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Crystal structure of tetrasodium-bis(μ_2-oxido)-hexafluoro-didioxo-molybdenum(V), $Na_2(Mo_2O_4F_6)$

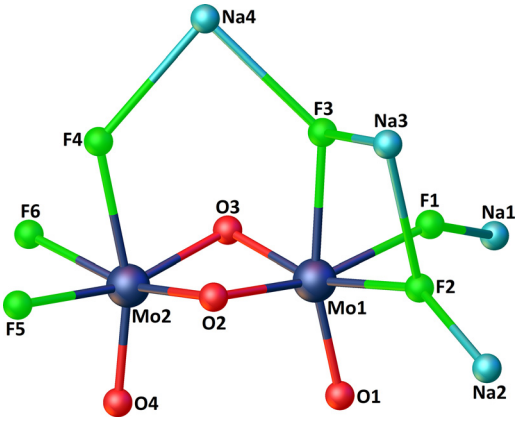

Table 1: Data collection and handling.

Crystal:	Block, brown
Size:	0.15 × 0.11 × 0.08 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	3.11 mm^{-1}
Diffractometer, scan mode:	Xcalibur, φ and ω-scans
θ_{max}, completeness:	29°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	3614, 2040, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1803
$N(param)_{refined}$:	145
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], OLEX2 [4]

https://doi.org/10.1515/ncrs-2022-0410
Received August 12, 2022; accepted September 13, 2022; published online September 23, 2022

Abstract

$O_4F_6Na_2Mo_2$, triclinic, $P\bar{1}$ (no. 2), a = 6.6154(6) Å, b = 7.8572(8) Å, c = 9.3588(11) Å, α = 95.257(9)°, β = 90.753(9)°, γ = 113.426(10)°, V = 443.83(9) Å^3, Z = 2, $R_{gt}(F)$ = 0.0431, w$R_{ref}(F^2)$ = 0.1125, T = 293(2) K.

CCDC no.: 2206943

A part of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of materials

A mixture containing $(NH_4)_2MoO_4{\cdot}4H_2O$ (4.830 g), NaF (1.350 g), citrin ($C_6H_8O_7$) (1.250 g), and deionized water (H_2O) (10.0 mL), with pH value 6.5, was prepared by mixing these components and sealed in a 25 mL Teflon-lined stainless steel autoclave (65% of the total volume of the autoclave). The resulting slurry was heated to 453 K in an oven and maintained at the temperature for three days. The brown purity-phase crystals of the title compound (about 25% yield based on Mo) were obtained.

Experimental details

All atoms were placed at calculated positions with the SHELX program.

Comment

Over the past decades, the study on fluorides has attracted more and more attention for its important applications in modern science and technology [5–8]. In general, inhomogeneous fluorides have widely different physicochemical properties, e.g. reactiveness, solubility and stability, and so on [9–11]. Meanwhile, fluorides were used in many important fields, such as organic synthesis, civilian chemical, biochemistry, nuclear chemistry, biomedicine, energy storage, battery technologies [12–15].

Herein, we report a new title fluoride, $Na_2(Mo_2O_4F_6)$. Single-crystal X-ray diffraction structure study reveals that the title compound, which has open 3D-network structure consists of Na^+ and a dinuclear molybdenum oxyfluoride.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.4985 (6)	0.0810 (5)	0.1538 (4)	0.0144 (9)
F2	0.6600 (7)	0.1721 (5)	0.4309 (5)	0.0160 (9)
F3	0.9145 (6)	0.2795 (5)	0.2147 (5)	0.0136 (8)
F4	1.1123 (6)	0.6928 (5)	0.1650 (5)	0.0140 (9)
F5	1.0212 (7)	0.9151 (5)	0.3497 (5)	0.0155 (9)
F6	0.8514 (7)	0.8167 (6)	0.0493 (5)	0.0176 (9)
Mo1	0.63801 (9)	0.33498 (7)	0.27620 (6)	0.00906 (17)
Mo2	0.80335 (9)	0.67789 (8)	0.22992 (7)	0.01020 (17)
Na1	0.2171 (5)	−0.0728 (4)	−0.0094 (3)	0.0161 (6)
Na2	0.6359 (4)	0.1092 (4)	0.6625 (3)	0.0143 (6)
Na3	1.0266 (4)	0.2022 (4)	0.4184 (3)	0.0139 (6)
Na4	1.2353 (5)	0.4610 (4)	0.1283 (3)	0.0188 (6)
O1	0.3855 (8)	0.3194 (7)	0.3244 (6)	0.0166 (11)
O2	0.8442 (8)	0.5530 (6)	0.3895 (5)	0.0139 (10)
O3	0.6730 (8)	0.4520 (6)	0.0993 (5)	0.0129 (10)
O4	0.5832 (8)	0.7283 (7)	0.2720 (6)	0.0192 (11)

The asymmetric unit of the compound contains a dinuclear anion, $[Mo_2O_4F_6]^{4-}$, and four Na^+ cations. The $[Mo_2O_4F_6]^{4-}$ anion is made up of two similar units, $[MoO_3F_3]$ (see the figure). The $[MoO_3F_3]$ buliding unit presents a deformed octahedral configuration with the Mo atom in the center. The six-coordinated Mo atoms show the bond distances (Mo–O_t) of 1.696(5) Å for terminal oxygen atoms and the bond distances (Mo–O_b) of 1.921(5)–1.940(5) Å for two-bridging oxygen atoms. The Mo–F bond distances are vary in the range of 2.055(4)–2.117(4) Å. O/F–Mo–O/F bond angles are in the range of 76.19(17)–165.4(2)°. The 3D title compound is formed by the Na^+ cations connecting $[Mo_2O_2F_6]^{4-}$ anions by means of Na–O and Na–F bonds. Bond valence calculations (BVS) [16] on Mo1 and Mo2 sites afford values of 5.105 and 5.108 respectively.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The work was supported by the Natural Science Foundation of Fujian Province (No. 2020J01367) and the Qimai Science and Technology Innovation Foundation of Xinluo County and Wuping County (No. 2022XLQM011, 2022WOQM04).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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