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Chemistry and structural chemistry of phosphides and polyphosphides 55*
Synthesis and structure of Na_6WP_4, Na_5SrNbP_4 and Na_5SrTaP_4**

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Abstract

The three novel tetraphosphametallates Na_6WP_4, Na_5SrNbP_4 and Na_5SrTaP_4 have been synthesized from the binary phosphides Na_3P and SrP, red phosphorus and the corresponding metals tungsten, niobium and tantalum in sealed niobium ampoules and characterized by single-crystal X-ray diffraction. The compounds crystallize hexagonally in the *hP*22 type of Na_6ZnO_4 (space group $P6_3mc$ (no. 186); Na_6WP_4: $a = 914.6(1)$ pm, $c = 717.2(1)$ pm; Na_5SrNbP_4: $a = 930.4(1)$ pm, $c = 734.9(1)$ pm; Na_5SrTaP_4: $a = 930.3(2)$ pm, $c = 734.7(3)$ pm; $Z = 2$). The structures consist of isolated cations Na^+ and Sr^{2+} and tetraphosphametallate anions $[WP_4]^{6-}$, $[NbP_4]^{7-}$ and $[TaP_4]^{7-}$ with mean bond lengths $\bar{d}$(W–P) = 231.5 pm, $\bar{d}$(Nb–P) = 240.1 pm and $\bar{d}$(Ta–P) = 239.9 pm respectively.

1. Introduction

The tetrahedral coordination of group 5 (vanadium, niobium and tantalum) and group 6 (chromium, molybdenum and tungsten) transition metals in chalcogenides has been extensively studied [1–5]. In contrast, it has not yet been reported that the corresponding anions $[MY_4]^{q-}$ ($Y \equiv P$, As) exist either in solution or the solid state, although a considerable number of pnictides of these transition metals are known [6]. A reason for this may be the higher negative formal charge $q-$ of the tetrapnictodometallate anion $[MY_4]^{q-}$, which leads to weaker bonds M–Y in pnictides as compared to those in the corresponding chalcogenides.

Recently some quarternary pnictides $M^I_4M^{II}_2MY_4$(M^I, alkali metal; M^{II}, alkali earth metal; M, group 14 element; $Y \equiv P$, As) [7] have been found to crystallize in the well-known Na_6ZnO_4 structure type [8], in which the group 14 atom is tetrahedrally coordinated by four pnicogen atoms. Therefore we are interested in knowing whether the corresponding compounds of group 5 or group 6 elements could also be formed with this structure. In this paper

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we report the successful synthesis of the compounds Na_6WP_4, Na_5SrNbP_4 and Na_5SrTaP_4 and their characterization by single-crystal X-ray diffraction and IR spectroscopy.

2. Experimental details

2.1. *Synthesis*

All the handling of starting materials as well as products was carried out in an argon-filled glove-box ($O_2 \leqslant 0.5$ ppm, $H_2O \leqslant 0.1$ ppm).

Na_6WP_4, Na_5SrNbP_4 and Na_5SrTaP_4 (1.5 g) were prepared from the binary phosphides Na_3P [9] and SrP [10], red phosphorus (red amorphous phosphorus, electronic grade purity, Hoechst AG., Knapsack) and the corresponding metal powder of tungsten, niobium or tantalum in sealed niobium ampoules ($\phi = 16$ mm, $l = 80$ mm) at 870 °C for 3 days. The first experiments were performed with stoichiometric ratios of the reactants. However, the products obtained in this way were always accompanied by considerable amounts of the starting materials and other unidentified phases. It has been found, after a number of experiments, that a considerable excess of sodium phosphide Na_3P is favourable for completing the reaction at this temperature; 25% excess of Na_3P was therefore employed in the later preparations; 5% excess of red phosphorus was also used for maintaining sufficient phosphorus vapour pressure during the reactions. The role of the excess Na_3P is not yet clear, but it may act as a flux and thus activate the refractory metals. We did not further purify the compounds from the excess Na_3P.

2.2. *Properties*

The crystals of Na_6WP_4, Na_5SrNbP_4 and Na_5SrTaP_4 are deep red and very air and moisture sensitive. They turn to pale yellow powders immediately when exposed to air.

2.3. *Structure determination*

In the first stage an X-ray powder pattern of Na_6WP_4, obtained at room temperature on a STOE X-ray diffractometer, was indexed with the programme INDEX [11] with a hexagonal unit cell ($a = 9.1$ Å, $c = 7.2$ Å). The simulated X-ray powder pattern, generated by the LAZY-PULVERIX programme [12] with these cell parameters and the positional parameters of Na_6ZnO_4, expected to be isostructural, showed very good agreement with the observed pattern. The additional lines of Na_3P, which was used in excess in the preparation, were also observed. The compounds Na_5SrNbP_4 and Na_5SrTaP_4 show similar patterns which are in agreement with the calculated ones.

The unit cell parameters were determined from single crystals by least-squares analysis of 22 reflections centred on a Syntex R3 diffractometer. The refined parameters and additional crystallographic data are compiled in Table 1.

The systematic absences, $hh2\bar{h}l$, $l \leqslant 2n$, indicate $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$ as possible space groups. Considering the good agreement of the

TABLE 1

Crystallographic data of Na_6WP_4, Na_5SrNbP_4 and Na_5SrTaP_4

	Na_6WP_4	Na_5SrNbP_4	Na_5SrTaP_4
Molar mass (a.m.u.)	445.67	419.36	507.40
Lattice constants (pm)	$a=914.6(1)$	$a=930.4(1)$	$a=930.3(2)$
	$c=717.2(1)$	$c=734.9(1)$	$c=734.7(3)$
	$c/a=0.784$	$c/a=0.790$	$c/a=0.790$
Space group (no.); Z	$P6_3mc$ (186); 2	$P6_3mc$ (186); 2	$P6_3mc$ (186); 2
V (cm^3 mol^{-1}); d_x(g cm^{-3})	156.5; 2.848	165.9; 2.528	165.8; 3.060
Data collection	Syntex R3 four-circle diffractometer; Mo Kα, $\lambda=71.073$ pm, graphite monochromator; scintillation counter, ω mode; $2\theta \leq 55.0°$; 296 K		
Structure determination	Refinement with SHELX-76; all atoms anisotropic, empirical absorption correction		
$N(hkl)$; $N'(hkl)$ with $I \geqslant 3\sigma$	258; 258	343; 340	268; 264
Variable parameters	26	26	26
$R_{(aniso)}$; $R_{w(aniso)}$	0.022; 0.022	0.025; 0.024	0.030; 0.029
Weighting scheme	$w=\sigma_F^{-2}$	$w=\sigma_F^{-2}$	$w=\sigma_F^{-2}$

observed X-ray powder patterns with the calculated ones, the positional parameters of Na_6ZnO_4 [8] were used as a starting parameter set in the structure refinement of Na_6WP_4. The refinement, with anisotropic displacement parameters for all atoms, yielded $R=0.022$ and the difference Fourier map did not show any significant chemical features. The structure of Na_5SrNbP_4 was refined starting with the positional parameters of Na_6WP_4. From the negative displacement parameter of Na1 it became apparent that the Na1 position is not entirely occupied by sodium atoms. Therefore we included strontium along with sodium in this 6*c* position. The site occupation factors (SOFs) of both Na1 and Sr1 were also refined with the constraint SOF(Na) + SOF(Sr) = 1 and result in 0.662(4) and 0.338 respectively. Since these values are very close to the values of 2/3 and 1/3 expected from the charge balance of the compound, we fixed them at SOF(Na1) = 2/3 and SOF(Sr) = 1/3 in the later refinement to account for the composition Na_5SrNbP_4. The structure of Na_5SrTaP_4 was refined in the same way. The positional and displacement parameters are given in Table 2 and important bond distances and angles are presented in Table 3. Refinements in the lower symmetry groups were done to prove a possible ordering of Na1 and strontium at site 6*c*, but did not yield significantly better results.

2.4. *IR spectroscopy*

Measurement of the IR spectra of Na_6WP_4, Na_5SrTaP_4 and Na_5SrNbP_4 was carried out on a Fourier Spectrometer IF3 113V (Bruker) with polyethylene pellets.

3. Results and discussion

3.1. *Structure description*

Figure 1 shows a perspective view of the Na_6WP_4 structure containing isolated Na^+ cations (Na1 and Na2) and tetrahedral $[WP_4]^{6-}$ anions. The phosphorus atoms form a slightly distorted hexagonal close packing (ABAB) along the *c* axis ($c/a=0.784$ instead of $1.633/2=0.816$). Figure 2 shows a projection of those layers around $z=1/2$. The tungsten and Na2 atoms fill half of the tetrahedral holes in an ordered way. The Na1 atoms fill three-quarters of the octahedral holes.

The coordination tetrahedron of the tungsten atom is slightly suppressed, in contrast to the elongated $[ZnO_4]$ tetrahedron in Na_6ZnO_4. The bond distances are d(W–P) = 226.9(6) (P1) and 233.0(2) pm (P2) respectively. The corresponding bond angles P–W–P are 109.14° and 109.80°, very close to the value for a regular tetrahedron. The coordination polyhedron of Na2 is an irregular tetrahedron having a common edge with the $[WP_4]$ tetrahedron (Fig. 2). The bond distances and bond angles range from 288.8 to 296.3 pm and from 77.3° to 134.9° respectively. The strong angular distortion results from the shift of the Na2 atom caused by the repulsive W–Na

TABLE 2

Positional and displacement parameters of Na_6WP_4, Na_5SrNbP_4 and Na_5SrTaP_4.
The U_{ij} (pm^2) are defined for $\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2U_{23}klb^*c^*)]$.
Standard deviations are given in parentheses

Compound	Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na_6WP_4	W	2b	1/3	2/3	0	123(2)	U_{11}	122(3)	62(1)	0	0
	Na1	6c	0.5318(3)	$-x$	0.1079(7)	252(17)	U_{11}	277(22)	134(19)	−20(10)	$-U_{13}$
	Na2	6c	0.1468(4)	$-x$	0.2848(7)	235(16)	U_{11}	392(29)	90(18)	31(13)	$-U_{13}$
	P1	2b	1/3	2/3	0.3163(8)	224(17)	U_{11}	157(21)	112(9)	0	0
	P2	6c	0.8056(2)	$-x$	0.3935(4)	178(8)	U_{11}	212(12)	96(10)	15(6)	$-U_{13}$
Na_5SrNbP_4	Nb	2b	1/3	2/3	0	138(3)	U_{11}	143(4)	69(1)	0	0
	M1[a]	6c	0.5292(1)	$-x$	0.1127(3)	256(5)	U_{11}	197(6)	143(5)	−14(3)	$-U_{13}$
	Na2	6c	0.1445(3)	$-x$	0.2855(5)	286(11)	U_{11}	522(23)	79(12)	64(10)	$-U_{13}$
	P1	2b	1/3	2/3	0.3255(4)	217(10)	U_{11}	149(13)	108(5)	0	0
	P2	6c	0.8082(1)	$-x$	0.3967(3)	167(5)	U_{11}	209(8)	83(6)	14(4)	$-U_{13}$
Na_5SrTaP_4	Ta	2b	1/3	2/3	0	163(4)	U_{11}	167(5)	81(2)	0	0
	M1[a]	6c	0.5303(2)	$-x$	0.1117(4)	217(10)	U_{11}	175(15)	133(12)	−10(7)	$-U_{13}$
	Na2	6c	0.1442(5)	$-x$	0.2829(13)	221(23)	U_{11}	464(44)	42(28)	70(19)	$-U_{13}$
	P1	2b	1/3	2/3	0.3247(9)	163(20)	U_{11}	90(30)	82(10)	0	0
	P2	6c	0.8086(2)	$-x$	0.3962(6)	102(11)	U_{11}	148(17)	50(13)	17(8)	$-U_{13}$

[a] The M1 site is occupied by (2/3) Na and (1/3) Sr.

TABLE 3

Bond distances (pm) and bond angles (deg) of Na_6WP_4, Na_5SrNbP_4 and Na_5SrTaP_4. Standard deviations are given in parentheses

Na_6WP_4		Na_5SrNbP_4		Na_5SrTaP_4		Multiplicity
W–P1	226.9(6)	Nb–P1	239.2(3)	Ta–P1	238.5(7)	1
P2	233.0(2)	P2	240.4(1)	P2	240.3(3)	3
Na1	323.7(4)	Na1	326.3(1)	Na1	327.9(2)	3
Na1–P1	299.0(6)	M1–P1	306.0(3)	M1–P1	304.5(5)	1
P2	298.4(5)	P2	306.8(2)	P2	306.3(4)	2
P2	318.9(4)	P2	323.8(2)	P2	324.7(3)	2
Na2	330.7(4)	Na2	335.1(3)	Na2	335.7(6)	2
P1	348.1(5)	P1	352.2(2)	P1	353.9(4)	1
Na2–P2	288.8(3)	Na2–P2	290.6(2)	Na2–P2	291.1(5)	2
P2	290.6(6)	P2	295.7(4)	P2	294.3(10)	1
P1	296.3(4)	P1	305.8(3)	P2	306.3(6)	1
P1–W	226.9(6)	P1–Nb	239.2(3)	P1–Ta	238.5(7)	1
Na2	296.3(4)	Na2	305.8(3)	Na2	306.3(5)	3
Na1	299.0(6)	M1	306.0(3)	M1	304.5(5)	3
Na1	348.1(5)	M1	352.2(2)	M1	353.9(4)	3
P2–W	233.0(2)	P2–Nb	240.4(1)	P2–Ta	240.3(3)	1
Na2	288.8(3)	Na2	290.6(2)	Na2	291.1(5)	2
Na2	290.6(6)	Na2	295.7(4)	Na2	294.3(10)	1
Na1	298.4(5)	M1	306.8(2)	M1	306.3(4)	2
Na1	318.9(4)	M1	323.8(2)	M1	324.7(3)	2
P1–W–P2	109.14(7)	P1–Nb–P2	108.05(8)	P1–Ta–P2	107.6(1)	3
P2–W–P2	109.80(7)	P2–Nb–P2	110.85(7)	P2–Ta–P2	111.3(1)	3

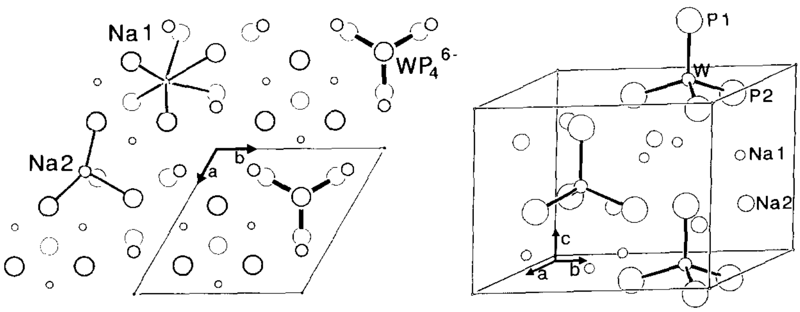

Fig. 1. *Left*. Projection of the Na_6WP_4 structure along [00.1] showing the WP_4^{6-} tetrahedra as well as the coordination polyhedra of sodium: small circles, Na1; medium circles, Na2; large circles, phosphorus atoms. ***Right***. Perspective view together with the atom labelling.

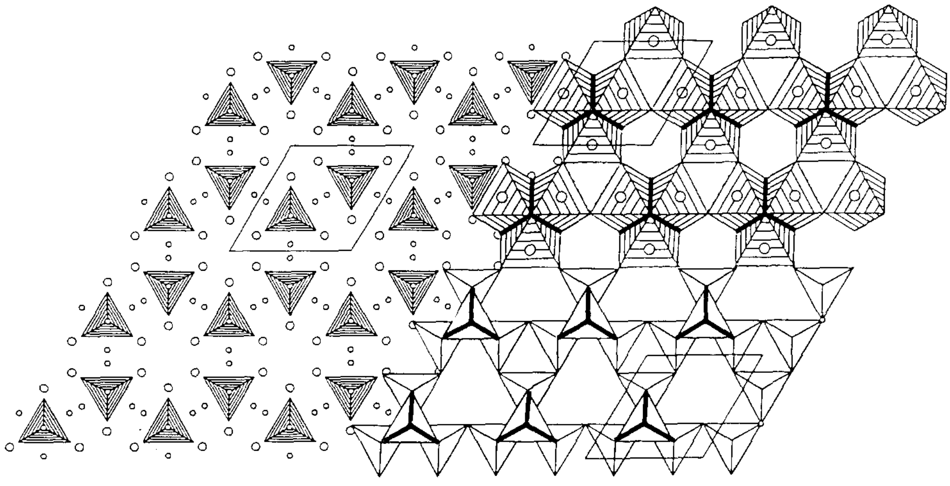

Fig. 2. *Left*. Polyhedral representation of the real structure of Na_6PW_4 along [00.1] emphasizing the WP_4 tetrahedra: small circles, Na1; large circles, Na2). ***Right***. Octahedral layer (around $z = 1/2$) of the idealized structure. The WP_4 tetrahedra are symbolized by a bold star. The Na(1) octahedra are hatched. Below the octahedral layer the edge connections of WP_4 tetrahedra and $Na(2)P_4$ tetrahedra are shown.

interaction. The coordination of Na1 is distorted octahedral (coordination number CN = 3 + 2 + 1) with the bond distances ranging from 299.0 (3×) to 318.9 (2×) and 348.1 pm (1×). The bond angles vary from 79.4° to 103.4°. This distortion results from the asymmetric surrounding of the octahedra by three [WP_4] tetrahedra (common face, common edge, common vertex). Similar bond distances and angles are found in Na_5SrNbP_4 and Na_5SrTaP_4. Here two sodium atoms together with one strontium atom occupy the M1 site with a distorted octahedral coordination (CN = 3 + 2 + 1).

The bond distances $\bar{d}$(W–P) = 231.5 pm, $\bar{d}$(Nb–P) = 240.1 pm and $\bar{d}$(Ta–P) = 239.9 pm are considerably shorter than the sum of the covalent radii, yielding single-bond distances of d_1(W–P) = 240 pm, d_1(Nb–P) = 244 pm and $d_1(\mathrm{Ta{-}P}) = 244$ pm. These smaller values might be caused by the low coordination number (CN = 4) as well as the highly charged ions (P^{3-} *vs.* W^{6+}, Nb^{5+} and Ta^{5+}).

Na_6WP_4 and the corresponding niobium and tantalum compounds are isotypic to Na_6ZnO_4 [8] (Pearson code *hP*22). The tetrahedral substructure formed by tungsten, Na2 and phosphorus atoms is an ordered wurtzite-type (2a) superstructure $Na_6W_2P_8 \equiv M_8Y_8$. This structure contains eight tetrahedral and eight octahedral holes, six of the octahedral holes being filled by Na1: $[Na_6{}^{tet}W_2{}^{tet}\Box_8{}^{tet}P_8][Na_6{}^{oct}\Box_2{}^{oct}] \equiv [(Na_3W\Box_4)^{tet}P_4][Na_3\Box]^{oct}$. A structure with completely filled octahedral holes is LiYSn [13] (Pearson code *hP*24). Table 4 gives the atomic parameters for that type, namely Na_6WP_4, Na_6ZnO_4, and LiYSn as the example for the superstructure [13]. The former two compounds are isotypic whereas LiYSn is isopointal to those if one includes the vacancies as regular sites. The crystal chemical formulae are therefore ${}^{3}_{\infty}[(Na_3Zn\Box_4)^{tet}O_4][Na_3\Box]^{oct}$ and ${}^{3}_{\infty}[(Li_4\Box_4)^{tet}Sn_4][Y_4]^{oct}$.

The sevenfold-coordinated P1 atom has a coordination sphere of a monocapped trigonal antiprism built from three Na1 and three Na2 atoms and a trigonal cap formed by the tungsten atom. The P2 atom is sixfold coordinated by a distorted trigonal prism formed by the tungsten atom, three Na2 and two Na1 atoms.

Figure 2 shows the structure along [00.1]. The WP_4 tetrahedra are emphasized. The structure is formed by h.c.p. layers of condensed octahedra and tetrahedra filled by Na1 (position idealized), Na2 and tungsten respectively. This polyhedra network is characterized by the formula ${}^{2}_{\infty}[Na_3{}^{oct}Na_3{}^{tet}W^{tet}P_{8/2}]$. The hexagonal packing of the layers results in columns of empty octahedra $\Box^{oct}$ and filled octahedra around $Na1^{oct}$ along [00.1]. However, the empty tetrahedra alternate with the filled ones, Na2–□–Na2··· and W–□–W···.

The hP22 type of Na_6ZnO_4 represents a remarkable structure type which tolerates a broad range of substitution with $0.75 \leq c/a \leq 0.79$. Na_6ZnO_4 and the isotypic alkali metal cobalt charcogenides [14] are in the very close range $0.770 \leq c/a \leq 0.778$. The lowest c/a ratios are observed with the oxide halides $Ba_4OCl_6 \equiv Cl_6OBa_4$ [15] and $Ln_4{}^{II}OCl_6 \equiv Cl_6OLn_4{}^{II}$ [16], having $c/a = 0.751$ and 0.758 respectively. The pnictides Na_6WP_4, Na_5SrTaP_4 and Na_5SrNbP_4 range in the upper limit ($0.784 \leq c/a \leq 0.790$). These compounds again demonstrate the stability of the Na_6ZnO_4 structure in tolerating the statistical distributions of Na^+ and Sr^{2+} at the same site. Finally, the c/a ratio of the pnictides $M_4{}^{I}M_2{}^{II}MY_4$ (see above) range from 0.761 to 0.789, which is an amazingly small range with respect to the variety of compounds.

Closer inspection of the observed U_{ij} values, especially those of the NbP_4 tetrahedron, indicates a rigid body behaviour of the tetrahedron ($U_{11}(P1) \gg U_{33}(P1)$; $U_{11}(P2) \ll U_{33}(P2)$). These displacements of the phosphorus atoms may be related to the ordering of Na1 and strontium atoms, leading to a superstructure. Such a superstructure has been observed with $K_5EuNbAs_4$ ($a' = 2a$, $c' = c$) [17]. However, in the case of $M_6{}^{I}CoSe_4$, similar U_{ij} ratios occur within the $CoSe_4$ tetrahedra [14], but here no ordering of

TABLE 4

Comparison of positional parameters of Na_6WP_4, Na_6ZnO_4 and LiYSn

Site	Na_6WP_4				Na_6ZnO_4				LiYSn			
	Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
2b	W	1/3	2/3	0	Zn	1/3	2/3	0	Li1	1/3	2/3	0
2b	P1	1/3	2/3	0.3163	O1	1/3	2/3	0.348	Sn1	1/3	2/3	0.407
6c	P2	0.8056	$-x$	0.3935	O2	0.811	$-x$	0.392	Sn2	0.830	$-x$	0.446
6c	Na1	0.5318	$-x$	0.1079	Na1	0.537	$-x$	0.114	Y1	0.518	$-x$	0.188
6c	Na2	0.1468	$-x$	0.2848	Na2	0.141	$-x$	0.286	Li2	0.174	$-x$	0.368
2a	□	0	0	z(Na1)	□	0	0	z(Na1)	Y2	0	0	0.188

the cations is necessary and therefore the displacement parameters indicate a dynamic process.

3.2. IR spectra

Assuming T_d–$\bar{4}3m$ symmetry for the MP_4^{q-} anions, one should expect four modes, A_1+E+2F_2, of which the F_2 are IR active. Indeed, in the IR spectra we observed absorption bands at 392 (Na_6WP_4), 370 (Na_5SrTaP_4) and 385 cm^{-1} (Na_5SrNbP_4) which were assigned to the F_2 stretching modes. Estimating the force constants with a simple model [18], we calculate $f_d = 2.66$ (WP_4^{6-}), 2.37 (TaP_4^{7-}) and 2.25 N cm^{-1} (NbP_4^{7-}). Comparing these force constants with those calculated with the same approach for the corresponding sulphides [18, 19], the obtained values $f_d = 4.11$ (WS_4^{2-}), 2.99 (TaS_4^{3-}) and 2.33 N cm^{-1} (NbS_4^{3-}) are significantly larger than those of the phosphides, indicating that the M–P bonds are much weaker than the M–S bonds.

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