



# A series of oxyfluoride chains containing asymmetric basic building units of both early- and late-transition metal cations



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## ABSTRACT

Four new transition metal oxyfluorides revealing chain structures composed of asymmetric basic building units of  $[\text{MO}_2\text{F}_4]^{2-}$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ ) and  $[\text{M}'(\text{pz}/\text{mpz})_4]^{2+}$  ( $\text{M}' = \text{Cu}$  and  $\text{Ni}$ ) polyhedra, i.e.,  $[\text{Cu}(\text{mpz})_4][\text{MoO}_2\text{F}_4]$  (1),  $[\text{Cu}(\text{pz})_4][\text{WO}_2\text{F}_4]$  (2),  $[\text{Ni}(\text{pz})_4][\text{MoO}_2\text{F}_4]$  (3), and  $[\text{Ni}(\text{pz})_4][\text{WO}_2\text{F}_4]$  (4) ( $\text{pz}$  = pyrazole;  $\text{mpz}$  = 3-methyl pyrazole) have been synthesized via hydrothermal reactions. The linear chain structures found from the title compounds are attributable to the *trans*-directing  $[\text{MO}_2\text{F}_4]^{2-}$  octahedral moiety and hydrogen bonding interactions. Strong Jahn–Teller distortions are observed for  $\text{Cu}^{2+}$  cations with  $d^9$  configuration in compounds 1 and 2. All the compounds show both lower-energy and higher-energy absorption band gaps, which originate from the  $d$ – $d$  transitions and the distortion of octahedral geometry of  $\text{M}^{2+}$  cations, respectively. The magnetism of  $[\text{Cu}(\text{mpz})_4][\text{MoO}_2\text{F}_4]$  turns out to be described by noninteracting  $\text{Cu}^{2+}$  spins rather than a spin chain due to long exchange path mediated via the nonmagnetic  $\text{Mo}^{6+}$  ions. The title compounds have been also thoroughly characterized using spectroscopic and thermal analyses along with calculations of local dipole moments and the extent of out-of-center distortions.

## 1. Introduction

Transition metal oxyfluorides have drawn extensive attentions in inorganic materials chemistry owing to their various attractive functional properties such as magnetism, catalysis, sorption, photochromic and electrochromic characteristics [1–6]. Especially, solid oxyfluoride materials containing magnetic cations may be applied in the electronic information technology [7–10]. Thus far, a variety of one-dimensional extended oxyfluoride frameworks have been constructed and broadly explored by the combination of distortive octahedra of early transition metals (ETM) and polarizable polyhedra of late transition metals (LTMs) with organic ligands through solvothermal reactions. In fact, the combinations of asymmetric basic building units (BBUs) of ETM, LTM, and organic ligands often resulted in many metal oxyfluorides with linear chain structures [11–13]. The tendency of the formation of linear chain structures for metal oxyfluorides should be closely related to the hard–soft acid–base chemistry: the ETM with high oxidation states as hard acids are bonded to the hard bases such as  $\text{F}^-$  and  $\text{O}^{2-}$ , whereas the LTM with low oxidation states as soft acids tend to be associated with the soft organic bases [14]. Transition metal oxyfluoride compounds presenting of low-dimensional arrangements with interesting magnetic properties have been investigated [15–20]. Moreover, the magnetic susceptibilities of organic-inorganic hybrids compounds have revealed unique characteristics such as para-

magnetic [21–23] and antiferromagnetic [3,24] properties. The asymmetric moiety of octahedrally coordinated  $d^0$  transition metal cations ( $\text{Mo}^{6+}$ ,  $\text{W}^{6+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ti}^{4+}$  etc.) have drawn a specific structure-directing property due to the varied nucleophilicities of  $\text{F}^-$  and  $\text{O}^{2-}$  ligands, and consequently, coordinated to the extended bond network in either *cis* or *trans* mode [25–27]. Herein, by taking the organic-inorganic oxyfluoride as a maternal structure, we have extended to the incorporation of two different amine ligands in *trans*-directing oxyfluoride systems comprising both types of Jahn–Teller distortive cations, and produced low-dimensional hybrid crystal structures. In this paper, four new 1D linear chain transition metal oxyfluorides by intimating distorted ETM octahedra ( $\text{Mo}^{6+}$  and  $\text{W}^{6+}$ ), polarizable LTM polyhedra ( $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ), and organic ligands [pyrazole ( $\text{pz}$ ) and 3-methylpyrazole ( $\text{mpz}$ )] are reported. Synthesis, structural description, spectroscopic characterization, thermal properties, and magnetic susceptibilities for the synthesized compounds are reported.

## 2. Experimental section

### 2.1. Caution: hydrofluoric acid is toxic and corrosive!

#### 2.1.1. Synthesis

$\text{CuO}$  (95.0%, Duksan),  $\text{NiO}$  (99.8%, Aldrich),  $\text{MoO}_3$  (99.5%, Alfa Aesar),  $\text{WO}_3$  (99.5%, Daejung),  $\text{C}_3\text{N}_2\text{H}_4$  (pyrazole), (98%, Alfa Aesar),

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C<sub>4</sub>H<sub>6</sub>N<sub>2</sub> (3-methylpyrazole) (97%, Alfa Aesar), and HF (aq. 48 wt%, J.T Baker) were used as received. Crystals of all the reported compounds were obtained via hydrothermal reactions. For [Cu(mpz)<sub>4</sub>][MoO<sub>2</sub>F<sub>4</sub>] (1),  $1.0 \times 10^{-3}$  mol (0.796  $\times 10^{-1}$  g) of CuO,  $1.0 \times 10^{-3}$  mol (0.144 g) of MoO<sub>3</sub>,  $6.0 \times 10^{-3}$  mol (0.508 g) of 3-methylpyrazole,  $5.0 \times 10^{-3}$  mol (0.208 g) of aqueous HF (48%), and 0.324 mL of H<sub>2</sub>O were mixed. For [Cu(pz)<sub>4</sub>][WO<sub>2</sub>F<sub>4</sub>] (2),  $3.0 \times 10^{-3}$  mol (0.239 g) of CuO,  $3.0 \times 10^{-3}$  mol (0.696 g) of WO<sub>3</sub>,  $1.8 \times 10^{-2}$  mol (1.225 g) of pyrazole, and  $1.5 \times 10^{-2}$  mol (0.625 g) of aqueous HF (48%), and 0.973 mL of H<sub>2</sub>O were mixed. For [Ni(pz)<sub>4</sub>][MoO<sub>2</sub>F<sub>4</sub>] (3),  $3.0 \times 10^{-3}$  mol (0.224 g) of NiO,  $3.0 \times 10^{-2}$  mol (0.432 g) of MoO<sub>3</sub>,  $1.8 \times 10^{-2}$  mol (1.225 g) of pyrazole,  $1.5 \times 10^{-2}$  mol (0.625 g) of aqueous HF (48%), and 1.946 mL of H<sub>2</sub>O were mixed. For [Ni(pz)<sub>4</sub>][WO<sub>2</sub>F<sub>4</sub>] (4),  $2.0 \times 10^{-3}$  mol (0.149 g) of NiO,  $2.0 \times 10^{-3}$  mol (0.464 g) of WO<sub>3</sub>,  $1.2 \times 10^{-2}$  mol (0.817 g) of pyrazole,  $1.0 \times 10^{-2}$  mol (0.417 g) of aqueous HF (48%), and 0.649 mL of H<sub>2</sub>O were mixed. Each reaction mixture was put in autoclaves with 23 mL Teflon cups. After tightly sealing, the autoclaves were heated to 150 °C (for compounds 1 and 4) or 180 °C (for compounds 2 and 3) for 72 h and slowly cooled to room temperature at a rate of 6 °C h<sup>-1</sup>. Blue crystals of compounds 1–4 were obtained by vacuum filtration in 81%, 69%, 70%, and 58% yields, respectively, based on CuO or NiO.

### 2.1.2. Structure determination

Single crystal X-ray diffraction data for compounds 1–4 were collected on a Bruker SMART BREEZE diffractometer (Mo K $\alpha$  radiation) with a 1 K CCD area detector at room temperature and on a BL2D-SMC at the Pohang Light Source II using 0.70000 Å radiation at 296 K. A blue plate (0.010 mm  $\times$  0.017 mm  $\times$  0.136 mm) for compound 1, a blue block (0.146 mm  $\times$  0.261 mm  $\times$  0.298 mm) for compound 2, a blue block (0.268 mm  $\times$  0.290 mm  $\times$  0.314 mm) for compound 3, and a blue block (0.184 mm  $\times$  0.201 mm  $\times$  0.204 mm) for compound 4 were selected. The structure solutions and refinements were obtained by SHELXS-97 and SHELXL-97 [28], respectively, in the software package WinGX-98 [29]. Crystallographic data for the title compounds are tabulated in Table 1.

### 2.1.3. Characterization

Powder X-ray diffraction (PXRD) data of the synthesized crystalline materials were collected on a Bruker D8-Advance diffractometer using Cu K $\alpha$  radiation with 40 kV and 40 mA in the  $2\theta$  range of 5–70° with a step size of 0.02° for 0.1 s. The measured PXRD patterns for the pure polycrystalline samples were in good agreement with the calculated data generated from single crystal X-ray diffraction experiments (see the Supporting information).

Infrared (IR) spectra for the reported materials were obtained by a Thermo Scientific Nicolet 6700 FT-IR spectrometer in the range of 400–4000 cm<sup>-1</sup> at room temperature.

**Table 1**

Crystallographic data for compounds 1–4.

	1	2	3	4
Formula	CuMoC <sub>16</sub> H <sub>24</sub> F <sub>4</sub> N <sub>8</sub> O <sub>2</sub>	Cu <sub>2</sub> W <sub>2</sub> C <sub>24</sub> H <sub>32</sub> F <sub>8</sub> N <sub>16</sub> O <sub>4</sub>	Ni <sub>2</sub> Mo <sub>2</sub> C <sub>24</sub> H <sub>32</sub> F <sub>8</sub> N <sub>16</sub> O <sub>4</sub>	NiWC <sub>12</sub> H <sub>16</sub> F <sub>4</sub> N <sub>8</sub> O <sub>2</sub>
fw	595.91	1255.43	1069.92	622.89
space group	P2 <sub>1</sub> /n (No. 14)	C2/c (No. 15)	C2/c (No. 15)	C2/c (No. 15)
a (Å)	9.5890(19)	20.773(3)	20.5906(3)	10.239(3)
b (Å)	17.185(3)	25.663(3)	24.4913(3)	12.290(3)
c (Å)	14.856(3)	15.0254(19)	15.3667(2)	15.440(4)
$\beta$ (°)	100.07(3)	97.565(10)	96.4090(10)	96.61(2)
V (Å <sup>3</sup> )	2410.3(9)	7940.3(17)	7700.85(18)	1929.9(9)
Z	4	8	8	4
T (K)	296(2)	296(2)	296(2)	296(2)
$\lambda$ (Å)	0.70000	0.71073	0.71073	0.71073
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.642	2.100	1.846	2.144
R(F) <sup>a</sup>	0.0431	0.0373	0.0568	0.0303
R <sub>w</sub> (F <sub>o</sub> <sup>2</sup> ) <sup>b</sup>	0.1161	0.0720	0.1202	0.0690

<sup>a</sup>  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ .

DC magnetic properties were investigated using a superconducting quantum interference device (SQUID) magnetometer (MPMS-XL7, Quantum Design). The dc magnetic susceptibilities were recorded down to 2 K at an applied magnetic field of  $H = 1$  kOe for zero-field-cooled (ZFC) and field-cooled (FC) processes. In addition, the isothermal magnetization curves were measured in the field range from –7 to 7 T at 2 K.

Electron spin resonance (ESR) measurements were conducted at an X-band ( $\nu = 9.443$  GHz) by using a JEOL JESFA200 spectrometer at room temperature.

UV–vis diffuse reflectance spectra for the title compounds were obtained on a Varian Cary 500 scan UV–Vis–NIR spectrophotometer in the spectral range of 200–2000 nm at room temperature. The measured reflectance data were converted to absorbance using the Kubelka-Munk function [30,31].

Thermogravimetric analysis (TGA) was performed on a SCINCO TGA N-1000 thermal analyzer from room temperature to 900 °C heating at a rate of 10 °C min<sup>-1</sup> under a constant flowing of Ar gas.

Elemental analysis was carried out on a Carlo Erba EA1108 analyzer. Elemental microanalysis for compound 1 obsrvd (calcd): C, 32.21% (32.25%); H, 4.06% (4.06%); N, 18.78% (18.80%). compound 2 obsrvd (calcd): C, 22.81% (22.96%); H, 2.61% (2.57%); N, 17.84% (17.85%). compound 3 obsrvd (calcd): C, 26.12% (26.94%); H, 3.10% (3.01%); N, 20.39% (20.95%). compound 4 obsrvd (calcd): C, 20.59% (23.14%); H, 2.59% (2.59%); N, 16.64% (17.99%).

## 3. Results and discussions

### 3.1. Crystal structure description of [Cu(mpz)<sub>4</sub>][MoO<sub>2</sub>F<sub>4</sub>] (1)

Compound 1 crystallizing in the centrosymmetric (CS) monoclinic space group, P2<sub>1</sub>/n (No. 14) exhibits a linear chain structure comprising of 3-methylpyrazole, MoO<sub>2</sub>F<sub>4</sub>, and CuN<sub>4</sub>F<sub>2</sub> polyhedra (Fig. 1a). A unique Mo<sup>6+</sup> in an asymmetric unit is coordinated to two oxygen and four fluorine atoms in a distorted octahedral moiety. In particular, the distortion in Mo(1)O<sub>2</sub>F<sub>4</sub> octahedra happens toward a distinct local C<sub>2</sub> direction and shows two long Mo–F [2.017(3) Å and 2.059(3) Å], two intermediate Mo–F [1.841(2) Å and 1.893(2) Å], and two short Mo–O [1.716(3) Å and 1.750(3) Å] bonds. Another unique Cu<sup>2+</sup> cation is also in the distorted octahedral geometry with four nitrogen and two fluorine atoms. The distortion in CuN<sub>4</sub>F<sub>2</sub> octahedra results in two long Cu–F [2.300(2)–2.307(2) Å] bonds along the axial locations and four normal Cu–N [2.008(3)–2.019(3) Å] bonds in the equatorial positions attributable to the Jahn-Teller distortions. 3-Methylpyrazole ligands coordinated to the equatorial position of CuN<sub>4</sub>F<sub>2</sub> octahedra exhibit C–C, C–N, and N–N

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