Synthesis, Crystal Structures, Magnetic Properties, and Lattice Dynamics of $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$ with $X = \text{Cl}, \text{Br}$

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ABSTRACT: We have synthesized $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$ with $X = \text{Cl}, \text{Br}$ by hydrothermal methods. The isotypic structures ($Pnma$, $Z = 4$, $a \approx 15.1 \text{ \AA}$, $b \approx 6.1 \text{ \AA}$, $c \approx 9.6 \text{ \AA}$) contain distorted hexagonal layers of Ba and X in a BN-type arrangement. Each halide is further coordinated by one out-of plane Ba atom in an alternate up-down fashion resulting in an overall ${}^2_\infty[\text{Ba}_2\text{X}]^{3+}$ structural feature. The planar Ba-X hexagonal rings are centered by divanadate groups in an eclipsed orientation. Edge-sharing chains of ${}^1_\infty[\text{CuO}_{2/2}(\text{OH})_{2/2}\text{O}_{2/1}]^{5-}$ complement the structure. The magnetic properties are associated with the magnetic Cu^{2+} ions and can be described as an antiferromagnetic quasi 1D $S = 1/2$ Heisenberg system. Confirmation is obtained from both magnetic and specific heat measurements. Furthermore, lattice dynamics are studied by DFT methods, IR, and Raman spectroscopy.

Keywords: crystal structure; multi-anionic compounds; vanadates; magnetic properties; one-dimensional $S=1/2$ Heisenberg system; lattice dynamics

INTRODUCTION

In recent years classical solid state synthesis methods employing reactive molten alkali and alkaline-earth metal halide salts at high temperatures have been reported.¹⁻⁹ Thereby, intriguing insights into the structural richness of the fascinating class of salt-inclusion type of compounds has been gained. These explorative studies indicate that extended halide/oxide lattices present opportunities to control the dimensionality of structural features. Controlling the interaction between the two chemically dissimilar lattices (halides and oxides) give rise to material design that await further exploitation for studies of structure-property relationships. For example, mesoporous solids,⁶ transition metal clusters,¹ anion exchange materials,^{8,9} noncentrosymmetric crystal structures and polar frameworks^{3,7,10-12} have been found. Interesting magnetic and luminescence properties add to the fascinating aspects that make this class of compounds exceptional for explorative research. So far, mainly phosphates,^{9-11,13,14} arsenates,^{3,4,18} silicates^{5,15-17}, and vanadates^{1,2,6,7,18-23} have been reported.

As an example, crystal structures of the chlorovanadate family have been reported. These exhibit low-dimensional cationic structural features, e.g. chains: ${}^1_\infty[\text{BaCl}]^+$ in $\text{BaVO}_3\text{Cl}^{23}$ or layers: ${}^2_\infty[\text{BaCl}]^+$ in $\text{KBa}_2\text{Cl}[\text{V}_2\text{O}_7]^{19}$ and $\text{Ba}_2\text{Cl}_2[\text{V}_2\text{O}_7]^{20}$. It is interesting to note, that the ${}^2_\infty[\text{BaCl}]^+$ layer is similar to the covalent boron nitride type of structure with the pseudo-hexagonal windows occupied by $[\text{V}_2\text{O}_7]^{4-}$.

Once magnetic transition metal cations are imbedded into the structures of the chlorovanadates one may distinguish three cases (i-iii). (i) In $\text{Cs}_2\text{FeV}_5\text{O}_{13}\text{Cl}_6$ complex entities of $[\text{FeCl}_6]^{3-}$ are present.² (ii) In $\text{KBaCu}[\text{V}_2\text{O}_7]\text{Cl}^{21}$ ($\text{CsCl})_2\text{Cu}(\text{VO}_3)_2$ and $(\text{CsCl})\text{Mn}_2[\text{V}_2\text{O}_7]_7[\text{MO}_4\text{Cl}_2]$ units with $M = \text{Mn}$ or Cu exist. Here, the halide and oxide parts of the

structures are interconnected via the (covalent) complex entity containing the magnetic ion. It can be directly seen that by reducing the halide salt content eventually pure oxide connectivity results, case (iii). For example, $[\text{CuO}_4]$ as has been reported to be present in $[\text{BaCl}][\text{CuPO}_4]^{13}$. In conclusion, the halide part of the structure may effectively reduce the dimensionality of the transition metal connectivity and alter the respective bonding for each complex entity.

Here, we present two multianionic compounds, $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$, containing $X = \text{Cl}^-$ or Br^- , $[\text{V}_2\text{O}_7]^{4-}$ and OH^- . These novel isotypic compounds were synthesized by hydrothermal synthesis. The magnetic transition metal, Cu^{2+} is coordinated exclusively by hydroxide ions and divanadate groups and not linked to halide ions. Such a complex structure is unexpected and intriguing and will be discussed in terms of structure-property relationships.

EXPERIMENTAL SECTION

Synthesis. Single crystals of $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ were synthesized by hydrothermal methods using 1.0 mmol of NH_4VO_3 , 1.5 mmol of CuCl_2 , 1.0 mmol of $\text{Ba}(\text{Ac})_2$, and 5.0 mmol of LiCl as starting materials. Instead of mixing all of the starting materials directly, we first dissolve the NH_4VO_3 in concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$ while gently heating ($\sim 60^\circ \text{C}$) and stirring. The other starting materials were easily dissolved in distilled water. All solutions were then mixed together in Teflon-lined stainless steel autoclaves. Drops of concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$ were used to adjust the pH of the solution to 8-10. The total volume was 20 ml and 26 ml Teflon-lined Parr containers were used. Typical reactions were carried out at 220°C for 3-4 days and subsequent cooling to 120°C at a rate of 6°C per hour. Crystals of $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ are synthesized by replacing the CuCl_2 and LiCl by the respective bromide.

The dark green-brown precipitate was collected, washed with distilled water several times, and then dried naturally in the

hood overnight. The main product of the crystals were needle shaped in the case of $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ (Fig. 1) and of varying morphology for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ (Fig. 2). Typical yields were $\approx 25(5)\%$ and $\approx 55(5)\%$ for $X \approx \text{Cl}$ and Br , respectively. The pH value has been shown to affect the growth of the crystals, as previously reported for hydrothermal synthesis routes, e.g. for Cu_2O and $\text{NH}_4\text{V}_3\text{O}_8$.^{24,25} We conducted a series of reactions under different pH values for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$. As the pH increases from 7.8 to 9.8, the crystal shape changes from needle, to rectangular, square and hexagonal (Fig. 2).

Chemical Analysis. Coating of the sample with a thin film of carbon (approximately 250 Å thicknesses) was performed in vacuum at 9.5×10^{-5} torr using a Ladd Research Industries carbon evaporator. SEM data were recorded on a Jeol JSM 8330 F scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS) using a silicon drift X-ray detector (SDD) by means of 15 kV accelerating voltage and 12 μA emission current from a cold-field emission gun. The acquisition time was 100 seconds/spot. The composition ratios Ba/X/Cu/V of 2 : 1 : 1 : 2 are confirmed with an average observed atomic-% of 38(1) Ba; 21(2) Cl; 18(2) Cu; 33(1) V from 11 measured spots for $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ and 35(2) Ba; 19(4) Br; 13(2) Cu; 32(3) V from 14 measured spots for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$, respectively. BaX_2 with $X = \text{Cl}, \text{Br}, \text{Cu}$ and V metal were used as standards.

Figure 1. (a) Photos of magnified $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ crystals. (b) Morphology of $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ crystals. (c) SEM picture of carbon-coated samples of $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ crystals. (d) Image of reflections for $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ showing three domains circled by different colors. The main domain is Domain 1 (blue). Matrices representing the orientations of the other two domains as related to Domain 1. Domain 2 (green) is clockwise rotated by 64.46° and Domain 3 (red) is counterclockwise rotated by 64.64° with respect to the a axis.

Structure Determination. Single crystal data sets of $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$ ($X = \text{Cl}, \text{Br}$) were collected on a Rigaku Rapid II instrument (Mo K α radiation with $\lambda = 0.71075 \text{ \AA}$) at room temperature. The program CrystalClear-SM Expert 2.0 r15 (Rigaku, 2011) was used to determine the unit cell parameters, absorption correction, and data reductions.²⁶ The structures were solved by direct methods and refined by

Difference-Fourier Synthesis (program system SHELX-2014),²⁷ implemented in the WinGX platform.²⁸ Crystallographic data for $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$ ($X = \text{Cl}, \text{Br}$) is included in Table 1 and atomic positions are listed in the supporting material.

The TwinSolve software integrated in *CrystalClear-SM* Expert 2.0 [ref. 26] was utilized to distinguish different domains indexed with the same unit cell. In Fig. 1, Domain 1 (blue) is the major component. Reflections circled by green and red are close to the reflections belonging to Domain 1, which indicates a twinning problem. The orientation of the additional two domains can be expressed as a function of Domain 1, with a rotation of approximately 64.5° with respect to the a axis, either clockwise or counterclockwise.

An Olympus BX 41-P polarizing microscope equipped with an Olympus DP12 microscope digital camera system was used to help selecting suitable single crystals of $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$, see Fig. 2. Crystals with a regular shape and single color were selected for single X-ray diffraction measurements. Domains are present for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ crystals (polarization microscope pictures) as well but splitting of reflections could not be resolved. Thus, we assume possible pseudo-merohedral twinning²⁹ as the origin here. Continuous streaks were found in between unique reflections for the crystal structure of $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ indicating the stacking faults. Moreover, all the streaks are along the a axis (Fig. 2).

Figure 2.(a-d) Photos of magnified $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ crystals showing the morphologies of crystals grown at different initial pH values: pH = 7.8 (a), 8.5 (b), 9.1 (c), 9.8 (d). (e) SEM picture of carbon-coated samples of $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ crystals. (f) Photos of $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ crystals under polarized light. (g) Image of reflections for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ showing streaks between unique reflections. (h) Indexed reflections showing the orientation of the streaks.

We solved the crystal structure using $P\bar{1}$ and applied the program system Platon³⁹ for finding the highest possible space group symmetry (space group $Pnma$). Systematic absence violations were found for both crystal data sets and can be eliminated by applying the same twin law as derived from the $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ data. The data for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ crystals of hexagonal platelet shapes gave smaller relative batch scale factors (BASF) for each component compared with $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$, BASF = 0.01808, 0.01455, 0.01396 and 0.01364, 0.00515, 0.00875 for X = Cl and Br, respectively. The first two values of each series relate to the two domains and the third to an inverted stacking order of the main domain.

Table 1. Crystallographic data for $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$, X = Cl, Br.

Powder Data		
Formula	$\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$	$\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$
Unit Cell (Å)	$a = 15.0889(2)$ $b = 6.0710(1)$ $c = 9.6076(1)$	$a = 15.1942(3)$ $b = 6.1182(1)$ $c = 9.6616(1)$
Volume (Å ³)	880.10(2)	898.15(2)
χ^2	4.63	6.11
R_{Bragg}	1.226	1.109
RF-factor	0.6767	0.7520
Single Crystal Data		
Formula	$\text{Ba}_2\text{ClCuV}_2\text{O}_8$	$\text{Ba}_2\text{BrCuV}_2\text{O}_8$
Molar Mass (g/mol)	603.55	648.01
Space group	orthorhombic, $Pnma$, $Z = 4$	
Lattice constants (Å)	$a = 15.1085(2)$ $b = 6.0802(1)$ $c = 9.6152(2)$	$a = 15.193(1)$ $b = 6.110(1)$ $c = 9.6658(1)$
Volume (Å ³)	883.28(2)	897.43(6)
Density (g/cm ³)	4.539	4.796
F(000)	1072	1144
Temperature (K)	293	293
Crystal size (mm)	0.10 × 0.05 × 0.04	0.16 × 0.10 × 0.04
Θ -Range (min – max)	2.5° – 30.0°	3.3° – 35.0°

Data range	-21 < h < 21 -8 < k < 8 -13 < l < 13	-24 < h < 23 -9 < k < 9 -15 < l < 15
R_{int}	0.036	0.031
Measured/Unique reflections	17443/1143	14620/2286
Parameter refined	68	78
R_1, wR_2, Goof	0.135, 0.310, 1.31	0.109, 0.258, 1.29
μ (Mo K α) (mm ⁻¹)	13.50	17.45
BASF [#]	0.01808, 0.01455, 0.01396	0.01364, 0.00515, 0.00875

[#] Refined as a 4-component inversion twin

A PANalytical X'Pert Pro Diffractometer (Cu radiation, $\lambda \text{K}\alpha_1 = 1.540562 \text{ \AA}$ and $\lambda \text{K}\alpha_2 = 1.544389 \text{ \AA}$) was used to collect diffraction patterns to confirm the phase purity and the structure model of the compounds. All samples were ground into fine powders and placed on a PW1817/32 zero background silicon crystal sample holder. All lattice constants were refined by profile-matching (LeBail fit) methods using the program Fullprof.³¹ Powder refinement data for $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$ (X = Cl, Br) are shown in Fig. 3.

Figure 3. Powder refinement data for $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ (top) and $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ (bottom). Observed (black), calculated (red), Bragg positions (green) and difference (blue).

Property Measurements. The title compounds have been studied by spectroscopic methods. Infrared spectra (IR) were collected in an argon filled glove box on an Alpha-P Infrared Spectrometer (Bruker) in reflectance mode. Raman spectra were recorded in the back-scattering geometry on a single crystal using a Horiba Jobin Yvon T 6400 Spectrometer with an optical microscope, a liquid nitrogen cooled CCD detector and a laser excitation of $\lambda = 633 \text{ nm}$. The experimental resolution did not exceed 1.5 cm^{-1} .

Magnetic and specific heat measurements were carried out on a Physical Property Measurement System (PPMS, Quantum Design) from 2 – 300 K in applied fields up to 8 T. Susceptibility data were obtained in field-cooled (fc) and zero-field-cooled (zfc) mode and corrected for diamagnetic contributions.

Calculations. First principle calculations of the electronic ground state of the $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ compound were performed within the generalized gradient approximation using Perdew-Burke-Ernzerhof local functional,³² as implemented in the CASTEP code.³³ Norm-conserving pseudopotentials were used. Prior to performing lattice dynamics calculations the structure was relaxed for experimentally determined lattice parameters, so that forces on atoms in the equilibrium position did not exceed 3 meV/Å. The integration within the Brillouin zone was performed over $1 \times 2 \times 1$ Monkhorst-Pack grid³⁴ in the reciprocal space. Fixed electron occupancy constraints were imposed on the self-consistent field energy minimization as a prerequisite for using the variational density functional perturbation theory (linear response scheme) in the phonon calculations.³⁵

RESULTS

Crystal Structure. Table 1 lists the crystallographic data. The atomic coordinates are included in the supporting material. Fig. 4 shows the unit cell of the structure of $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$ with $X = \text{Cl}$ or Br ; containing multi-anions: hydroxide, vanadate, and halide. Ba/halide layers are stacked along the a axis. Overall, the crystal structure can be divided into three features: $\frac{2}{3}[\text{Ba}_2\text{X}]^{3+}$ layers, $[\text{V}_2\text{O}_7]^{4-}$ dimers and $\frac{1}{2}[\text{CuO}_{2/2}(\text{OH})_{2/2}\text{O}_{2/1}]^{5-}$ chains.

The main symmetry of the $\text{Ba}_2\text{XCu}[\text{V}_2\text{O}_7](\text{OH})$ type of structures is given by the arrangement of the pseudo-hexagonal $\frac{2}{3}[\text{Ba}_2\text{X}]^{3+}$ layers. (Fig. 5) Three Ba^{2+} and three X^- ions form a slightly distorted hexagon with interior angles quite close to 120° (117° , 117° , 126°). (Table 2) Infinite layers with an alternating Ba_2/X arrangement (BN-structure type analogy) are stacked along the a axis. Each X^- is connected to an extra out-of plane Ba^{2+} ion (Ba1). Each hexagon is centered by a $[\text{V}_2\text{O}_7]^{4-}$ dimer. As shown in Fig. 5, the $\frac{2}{3}[\text{Ba}_2\text{X}]^{3+}$ layer is weakly coupled to the $[\text{V}_2\text{O}_7]^{4-}$ dimer. Thus, there is no restriction for the rotation of $\frac{2}{3}[\text{Ba}_2\text{X}]^{3+}$ and $[\text{V}_2\text{O}_7]^{4-}$, respectively. This might explain the random orientation of layers as the origin of default stacking, see domain structure refinement and twinning.

Figure 4. The unit cell of $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$ with $X = \text{Cl}$ or Br .

The orientation of the eclipsed $[\text{V}_2\text{O}_7]^{4-}$ group with respect to the Ba-X layer is shown in Fig. 5. Divanadate groups connected to Cu^{2+} via O2 and O5 in a bridging fashion. The C.N. for Cu^{2+} is complemented by two bridging O6(OH). Cu^{2+} is found in a distorted octahedral environment. Within a plaquette, four Cu-O (Cu-O2 and Cu-O6) distances are similar, while the Cu-O5 distances perpendicular to the plaquette are much longer and typical for elongated CuO_6 units of approximately D_{4h} symmetry. Cu-O distances and bridging Cu-O-Cu angles are listed in Table 2. Adjacent Cu ions are connected via edge-sharing and form trans $\frac{1}{2}[\text{CuO}_{2/2}(\text{OH})_{2/2}\text{O}_{2/1}]^{5-}$ chains (Fig. 6).

Table 2. Selected distances (Å) and angles (in deg) for $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$, $X = \text{Cl}, \text{Br}$.

$\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$	$X = \text{Cl}$	$X = \text{Br}$
Ba1-X	3.186(8)	3.268(2)
Ba2-X (2×)	3.409(4)	3.415(1)
Ba2-X	3.266(8)	3.308(2)
Ba2-X-Ba2 (2×)	116.9(1)	116.51(3)
Ba2-X-Ba2	126.2(2)	126.97(7)
Cu-O6(OH) (2×)	1.99(2)	1.989(9)
Cu-O2 (2×)	2.09(2)	2.056(9)
Cu-O5 (2×)	2.29(2)	2.35(1)
Cu-O6(OH)-Cu	99(1)	100.4(6)
Cu-O5-Cu	83.1(8)	81.1(4)
V1-(O1) ^t	1.64(3)	1.67(1)
V1-(O2) ^t (2×)	1.70(2)	1.710(9)
V2-(O5) ^t	1.70(3)	1.68(2)
V2-(O3) ^t (2×)	1.69(2)	1.68(1)
V1-(O4) ^b	1.76(3)	1.78(1)
V2-(O4) ^b	1.83(2)	1.82(1)
V1-(O4) ^b -V2	161(2)	162(1)

t = terminal, b = bridging

Figure 5. (Top) Projection of the intergrown ${}^2[\text{Ba}_2\text{X}]^{3+}$ layer with the incorporated $[\text{V}_2\text{O}_7]^{4-}$ unit in the center of a pseudo-BN-type of arrangement in $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$, $\text{X} = \text{Cl}, \text{Br}$. (Bottom) Perspective view of $[\text{V}_2\text{O}_7]^{4-}$ in the center of a distorted hexagon within a ${}^2[\text{Ba}_2\text{X}]^{3+}$ layer indicating the freedom of rotation between the $[\text{V}_2\text{O}_7]^{4-}$ dimer and the ${}^2[\text{Ba}_2\text{X}]^{3+}$ layer.

Figure 6. Perspective view of the ${}^1[\text{CuO}_{2/2}(\text{OH})_{2/2}\text{O}_{2/1}]^{5-}$ feature in $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$, $\text{X} = \text{Cl}, \text{Br}$.

In summary, the structure features ${}^2[\text{Ba}_2\text{X}]^{3+}$ layers containing $[\text{V}_2\text{O}_7]^{4-}$ dimers. These link exclusively via terminal O-atoms to ${}^1[\text{CuO}_{2/2}(\text{OH})_{2/2}\text{O}_{2/1}]^{5-}$ chains. Note that the Cu-chains and the out of plane Ba-atoms (Ba1) are oriented parallel to $[010]$ and alternate within the bc -plane. Thus, each twinning domain by rotation (see above) creates a domain boundary, where mainly O6 and Ba1 are exchanged. This might offer an explanation of observed residue electron density due to mismatch of size and displacement on this site.

IR and RA Spectroscopy. Infrared and Raman spectroscopy were used to study the lattice dynamics of $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$. Since there are 56 atoms excluding H atoms (positions not refined by x-ray diffraction data) within one unit cell, the total number of normal modes equals

$56 \times 3 = 168$. Expected IR and Raman active modes are: $\Gamma_{\text{total}} = 24A_g(\text{R}) + 18A_u(\text{inactive}) + 15B_{1g}(\text{R}) + 27B_{1u}(\text{IR}) + 24B_{2g}(\text{R}) + 18B_{2u}(\text{IR}) + 15B_{3g}(\text{R}) + 27B_{3u}(\text{IR})$. The Density Functional Theory (DFT) method is used to calculate the frequencies for all the modes. The supplement material contains the tabulated assignment of experimental and calculated modes for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ and a comparison with $[\text{V}_2\text{O}_7]^{4-}$ in an aqueous solution.³⁶

Comparing the two compounds of $\text{X} = \text{Cl}$ and Br , almost the same mid-infrared (MIR) spectra are observed, see Fig. 7. The modes at 3387 cm^{-1} and 3420 cm^{-1} can be assigned as the O-H stretching modes. For comparison, in natural minerals, e.g. $\text{Cu}_2(\text{OH})_3\text{Cl}$, similar OH^- stretching mode frequencies of hydroxide bonded to Cu^{2+} ranging from 3315 cm^{-1} to 3450 cm^{-1} have been reported.³⁷ On the other hand, the OH^- stretching modes of a “free” and isolated hydroxide ions are found at $\sim 3550\text{ cm}^{-1}$ as observed for NaOH ^{38,39} and $\text{Na}_5[\text{FeO}_3](\text{OH})$,⁴⁰ respectively.

Figure 7. Experimental MIR-spectra for $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$, $\text{X} = \text{Cl}, \text{Br}$ and calculated displacements.

Assignments for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ are referenced in the range between 700 and 950 cm^{-1} as V–O stretching; around 525 cm^{-1} as Cu–O6 stretching; and below 500 cm^{-1} as V–O deformation modes and lattice modes. Compared with the fundamental vibrational modes for the $[\text{V}_2\text{O}_7]^{4-}$ in aqueous solution,³⁶ assignments for the $[\text{V}_2\text{O}_7]^{4-}$ in our compounds are much more complicated, but in good agreement with the general trend. Experimental and theoretical values match well in energies for V–O modes, $\Delta\nu^{\text{calc.-exp.}} \approx 38(4)\text{ cm}^{-1}$. Prominent blue shifts of $\approx 100\text{ cm}^{-1}$ for the calculated Cu–O6 stretching modes in comparison with the experimental data are observed. This can be explained by the fact that hydrogen has not been considered in the structure model used for the DFT calculation, because we were unable to localize the H-positions from our X-ray data. An “over-charged” Cu cation (formally Cu^{3+}) results and hence increases the frequency of the Cu–O6 stretching modes. Thus, it is conceivable that the H-atom is localized on the O6 atom (assigned OH-group), which then results in Cu^{2+} , see also the magnetic property measurements for confirmation. Cu–O6 displacements are isolated from the divanadate group (Fig. 8). Further details are given in the supporting material.

Figure 8. Displacement patterns of IR modes from DFT calculations for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ related to Cu–O6 displacements: (Top) B_{2u} at 632 cm^{-1} and (Bottom) B_{3u} at 586 cm^{-1} . Cu (cyan), O6 (purple).

The polarized single-crystal Raman data of $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ reveals the expected number of high intensity A_g modes from the DFT calculations, see Fig. 9. In summary, the experimental and theoretical data are in good agreement with an overall small blue shift of $\approx 6\%$ for the V–O stretching modes in the high energy region. This further confirms the accuracy of the structure model derived from the single crystal X-ray diffraction data. It is noteworthy, that we do not find the proposed empirical relation of mode energies of pure V–O^b versus V–O^t vibration dependencies on the bridging angle, V–O^b–V, of the $[\text{V}_2\text{O}_7]^{4-}$ unit.⁴¹ Our lattice dynamic calculations indicate a rather surprising result of mixed V–O^b and V–O^t modes at high energies. Selected Raman displacements as obtained from our theoretical work are presented in Fig. 10.

Figure 9. Polarized single crystal Raman data for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$.

Figure 10. Displacement patterns of Raman modes for $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ from DFT calculations. (Top) A_g at 976 cm^{-1} , (Bottom) B_{2g} at 946 cm^{-1} .

Magnetic Properties. The magnetic properties originate from the presence of $\text{Cu}^{2+}(d^9)$ located within the $^{1}_{\infty}[\text{CuO}_{2/2}(\text{OH})_{2/2}\text{O}_{2/1}]^5$ chain present in the structure. The magnetic active orbital for an elongated $[\text{CuO}_6]$ -entity is the $d_{x^2-y^2}$ orbital, which is indicated by the plaquette depiction in Fig. 6. Based on the Goodenough-Kanamori rules,⁴² the Cu–O6–Cu bridging angle, which is $\approx 100^\circ$, should yield antiferromagnetic (AFM) exchange interactions. Therefore, we will evaluate our data within the quasi one-dimensional $S = 1/2$ Heisenberg AFM model.⁴³

Figure 11. Insets: The normalized field dependent magnetization data measured at 2 K for $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$,

$X = \text{Cl}$ (bullets) or Br (circles) with an overall fit (red) consisting of the paramagnetic defect concentration (green), and the assumed linear behavior in H for an AFM chain compound (blue), see text. *Main panels:* Measured susceptibility in applied fields of 1 T (ZFC) for $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$, $X = \text{Cl}$ or Br . The fit (red) to the experimental data is given by the combination of an AFM $S = 1/2$ chain (blue) and a defect (green) contribution.

The magnetization, $M(H)$, divided by the saturation magnetization, $M_{\text{sat}}(H_{\infty})$, at 2 K for both compounds is shown in Fig. 11. We use the Brillouin function, $B_J(y)$,⁴³ to determine the paramagnetic defect concentration for uncorrelated Cu^{2+} ($S = 1/2$). These mainly originate from chain endmembers, which concentration should be enhanced by domain boundaries due to the twinning discussed above. The magnetization contribution of a Heisenberg 1D-AFM $S = 1/2$ chain is considered to exhibit a linear field dependence (prefactor: a) for $\mu_B H/k_B \ll J_{\text{AFM}}$. A fit of the low temperature magnetization data to eq. 1 for a constant temperature and $J = S$ is shown in Fig. 11 with $g = 2.18$ (Cl) and 2.16 (Br), respectively. We find the defect concentration of the paramagnetic impurity (x) to be 8% and 5% for $X = \text{Cl}$ and Br, respectively.

$$M(H) = (1-x)aH + xNgJ\mu_B B_J(y) \quad (1)$$

For the susceptibility data (Fig. 11) of $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$, we see a significant difference from a Curie or Curie-Weiss type of behavior. For a typical AFM, $\chi(T)$ is expected to show a maximum and a continuous decrease while approaching 0 K. Here, we observe a Curie-tail that can be attributed to defects (see magnetization above), which is a common feature for small spin systems and low-dimensional features, here a 1D-AFM. The defects exhibit a paramagnetic behavior and obey a Curie law with C presenting the Curie constant. Consequently, we account for these paramagnetic impurities by using the respective percentages for the Curie-paramagnetic part of the susceptibility. Hence, the temperature dependent susceptibility, $\chi(T)$, is composed of two components: defects ($x = 8\%$ or 5%) and the remaining $(1-x) = 92\%$ or 95% related to the $S = 1/2$ AFM chain. We have calculated and plotted two contributions separately and give the sum as a fit to the experimental data, Fig. 11 and eq. 2. For the uniform AFM-Heisenberg chain ($\chi^{\text{B.F.}}$) eq. 3, the Bonner-Fisher model^{43,44} is used with the g value as given above and the antiferromagnetic coupling constant, J_{AFM} , with $J_{\text{Cl}} = 87$ K for $X = \text{Cl}$ and $J_{\text{Br}} = 110$ K for $X = \text{Br}$. Taking a closer look where χ reaches T_{max} for the AFM chain model, the theoretical relationship of $T_{\text{max}}/J_{\text{AFM}} = 0.641$ is obeyed. J_{AFM} for $X = \text{Br}$ is larger than that for $X = \text{Cl}$.

$$\chi(T) = (1-x)\chi(T)^{\text{B.F.}} + x\frac{C}{T} \quad (2)$$

$$\chi(T)^{\text{B.F.}} = \frac{Ng^2\mu_B}{k_B T} \cdot \frac{0.25 + 0.07497z + 0.075235z^2}{1.0 + 0.9931z + 0.172135z^2 + 0.757825z^3} \quad (3)$$

with $z = J_{\text{AFM}}/T$

Specific heat measurements were conducted to provide further information on the 1D antiferromagnetic system. The total specific heat, $C_p(T)$ is given in Fig. 12. No anomaly

indicative of magnetic long range order (3D) is observed which provides further support for the realization of a uniform quasi 1D-AFM Heisenberg system.⁴⁵ Considering the Debye model,⁴⁶ which predicts, at very low temperatures, a T^3 -dependency of the phonon contribution to the total specific heat, $C_p(T)$, we plot $C_p(T)/T$ versus T^2 (Fig. 12). Then the phonon contributions become linear in T^2 and pass through the origin at very low temperatures, see eq. 4. The green curve represents the simulated C_{phonon}/T vs. T^2 with the slope obtained from the linear fit of the appropriate range in the experimental data. The magnetic part of the specific heat, $C_m(T) = AT$ at low temperatures, can then be attributed to the offset. This constant value, A , is related to J_{AFM} which can be obtained from the high temperature series expansions for the magnetic specific heat of a $S = 1/2$ antiferromagnetic uniform Heisenberg chain, as reported by Johnston *et al.*⁴⁷ The best fit is achieved for $J_{\text{AFM}} = 87$ K for $X = \text{Cl}$ and $J_{\text{AFM}} = 110$ K for $X = \text{Br}$ which is consistent with our results from the susceptibility measurements. This confirms the $S = 1/2$ Heisenberg quasi 1D-AFM properties of these compounds.

$$C_p(T) = C_m(T) + C_{\text{phonon}}(T) = AT + BT^3 \quad (4)$$

for $T \rightarrow 0$ K

Figure 12. *Top panel:* The total specific heat data measured in zero-field is given. *Bottom panels:* C_p/T versus T^2 for $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$, $X = \text{Cl}$ (black bullets) and Br (black circles) at low temperatures. The fits (red) to the experimental data are composed of the phonon (green) and magnetic (blue) contributions at low temperatures.

The type of oxygen bridging connectivity within the Cu-chains present in the title compounds is rather similar to the reported $S = 1/2$ chain compound AgCuVO_4 .⁴⁸ Since the Cu–O–Cu bridging angle is slightly larger by 13° for AgCuVO_4 , it is conceivable that J_{AFM} is larger thus leading to a more reduced moment at low temperatures. However, interchain coupling gives rise to magnetic long range order at around 10 K in AgCuVO_4 . This is not observed for the title compounds, despite the fact that the magnetic moments should be larger in comparison with AgCuVO_4 . In conclusion, we have successfully suppressed magnetic long-range order for $\text{Ba}_2\text{XCu}(\text{OH})[\text{V}_2\text{O}_7]$, $X = \text{Cl}$ and Br - at least down to 2 K. The effective separation of the magnetic chains through divanadates, weakly coupled Ba-halide layers, as well as multianionic systems seems to be a feasible strategy to gain access to low-dimensional spin-systems.

CONCLUSIONS

Two new compounds with an unprecedented type of structure have been successfully synthesized by application of hydrothermal methods. The high halide content plays a crucial role for the product formation, e.g. acentric $\text{Cu}_2(\text{OH})[\text{VO}_4]$ was obtained in the absence of LiCl at $\text{pH} \approx 9$. However, attempts of replacing Ba^{2+} by K^+ or Cu^{2+} by Mn^{2+} were so far unsuccessful in preparing multi-anionic compounds with $\text{X} = \text{Cl}^-$ or Br^- , OH^- , and vanadate(s). Crystals of the title compounds have been grown with different morphologies in the pH range between 8 and 10 indicating the main crystal growth parameter in these systems. Intriguingly, the two sublattices (halide-oxygen) are only weakly coupled, an aspect that may lead to the future development of extended 2D structures for exfoliation studies. Thereby, artificially stacked hybrid superlattices may be obtained, facilitating the exploration of tailor-made electronic, optical and magnetic materials.

We found evidence of stacking faults for both compounds as well as twinning for needle-shaped $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ and elongated hexagonal plate-shaped $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ crystals. Lattice dynamics were studied to confirm the structure model solved from the single X-ray data. The magnetic Cu^{2+} ions are linked to chains which can be described by theory as a quasi 1D $S = 1/2$ Heisenberg AFM system. Confirmation is obtained from both magnetic and specific heat measurements. Furthermore, increasing the size of the halide ion (here: Cl^- to Br^-) leads to the expansion of cell parameters. This structural difference impacts the magnetic behavior of $\text{Ba}_2\text{ClCu}(\text{OH})[\text{V}_2\text{O}_7]$ and $\text{Ba}_2\text{BrCu}(\text{OH})[\text{V}_2\text{O}_7]$ and finds its manifestation in the increasing value of the coupling parameter J_{AFM} .

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