SPECIAL TOPIC: Dedicated to the 70th Birthday of Professor Kenneth R. Poeppelmeier

Synthesis and characterization of a new quasi-one-dimensional antiferromagnet $\text{CoF}_2(\text{H}_2\text{O})_2(\text{pyrazine})$

Yanhong Wang, Hang Liu, Peng Fu and Hongcheng Lu*

ABSTRACT A new one-dimensional (1D) antiferromagnetic transition metal hybrid fluoride $\text{CoF}_2(\text{H}_2\text{O})_2(\text{pyz})$ (pyz = pyrazine) together with two new isostructural $\text{MF}_2(\text{H}_2\text{O})_2(\text{pyz})$ ($\text{M} = \text{Ni}^{2+}, \text{Zn}^{2+}$) have been successfully synthesized by the hydrothermal method. Their structures were determined by single crystal X-ray diffraction and they all crystallize in the same space group of $C2/m$. The magnetic property of $\text{CoF}_2(\text{H}_2\text{O})_2(\text{pyz})$ **1** was measured and discussed. The Weiss constant of -20.6 K indicates dominant antiferromagnetic interaction and the effective magnetic moment of about $5.66 \mu_B$ suggests large unquenched orbital contribution and anisotropy in **1**. The quantum fluctuations in the quasi-1D antiferromagnet of **1** prevent the appearance of long range magnetic order until 2.9 K, suggesting good 1D magnetism.

Keywords: fluoride, hydrothermal synthesis, low-dimensional magnetism, quantum magnetism

INTRODUCTION

Low dimensional quantum magnets are of great interest owing to the exotic quantum phenomena like spin liquid state, the relation to the high-temperature superconductivity and the potential application in quantum computing [1–6]. As the simple low dimensional quantum magnets, one-dimensional (1D) magnets have been firstly studied. Comparing to the single chain magnets or single molecule magnets requiring ferromagnetic interaction for magnetic relaxation, the 1D Heisenberg antiferromagnetic (AFM) spin chains have also been extensively investigated for their intriguing phenomena such as spin-charge separation, quantum disordered state and high-temperature superconductivity [7–9]. To experimentally realize ideal 1D magnets ($J'/J \ll 1$), the

interchain interaction J' need be negligible besides strong intrachain interaction J . The inorganic ionic groups such as $[\text{ClO}_4]^-$, $[\text{PO}_4]^{3-}$, and $[\text{SeO}_3]^{2-}$ were usually used for obtaining 1D AFM spin chain compounds including Haldane-gap compound $[\text{Ni}(\text{en})_2(\text{NO}_2)]\text{ClO}_4$ [10–12]. Also, the fluorine plays an important role in the regulation of structure, magnetic and optical properties [13–15]. In addition, it is recently reported that the organic molecule could be more efficient to separate spin chains with negligible interchain interaction J' for experimentally realizing the nearly ideal 1D $S = 5/2$ antiferromagnet $(4,4'\text{-bpy})\text{FeF}_3$ ($4,4'\text{-bpy}$ = $4,4'\text{-bipyridyl}$) [15].

Besides the organic molecule of $4,4'\text{-bipyridyl}$, pyrazine (pyz) has also been widely used as bridging ligands for targeting novel low-dimensional antiferromagnets such as $\text{Cu}(\text{pyz})(\text{NO}_3)_2$, $[\text{CuX}(\text{pyz})_2](\text{BF}_4)$ ($\text{X} = \text{Cl}, \text{Br}$), $\text{Cu}(\text{HF}_2)(\text{pyz})_2\text{BF}_4$, $\text{Cu}(\text{HCO}_2)_2(\text{pyz})$, and $[\text{Ni}(\text{HF}_2)(3\text{-Clpy})_4]\text{BF}_4$ (py = pyridine) [16–20]. However, most of them are focused on copper-based compounds with $S = 1/2$. For the low-dimensional antiferromagnets with magnetic ion of Cu^{2+} in octahedron environment, the magnetic orbital $d_{x^2-y^2}$ is oriented in the equatorial CuL_4 (L = ligand) plane, perpendicular to the elongated Jahn-Teller (JT) axis with d_{z^2} orbital. The unique magnetic orbital $d_{x^2-y^2}$ of Cu^{2+} which could be easily determined based on elongated z axis makes it easier to study magnetic properties of copper-based low-dimensional antiferromagnets with $S = 1/2$, even under successive change of external environment. For example, magnetic properties of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ under pressure have been studied because the JT axis (z axis) could be reoriented under pressure, which was from along Cu–N bonds under ambient

Key Laboratory of Material Chemistry for Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Hubei Key Laboratory of Bioinorganic Chemistry & Materia Medica, Hubei Key Laboratory of Material Chemistry and Service Failure, Huazhong University of Science and Technology, Wuhan 430074, China

* Corresponding author (email: hcl@hust.edu.cn)

pressure to be reoriented along Cu–O bonds then along Cu–F bonds with the increase of pressure [21,22]. To intensively investigate more low-dimensional antiferromagnets with the pyrazine molecule, it is crucial to experimentally realize 1D AFM spin chain systems with other spin values such as $S = 1$ or $3/2$ besides for $S = 1/2$. Thus, in this work, we have hydrothermally targeted two new 1D AFM chain compounds $\text{MF}_2(\text{H}_2\text{O})_2(\text{pyz})$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}$), one is with $S = 3/2$ and another is with $S = 1$. The magnetic properties of $\text{CoF}_2(\text{H}_2\text{O})_2(\text{pyz})$ are measured and discussed.

EXPERIMENTAL SECTION

Caution

Hydrofluoric acid (HF) is toxic and corrosive! It must be handled with extreme caution and appropriate protective gear [23–25].

Synthesis

Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, aladdin), nickel oxide (NiO , 99%, aladdin), zinc oxide (ZnO , 99%, aladdin), pyrazine ($\text{C}_4\text{H}_4\text{N}_2$, 98%, aladdin), and aqueous HF (>40.0% HF by weight, aladdin) were used as received. All reagents were sealed with a sealer in Teflon pouches made as described previously, which has been widely used in Poeppelmeier's group [26–30]. And then the Teflon pouches were placed into a 120 mL autoclave (Fuzhou Fuleisi co.) with a backfill of 40 mL distilled water. The autoclave was quickly heated to 200°C, held at this temperature for 24 h and cooled to ambient temperature for 30 h.

$\text{CoF}_2(\text{H}_2\text{O})_2(\text{pyz})$ 1. Single crystals of $\text{CoF}_2(\text{H}_2\text{O})_2(\text{pyz})$ 1 were synthesized as described above with 0.300 g (1.03 mmol) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.400 g (5 mmol) of pyrazine, 0.8 mL (~22.08 mmol) of 40% aqueous HF. A small amount of orange single crystals were recovered in air after vacuum filtration for single crystal X-ray diffraction (XRD) and magnetic susceptibility measurement.

$\text{NiF}_2(\text{H}_2\text{O})_2(\text{pyz})$ 2. Green single crystals of $\text{NiF}_2(\text{H}_2\text{O})_2(\text{pyz})$ 2 were synthesized as described above with 0.200 g (2.68 mmol) of NiO , 0.400 g (5 mmol) of pyrazine, 0.8 mL (~22.08 mmol) of 40% aqueous HF. After vacuum filtration in air, very tiny green single crystals selected from black powder were only suitable for single crystal XRD.

$\text{ZnF}_2(\text{H}_2\text{O})_2(\text{pyz})$ 3. Colorless single crystals of $\text{ZnF}_2(\text{H}_2\text{O})_2(\text{pyz})$ 3 were synthesized as described above with 0.200 g (2.46 mmol) of ZnO , 0.400 g (5 mmol) of pyrazine, 0.8 mL (~22.08 mmol) of 40% aqueous HF. Very

tiny colorless single crystals were recovered in air after vacuum filtration for single crystal XRD.

Crystallographic determination

Single crystal XRD experiments were conducted on a Rigaku X-ray diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 123 K for 1, and 296 K for 2 and 3. The structures were determined by direct methods, completed by Fourier difference syntheses with SIR97 [31], and refined using SHELXL-2018 [32]. Additional symmetry elements were checked using the program PLATON [33]. Crystallographic data are reported in Table 1.

Magnetometer

A Quantum Design superconducting quantum interference device (SQUID) magnetometer was used to collect direct-current (DC) magnetic susceptibility data for 1 at 0.1 T in the range of 2–350 and 1.85–20 K. A small amount of single crystals were ground into fine powder and loaded into Al foil then inserted into a straw to connect magnetic property measurement system (MPMS) stick for magnetic measurements.

RESULTS

Crystal structures

Compounds $\text{MF}_2(\text{H}_2\text{O})_2(\text{pyz})$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$) 1–3 all crystallize in the space group $C2/m$ of the monoclinic system. The crystallographic data of 1–3 is summarized in Table 1. Since three compounds 1–3 are isostructural, only the structure of $\text{CoF}_2(\text{H}_2\text{O})_2(\text{pyz})$ 1 was discussed in detail. The unit cell parameters of 1 are $a = 7.047(6) \text{ \AA}$, $b = 7.738(6) \text{ \AA}$, $c = 7.149(6) \text{ \AA}$, $\beta = 111.21(2)^\circ$, and $Z = 2$. In its asymmetric unit, there are one unique Co atom, one unique F atom, one unique N atom, two unique C atoms and one unique O atom of water molecule. As shown in Fig. 1a, the Co-centered octahedra are bridged with each other through one pyrazine molecule to form the 1D linear chains along the c axis with intrachain Co...Co separation of $7.149(6) \text{ \AA}$. The uniform Co–pyz–Co linear chains are linked with each other by hydrogen bonds through $\text{O} \cdots \text{H}^+ \cdots \text{F}$ in the ab plane to stabilize the 3D frameworks (Fig. 1b). The hydrogen bond distance of $\text{H}^+ \cdots \text{F}$ is $1.91 \text{ \AA}$ and the $\text{F} \cdots \text{H}^+ \cdots \text{O}$ bond angle is 143.1° . The shortest interchain Co...Co distance is $5.233(3) \text{ \AA}$ in the ab plane. Within the chains, the pyrazine molecules for bridging the Co-centered octahedra are disordered with the two aromatic plane angle of 83.4° which are all independently determined in the crystal structures of 1–3 by single crystal XRD. As shown in Fig. 1c, for the

Table 1 Crystal data, structure solutions and refinements for 1–3

Compounds	1	2	3
λ (K $_{\alpha}$) (Å)	0.71073	0.71073	0.71073
Formula	CoF ₂ (H ₂ O) ₂ C ₄ H ₄ N ₂	NiF ₂ (H ₂ O) ₂ C ₄ H ₄ N ₂	ZnF ₂ (H ₂ O) ₂ C ₄ H ₄ N ₂
Weight (g mol ⁻¹)	213.05	212.81	219.51
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>C2/m</i>	<i>C2/m</i>
<i>a</i> (Å)	7.047(6)	7.021(2)	7.041(2)
<i>b</i> (Å)	7.738(6)	7.778(2)	7.813(2)
<i>c</i> (Å)	7.149(6)	7.044(2)	7.257(2)
β (°)	111.21(2)	109.79(3)	110.66(3)
<i>V</i> (Å ³)	363.4(5)	361.9(1)	373.6(2)
<i>Z</i>	2	2	2
<i>T</i> (K)	123	296	296
Maximum θ (°)	27.5	27.5	27.3
ρ_{calc} (g cm ⁻³)	1.947	1.953	1.952
R_1^a	0.065	0.060	0.020
wR_2^a	0.179	0.145	0.058
Goodness-of-fit (χ^2)	1.06	1.17	1.10

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| \text{ and } wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2} \text{ for } F_o^2 > 2\sigma(F_o^2).$$

Figure 1 Crystal structure of **1**. (a) View along the *c* axis for the Co-pyz-Co chains; (b) view along the *ab* plane for interchain networks through hydrogen bonding; (c) view for the CoF₂O₂N₂ octahedron.

CoF₂O₂N₂ octahedra, it is distorted with distortion of $\delta = 9.2\%$ [$\delta = (d_{\text{max}} - d_{\text{min}})/d_{\text{min}}$] and elongated along the N-Co-N axis. Each CoF₂O₂N₂ octahedra is composed of two equatorial Co-F bonds with bond length Co-F_{terminal} = 1.987(5) Å, two equatorial Co-O bonds with bond length Co-O_{terminal} = 2.081(5) Å and two apical Co-N bonds with bond length Co-N_{trans} = 2.170(6) Å. Their bond lengths are in agreement with those reported in other Co-based compounds [34,35]. The oxidation state of +2 in cobalt, nickel and zinc are confirmed by bond valence sum (BVS) calculations using values reported by Brese

and O'Keefe (Table 2) [36]. Other bond lengths for 1–3 are summarized in Table 2.

Magnetic properties

The temperature dependence of magnetization of **1** was firstly measured within 2–350 K, as shown in Fig. 2a. The curve of magnetic susceptibility χ increasing with the decrease of temperature is similar with conventional paramagnetic behavior. Then it seems to appear decreasing at low temperature, which may suggest a long range magnetic order (LRO). To confirm this peak

Table 2 Selected bond lengths, and BVS calculations for **1**–**3**

Bond	Bond Length (Å)	S_{ij}
1		
Co–F	2×1.987 (5)	2×0.391
Co–O	2×2.081 (5)	2×0.350
Co–N	2×2.170 (6)	2×0.409
		$\Sigma S_{ij} = 2.30$
2		
Ni–F	2×1.987 (5)	2×0.350
Ni–O	2×2.051 (5)	2×0.342
Ni–N	2×2.125 (6)	2×0.363
		$\Sigma S_{ij} = 2.11$
3		
Zn–F	2×1.989 (2)	2×0.368
Zn–O	2×2.095 (2)	2×0.347
Zn–N	2×2.237 (3)	2×0.283
		$\Sigma S_{ij} = 1.996$

Figure 2 Temperature dependence of (a) χ between 2 and 350 K; (b) χ between 1.8 and 20 K; (c) χ^{-1} (blue) and (d) χT (green) for **1** measured at 0.1 T.

anomaly, more magnetic susceptibility data points were then collected between 1.8 and 20 K. As shown in Fig. 2b, the peak around 2.9 K suggesting a LRO was clearly observed. A Curie-Weiss fitting in a high temperature range (100–350 K) (Fig. 2c) was applied, yielding the effective magnetic moment of $P_{\text{eff}} = 5.66(1) \mu_{\text{B}}$ and the Weiss temperature of $\theta = -20.6(1)$ K. The negative Weiss constant indicates that the dominant magnetic interaction in **1** is AFM, which is also moderately-strong for $S = 3/2$. The larger P_{eff} suggests unquenched orbital contribution,

which have been usually observed in other reported Co^{2+} compounds [34,37–39]. Compared with the theoretical value of $5.40 \mu_{\text{B}}$ for spin and orbital angular momenta, the high anisotropy ($g > 2$) may be proposed in the 1D chain structure of **1** based on the large value of P_{eff} . In Fig. 2d, the susceptibility temperature product χT value was $3.77 \text{ emu K mol}^{-1}$ at 350 K which is larger than the spin-only value owing to the aforementioned large orbital contribution. It slowly decreased to $3.32 \text{ emu K mol}^{-1}$ around 100 K, then rapidly decreased toward zero upon further cooling owing to enhanced AFM correlations between Co^{2+} sites, which further confirmed the dominant antiferromagnetic interactions in **1** as mentioned above.

DISCUSSION

The energy levels (^4F) of a single Co^{2+} ion with $3d^7$ electronic configuration are split into three terms in an ideal octahedra environment (O_{h}) with the ground state of triplet state $^4\text{T}_{1\text{g}}$. Due to the triplet nature of the ground state $^4\text{T}_{1\text{g}}$, unquenched orbital contribution is exhibited [35]. Thus, larger effective magnetic moments are usually observed experimentally in the compounds with Co^{2+} in high spin state [34,37–39]. Consistently, the effective magnetic moment P_{eff} in **1** in this work is produced as $5.66 \mu_{\text{B}}$ from the magnetic susceptibility data in the high temperature region, which is reasonably expected to be larger than the spin only value of $3.87 \mu_{\text{B}}$ for free high spin state of Co^{2+} . Meanwhile, the strong magnetic anisotropy could be induced by this orbital contribution to the effective magnetic moment together with the presence of the ligand field [34]. Moreover, the slightly larger distortion of $\text{CoF}_2\text{N}_2\text{O}_2$ octahedra which may further lift the ground state of $^4\text{T}_{1\text{g}}$ and one dimensionality in **1** could also lead to the larger anisotropy. These could be another reason for the slightly larger effective magnetic moment P_{eff} than those in other reported Co^{2+} compounds.

Now let's discuss the low temperature magnetic behavior. In **1**, the intrachain interaction J in the linear chain along the c axis is through Co-pyz-Co with the shortest intrachain $\text{Co}\cdots\text{Co}$ distance of $7.149(6)$ Å (Fig. 1a). Because the antiferromagnetic interaction should be strongest when the path is linear [19,40], this intrachain interaction J should be antiferromagnetic and strong. While the interchain interaction J' along the ab plane is through $\text{Co-(F}\cdots\text{H-O)}_2\text{-Co}$ with the shortest interchain $\text{Co}\cdots\text{Co}$ distance of $5.233(3)$ Å (Fig. 1b). Compared with the magnetic interaction through ligand covalently-bonded to the magnetic ion, the magnetic interaction through

hydrogen bonding with more atoms should be weaker, in particular the Co-(F...H-O)₂-Co bridge in **1** is in the more orthogonality way. Given to the abovementioned reason, **1** should exhibit as a 1D chain model in which the Co-pyz-Co chains along the *c* axis are separated by hydrogen bonding in the *ab* plane. The 1D nature would enhance the quantum fluctuations and prevent the conventional 3D long range magnetic order. This is confirmed by the experimental data. Based on the magnetic susceptibility results, no LRO is observed until 2.9 K in **1**. If we calculate the ratio of $|T_N/\theta|$, the value of 0.14 is pretty small, which could further confirm the good 1D magnetism in **1**.

To further investigate the origin of magnetic properties of **1** with $S = 3/2$, it is necessary to perform more experiments such as heat capacity at various magnetic field and electron spin resonance (ESR) experiments at low and high magnetic fields, which are in progress in Wuhan National High Magnetic Field Center.

CONCLUSION

Three new 1D hybrid fluorides MF₂(H₂O)₂(pyz) (M = Co²⁺, Cu²⁺, Zn²⁺) have been hydrothermally synthesized and structurally characterized. The magnetic susceptibility results of CoF₂(H₂O)₂(pyz) suggest, owing to strong 1D quantum fluctuations, no conventional 3D long range antiferromagnetic order was observed until 2.9 K, indicating good 1D magnetism in nature in CoF₂(H₂O)₂(pyz). This work provides more experimental models of 1D AFM chains with different spin values of $S = 3/2$ and $S = 1$ for further study about quantum magnetism.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information CIF files for compounds 1–3 $\text{MF}_2(\text{H}_2\text{O})_2(\text{pyz})$ ($\text{M} = \text{Co}, \text{Ni}, \text{Zn}$) (CCDC 1046149–104651) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Yanhong Wang was born in Hunan, China. She received her Master's degree in chemical engineering and technology from Hunan Institute of Technology in China (2019). Her current research focuses on exploration and characterization of low dimensional quantum magnetic materials.

Hongcheng Lu received his Bachelor's (2008), Master's, and PhD degrees (2014) in materials science at Northwestern Polytechnical University in China. He did his PhD research work under supervision of Professor Kenneth Poeppelmeier at Northwestern University in USA (2010–2014). Then he worked as a postdoctoral fellow with Professor Hiroshi Kageyama at Kyoto University in Japan (2014–2016), with Professor Tyrel McQueen at Johns Hopkins University (2016–2017) and with Professor Sara Haravifard at Duke University (2017–2018) in USA. From 2019, he has been working as a full professor at Huazhong University of Science and Technology. His research interest is focused on the design, synthesis, crystal growth, and characterization of novel inorganic or hybrid functional crystal materials.

一种新型准一维反铁磁体 $\text{CoF}_2(\text{H}_2\text{O})_2(\text{pyrazine})$ 的制备与表征

王艳红, 刘航, 符鹏, 卢红成*

摘要 本文通过水热法成功合成出了一种新型一维反铁磁性的过渡金属杂化氟化物 $\text{CoF}_2(\text{H}_2\text{O})_2(\text{pyz})$ ($\text{pyz} = \text{吡嗪}$)及其两种新同构体 $\text{MF}_2(\text{H}_2\text{O})_2(\text{pyz})$ ($\text{M} = \text{Ni}^{2+}, \text{Zn}^{2+}$)。通过单晶X射线衍射方法解析出它们的晶体结构都属于相同的空间群 $C2/m$ 。并且对化合物1 $\text{CoF}_2(\text{H}_2\text{O})_2(\text{pyz})$ 的磁性进行了测试和讨论。Weiss常数为 -20.6 K , 表明化合物1中主要存在显著的反铁磁性交换作用。同时, 大约为 $5.66 \mu_B$ 的有效磁矩说明化合物1中有较大未遏制的轨道磁矩贡献和各向异性。由于强量子涨落的阻止作用, 当温度低于 2.9 K 时, 准一维反铁磁体1才呈现出长程磁有序, 这表明其具有良好的二维磁性。