, high purity) in appropriate amounts. After ammonia was condensed onto the metal, the resulting alkali metal solution was added to the sulfur. The mixture was stirred by shaking and then allowed to slowly warm up. The ammonia was evaporated over several hours. Na_2S_2 was obtained as a yellow powder. X-ray powder diffraction showed some Na_2S and higher polysulfides as well as the majority phase Na_2S_2, but since the overall alkali metal sulfur ratio had to be 1 : 1 we used this material for the following reactions. Rb_2S_3 is an orange-yellow powder, which was X-ray single phase as determined by X-ray powder diffraction.

Na_3TaS_4 was prepared from two different reaction mixtures: (i) Na_2S powder (Cerac, 99.9%), elemental sulfur powder, and Ta_3N_5 and (ii) Na_2S, elemental sulfur, and

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TaN. Both mixtures corresponded to a Na/Ta/S molar ratio of approximately 10 : 1 : 10. The reactants were sealed in evacuated silica tubes, heated to 800°C within 24 h, kept at 800°C for 100 h, and slowly cooled down to room temperature within 100 h. After the treatment the products in both tubes looked like solidified red melts. Two kinds of crystals were visually observed under a microscope in the raw powder: yellow hexagonal plates (excess Na_2S_2) and yellow-orange needles. The sample was then washed with dry DMF under inert atmosphere to remove excess sodium sulfides.

Na_3NbS_4 can be prepared in an analogous fashion from Na_2S, sulfur, and niobium powder (Na : Nb : S = 10 : 1 : 10). Rb_3NbS_4 was prepared from excess Rb_2S_3 and niobium powder and Rb_3TaS_4 from Rb_2S_3 and Ta_3N_5 (Rb : M : S = 5 : 1 : 7.5). Na_3NbS_4 crystallizes as yellow needles, Rb_3NbS_4 (yellow) and Rb_3TaS_4 (orange) as crystals with bulky shape.

Crystals of each compound were manually selected and sealed in glass capillaries for single-crystal X-ray studies. All products are moisture-sensitive.

After the A_3MS_4 stoichiometry was established from the structure solutions, preparation of single-phase Na_3TaS_4 samples was attempted. For that purpose mixtures of Ta_3N_5 with Na_2S_2 powder and elemental sulfur and of TaN, Na_2S_2, and elemental sulfur at the molar ratio of 3 : 1 : 4 (Na : Ta : S) were prepared. The two reaction mixtures were pressed into pellets, placed separately in aluminum oxide crucibles in sealed evacuated silica tubes, and heated to 800°C (from room temperature to 800°C within 50 h, at 800°C for 100 h, slow cooling over a period of 100 h). Both pellets melted in the course of the reactions. Products in both tubes had a black coating on the surface, but they were beige powders in the bulk. Powder X-ray diffraction data were collected and analyzed for both samples. The weight changes of these mixtures during the reactions were not established, but we suspect the formation of N_2 in a redox reaction with sulfur or polysulfide ions, respectively. Since no other solid product was found anywhere in the tubes and the products appeared to be single phase, the yields are approximately quantitative. Analogues experiments to prepare single phase samples of the three other compositions were not carried out.

EDX Analysis of Na_3TaS_4

To establish the approximate composition of the yellow-orange needles of the sodium tantalum sulfide, EDX analysis of several such crystals was carried out on a scanning electron microscope (JEOL 733). Measurements yielded an

TABLE 1
Crystallographic Data Concerning the Compounds A_3MS_4 (A = Na, Rb; M = Nb, Ta)

Compound	Na_3NbS_4	Na_3TaS_4	Rb_3NbS_4	Rb_3TaS_4
Crystal shape	Needle	Needle	Bulk	Bulk
Dimensions/mm	0.08 × 0.08 × 0.2	0.08 × 0.1 × 0.33	0.1 × 0.1 × 0.1	0.15 × 0.15 × 0.15
Space group, Z	$Fdd2$ (No. 43), 32		$Pnma$ (No. 62), 4	
a, Å	27.3034(4)	27.2322(2)	9.6109(6)	9.6084(5)
b, Å	28.4662(1)	28.4264(2)	11.1013(7)	11.1067(6)
c, Å	7.9642(1)	7.9634(6)	9.6390(6)	9.6426(5)
Cell volume, Å^3	6190.0(2)	6164.6(2)	1028.4(2)	1029.0(1)
Calculated density/g/cm^3	2.49	3.26	3.08	3.65
Radiation	Mo$K\alpha$			
Monochromator	Graphite			
Absorption correction	SADABS (25)			
Min. transmission	0.638	0.393	0.375	0.445
μ/mm^{-1}	2.69	15.40	15.99	25.49
$2\theta_{max}$/deg	56.7	52.8	55.6	55.7
h, k, l	−36 to 35	−23 to 33	−12 to 11	−11 to 12
	−29 to 37	−33 to 35	−14 to 10	−14 to 14
	−10 to 10	−9 to 7	−9 to 12	−12 to 9
Independent reflections	3288	2718	1211	1193
Reflections with $F_0^2 \geq 4\sigma F_0^2$	3020	2630	1031	1080
Variables	147	146	44	44
Goodness of fit (goof)	0.989	1.160	1.028	1.223
R_{int}	0.038	0.051	0.048	0.046
R/R_w	0.024/0.048	0.066/0.177	0.030/0.072	0.031/0.070
Extinction parameter	0.00028(1)	—	0.0217(9)	0.0050(3)
Largest difference peak	0.67	6.68	1.01	1.84
Flack parameter	0.02(4)	0.05(3)	—	—

average stoichiometry of $Na_{2.3}TaS_{4.0}$. As partial loss of sodium in our experience sometimes takes place in high vacuum during analysis of crystal surfaces, and since the error on the sodium content should be the largest and this is a standardless determination, these results are consistent with the ideal Na_3TaS_4 stoichiometry.

TABLE 2
Atomic Coordinates for Na_3MS_4 (M = Nb, Ta)[a]

Atom	Site	x	y	z	U_{iso} (Å^2)
Ta(1)	**16*b***	**0.00973(3)**	**0.11555(3)**	**0.5528(1)**	**0.0126(3)**
		0.24027	0.13445	0.4472	
Nb(1)		*0.24010(1)*	*0.13465(1)*	*0.44859(4)*	*0.01379(9)*
Ta(2)	**16*b***	**0.12245(4)**	**0.00614(3)**	**0.0484(1)**	**0.0139(3)**
		0.12755	0.24386	0.9516	
Nb(1)		*0.12737(1)*	*0.24385(1)*	*0.95322(4)*	*0.01511(9)*
S(1)	**16*b***	**0.2491(2)**	**0.0937(2)**	**0.562(1)**	**0.020(1)**
		0.0009	0.1563	0.438	
		0.00085(4)	*0.15611(4)*	*0.4400(2)*	*0.0259(2)*
S(2)	**16*b***	**0.1864(3)**	**0.1563(2)**	**0.9129(9)**	**0.019(1)**
		0.0637	0.0937	0.0871	
		0.06387(4)	*0.09382(4)*	*0.0864(1)*	*0.0232(2)*
S(3)	**16*b***	**0.0840(3)**	**0.2477(2)**	**0.056(1)**	**0.025(1)**
		0.1661	0.0023	0.944	
		0.16596(4)	*0.00226(4)*	*0.9463(2)*	*0.0255(2)*
S(4)	**16*b***	**0.1556(3)**	**0.1859(2)**	**0.4000(9)**	**0.023(2)**
		0.0944	0.0641	0.6000	
		0.09485(4)	*0.06423(4)*	*0.6030(2)*	*0.0240(2)*
S(5)	**16*b***	**0.0544(3)**	**0.0503(2)**	**0.4973(9)**	**0.021(1)**
		0.1956	0.1997	0.5027	
		0.19527(4)	*0.20005(4)*	*0.5052(1)*	*0.0224(2)*
S(6)	**16*b***	**0.0500(3)**	**0.1594(2)**	**0.7483(9)**	**0.021(1)**
		0.2000	0.0906	0.2517	
		0.19999(4)	*0.09083(3)*	*0.2530(1)*	*0.0212(2)*
S(7)	**16*b***	**0.1722(3)**	**0.0381(2)**	**0.2480(9)**	**0.024(2)**
		0.0778	0.2119	0.7512	
		0.07734(4)	*0.21199(4)*	*0.7540(1)*	*0.0249(3)*
S(8)	**16*b***	**0.0566(3)**	**0.0531(2)**	**0.9997(9)**	**0.022(1)**
		0.1934	0.1969	0.0003	
		0.19333(4)	*0.19697(4)*	*0.0021(1)*	*0.0238(2)*
Na(1)	**16*b***	**0.0953(6)**	**0.1375(6)**	**0.150(3)**	**0.070(6)**
		0.1547	0.1125	0.850	
		0.15426(7)	*0.11237(9)*	*0.8531(4)*	*0.0681(8)*
Na(2)	**16*b***	**0.1368(6)**	**0.0922(5)**	**0.676(3)**	**0.052(4)**
		0.1132	0.1578	0.324	
		0.11229(8)	*0.15697(7)*	*0.3283(3)*	*0.0544(6)*
Na(3)	**16*b***	**0.1297(4)**	**0.2219(4)**	**0.728(2)**	**0.022(2)**
		0.1203	0.0281	0.272	
		0.12012(6)	*0.02762(6)*	*0.2718(2)*	*0.0255(4)*
Na(4)	**16*b***	**0.0022(5)**	**0.2463(4)**	**0.766(2)**	**0.034(3)**
		0.2478	0.0037	0.234	
		0.24785(7)	*0.00362(6)*	*0.2317(3)*	*0.0395(5)*
Na(5)	**16*b***	**0.2261(5)**	**0.1264(4)**	**0.236(2)**	**0.026(2)**
		0.0239	0.1236	0.764	
		0.02433(6)	*0.12300(6)*	*0.7668(2)*	*0.0261(4)*
Na(6)	**8*a***	$\frac{1}{4}$	$\frac{1}{4}$	**0.000(2)**	**0.038(5)**
		0	0	0.000	
		0	*0*	*0.0000(4)*	*0.0391(7)*
Na(7)	**8*a***	$\frac{1}{4}$	$\frac{1}{4}$	**0.488(2)**	**0.035(4)**
		0	0	0.512	
		0	*0*	*0.5122(4)*	*0.0396(7)*

[a] Boldface type refers to Na_3TaS_4; lightface roman type refers to Na_3TaS_4 data transformed to the other enantiomeric form; italic refers to Na_3NbS_4.

TABLE 3
Atomic Thermal Displacement Parameters (Å^2) for Na_3MS_4 (M = Nb, Ta)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ta(1)	**0.0195(5)**	**0.0089(4)**	**0.0096(5)**	**0.0005(4)**	**− 0.0006(5)**	**− 0.0006(3)**
Nb(1)	*0.0127(2)*	*0.0147(2)*	*0.0139(2)*	*− 0.0005(2)*	*− 0.0004(2)*	*− 0.0003(1)*
Ta(2)	**0.0205(5)**	**0.0118(4)**	**0.0096(5)**	**− 0.0003(4)**	**− 0.0009(5)**	**− 0.0022(3)**
Nb(2)	*0.0133(2)*	*0.0176(2)*	*0.0144(2)*	*− 0.0007(2)*	*0.0000(2)*	*− 0.0016(1)*
S(1)	**0.031(3)**	**0.020(3)**	**0.009(3)**	**− 0.004(3)**	**− 0.003(3)**	**0.004(2)**
	0.0318(6)	*0.0257(5)*	*0.0201(6)*	*− 0.0053(5)*	*− 0.0037(5)*	*− 0.0016(4)*
S(2)	**0.022(3)**	**0.022(3)**	**0.014(3)**	**0.000(2)**	**0.002(3)**	**0.007(3)**
	0.0150(5)	*0.0324(6)*	*0.0223(6)*	*0.0018(5)*	*0.0010(4)*	*0.0060(4)*
S(3)	**0.030(3)**	**0.032(3)**	**0.015(4)**	**− 0.001(3)**	**− 0.007(3)**	**− 0.005(3)**
	0.0236(5)	*0.0341(6)*	*0.0188(6)*	*− 0.0036(5)*	*− 0.0032(5)*	*− 0.0005(4)*
S(4)	**0.036(4)**	**0.014(3)**	**0.019(4)**	**0.003(2)**	**− 0.002(3)**	**0.010(3)**
	0.0274(6)	*0.0210(6)*	*0.0237(6)*	*− 0.0003(4)*	*0.0008(5)*	*0.0064(4)*
S(5)	**0.028(4)**	**0.018(3)**	**0.017(4)**	**− 0.002(2)**	**0.000(3)**	**0.004(3)**
	0.0228(5)	*0.0212(5)*	*0.0232(6)*	*− 0.0040(4)*	*− 0.0007(4)*	*0.0054(4)*
S(6)	**0.027(3)**	**0.018(3)**	**0.019(4)**	**− 0.007(2)**	**0.001(3)**	**− 0.006(3)**
	0.0195(5)	*0.0208(5)*	*0.0232(6)*	*− 0.0040(4)*	*− 0.0020(4)*	*− 0.0045(4)*
S(7)	**0.032(4)**	**0.028(3)**	**0.012(4)**	**− 0.005(3)**	**0.001(3)**	**− 0.013(3)**
	0.0242(5)	*0.0294(6)*	*0.0211(6)*	*− 0.0031(5)*	*− 0.0024(4)*	*− 0.0096(4)*
S(8)	**0.035(4)**	**0.019(3)**	**0.011(4)**	**0.001(2)**	**0.002(3)**	**0.005(3)**
	0.0216(5)	*0.0254(5)*	*0.0243(6)*	*0.0005(5)*	*− 0.0022(4)*	*0.0053(4)*
Na(1)	**0.041(9)**	**0.07(1)**	**0.104(17)**	**− 0.05(1)**	**− 0.001(9)**	**− 0.015(8)**
	0.033(1)	*0.079(2)*	*0.093(2)*	*− 0.054(2)*	*0.007(1)*	*− 0.013(1)*
Na(2)	**0.056(9)**	**0.033(7)**	**0.07(1)**	**− 0.017(7)**	**− 0.025(8)**	**− 0.001(7)**
	0.038(1)	*0.042(1)*	*0.083(2)*	*− 0.015(1)*	*− 0.027(1)*	*0.0016(9)*
Na(3)	**0.024(6)**	**0.023(5)**	**0.020(6)**	**− 0.002(4)**	**− 0.003(4)**	**− 0.002(4)**
	0.0251(9)	*0.0254(9)*	*0.026(1)*	*0.0022(7)*	*0.0010(7)*	*− 0.0035(7)*
Na(4)	**0.038(6)**	**0.025(5)**	**0.04(1)**	**0.000(5)**	**− 0.003(6)**	**0.002(5)**
	0.0265(9)	*0.0300(9)*	*0.062(2)*	*0.0044(10)*	*− 0.002(1)*	*0.0033(7)*
Na(5)	**0.030(6)**	**0.032(6)**	**0.017(6)**	**0.002(5)**	**− 0.002(5)**	**0.002(5)**
	0.0251(9)	*0.0318(9)*	*0.0214(9)*	*0.0017(7)*	*0.0015(7)*	*0.0002(7)*
Na(6)	**0.06(1)**	**0.033(9)**	**0.02(1)**	**0**	**0**	**0.014(9)**
	0.056(2)	*0.036(2)*	*0.026(2)*	*0*	*0*	*0.017(1)*
Na(7)	**0.05(1)**	**0.05(1)**	**0.007(9)**	**0**	**0**	**0.015(9)**
	0.032(2)	*0.062(2)*	*0.025(2)*	*0*	*0*	*0.017(1)*

[a] Boldface type refers to Na_3TaS_4, and italic type refers to Na_3NbS_4.

Crystal Structure Determination

Selected crystals were first tested on a precession camera. Well-diffracting crystals showing sharp reflections were then studied on a CCD diffractometer (Bruker SMART) at room temperature. Yellow (Na_3NbS_4) and yellow-orange (Na_3TaS_4) needles were indexed with an F-centered orthorhombic unit cell. Intensity data were taken for each crystal in a hemisphere scan mode with 1321 frames (886 for Na_3TaS_4) taken via ω rotation ($\Delta\omega = 0.3°$) and 30 s per frame. Systematic extinctions were consistent with space groups *Fddd* and *Fdd*2. Structure solution using direct

TABLE 4
Atomic Coordinates for Rb_3MS_4 (M = Nb, Ta)[a]

Atom	Site	x	y	z	U_{iso} (Å^2)
Ta (1)	**4c**	**0.28174(4)**	$\frac{1}{4}$	**0.01461(4)**	**0.0136(2)**
Nb(1)		*0.28145(5)*	$\frac{1}{4}$	*0.01456(5)*	*0.0154(2)*
Rb(1)	**8d**	**0.05029(8)**	**0.04291(7)**	**0.28959(8)**	**0.0244(2)**
		0.05018(5)	*0.04318(4)*	*0.29011(5)*	*0.0267(2)*
Rb(2)	**4c**	**0.3544(1)**	$\frac{1}{4}$	**0.5840(1)**	**0.0382(3)**
		0.35454(7)	$\frac{1}{4}$	*0.58452(7)*	*0.0401(2)*
S(1)	**8d**	**0.1678(2)**	**0.4193(2)**	**0.9481(2)**	**0.0301(5)**
		0.1678(1)	*0.4196(1)*	*0.9482(1)*	*0.0330(3)*
S(2)	**8d**	**0.0003(3)**	$\frac{1}{4}$	**0.5781(3)**	**0.0217(5)**
		– 0.0002(2)	$\frac{1}{4}$	*0.5780(2)*	*0.0247(4)*
S(3)	**8d**	**0.2992(3)**	$\frac{1}{4}$	**0.2488(3)**	**0.0207(5)**
		0.2990(2)	$\frac{1}{4}$	*0.2496(2)*	*0.0228(4)*

[a] Boldface type refers to Rb_3TaS_4; italic type refers to Rb_3NbS_4.

TABLE 5
Atomic Thermal Displacement Parameters (Å^2) for Rb_3MS_4 (M = Nb, Ta)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ta(1)	**0.0112(2)**	**0.0183(2)**	**0.0113(2)**	**0**	**– 0.0005(1)**	**0**
Nb(1)	*0.0153(3)*	*0.0165(3)*	*0.0145(3)*	*0*	*– 0.0005(2)*	*0*
Rb(1)	**0.0236(4)**	**0.0233(4)**	**0.0263(4)**	**0.0017(3)**	**– 0.0012(3)**	**0.0011(3)**
	0.0284(3)	*0.0216(3)*	*0.0302(3)*	*0.0017(2)*	*– 0.0012(2)*	*0.0010(2)*
Rb(2)	**0.0242(6)**	**0.0666(9)**	**0.0239(6)**	**0**	**– 0.0042(4)**	**0**
	0.0287(4)	*0.0649(6)*	*0.0265(4)*	*0*	*– 0.0046(3)*	*0*
S(1)	**0.025(1)**	**0.032(1)**	**0.034(1)**	**0.0117(9)**	**0.0015(9)**	**0.0098(8)**
	0.0291(6)	*0.0312(7)*	*0.0387(7)*	*0.0145(6)*	*0.0009(5)*	*0.0094(5)*
S(2)	**0.013(1)**	**0.031(1)**	**0.021(1)**	**0**	**– 0.005(1)**	**0**
	0.0183(8)	*0.0305(9)*	*0.0253(8)*	*0*	*– 0.0037(6)*	*0*
S(3)	**0.024(1)**	**0.025(1)**	**0.014(1)**	**0**	**0.001(1)**	**0**
	0.0272(8)	*0.0259(9)*	*0.0152(7)*	*0*	*0.0000(6)*	*0*

[a] Boldface type refers to Rb_3TaS_4; italic type refers to Rb_3NbS_4.

methods (11) showed that the *Fdd*2 space group is the correct one. For the Na_3TaS_4 crystal some reflections could not be indexed with the resulting orientation matrix. They were indexed independently with the same unit cell, but a matrix rotated 90° around the *c* axis. This rotation superimposes the crystallographic *a* and *b* axes, which show a difference in length of about 4%. No untwinned crystal was obtained. Since the overall intensity of the second individuum is as low as 10% compared with the main individuum, no twin refinement was attempted. Still it was possible to determine clearly the sense of the polar axis in this particular crystal. Because the structure refinements on the crystals for both sodium compounds led to the opposite enantiomers, the original and the transformed data for Na_3TaS_4 and the original data for Na_3NbS_4 are reported in Table 2. All structure refinements were performed using SHELXL-93 (12).

The crystals of the rubidium containing compounds were treated in the same manner as that mentioned for the sodium sulfides. The unit cell parameters and extinction

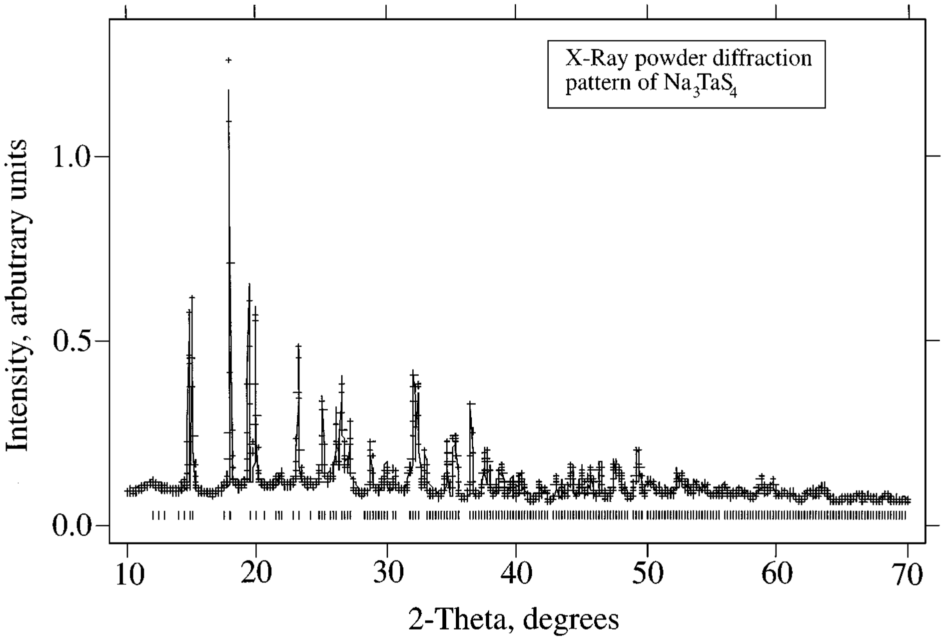

FIG. 1. Powder X-ray diffraction pattern for Na_3TaS_4 (crosses), fit based on the single-crystal X-ray data (solid line), and the positions of the peaks (marks at the bottom of the plot).

conditions of data sets on yellow (Rb_3NbS_4) and orange (Rb_3TaS_4) crystals led to the space group *Pnma*.

Additional information on the structure solution is given in Table 1, fractional atomic coordinates are listed in Tables 2 and 4, and the thermal displacement parameters in Tables 3 and 5.

Both supposedly polycrystalline samples of Na_3TaS_4 prepared from stoichiometric components yielded essentially identical powder X-ray diffraction patterns (Scintag XDS 2000 diffractometer with Cu$K\alpha$ radiation). One is shown in Fig. 1. Also shown are the positions of reflections expected for Na_3TaS_4 and the theoretical powder X-ray pattern based on the single crystal data. The positional and thermal displacement parameters of the atoms could not be refined based on the powder X-ray diffraction data (program GSAS (13) was employed), although the match of the experimentally observed diffraction pattern and the one expected based on the single-crystal structure solution is visually flawless. The orthorhombic unit cell parameters of the powders were refined to the following values: $a = 27.259(2)$ Å, $b = 28.400(2)$ Å, and $c = 7.9647(4)$ Å, which agree with the single-crystal data within reasonable estimates of potential errors.

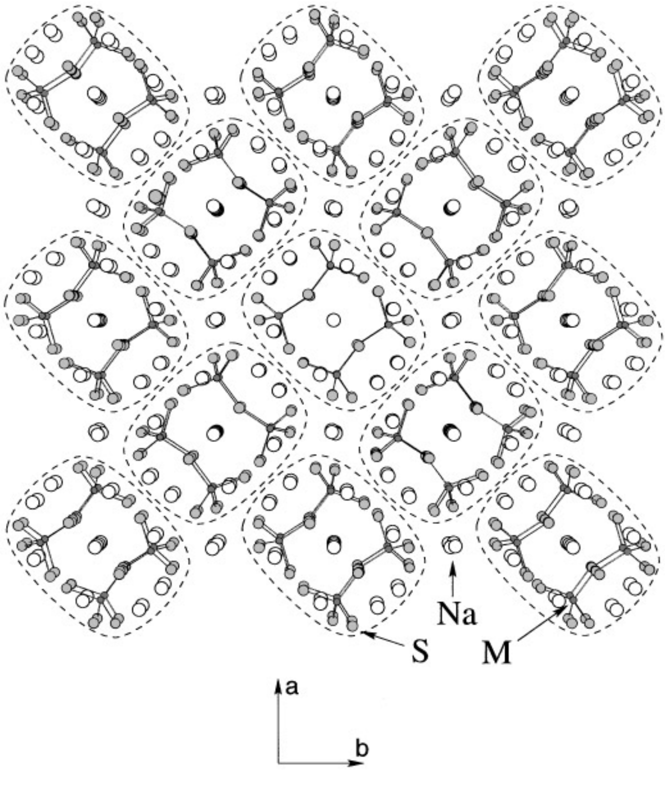

FIG. 2. The Na_3MS_4 (M = Nb, Ta) crystal structure viewed along the c axis. One-dimensional columns of MS_4 tetrahedra surrounding chains of sodium ions are emphasized. Despite the appearance, the MS_4 tetrahedra are not directly connected to each other.

STRUCTURE DESCRIPTIONS AND DISCUSSION

Na_3NbS_4 and Na_3TaS_4 crystallize in a new structure type. A view in this crystal structure is drawn in Fig. 2. It can be described very simply as consisting of isolated MS_4^{3-} units (M = Nb, Ta) separated by sodium cations. However, the packing arrangement in this crystal is quite complex. Figure 2 visually separates the structure into one-dimensional columns running along the c axis. This special arrangement of the MS_4^{3-} units leads to the large a and b axes.

Rb_3NbS_4 and Rb_3TaS_4 crystallize isotypically with compounds such as K_3NbS_4 (2), K_3VS_4 (14), and Cs_3MSe_4 (M = Nb, Ta) (15). Analogous to the sodium compounds the structures are built up from stacking of isolated MS_4^{3-} units together with alkali metal cations, but due to the larger size of the latter the stacking occurs in a different manner than that in the sodium compounds. The structure of Rb_3MS_4, viewed along the a axis, shows chains of MS_4^{3-} tetrahedra similar to that in the channels of Na_3MS_4 (Fig. 3).

Bond valence sums (16) and Madelung potentials using the Ewald method (17) were calculated for all four title compounds with the program Eutax (18). They are summarized in the Table 6a, b. Important M–S and A–S distances, as well as the S–M–S angles, for all four compounds are listed in the Tables 7a, b and 8a, b. The coordination of the transition metal atoms is nearly tetrahedral, as evidenced by the values of the S–M–S angles, which range from 107.6 to 112.4°. As expected, the M–S bond lengths (2.26–2.29 Å) show no significant differences between niobium and tantalum. They are characteristic of double bonds. For

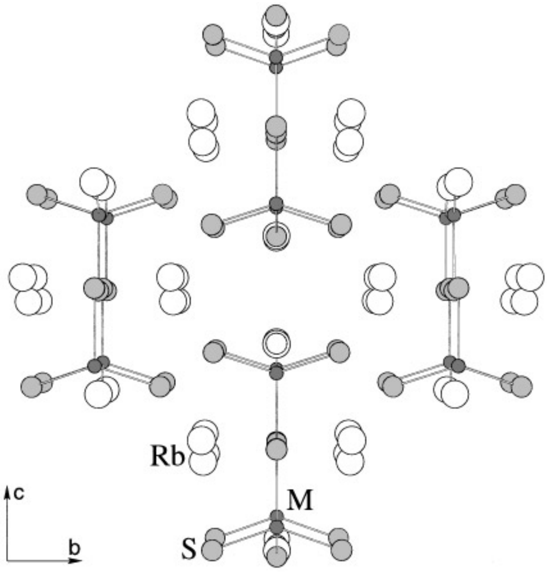

FIG. 3. Crystal structure of Rb_3MS_4 (M = Nb, Ta) viewed along the a axis. Rows of MS_4^{3-} tetrahedra, similar to that in Na_3MS_4 (Fig. 2), are visible. The tetrahedra are not directly connected to each other.

TABLE 6a
Bond Valence Sums and Madelung Potentials (in V) for Na_3MS_4 (M = Nb, Ta)[a]

Atom	Bond valence sum	Charge	Potential (V)
Ta(1)	**5.592**	**5.00**	**− 39.185**
Nb(1)	*5.167*		*− 39.004*
Ta(2)	**5.420**	**5.00**	**− 38.906**
Nb(2)	*5.087*		*− 38.885*
Na(1)	**0.734**	**1.00**	**− 9.982**
	0.737		*− 10.055*
Na(2)	**0.759**	**1.00**	**− 9.458**
	0.712		*− 9.452*
Na(3)	**1.158**	**1.00**	**− 11.862**
	1.140		*− 11.817*
Na(4)	**0.993**	**1.00**	**− 11.897**
	0.979		*− 11.932*
Na(5)	**1.110**	**1.00**	**− 12.020**
	1.110		*− 12.016*
Na(6)	**0.882**	**1.00**	**− 7.887**
	0.866		*− 7.793*
Na(7)	**0.915**	**1.00**	**− 8.270**
	0.903		*− 8.202*
S(1)	**2.143**	**− 2.00**	**19.143**
	2.035		*19.089*
S(2)	**2.122**	**− 2.00**	**20.587**
	1.997		*20.475*
S(3)	**2.000**	**− 2.00**	**19.025**
	1.907		*18.947*
S(4)	**2.008**	**− 2.00**	**20.238**
	1.933		*20.251*
S(5)	**2.178**	**− 2.00**	**21.119**
	2.061		*21.090*
S(6)	**2.164**	**− 2.00**	**19.026**
	2.061		*18.985*
S(7)	**1.908**	**− 2.00**	**18.719**
	1.818		*18.654*
S(8)	**2.142**	**− 2.00**	**21.091**
	2.006		*21.018*

[a] Boldface type refers to Na_3TaS_4, and italic type refers to Na_3NbS_4.

TABLE 6b
Bond Valence Sums and Madelung Potentials (in V) for Rb_3MS_4 (M = Nb, Ta)[a]

Atom	Bond valence sum	Charge	Potential (V)
Ta	**5.520**	**5.00**	**− 39.242**
Nb	*5.208*		*− 39.212*
Rb(1)	**0.949**	**1.00**	**− 8.214**
	0.952		*− 8.215*
Rb(2)	**0.733**	**1.00**	**− 9.007**
	0.734		*− 9.005*
S(1)	**1.941**	**2.00**	**18.970**
	1.866		*18.967*
S(2)	**1.959**	**2.00**	**19.861**
	1.899		*19.893*
S(3)	**2.310**	**2.00**	**19.594**
	2.215		*19.516*

[a] Boldface type refers to Rb_3TaS_4; italic type refers to Rb_3NbS_4.

comparison, $K_4Ta_2S_{11}$ (1) (with Ta^V) features two sets of Ta–S bond lengths: average of 2.235 Å for formally double bonds and a range of 2.465–2.579 Å for formally single bonds. Similar Ta–S bond lengths are found in a complex $Ta_6S_{17}^{4-}$ polyanion in $(Et_4N)_4[Ta_6S_{17}]\cdot 3CH_3CN$ (19): 2.179–2.204 Å for double bonds and 2.400–2.593 Å for single bonds. In the latter compound there are also longer Ta–S contacts of 2.615–2.992 Å. $CsTaS_3$ (3) features Ta–S bond lengths of 2.339 and 2.582 Å, in the single bond range. In K_3NbS_4 the average bond length is 2.250 Å. Cu_3TaS_4 (4), Tl_3TaS_4 (5), and K_3TaS_4 (2) all contain TaS_4^{3-} tetrahedra, but the atomic positions in these compounds are not well established.

The sodium atoms in the Na_3MS_4 compounds are coordinated by five (Na(1) and Na(2)) or six (Na(3)–Na(7)) sulfur atoms. The Na(6) and Na(7) are surrounded by distorted octahedra of sulfur; other polyhedra are rather irregular. The Na–S bond lengths range from 2.79 to 3.26 Å. These are comparable to the Na–S distances in Na_2S (20) (2.82 Å) and in Na_2S_2 (21) (2.81 and 2.99 Å). The sum of Shannon (22) ionic radii for Na^+ (1.02 Å) and S^{2-} (1.84 Å) is 2.86 Å. The sodium atoms Na(1) and Na(2) exhibit relatively large thermal parameters (compare Tables 2 and 3), which are mainly the result of large thermal motion in the c direction along the columns. Both these sodium atoms are five-

TABLE 7a
Ta–S and Na–S Bond Lengths (Å) and S–Ta–S Angles (deg) in Na_3TaS_4

Ta(1)–S(5)	2.262(6)	Na(3)–S(6)	2.81(1)	Na(6)–S(5) 2 ×	2.88(2)
Ta(1)–S(1)	2.262(7)	Na(3)–S(2)	2.83(1)	Na(6)–S(8) 2 ×	2.93(2)
Ta(1)–S(2)	2.269(7)	Na(3)–S(5)	2.86(1)	Na(6)–S(2) 2 ×	3.252(8)
Ta(1)–S(6)	2.276(7)	Na(3)–S(4)	2.90(1)		
		Na(3)–S(7)	2.98(1)	Na(7)–S(8) 2 ×	2.87(1)
Ta(2)–S(8)	2.269(7)	Na(3)–S(3)	2.99(2)	Na(7)–S(5) 2 ×	2.92(2)
Ta(2)–S(7)	2.276(7)			Na(7)–S(4) 2 ×	3.230(9)
Ta(2)–S(3)	2.277(8)	Na(4)–S(1)	2.79(1)		
Ta(2)–S(4)	2.287(6)	Na(4)–S(6)	2.80(1)	S(1)–Ta(1)–S(5)	108.9(3)
		Na(4)–S(3)	2.89(2)	S(1)–Ta(1)–S(6)	111.3(2)
Na(1)–S(8)	2.88(2)	Na(4)–S(7)	3.02(2)	S(2)–Ta(1)–S(5)	108.9(3)
Na(1)–S(4)	2.92(2)	Na(4)–S(3)	3.20(2)	S(2)–Ta(1)–S(6)	108.1(3)
Na(1)–S(1)	2.97(2)	Na(4)–S(7)	3.21(2)	S(5)–Ta(1)–S(6)	108.9(3)
Na(1)–S(2)	3.16(2)			S(1)–Ta(1)–S(2)	110.8(3)
Na(1)–S(3)	3.23(2)	Na(5)–S(1)	2.83(1)		
		Na(5)–S(4)	2.87(1)	S(3)–Ta(2)–S(4)	112.4(3)
Na(2)–S(5)	2.91(2)	Na(5)–S(7)	2.91(1)	S(3)–Ta(2)–S(7)	108.9(3)
Na(2)–S(2)	2.95(2)	Na(5)–S(2)	2.91(1)	S(3)–Ta(2)–S(8)	109.2(3)
Na(2)–S(3)	2.99(2)	Na(5)–S(6)	2.94(1)	S(4)–Ta(2)–S(7)	107.4(3)
Na(2)–S(6)	3.09(2)	Na(5)–S(8)	2.97(1)	S(4)–Ta(2)–S(8)	108.1(3)
Na(2)–S(1)	3.19(2)			S(7)–Ta(2)–S(8)	110.8(3)
Na–Na ≥	3.52(2)			Na–Ta ≥	3.54(4)

TABLE 7b
Nb–S and Na–S Bond Lengths (Å) and S–Nb–S Angles (deg) in Na_3NbS_4

Nb(1)–S(6)	2.277(1)	Na(3)–S(6)	2.831(2)	Na(6)–S(5) 2 ×	2.896(2)
Nb(1)–S(5)	2.273(1)	Na(3)–S(5)	2.843(2)	Na(6)–S(8) 2 ×	2.928(2)
Nb(1)–S(1)	2.264(1)	Na(3)–S(2)	2.844(2)	Na(6)–S(2) 2 ×	3.263(1)
Nb(1)–S(2)	2.287(1)	Na(3)–S(4)	2.919(2)		
		Na(3)–S(3)	2.967(2)	Na(7)–S(8) 2 ×	2.885(2)
Nb(2)–S(8)	2.275(1)	Na(3)–S(7)	2.995(2)	Na(7)–S(5) 2 ×	2.906(2)
Nb(2)–S(7)	2.282(1)			Na(7)–S(4) 2 ×	3.251(1)
Nb(2)–S(3)	2.282(1)	Na(4)–S(6)	2.810(2)		
Nb(2)–S(4)	2.286(1)	Na(4)–S(1)	2.796(2)	S(1)–Nb(1)–S(2)	110.77(4)
		Na(4)–S(3)	2.914(2)	S(1)–Nb(1)–S(5)	108.73(4)
Na(1)–S(8)	2.889(2)	Na(4)–S(7)	2.993(2)	S(1)–Nb(1)–S(6)	111.26(4)
Na(1)–S(4)	2.911(2)	Na(4)–S(3)	3.188(2)	S(2)–Nb(1)–S(5)	109.40(4)
Na(1)–S(1)	2.986(3)	Na(4)–S(7)	3.213(2)	S(2)–Nb(1)–S(6)	107.65(4)
Na(1)–S(2)	3.134(3)			S(5)–Nb(1)–S(6)	108.99(4)
Na(1)–S(3)	3.237(3)	Na(5)–S(1)	2.841(2)		
		Na(5)–S(4)	2.865(2)	S(3)–Nb(2)–S(4)	112.10(4)
Na(2)–S(5)	2.936(2)	Na(5)–S(2)	2.887(2)	S(3)–Nb(2)–S(7)	108.75(4)
Na(2)–S(2)	2.948(2)	Na(5)–S(7)	2.919(2)	S(3)–Nb(2)–S(8)	109.09(4)
Na(2)–S(3)	3.010(3)	Na(5)–S(6)	2.953(2)	S(4)–Nb(2)–S(7)	107.71(4)
Na(2)–S(6)	3.104(2)	Na(5)–S(8)	2.979(2)	S(4)–Nb(2)–S(8)	108.13(4)
Na(2)–S(1)	3.170(3)			S(7)–Nb(2)–S(8)	111.08(4)
Na–Na ≥	3.553(3)			Na–Nb ≥	3.544(2)

fold coordinated by sulfur atoms in a distorted rectangular pyramid. The thermal vibration ellipsoid points directly through the base of these polyhedra with the next sulfur atoms in a distance of more than 3.46 Å. These sodium atoms are also the ones with the lowest bond valence sums (compare Table 6a). In a similar manner the Rb(2) atoms in the rubidium sulfides show a large thermal parameter (see Tables 4 and 5) and exhibit the smallest bond valence sums (Table 6b). The rubidium ions are all sevenfold coordinated by sulfur at distances in the range from 3.28 to 3.91 Å. Comparable distances are found in Rb_2S (3.313Å) (23) and Rb_2S_3 (3.306 to 3.454 Å) (24).

TABLE 8a
Ta–S and Rb–S Bond Lengths (Å) and S–Ta–S Angles (deg) in Rb_3TaS_4

Ta(1)–S(3)	2.267(3)	Rb(2)–S(3)	3.279(3)
Ta(1)–S(1) 2 ×	2.268(2)	Rb(2)–S(2)	3.401(3)
Ta(1)–S(2)	2.282(3)	Rb(2)–S(2)	3.550(3)
		Rb(2)–S(1) 2 ×	3.563(3)
Rb(1)–S(3)	3.341(2)	Rb(2)–S(1) 2 ×	3.906(2)
Rb(1)–S(3)	3.353(2)		
Rb(1)–S(1)	3.397(2)	S(1)–Ta(1)–S(1)	112.0(1)
Rb(1)–S(1)	3.400(2)	S(1)–Ta(1)–S(2) 2 ×	109.44(6)
Rb(1)–S(1)	3.509(2)	S(1)–Ta(1)–S(3) 2 ×	108.53(7)
Rb(1)–S(2)	3.529(1)	S(2)–Ta(1)–S(3)	108.83(9)
Rb(1)–S(2)	3.643(2)		
		Rb–Rb ≥	3.919(1)
		Rb–Ta ≥	3.9390(9)

TABLE 8b
Nb–S and Rb–S Bond Lengths (Å) and S–Nb–S Angles (deg) in Rb_3NbS_4

Nb(1)–S(3)	2.275(2)	Rb(2)–S(3)	3.277(2)
Nb(1)–S(1) 2 ×	2.269(1)	Rb(2)–S(2)	3.408(2)
Nb(1)–S(2)	2.280(2)	Rb(2)–S(2)	3.544(2)
		Rb(2)–S(1) 2 ×	3.563(2)
Rb(1)–S(3)	3.338(1)	Rb(2)–S(1) 2 ×	3.905(2)
Rb(1)–S(3)	3.353(1)		
Rb(1)–S(1)	3.400(1)	S(1)–Nb(1)–S(1)	112.17(8)
Rb(1)–S(1)	3.399(1)	S(1)–Nb(1)–S(2) 2 ×	109.39(4)
Rb(1)–S(1)	3.513(2)	S(1)–Nb(1)–S(3) 2 ×	108.50(4)
Rb(1)–S(2)	3.529(1)	S(2)–Nb(1)–S(3)	108.83(6)
Rb(1)–S(2)	3.638(1)		
		Rb–Rb ≥	3.921(1)
		Rb–Nb ≥	3.936(1)

It is surprising that the presence of such a simple structural motif as MS_4^{3-} in Na_3MS_4 results in complex stackings of the anions and alkali metal cations. In trying to rationalize this, comparison with the simpler copper and thallium analogues is instructive. The structures of cubic Cu_3TaS_4 (4) and Tl_3TaS_4 (5) are drawn in Fig. 4. Approximate values for the positional parameters of the sulfur

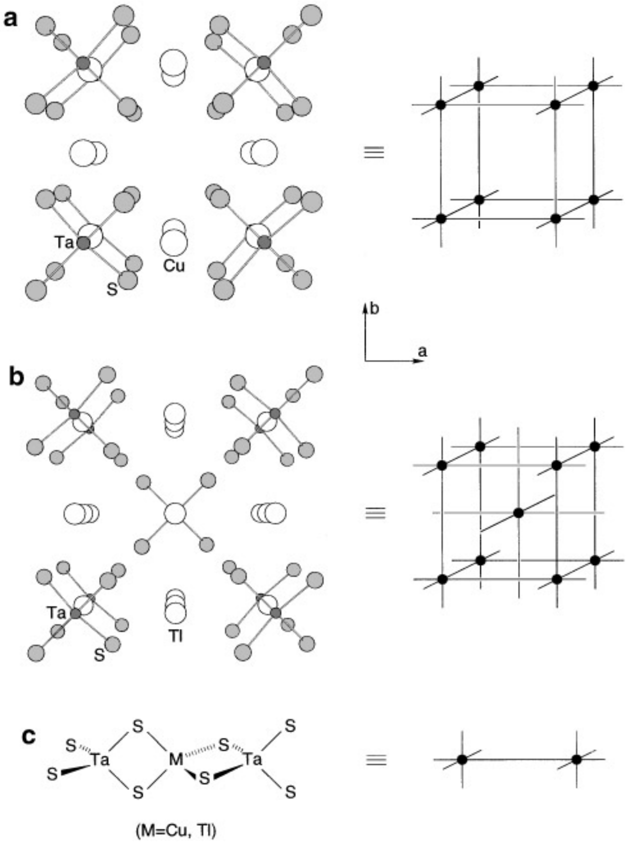

FIG. 4. Crystal structures of cubic Cu_3TaS_4 (a) and Tl_3TaS_4 (b). The schematic drawings on the right are constructed according to the legend (c) at the bottom.

ligands (all metal atoms are in special positions) are used, since a complete single-crystal structure refinement is not available. Cu_3TaS_4 can be thought of as a simple cubic array of TaS_4^{3-} units connected by Cu^+ centers. Each TaS_4^{3-} moiety is bound to six copper cations via its six edges; each copper center, tetrahedrally coordinated by four sulfur atoms, bridges two TaS_4^{3-} tetrahedra. Tl_3TaS_4 has a very similar structure: it consists of two interpenetrating cubic Cu_3TaS_4-like networks. This increases the coordination number of thallium atoms from 4 to 8. Although the crystal structures of A_3MS_4 (A = Cu, Na, K, Rb, Tl) are quite different from each other, the following two features are apparent. Firstly, the MS_4^{3-} tetrahedra are present in all of them; secondly, the packing of MS_4^{3-} and A^+ correlates fairly with the ionic radii (22) of A^+: Cu^+ (0.77 Å) is four-coordinate, Na^+ (1.02 Å) is five- or six-coordinate, K^+ (1.38 Å) and Rb^+ (1.52 Å) are surrounded by seven sulfur centers, and Tl^+ (1.50 Å) is eight-coordinate.

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