

YF[MoO₄] and YCl[MoO₄]: Two Halide Derivatives of Yttrium *ortho*-Oxomolybdate: Syntheses, Structures, and Luminescence Properties

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The halide derivatives of yttrium *ortho*-oxomolybdate YX[MoO₄] (X = F, Cl) both crystallize in the monoclinic system with four formula units per unit cell. YF[MoO₄] exhibits a primitive cell setting (space group *P2₁/c*; *a* = 519.62(2) pm, *b* = 1225.14(7) pm, *c* = 663.30(3) pm, β = 112.851(4)°), whereas the lattice of YCl[MoO₄] shows face-centering (space group *C2/m*; *a* = 1019.02(5) pm, *b* = 720.67(4) pm, *c* = 681.50(3) pm, β = 107.130(4)°). The two compounds each contain crystallographically unique Y³⁺ cations, which are found to have a coordination environment of six oxide and two halide anions. In the case of YF[MoO₄], the coordination environment is seen as square antiprisms, and for YCl[MoO₄], trigon-dodecahedra are found. The discrete tetrahedral [MoO₄]²⁻ units of the fluoride derivative are exclusively bound by six terminal Y³⁺ cations, while those of the chloride compound show a 5-fold coordination around the tetrahedra with one edge-bridging and four terminal Y³⁺ cations. The halide anions in each compound exhibit a coordination number of two, building up isolated planar rhombus-shaped units according to [Y₂F₂]⁴⁺ in YF[MoO₄] and [Y₂Cl₂]⁴⁺ in YCl[MoO₄], respectively. Both compounds were synthesized at high temperatures using Y₂O₃, MoO₃, and the corresponding yttrium trihalide in a molar ratio of 1:3:1. Single crystals of both are insensitive to moist air and are found to be coarse shaped and colorless with optical band gaps situated in the near UV around 3.78 eV for the fluoride and 3.82 eV for the chloride derivative. Furthermore, YF[MoO₄] seems to be a suitable material for doping to obtain luminescent materials because the Eu³⁺-doped compound shows an intense red luminescence, which has been spectroscopically investigated.

Introduction

Since energy saving became a serious issue throughout all fields of daily life, the importance of finding suitable materials grew, including the search for efficient luminescent materials. For that purpose, tungstates and molybdates are known as rather good host lattices, especially because *scheelite*-type compounds, such as Ca[WO₄] or Pb[WO₄], show luminescence even when not doped with other divalent cations.^{1,2} To adjust luminescence properties for special

needs, the doping of appropriate host lattices with di- or trivalent rare-earth metal cations usually leads to a set of suitable materials. The *scheelite* structure type naturally contains divalent cations, but the number of divalent lanthanides for doping is limited (e.g., Eu²⁺ is a widely used and therefore also well-investigated dopant). Thus, if doping with trivalent lanthanides is desired, two possibilities exist for using molybdates or tungstates with the respective M³⁺ cations (M = lanthanoid). The first one is modifying the M^{II}[WO₄] structure into M^IM^{III}[WO₄]₂ with M^I usually found as, but not limited to, an alkali metal and with M^{III}, found as a rare-earth metal cation, preferably without f-electrons (like Y³⁺ and La³⁺) or sometimes Gd³⁺ (4f⁷) because its f → f transitions are in an energy range much greater than

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that of visible light.^{3–5} This approach to the problem has resulted in a very large area of chemical and physical research, such that the given referenced examples serve only as a subset of the breadth of important work. However, the one feature that this structural class of compounds has in common is that alkali metal, rare-earth metal, and dopant cations are all positioned on the same crystallographic site.

A different approach to the above-mentioned challenge is to customize the structure for doping with trivalent cations by designing compounds in which the cationic part of the host lattice should comprise exclusively M³⁺ cations. Since tetrahedral oxomolybdates(VI) and -tungstates(VI) hold a charge of –2, another monovalent anion (preferably a halide) could be incorporated into the structure to perfectly balance with a rare-earth metal trication. In contrast to the *scheelite*-type approach, very little is known in the case of halide derivatives of rare-earth metal tungstates. Only a few compounds have been prepared, for example, La₃Cl₃[WO₆]^{6,7} and Pr₃Cl₃[WO₆],⁸ which are isostructural. These compounds contain octahedral [WO₆]^{6–} units rather than tetrahedral units, as also seen in LaCl[WO₄],⁹ a compound that crystallizes as twinned structures in the orthorhombic system, and GdCl[WO₄],⁹ which is *non-isotypic* to the lanthanum compound. So far, no other halide derivatives are known, especially no compounds containing F[–] anions. The softer halide anions like Cl[–], Br[–], and I[–] sometimes cause charge-transfer luminescence quenching, but the hard fluoride anions usually provide lattices without negative impact on the luminescent properties of the respective compound (e.g., La₃F₃[Si₃O₉]:Ce³⁺).¹⁰ On the other hand, the harder the structural building blocks are, the higher is the energy of lattice vibrations, and therefore, luminescence could be quenched by interaction between the luminophor and the crystal lattice. In contrast to the tungstates, no monovalent anionically derivatized rare-earth metal molybdates are known in the literature. The two title compounds display the first representatives of this new group of rare-earth metal halide *ortho*-oxomolybdates.

Experimental Section

Synthesis. Both YF[MoO₄] and YCl[MoO₄] are obtained by classical solid-state synthesis methods. A mixture of yttrium trifluoride (YF₃; 99.9%; ChemPur, Karlsruhe, Germany), yttrium sesquioxide (Y₂O₃; 99.9%; ChemPur, Karlsruhe, Germany), and molybdenum trioxide (MoO₃; *pro analysi*; Merck, Darmstadt,

Germany) with the components in the molar ratio 1:1:3 was sintered together in an evacuated silica ampule for seven days at 850 °C according to



From this reaction, colorless, transparent, bulky single crystals were obtained, which remained stable to air and water. The reaction gives a yield of about 60% showing a contamination of SiO₂, which could be identified via infrared spectroscopy and X-ray powder diffractometry. The silicon dioxide arises probably from the wall of the silica tube, which has been attacked by the yttrium trifluoride. YCl[MoO₄] was prepared by a reaction of yttrium trichloride (YCl₃; 99.9%; ChemPur, Karlsruhe, Germany) with yttrium sesquioxide, and molybdenum trioxide according to



in an evacuated silica ampule at 850 °C for seven days as well. This experiment yielded colorless, transparent, coarse single crystals of YCl[MoO₄]. The product turned out to be air- and water-stable and appeared to be phase pure, as confirmed by infrared spectroscopy and powder X-ray diffractometry. Both reactions were repeated several times, and finally conducted with the admixture of about 3% EuF₃ or EuCl₃, respectively, to produce Eu³⁺-doped materials. While YF[MoO₄]:Eu³⁺ shows a bright red luminescence under UV illumination (excitation wavelength λ = 254 nm), YCl[MoO₄]:Eu³⁺ remains disappointingly *non-luminescent* at room temperature. Because of the small amount of dopant, it is not possible to determine how many Eu³⁺ cations were incorporated into the host material. The assumption is that the level of dopant in the fluoride compound is smaller than 3% because of the reaction of EuF₃ with the wall of the silica tube, while the percentage of Eu³⁺ cations in YCl[MoO₄] is presumably 3%, which could possibly be too high and cause concentration quenching.

X-ray Crystallography. The X-ray powder patterns were measured on a Stoe STADI P diffractometer with a position-sensitive detector using germanium-monochromatized Cu Kα radiation (wavelength: λ = 154.060 pm). The experimental diffractograms together with the corresponding theoretical powder patterns are given in the Supporting Information. Intensity data sets for the single crystals of YF[MoO₄] and YCl[MoO₄] were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromatized Mo Kα radiation (wavelength: λ = 71.067 pm). In both cases, numerical absorption correction was performed with help of the program HABITUS.¹¹ The structure solutions and refinements were carried out by use of the program package SHELX-97.¹² Details of the data collections and the structure refinements¹³ are noted in Table 1; atomic positions and coefficients of the isotropic thermal displacement parameters¹⁴ are shown in Table 2, and motifs of mutual adjunction,¹⁵ interatomic distances, and selected bond angles are given in Table 3. Further details of the crystal structure

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Table 1. Crystallographic Data for YF[MoO₄] and YCl[MoO₄]

		YF[MoO ₄]	YCl[MoO ₄]
crystal system			monoclinic
space group		<i>P</i> ₂ ₁ / <i>c</i> (no. 14)	<i>C</i> ₂ / <i>m</i> (no. 12)
formula units			4
lattice constants	<i>a</i> /pm	519.62(2)	1019.02(5)
	<i>b</i> /pm	1225.14(7)	720.67(4)
	<i>c</i> /pm	663.30(3)	681.50(3)
	β /deg	112.851(4)	107.130(4)
calculated density	$D_x/g \cdot cm^{-3}$	4.572	3.948
molar volume	$V_m/cm^3 \cdot mol^{-1}$	58.583	72.005
<i>F</i> (000)		488	520
index range	$\pm h / \pm k / \pm l$	6/16/8	13/9/9
θ range	$\theta_{min} - \theta_{max}$	3.33–28.26	3.13–28.28
absorption coefficient	μ/mm^{-1}	17.97	15.14
data corrections		background, polarization, and Lorentz factors; numerical absorption correction by the program <i>HABITUS</i> ¹¹	
collected/unique reflections		8784/956	6088/646
R_{int}/R_σ		0.078/0.030	0.084/0.032
scattering factors		International Tables, Vol. C ¹³	
R_1 for no. reflections with $ F_o \geq 4\sigma(F_o)$		0.021/930	0.019/625
R_1/wR_2 for all reffns		0.022/0.047	0.020/0.043
goodness of fit	<i>S</i>	1.067	1.088
extinction	<i>g</i>	0.102(2)	0.0211(7)
residual electron density	max.	0.73	0.77
($\rho/e^- 10^{-6} pm^{-3}$)	min.	-1.19	-0.94

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Displacement Parameters, U_{eq}^a , for YF[MoO₄] and YCl[MoO₄]

	Wyckoff position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}/pm^2
YF[MoO ₄]					
Y	4 <i>e</i>	0.63957(6)	0.44939(2)	0.29985(4)	35(1)
F	4 <i>e</i>	0.4528(4)	0.0988(2)	0.0352(3)	101(4)
Mo	4 <i>e</i>	0.07718(5)	0.64392(2)	0.12920(4)	33(1)
O1	4 <i>e</i>	0.2368(5)	0.3449(2)	0.0914(4)	101(5)
O2	4 <i>e</i>	0.1921(5)	0.7765(2)	0.2066(4)	98(5)
O3	4 <i>e</i>	0.0048(5)	0.5698(2)	0.3366(4)	73(5)
O4	4 <i>e</i>	0.6932(5)	0.0649(2)	0.4622(4)	71(5)
YCl[MoO ₄]					
Y	4 <i>i</i>	0.22105(3)	0	0.11038(5)	68(1)
Cl	4 <i>i</i>	0.00979(9)	0	0.76222(14)	169(2)
Mo	4 <i>i</i>	0.36315(3)	0	0.73080(4)	63(1)
O1	4 <i>i</i>	0.2958(3)	0	0.4662(4)	187(7)
O2	4 <i>i</i>	0.4583(3)	0	0.2030(4)	149(6)
O3	8 <i>j</i>	0.1987(2)	0.3109(3)	0.1532(3)	126(4)

$$^a U_{eq} = \frac{1}{3}[U_{22} + \frac{1}{2}(\sin^2 \beta)(U_{11} + U_{33} + 2U_{13} \cos \beta)].^{14}$$

investigations are available from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax +49(0)7247/808-666; e-mail crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-418411 for YF[MoO₄] and CSD-418412 for YCl[MoO₄].

IR Spectroscopy. The infrared spectra of both compounds were taken on a Nicolet 6700 FT-IR spectrometer equipped with an ATR unit using a diamond crystal, measuring the reflection of the powder sample. The spectrum of YCl[MoO₄] shows a wide band with several shoulder peaks at around 850 cm⁻¹ which correspond to the [MoO₄]²⁻ stretching vibrations. They are also visible in the spectrum of YF[MoO₄], but in this spectrum a wide band at about 1070 cm⁻¹ occurs as well, indicating the presence of SiO₂.

Raman Spectroscopy. The bulk solid-state Raman spectra of the two title compounds were collected on a Nicolet Magna-IR 760 spectrometer with a FT-Raman module attachment by use of a Nd:YAG excitation laser (wavelength $\lambda = 1064$ nm).

UV-visible Spectroscopy. Diffuse reflectance spectra have been collected on a Varian Cary 500 Scan UV-vis-NIR spectrophotometer equipped with a Praying Mantis accessory. A polytetrafluoroethylene standard was used as reference. The Kubelka-Munk

function was applied to obtain band gap information.¹⁶ For YF[MoO₄], the band gap was calculated to be 3.78 eV; the band gap of YCl[MoO₄] amounts to 3.82 eV. Thus, absorption is situated in the UV range and therefore the substances appear to be white.

Luminescence Spectroscopy. Photoluminescence spectra in the visible region have been recorded on an Edinburgh Instruments FS900 spectrofluorimeter. This instrument is equipped with a xenon arc lamp, a microsecond flashlamp (pulse length: 2 μ s) and a red-sensitive photomultiplier (300–850 nm). Quantum yields were measured on an Edinburgh Instruments FS920P visible/near-infrared spectrometer, with a 450 W xenon lamp as the excitation source, a double excitation monochromator (1800 lines mm⁻¹), and an emission monochromator (600 lines mm⁻¹). The sample compartment has been equipped with an integrating sphere coated with BaSO₄ for quantum yield measurements. All photoluminescence spectra have been recorded at room temperature.

Results and Discussion

Crystal Structure and Raman Spectroscopy. Both YF[MoO₄] and YCl[MoO₄] crystallize in the monoclinic system, but while the fluoride-containing compound corresponds to the primitive space group *P*₂₁/*c* ($a = 519.62(2)$ pm, $b = 1225.14(7)$ pm, $c = 663.30(3)$ pm, $\beta = 112.851(4)^\circ$, $Z = 4$), the chloride derivative crystallizes in the face-centered space group *C*₂/*m* ($a = 1019.02(5)$ pm, $b = 720.67(4)$ pm, $c = 681.50(3)$ pm, $\beta = 107.130(4)^\circ$, $Z = 4$). The two structures each contain a single crystallographically unique Y³⁺ cation site. The rare-earth metal cation on this site displays a coordination number of eight. In YF[MoO₄], six O²⁻ and two F⁻ anions form a distorted square antiprism about the yttrium trications, while six oxide and two chloride ligands surround the Y³⁺ cations in YCl[MoO₄] to build up a trigonal-dodecahedron (Figure 1). The two halide anions in either polyhedron constitute an edge of the coordination figure.

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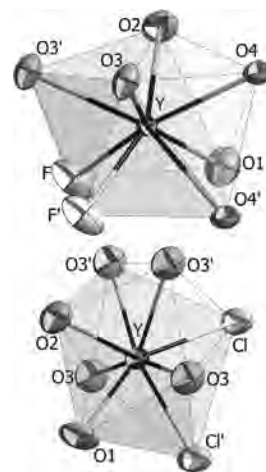
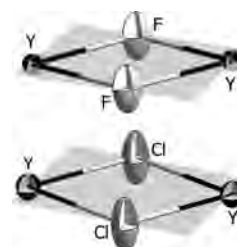
Table 3. Motifs of Mutual Adjunction,¹⁵ Internuclear Distances (*d*/pm), and Selected Angles (\angle /deg) for YF[MoO₄] and YCl[MoO₄]

YF[MoO ₄]	F	O1	O2	O3	O4	CN
Y	2/2 221.5(2) 227.7(2)	1/1 238.4(2)	1/1 229.8(2)	2/2 234.0(2) 241.3(2)	2/2 236.8(2) 238.3(2)	8
Mo	0/0	1/1 172.3(3) -O2: 106.3(1) -O3: 106.2(1) -O4: 106.7(1)	1/1 173.8(2) -O3: 113.2(1) -O4: 113.7(1)	1/1 180.6(2) -O4: 110.2(1)	1/1 181.4(3)	4
CN	2	2	2	3	3	
YCl[MoO ₄]	Cl	O1	O2	O3		CN
Y	2/2 269.4(1) 273.7(1)	1/1 231.8(3)	1/1 231.2(3)	4/2 228.0(2) 257.3(2)		8
Mo	0/0	1/1 173.0(3) -O2: 109.5(1) -O3: 112.3(1) (2 \times)	1/1 174.1(3) -O3: 111.4(1) (2 \times)	2/1 178.1(2) -O3: 99.8(1)		4
CN	2	2	2	3		

The yttrium–oxygen distances in the two title compounds display values of $d(\text{Y}^{3+}-\text{O}^{2-}) = 228\text{--}257$ pm, which correspond very well to those of yttrium sesquioxide (C-type Y_2O_3 , $d(\text{Y}^{3+}-\text{O}^{2-}) = 225\text{--}235$ pm).¹⁷ Although the distance of 257 pm seems to be rather long, it is not that unusual since in the yttrium chloride oxosulfate $\text{Y}_3\text{Cl}[\text{SiO}_4]_2$ a distance of 265 pm between Y^{3+} and O^{2-} is found.¹⁸ The distances of Y^{3+} to the halide anions cover values of $d(\text{Y}^{3+}-\text{F}^-) = 221\text{--}227$ pm and $d(\text{Y}^{3+}-\text{Cl}^-) = 269\text{--}274$ pm that lie in the same range as those of the respective trihalides (YF_3 , $d(\text{Y}^{3+}-\text{F}^-) = 226\text{--}232$ pm;¹⁹ YCl_3 , $d(\text{Y}^{3+}-\text{Cl}^-) = 258\text{--}270$ pm).²⁰ The halide anions themselves exhibit a coordination number of two in either structure forming an angled environment with the surrounding yttrium cations. This low coordination number is also seen in the formula-analogous yttrium fluoride oxosulfate $\text{YF}[\text{SO}_4]$;²¹ however, this structure contains infinite chains described by the formula ${}_{\infty}[\text{YF}_2\text{O}_2]^{2+}$, whereas in $\text{YF}[\text{MoO}_4]$, as well as in $\text{YCl}[\text{MoO}_4]$, isolated planar rhombus-shaped units $[\text{Y}_2\text{F}_2]^{4+}$ or $[\text{Y}_2\text{Cl}_2]^{4+}$ exist (Figure 2).

The deviation of these rhombuses from an ideal rectangular or square shape is reflected in the different angles between the Y^{3+} cations and the halide anions. In $\text{YF}[\text{MoO}_4]$, the $\text{F}-\text{Y}-\text{F}$ angle is 69.1° , while the complementary $\text{Y}-\text{F}-\text{Y}$ angle is 110.9° . The situation in $\text{YCl}[\text{MoO}_4]$ is comparable; here the $\text{Cl}-\text{Y}-\text{Cl}$ angle is found as 75.0° , and the complementary $\text{Y}-\text{Cl}-\text{Y}$ angle is 105.0° . On the one hand, this leads to relatively large $\text{Y}^{3+}-\text{Y}^{3+}$ distances of 370 pm for the fluoride and 431 pm for the chloride derivative. On the other hand, the distances between the halide anions within these rhombuses appear to be rather short. The F^--F^- distance in $\text{YF}[\text{MoO}_4]$ is found as 255 pm, which, however,

is about double the size of the F^- ionic radius ($r_i = 125$ pm for $\text{CN} = 2$).²² The same is true for the corresponding Cl^--Cl^- distance ($d = 331$ pm) in $\text{YCl}[\text{MoO}_4]$ ($r_i(\text{Cl}^-) = 171$ pm, calculated as Mean Fictive Ionic Radius (MEFIR),²³ with the help of the program MAPLE (Madelung Part of Lattice Energy),¹⁵ since Shannon does not provide radii data for chloride with a coordination number of two).²² Nevertheless, the halide anions are situated quite close together in both of the crystal structures; therefore, these atoms have to find a way to avoid each other in the structure. Since both anions show a certain amount of polarizability and bear only a charge of -1 , the shape of their electron shells determined

**Figure 1.** Coordination environment around the Y^{3+} cations in $\text{YF}[\text{MoO}_4]$ (top) and $\text{YCl}[\text{MoO}_4]$ (bottom).**Figure 2.** Isolated planar rhombus-shaped $[\text{Y}_2\text{X}_2]^{4+}$ units in the crystal structures of $\text{YF}[\text{MoO}_4]$ ($\text{X} = \text{F}$, top) and $\text{YCl}[\text{MoO}_4]$ ($\text{X} = \text{Cl}$, bottom).(17) Paton, M. G.; Maslen, E. N. *Acta Crystallogr.* **1965**, *19*, 307–310.(18) Hartenbach, I.; Schleid, Th. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2493–2498.(19) Zalkin, A.; Templeton, D. H. *J. Am. Chem. Soc.* **1953**, *75*, 2453–2458.(20) Templeton, D. H.; Carter, G. F. *J. Phys. Chem.* **1954**, *58*, 940–944.(21) Wang, X.-Q.; Liu, L.-M.; Ross, K.; Jacobson, A. J. *Solid State Sci.* **2000**, *2*, 109–118.(22) Shannon, R. D. *Acta Crystallogr.* **1976**, *A 32*, 751–767.(23) Hoppe, R. *Z. Kristallogr.* **1979**, *150*, 23–52.

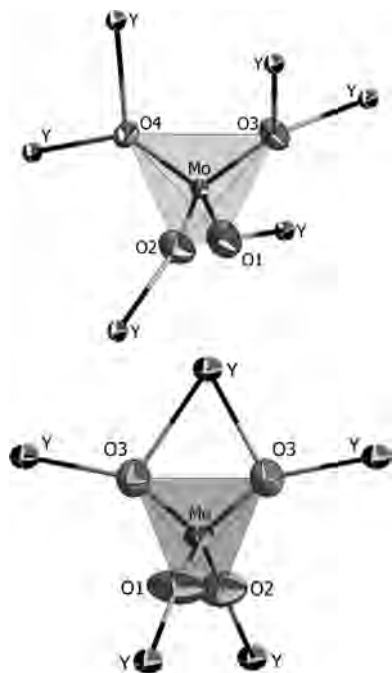


Figure 3. Cation coordination around the $[\text{MoO}_4]^{2-}$ tetrahedra in $\text{YF}[\text{MoO}_4]$ (top) and $\text{YCl}[\text{MoO}_4]$ (bottom).

in the crystal structure do not appear ideally spherical, but rather ellipsoidal, with the longest main axis perpendicular to the plane of the respective $[\text{Y}_2\text{X}_2]^{4+}$ rhombuses. A closer look at the distances reveals that the lesser polarizable fluoride anions feature a distance which is 2.0% longer than twice their ionic radii, whereas the more polarizable chloride anions feature distances that are 3.5% shorter as compared to their doubled ionic radii. So both structures can be considered as fragmented in discrete complex $[\text{Y}_2\text{X}_2]^{4+}$ cations ($\text{X} = \text{F}, \text{Cl}$) and isolated *ortho*-oxomolybdate(VI) anions $[\text{MoO}_4]^{2-}$, described by a formula: $[\text{Y}_2\text{X}_2][\text{MoO}_4]_2$. In both compounds, the oxomolybdate units are tetrahedral, with $\text{Mo}^{6+}-\text{O}^{2-}$ bond lengths in the range of 172–181 pm, which coincide with other structures comprising discrete tetrahedral $[\text{MoO}_4]^{2-}$ entities (e.g., $\text{La}_2[\text{MoO}_4]_3$, $d(\text{Mo}^{6+}-\text{O}^{2-}) = 173\text{--}182$ pm).²⁴ In the fluoride-containing yttrium molybdate, the coordination environment around the $[\text{MoO}_4]^{2-}$ tetrahedra consists solely of terminal Y^{3+} cations, while in the chloride derivative, one edge-bridging Y^{3+} cation is present in addition to four Y^{3+} terminal cations (Figure 3).

In $\text{YF}[\text{MoO}_4]$, the O–Mo–O angles within these tetrahedra cover an interval of 106–114°, which represents a deviation of just $\pm 4^\circ$ from the ideal tetrahedral angle of 109.5°. The corresponding angles for the $[\text{MoO}_4]^{2-}$ tetrahedra in $\text{YCl}[\text{MoO}_4]$ are even closer to ideal ($\angle(\text{O}–\text{Mo}–\text{O}) = 109\text{--}112^\circ$, $5\times$), with the exception of the O3–Mo–O3 angle, which is remarkably small (99.8°). This particular angle, however, is the one which is affected by the bridging Y^{3+} cation and thus subject to some geometric tension. Furthermore, the isolated oxomolybdate units display different symmetry. While in $\text{YCl}[\text{MoO}_4]$ a mirror plane runs through each tetrahedron resulting in C_s symmetry, the respective

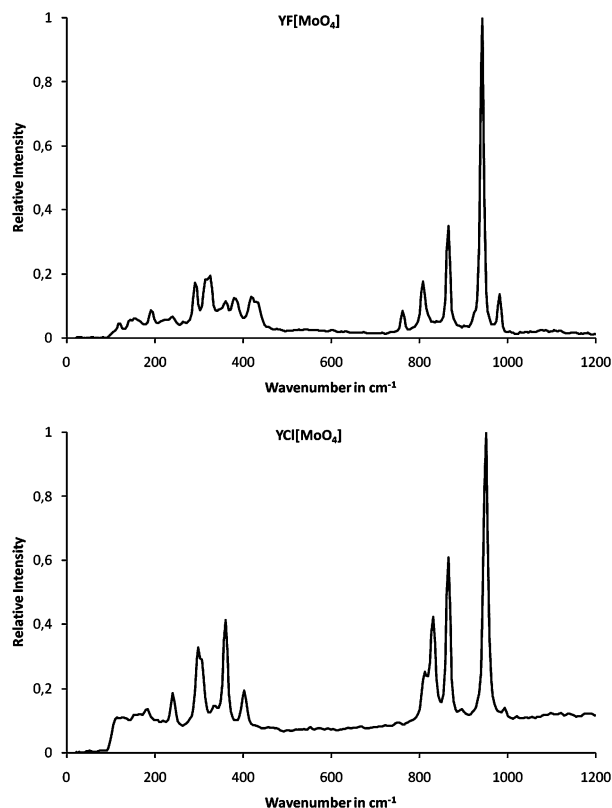


Figure 4. Raman spectra of $\text{YF}[\text{MoO}_4]$ (top) and $\text{YCl}[\text{MoO}_4]$ (bottom).

tetrahedra in $\text{YF}[\text{MoO}_4]$ sit on a site symmetry of only C_1 . This symmetry is reflected by the different Raman spectra of the title compounds as seen in Figure 4.

The stretching modes of the $[\text{MoO}_4]^{2-}$ tetrahedra can be found in the range of 800–980 cm^{-1} , and the deformation modes are situated between 200 and 400 cm^{-1} .²⁵ In the range of the deformation modes, the Y–F,²⁶ as well as the Y–O,²⁷ vibrations are commonly visible too; thus, the peaks in this energy range cannot be assigned reliably to a particular mode. According to Busca,²⁵ for C_1 symmetry, one symmetric stretching and three asymmetric modes are visible with the symmetric one found at higher energy than the asymmetric ones. Therefore, we assume that the peak at 943 cm^{-1} in the spectrum of $\text{YF}[\text{MoO}_4]$ belongs to the symmetric, and those at 866, 808, and 762 cm^{-1} belong to the asymmetric modes. This assumption is endorsed by the fact that the symmetric mode usually shows the most intense Raman bands,²⁸ as seen in Figure 4. The same is true for the spectrum of $\text{YCl}[\text{MoO}_4]$ in which the strongest peak emerges at 951 cm^{-1} , which we assign to the symmetric stretching vibration. Although the $[\text{MoO}_4]^{2-}$ units in this compound show a higher symmetry (C_s), one symmetric and three asymmetric stretching vibrations can be observed as well. Presumably because of the higher symmetry, the latter are visible in a smaller range causing two of them at 831 cm^{-1}

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with a shoulder at 812 cm⁻¹ to almost merge. The third asymmetric mode is visible at 866 cm⁻¹. To describe the crystal structure with the building blocks discussed earlier in the paper, it is most useful to look at the connectivity of the individual [YX₂O₆]¹¹⁻ polyhedra. In YF[MoO₄], these polyhedra share three common edges: F–F', O3–O3', and O4–O4', to form a corrugated layer parallel to (010). The (O1)²⁻ and (O2)²⁻ anions of a given [YF₂O₆]¹¹⁻ polyhedron individually connect to a molybdenum atom and *not* to other Y³⁺ cations in the unit cell. The situation in YCl[MoO₄] is similar, wherein the corresponding layer is built up by three edges (Cl–Cl' and two O3–O3', doubled by the mirror plane running through the idealized trigonal [YCl₂O₆]¹¹⁻ dodecahedron). The (O1)²⁻ and (O2)²⁻ anions exclusively belong to the coordination sphere of one Y³⁺ and one Mo⁶⁺ cation as found in YF[MoO₄]. Both of the layers, described by the Niggli formula $\frac{2}{3}\{[YX\frac{5}{2}O\frac{3}{2}O\frac{2}{1}]^{6-}\}$ (X = F, Cl; e = edge-connecting, t = terminal), provide hexagonal-shaped voids built up by two F–F' edges, two (O3)²⁻ anions, and two (O4)²⁻ anions in case of YF[MoO₄], but with two Cl–Cl' edges and four (O3)²⁻ anions for YCl[MoO₄]. The difference between the two described layers manifests itself in the particular arrangement of these voids. While in the fluoride derivative the layout corresponds to a sheered primitive alignment, in the chloride derivative the voids are ordered according to a hexagonal closest-packing arrangement (Figure 5).

In both of the title compounds, these layers are connected via Mo⁶⁺ cations in the *b* or *c* direction, respectively, to build up a three-dimensional structure. Those cations connected through oxide bonds, comprise [MoO₄]²⁻ tetrahedra, which are located above and below the hexagon-shaped voids of the $\frac{2}{3}\{[YX\frac{5}{2}O\frac{3}{2}O\frac{2}{1}]^{6-}\}$ layers (X = F, Cl). Describing the two different structures using the isolated complex [Y₂X₂]⁴⁺ cations and [MoO₄]²⁻ anions, the [Y₂F₂]⁴⁺ rhombuses in YF[MoO₄] show a two-dimensional hexagonally closest-packed arrangement with the [MoO₄]²⁻ tetrahedra surrounding them above and below (Figure 6).

In YCl[MoO₄], the discrete [Y₂Cl₂]⁴⁺ units are aligned in strands along [001] with adjacent strands at [1/2 1/2 1], reflecting the architecture of a tetragonal rod-packing. The [MoO₄]²⁻ tetrahedra are situated in the rectangular interstices in between; therefore, they also appear in a strand-like formation. Thus, the strand pattern can be described as two interpenetrating tetragonal rod-packings (Figure 7), in which the “molybdate strands” consist of twice as many [MoO₄]²⁻ tetrahedra as compared with the “rhombus strands” that contain the [Y₂Cl₂]⁴⁺ units.

Although from this point of view the two yttrium halide oxomolybdates could well be considered as AB₂-type structures (according to [Y₂X₂][MoO₄]₂), it is not possible to compare either structure easily with common AB₂ compounds like CdI₂, CdCl₂, CaF₂, or CaCl₂.

Luminescence Properties. Since both of the compounds contain exclusively cations (Y³⁺ and Mo⁶⁺) and anions (F⁻ or Cl⁻ and O²⁻) with *no* valence electrons, these oxomolybdates(VI) could be very likely used as host materials for luminescence applications without the risk of reductive

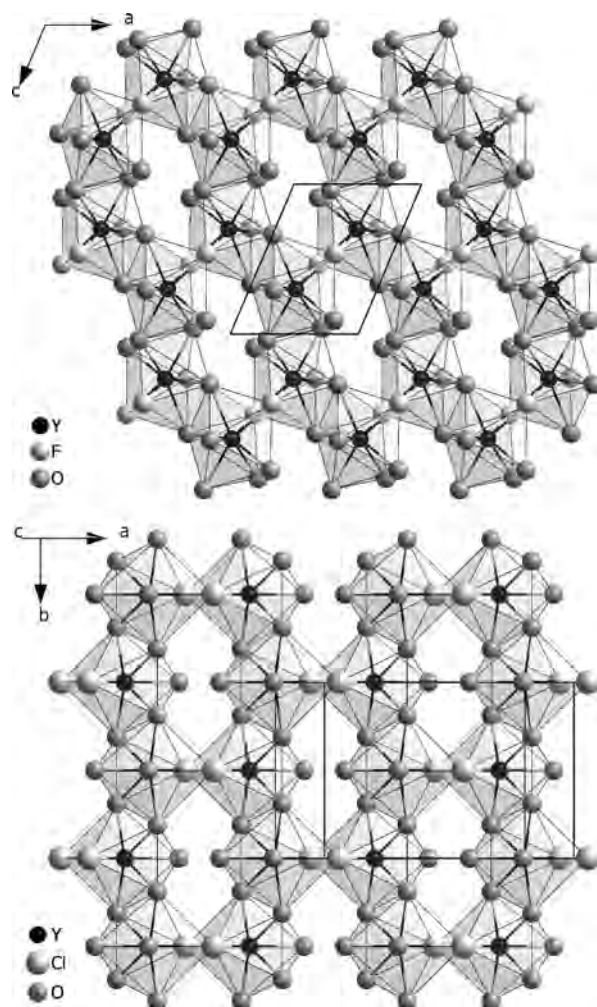


Figure 5. View of the $\frac{2}{3}\{[YX\frac{5}{2}O\frac{3}{2}O\frac{2}{1}]^{6-}\}$ layers of edge-shared [YX₂O₆]¹¹⁻ polyhedra (with X = F in YF[MoO₄], top, and X = Cl in YCl[MoO₄], bottom) with special emphasis on the hexagon-shaped voids in a sheered primitive (top) and a hexagonal-closest-packed arrangement (bottom).

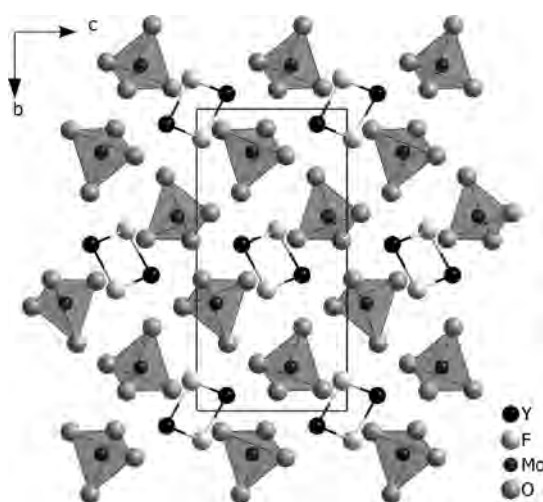


Figure 6. View of the structure of YF[MoO₄] along [100], showing the hexagonally closest-packed layer arrangement of the [Y₂F₂]⁴⁺ rhombuses.

quenching. Considering the size of the Y³⁺ cations (*r*₁ = 105 pm),²² doping in lanthanoid cations with ±10 % of this size should be possible. Our first attempts with EuF₃ and EuCl₃,

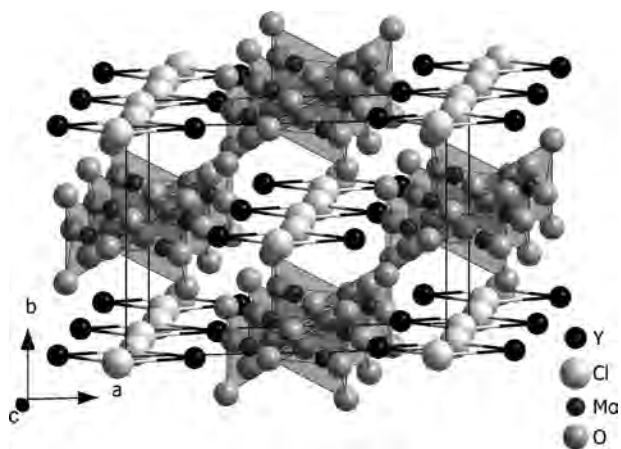


Figure 7. View of the structure of $\text{YCl}[\text{MoO}_4]$ along $[001]$, showing the tetragonal rod-packed arrangements of the $[\text{Y}_2\text{Cl}_2]^{4+}$ rhombuses with interpenetrating double strands consisting of $[\text{MoO}_4]^{2-}$ tetrahedra.

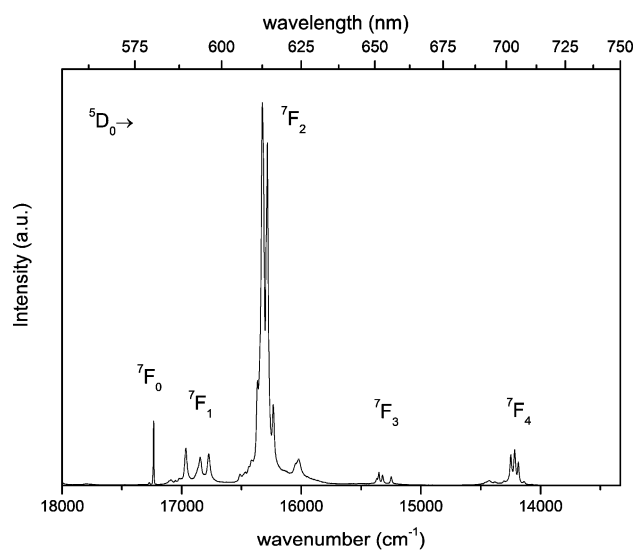


Figure 8. Luminescence spectrum of $\text{YF}[\text{MoO}_4]:\text{Eu}^{3+}$ in the solid state. The spectrum was recorded at room temperature with an excitation wavelength of 391 nm.

respectively, as doping agents were only partially successful. While the europium(III)-doped fluoride derivative shows rather bright red luminescence under UV illumination (excitation wavelength $\lambda = 254$ nm) at room temperature, the Eu^{3+} -containing chloride derivative remained non-luminescent under the same conditions. In the latter case, we assume luminescence quenching takes place, of which we cannot prove or deny if it is a concentration or a charge-transfer effect. Therefore only $\text{YF}[\text{MoO}_4]:\text{Eu}^{3+}$ could be further investigated by luminescence spectroscopy and its solid-state luminescence spectrum is shown in Figure 8.

The spectrum is typical for a europium(III)-doped compound featuring the hypersensitive transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ at 16330 cm^{-1} (612 nm), which is the most intense peak in the luminescence spectrum, much more intense than the magnetic dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$. The three crystal-field transitions for the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ branch indicate a strong distortion from an ideal coordination polyhedron, which is also seen in the crystal structure (Figure 1, top). The presence of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition itself rules out the possibility of D_2 symmetry. As just one peak is observed for this transition, only a local

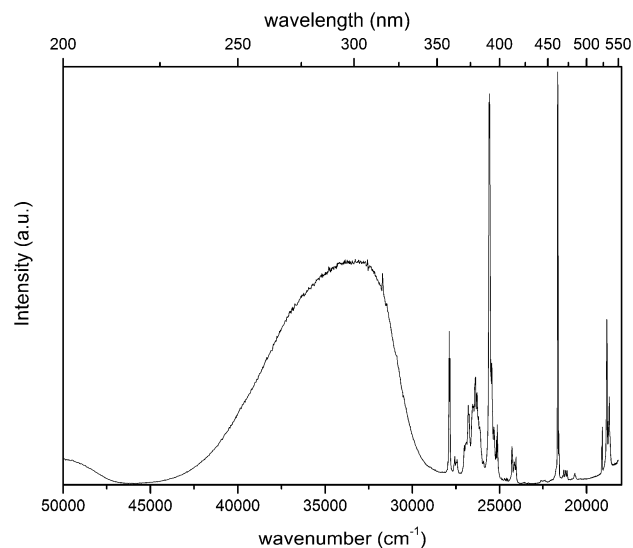


Figure 9. Excitation spectrum of $\text{YF}[\text{MoO}_4]:\text{Eu}^{3+}$ in the solid state at room temperature. The detection wavelength was set at 614 nm.

site with C_1 , C_2 , C_s , or C_{2v} symmetry can be present. Because of the five peaks for the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition, C_{2v} symmetry is not possible. The intensity ratio $I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)/I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$ is equal to 6.4. The luminescence decay of the ${}^5\text{D}_0$ -state transition (monitored via the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition at 614 nm upon excitation into the ${}^5\text{L}_6$ level at 391 nm) was found to be single exponential, and the radiative lifetime was measured as 0.67 ms. The monoexponential decay together with the presence of only one component for the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transition indicates that there is only one rather well-defined europium(III) site present. The excitation spectrum (performed by monitoring the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission at 614 nm, Figure 9) exhibits a broad band in addition to the typical fine-resolved f–f transition lines of Eu^{3+} .

The broad band between 250 and 330 nm can be attributed to the $\text{O} \rightarrow \text{Mo}$ and $\text{O} \rightarrow \text{Eu}$ ligand-to-metal charge-transfer transition (LMCT). Excitation at 281 nm into this charge-transfer band results in an emission spectrum that does not show any significant differences to the excitation at 391 nm. The absolute quantum yield of the investigated compound was determined at room temperature by means of an integrating sphere and comes out to be 3.3(3) %. Although this value is rather small as compared to other Eu^{3+} compounds, these are quite promising results and stimulate further work in this area. When the still dissatisfying problem of phase-pure synthesis can be solved in the near future, experiments with precise levels of the dopant will follow as well as doping and co-doping with other lanthanoid trications. The yttrium fluoride *ortho*-oxomolybdate $\text{YF}[\text{MoO}_4]$ has thus proven to be a suitable host material for luminescent light emission in principle, so the first step towards a possible high-performance application is made.

Conclusions

In the present paper, the syntheses, structures, and some spectroscopic properties of the two new rare-earth metal halide *ortho*-oxomolybdates $\text{YF}[\text{MoO}_4]$ and $\text{YCl}[\text{MoO}_4]$ have been reported. In addition to tetrahedral $[\text{MoO}_4]^{2-}$ entities,

both structure types contain very peculiar [Y₂X₂]⁴⁺ units in the shape of planar rhombuses. Furthermore, the Eu³⁺-doped fluoride derivative shows red luminescence, which has been investigated by luminescence spectroscopy, including a determination of the quantum yield.

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Supporting Information Available: Crystallographic information files (CIFs), IR, and DRS spectra, as well as X-ray powder diffractograms of YF[MoO₄] and YCl[MoO₄]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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