

# Large Positive Zero-Field Splitting in the Cluster Magnet Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub>

Qiang Chen,<sup>†</sup> Shiyu Fan,<sup>†</sup> Keith M. Taddei,<sup>§</sup> Matthew B. Stone,<sup>§</sup> Alexander I. Kolesnikov,<sup>§</sup> Jinguang Cheng,<sup>||,⊥</sup><sup>®</sup> Janice L. Musfeldt,<sup>†,‡</sup><sup>®</sup> Haidong Zhou,<sup>†</sup> and Adam A. Aczel<sup>\*,†,§</sup><sup>®</sup>

<sup>†</sup>Department of Physics and Astronomy, and <sup>‡</sup>Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

<sup>§</sup>Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

 $^{\perp}$ Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China

Supporting Information

ABSTRACT: We present the synthesis and magnetic characterization of a polycrystalline sample of the 6Hperovskite Ba3CeRu2O9, which consists of Ru dimers based on face-sharing RuO<sub>6</sub> octahedra. Our low-temperature magnetic susceptibility, magnetization, and neutron powder diffraction results reveal a nonmagnetic singlet ground state for the dimers. Inelastic neutron scattering, infrared spectroscopy, and the magnetic susceptibility over a wide temperature range are best explained by a molecular orbital model with a



zero-field splitting parameter D = 85 meV for the  $S_{tot} = 1$  electronic ground-state multiplet. This large value is likely due to strong mixing between this ground-state multiplet and low-lying excited multiplets, arising from a sizable spin molecular orbital coupling combined with an axial distortion of the Ru<sub>2</sub>O<sub>9</sub> units. Although the positive sign for the splitting ensures that Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> is not a single molecule magnet, our work suggests that the search for these interesting materials should be extended beyond Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> to other molecular magnets based on metal-metal bonding.

# INTRODUCTION

Zero-field splitting (ZFS) is a ubiquitous phenomenon leading to anisotropy in magnetic materials.<sup>1</sup> This effect lowers the degeneracy of the energy levels in zero applied magnetic field for magnetic ions with more than one unpaired electron. For magnetic ions or molecules with no first-order orbital angular momentum contribution to the electronic ground state, ZFS arises from spin-orbit coupling  $\lambda$  and a symmetry-lowering structural distortion of the local environment, as these combined effects lead to a mixing of the ground-state multiplet with the excited-state multiplets. In this case, the strength of ZFS is quantified through the two parameters D and E, which define its axial and transverse components, respectively. For magnetic systems based on mononuclear, 3d transition metal building blocks, typically |D| < 5 meV, although an exceptionally large value of ~54 meV has recently been obtained in a Ni-based magnet with an unusual local geometry.<sup>2</sup>

ZFS plays an important role in single molecule magnets (SMMs), a class of materials with potential applications in nanoscale magnetic devices such as quantum computers and spin transistors.<sup>3–6</sup> These systems consist of isolated magnetic ions or molecules with spin S and a bistable ground state consisting of the microstates  $S_z = \pm S$  arising from an easy-axis magnetic anisotropy with magnitude |D|. These properties enable an applied magnetic field to induce a net magnetization that can be maintained for relatively long periods of time once the field is switched off. Because the energy barrier to the loss of magnetization is given by  $U_{\rm eff} \propto |D|S^2$ , an extremely large, negative zero-field splitting and/or a high spin ground state are prerequisites for a long magnetic relaxation time at elevated temperatures, which is extremely desirable for most SMM applications. Another important parameter for characterizing SMMs is the blocking temperature  $T_{\rm B}$ , which is defined as the highest temperature where magnetic hysteresis is observed in a plot of the magnetization versus applied magnetic field. Higher blocking temperatures are obtained by increasing  $U_{\rm eff}$ .

The first SMM studied in significant detail was based on the  $Mn_{12}$  acetate molecule<sup>7</sup> with S = 10 and |D| < 0.1 meV, so early SMM design efforts focused on maximizing S. While this was accomplished by generating other molecular magnets based on large transition metal complexes,<sup>5,8,9</sup> it has proven to be extremely difficult to significantly increase  $U_{\rm eff}$  with this approach.<sup>10–12</sup> For this reason, more recent SMM synthesis efforts have concentrated on maximizing |D| instead. This



Received: March 28, 2019 Published: May 28, 2019

## Journal of the American Chemical Society

strategy has been extremely fruitful, as it has led to the discovery of several SMMs based on rare earth<sup>4,13</sup> or transition metal ions.<sup>6,14</sup> The blocking temperatures have also been increasing steadily, with the record now slightly above the nitrogen liquefaction temperature of 77 K.<sup>15</sup> Despite the breakthroughs of identifying SMMs that function at elevated temperatures, it is important to establish design principles to increase  $U_{\rm eff}$  and  $T_{\rm B}$  even further. To this end, molecular magnets with metal–metal bonding should be considered, as recent work has shown that  $|D| \ge 10$  meV can be realized in binuclear Ru paddlewheel compounds with extremely short Ru–Ru distances.<sup>16–19</sup>

The 6H-perovskites, with the general formula  $Ba_3MA_2O_9$ , may also be interesting in this context. The versatility of the crystal structure, shown in Figure 1, enables the A site to



**Figure 1.** (a) Crystallographic unit cell of  $Ba_3CeRu_2O_9$ . (b) Local structure of a Ru dimer, which shows the inequivalent red and blue triangles composed of  $O_1$  and  $O_2$  ions, respectively. These inequivalent oxygen triangles arise from an octahedral off-centering of the two Ru ions along the *c*-axis.

accommodate a wide variety of 4d and 5d transition metals, which form spin dimers due to the short nearest-neighbor A-A distance arising from the AO<sub>6</sub> face-sharing octahedral geometry. Most previous work on 6H-perovskites with a magnetic A site has assumed that a single ion, local moment picture is a valid starting point for understanding the electronic ground states of the individual dimers.<sup>20-24</sup> However, we recently showed that metal-metal bonding occurs in  $Ba_3MRu_2O_9$  (M = In, Lu, Y)<sup>25</sup> due to significant orbital hybridization, resulting in an  $S_{tot} = 1/2$  Heisenberg moment distributed equally over the two Ru sites. This behavior likely arises due to the large spatial extent of the Ru 4d orbitals combined with the extremely short intradimer Ru-Ru distances (2.54-2.56 Å at room temperature).<sup>25</sup> These distances are smaller than the values reported for both Ru metal and many other members of this family, as indicated in Table 1.

Intriguingly,  $Ba_3MRu_2O_9$  (M = Ce, Pr, Tb)<sup>22</sup> has eight valence electrons per Ru dimer and even shorter intradimer Ru–Ru distances, which likely leads to metal–metal bonding as well. Large ZFS may play an important role in these materials, as an  $S_{tot} = 1$  electronic ground-state multiplet is predicted in a molecular orbital scenario.<sup>26</sup> Because  $Ba_3CeRu_2O_9$  consists of well-separated Ru dimers due to nonmagnetic Ce<sup>4+</sup> occupying the M site and no evidence for long-range magnetic order was found previously down to 2  $K_r^{22}$  it should be considered a SMM candidate. In this work, we combine magnetometry, neutron powder diffraction,

Table 1. Nearest-Neighbor Ru-Ru Distances in Ru Metal and Selected 6H-Perovskite Ruthenate Compounds at Room Temperature

material	4d electrons per dimer	nominal Ru valence	intradimer distance (Å)	ref
Ru metal			2.65	27
Ba <sub>3</sub> NaRu <sub>2</sub> O <sub>9</sub>	5	5.5	2.75	28
Ba3LiRu2O9	5	5.5	2.77	28
Ba <sub>3</sub> CaRu <sub>2</sub> O <sub>9</sub>	6	5	2.65	21
Ba <sub>3</sub> ZnRu <sub>2</sub> O <sub>9</sub>	6	5	2.67	29
Ba <sub>3</sub> CoRu <sub>2</sub> O <sub>9</sub>	6	5	2.68	30
Ba <sub>3</sub> YRu <sub>2</sub> O <sub>9</sub>	7	4.5	2.54	23
Ba <sub>3</sub> InRu <sub>2</sub> O <sub>9</sub>	7	4.5	2.56	23
Ba <sub>3</sub> LuRu <sub>2</sub> O <sub>9</sub>	7	4.5	2.55	23
Ba3PrRu2O9	8	4	2.49	22
Ba <sub>3</sub> TbRu <sub>2</sub> O <sub>9</sub>	8	4	2.49	22
Ba <sub>3</sub> CeRu <sub>2</sub> O <sub>9</sub>	8	4	2.46	this work

inelastic neutron scattering, and infrared spectroscopy to establish the nature of the magnetic building blocks and to investigate the SMM candidacy of  $Ba_3CeRu_2O_9$ .

## EXPERIMENTAL DETAILS

**Sample Preparation and Magnetometry.** Polycrystalline Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> was prepared by a solid-state chemistry method using a stoichiometric amount of the starting materials BaCO<sub>3</sub>, Ru, and CeO<sub>2</sub> (predried at 950 °C overnight) with phase purities of 99.9% or greater. The starting materials were mixed in agate mortars, pressed into pellets, annealed in air at 900 °C for 12 h, and then annealed for another 30 h at 1350 °C with intermediate grinding and pelletizing. X-ray powder diffraction using a HUBER image-plate Guinier camera with Cu K<sub>a1</sub> radiation (1.54 Å) confirmed the phase purity of the sample. The magnetization was measured with both a Quantum Design Vibrating Sample magnetometer and a Magnetic Property Measurement System in the temperature intervals 2–320 K and 300–600 K, respectively.

Neutron Scattering. Neutron powder diffraction (NPD) on the Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> polycrystalline sample was performed using the HB-2A powder diffractometer of the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). The sample was loaded in an aluminum can, and the data were collected at temperatures T =0.3, 100, and 300 K with a neutron wavelength of 1.54 Å and a collimation of open-21'-12'. Inelastic neutron-scattering (INS) measurements were performed on the direct-geometry time-of-flight chopper spectrometer SEQUOIA<sup>31</sup> of the Spallation Neutron Source (SNS) at ORNL, using the same polycrystalline sample loaded in an aluminum can. Spectra were collected at 4 and 300 K with incident energies  $E_i = 25$ , 100, and 300 meV. An empty aluminum can was measured in identical experimental conditions for a similar counting time. The resulting background spectra were subtracted from the corresponding sample spectra after normalization with a vanadium standard to account for variations of the detector response and the solid angle coverage.

**Infrared Spectroscopy.** The infrared response was measured using a series of Fourier transform spectrometers with an open flow cryostat (3–100 meV, 20–300 K) on polycrystalline Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> mixed with paraffin or KBr to optimize the optical density. Absorption was calculated as  $\alpha(\omega) = -\frac{1}{hd} \ln[T(\omega)]$ , where  $T(\omega)$  is the measured transmittance, *h* is the mass concentration of Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub>, and *d* is the thickness. Oscillator strength was calculated as  $f = \frac{2\epsilon}{N_e \pi \omega_p^2} \int_{\omega_1}^{\omega_2} n\alpha(\omega) d\omega$ , where  $N_e$  is the number of electrons per Ru site, *n* is the refractive index,  $\omega_p$  is the plasma frequency  $\omega_p = \sqrt{\frac{e^2\rho}{me_0}}$ , *e* is the electron charge,  $\rho$  is the number of Ru atoms per unit



**Figure 2.** (a) Magnetic susceptibility versus temperature for  $Ba_3CeRu_2O_9$  measured in an applied magnetic field of 1 kOe between 2 and 300 K. (b) Low-temperature data only with the best fit to the Curie–Weiss law superimposed as a solid curve. (c) Isothermal magnetization at 2 K (open symbols) with the best Brillouin function fit superimposed on the data. The small value of the magnetization measured over the entire field range investigated, which we attribute to a magnetic impurity phase or defects, is consistent with a nonmagnetic spin-singlet ground state for  $Ba_3CeRu_2O_9$ . (d) The refined neutron powder diffraction pattern with T = 0.3 K. The ticks below the diffraction pattern correspond to the expected Bragg peak positions for the  $Ba_3CeRu_2O_9$  sample and the Al can. The gray arrow identifies the region where the largest impurity peaks are observed. (e) A rescaled version of the diffraction data over a limited  $2\theta$  range, which highlights the small impurity peaks.

cell, *m* is the electron mass, *c* is the speed of light, and  $\varepsilon_0$  is the vacuum dielectric constant.<sup>32,33</sup>

## RESULTS AND DISCUSSION

**Low-Temperature Magnetic Properties and Crystal Structure.** Figure 2a shows the magnetic susceptibility  $\chi$  (plotted as M/H) versus temperature for Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> measured between 2 and 300 K in an applied magnetic field of 1 kOe. No features indicative of magnetic order are observed down to 2 K, which is in good agreement with previous work<sup>22</sup> and in sharp contrast to the seven 4d-electron dimer analogues Ba<sub>3</sub>MRu<sub>2</sub>O<sub>9</sub> (M = In, Lu, Y).<sup>23-25,34</sup> The low-*T* data between 2 and 20 K, shown in Figure 2b, fit well to the Curie–Weiss law:

$$\chi = \frac{C}{T - \theta} + \chi_0 \tag{1}$$

where *C* is the Curie–Weiss constant,  $\theta$  is the Weiss temperature, and  $\chi_0$  is a *T*-independent contribution. Our best fit yields C = 0.00351 emu-K/mol-FU (Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> formula unit),  $\theta = -0.5$  K, and  $\chi_0 = 9.3 \times 10^{-4}$  emu/mol-FU. The large value for  $\chi_0$  implies that there are other contributions to this term beyond the usual core diamagnetism and van Vleck paramagnetism; this issue will be revisited later when a more complete model of the magnetic susceptibility over a wider temperature range is presented. The most important result from this simple low-temperature fit is that the Curie–Weiss constant corresponds to an effective moment of only 0.17  $\mu_{\rm B}$ , which is extremely small and possibly indicative of a nonmagnetic dimer ground state.

To investigate this possibility further, we collected isothermal magnetization data at 2 K. Figure 2c illustrates that simple Brillouin function behavior corresponding to a dense array of paramagnetic spin-1 moments arising from either single ion Ru<sup>4+</sup> (e.g., S = 1, saturation magnetization  $M_{\text{sat}} = 2 \mu_{\text{B}}/\text{Ru}$ ) or molecular orbital formation (e.g.,  $S_{\text{tot}} = 1$ ,  $M_{\text{sat}} = 2 \mu_{\text{B}}/\text{dimer}$ ) was not observed. Although nearly full saturation at 2 K is expected by 70 kOe, we instead observe a drastically reduced signal throughout the entire field range investigated. This small magnetization may arise from impurities and/or defects in the sample and provides additional support for the nonmagnetic dimer ground state. We can estimate the molar fraction *f* of the magnetic impurities or defects by assuming that they arise from spin-1/2 moments and then fitting our magnetization data to the appropriate Brillouin function  $B_{\text{s}}(x)$ :

$$M^{\text{mol}}(H, T) = \chi_0(T)H + fN_A\mu_BgSB_S(x)$$
<sup>(2)</sup>

where

$$x = \frac{gS\mu_{\rm B}H}{k_{\rm B}T} \tag{3}$$

and  $\chi_0(T)$  is the field-independent susceptibility of Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> at temperature *T*, *N*<sub>A</sub> is Avogadro's constant, *g* = 2 is the Landé *g*-factor,  $\mu_{\rm B}$  is the Bohr magneton, and  $k_{\rm B}$  is the Boltzmann constant. Our best fit to this expression, shown by the solid curve in Figure 2c, yields *f* = 0.29% paramagnetic, *S* = 1/2 Ru moments (0.58% paramagnetic Ru dimers), which are consistent with a very small concentration of defects or impurities.

Previous X-ray diffraction work found that  $Ba_3CeRu_2O_9$  crystallizes in the hexagonal  $P6_3/mmc$  space group at room temperature.<sup>22</sup> We performed neutron powder diffraction between 0.3 and 300 K to search for signatures of structural phase transitions or long-range magnetic order. A representative diffraction pattern at 0.3 K is shown in Figure 2d. No magnetic Bragg peaks are observed, which is consistent with the nonmagnetic ground-state scenario inferred from the magnetization measurements. Furthermore, no evidence for

structural transitions is found in these data, as the diffraction patterns refine well in the hexagonal  $P6_3/mmc$  space group at all temperatures. On the other hand, there are a few extra, temperature-independent Bragg peaks in these patterns corresponding to a small amount of impurity. The largest extra peaks are highlighted in Figure 2e and are best indexed by ~1.2(3)% and 1.5(3)% of BaCeO<sub>3</sub> and 9R-BaRuO<sub>3</sub>, respectively; the latter should contribute an extrinsic paramagnetic contribution to the magnetic susceptibility.<sup>35,36</sup>

A schematic of the crystal structure for  $Ba_3CeRu_2O_9$  is presented in Figure 1a. Face-sharing  $RuO_6$  octahedra produce Ru dimers with an intradimer Ru–Ru distance shorter than that reported for Ru metal.<sup>27</sup> The  $Ru_2O_9$  units consist of two crystallographically inequivalent oxygen ions, which are labeled  $O_1$  and  $O_2$  in Figure 1b. Table 2 summarizes the lattice

Table 2. Lattice Constants and Selected Structural Parameters for Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> at Various Temperatures Extracted from Refinements of the NPD Data

	temp (K)			
	0.3	100	300	
a (Å)	5.8804(2)	5.8825(2)	5.8933(2)	
c (Å)	14.6487(5)	14.6481(4)	14.6492(5)	
Ba <sub>2</sub> z	0.9022(3)	0.9024(3)	0.9023(3)	
Ru z	0.1654(2)	0.1661(2)	0.1659(2)	
$O_1 x$	0.4904(8)	0.4908(10)	0.4900(10)	
$O_2 x$	0.1754(6)	0.1734(7)	0.1732(7)	
$O_2 z$	0.4121(1)	0.4125(1)	0.4126(1)	
$R_{wp}$ (%)	8.33	6.99	7.03	
Ru–Ru (Å)	2.479(4)	2.458(4)	2.464(4)	
$Ru-O_1$ (Å)	2.023(4)	2.021(4)	2.019(4)	
Ru $-O_2$ (Å)	1.969(3)	1.995(5)	1.999(5)	
$O_1$ -Ru- $O_1$ (deg)	86.4(2)	86.9(4)	86.6(4)	
$O_2$ -Ru- $O_2$ (deg)	90.1(3)	90.0(2)	90.2(2)	
$O_1$ -Ru- $O_2$ (deg)	91.7(2)	91.5(3)	91.6(3)	
$O_1 - O_1$ (Å)	2.771(5)	2.779(9)	2.770(6)	
$O_2 - O_2$ (Å)	2.787(6)	2.822(7)	2.832(4)	
$O_1 - O_2$ (Å)	2.866(4)	2.877(4)	2.879(5)	
Ru off-centering (Å)	0.050(3)	0.039(3)	0.041(3)	

constants, atomic fractional coordinates, refinement quality, and selected bond lengths and angles at various temperatures. The short intradimer Ru-Ru distance remains essentially unchanged down to 0.3 K, and therefore a molecular orbital scheme may be appropriate for this material over a wide temperature range. We also note that the Ru<sub>2</sub>O<sub>9</sub> units have a trigonal elongation along the c-axis and the Ru ions are not centered in their respective oxygen octahedra. Instead, they are displaced away from one another along the c-axis due to the electrostatic repulsion between them, generating inequivalent  $Ru-O_1$  and  $Ru-O_2$  bonds and producing a size mismatch between the *ab*-plane triangles formed by the  $O_1$  and  $O_2$ oxygen ions in this material [see Figure 1b]. The magnitude of this displacement is presented at various temperatures in Table 2. Table 1 highlights the importance of electrostatic repulsion throughout this family, as the metal-metal distance increases systematically as the nominal valence of the Ru site increases.

**Spectroscopy Measurements.** There are two likely ways to produce a nonmagnetic dimer ground state in  $Ba_3CeRu_2O_9$ : (1) via antiferromagnetic superexchange between local moments of the Ru ions, or (2) via significant positive zero-field splitting (D > 0) of the ground-state multiplet in a molecular orbital picture. The temperature-dependence of the magnetic susceptibility is very different for these two cases, and therefore it can be used to help distinguish between them. However, the appropriate fit functions are generally overparameterized, so first establishing the energy scales of the excited states with other measurements is desirable. To this end, we used spectroscopy techniques to identify the possible magnetic excitations in Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub>.

Inelastic neutron scattering measurements were performed on the SEQUOIA spectrometer with incident energies  $E_i = 25$ , 100, and 300 meV. Figure 3a-c shows T = 4 K color contour plots of the dynamical structure factor  $S(Q,\omega)$  multiplied by the magnetic form factor squared  $f(Q)^2$  for the  $E_i = 25$ , 100, and 300 meV data sets, respectively. The sample spectra are dominated by Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> phonon modes over a wide energy transfer range up to  $\sim$ 70 meV. This large phonon contribution makes it extremely challenging to identify weak magnetic scattering in these color contour plots or in the 4 K constant-Q cuts of  $S(Q,\omega)$  presented in Figure 3d-f. Typically, in this situation one examines  $f(Q)^2 \Delta \chi''(Q,\omega)$  instead, where  $\chi''(Q,\omega) = S(Q,\omega)^*[1 - e^{(-\hbar\omega/k_BT)}]$  is the imaginary part of the dynamical magnetic susceptibility and  $\Delta \chi''(Q,\omega) =$  $\chi''(T_{\rm low}) - \chi''(T_{\rm high})$ . While the single phonon contribution to  $\chi''(Q,\omega)$  should be T-independent, the magnetic component generally increases with decreasing T. In this spirit, constant-Q cuts of  $f(Q)^2 \Delta \chi''(Q,\omega)$  with  $T_{\text{low}} = 4$  K,  $T_{\text{high}} = 300$ K, and  $E_i = 25$ , 100, or 300 meV are shown in Figure 3g-i. Several peaks indicated by gray arrows, corresponding to candidate magnetic excitations, appear in these plots. However, these features can also arise from an imperfect subtraction of the single phonon contribution in  $\chi''(Q,\omega)$  due to the presence of multiphonon scattering or temperature-independent multiple scattering.<sup>37,38</sup> To differentiate between these two possibilities, we examined the Q-dependence of  $S(Q,\omega)$  for these excitations and present the results in Figure 3j-l. While multiple scattering will lead to a Q-independent contribution at low Q and multiphonon scattering will increase with increasing  $Q_{\rm s}^{37,38}$  the intensity of magnetic modes will increase with decreasing Q. The 70 and 90 meV peaks are the only ones that satisfy this third criterion, and therefore they correspond to the magnetic excitations in these data.

Because the intensity of the magnetic modes observed with INS is extremely weak, we performed complementary infrared measurements in an effort to confirm the excitation scheme. Although this technique cannot reveal the Q-dependence, the energy resolution is much better than INS. Figure 4a displays the infrared absorption spectra at 20, 110, 200, and 300 K. Several features are clearly observed with energy scales consistent with assignment as either phonons or magnetic excitations. Examination of the line shape trends reveals subtle differences between the various structures. The majority of peaks behave as simple phonons, although the 29, 72, and 85 meV features have a more complex origin. To differentiate between the two possible assignments, we extracted the oscillator strength f of each feature and plotted these values as a function of temperature [Figure 4b]. A peak with a pure phonon origin may red shift and broaden with increasing temperature, but the oscillator strength will be conserved.<sup>33</sup> On the other hand, the oscillator strength of a peak with a more complicated origin (e.g., a mixed mode with both phononic and magnetic components) may have significant temperature dependence because the magnetic component is not required to obey the f sum rule. Our analysis reveals that the oscillator

## Journal of the American Chemical Society



**Figure 3.** (a-c) Color contour plots of the dynamical structure factor  $S(Q_i\omega)$  multiplied by the magnetic form factor squared  $f(Q)^2$  at T = 4 K for the incident energy  $E_i = 25$ , 100, and 300 meV SEQUOIA data sets. The spectra are dominated by Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> phonon contributions up to 70 meV, and no magnetic excitations are clearly visible. (d-f) Constant-Q cuts of  $f(Q)^2S(Q_i\omega)$  at low Q (integration ranges shown on each panel) with T = 4 and 300 K for  $E_i = 25$ , 100, or 300 meV. (g-i) Constant-Q cuts for  $f(Q)^2\Delta\chi''(Q_i\omega) = f(Q)^2[\chi''(4 \text{ K}) - \chi''(300 \text{ K})]$  with  $E_i = 25$ , 100, or 300 meV. The peaks in these plots, indicated by the gray arrows, arise from magnetic scattering or an imperfect subtraction of the single phonon contribution in  $\chi''(Q_i\omega)$  due to multiphonon scattering or temperature-independent multiple scattering. (j-1) Constant-*E* cuts of  $f(Q)^2S(Q_i\omega)$ (integration ranges shown on each panel) at T = 4 K corresponding to the candidate magnetic excitations in panels (g)-(i). The 70 and 90 meV peaks in  $\Delta\chi''(Q_i\omega)$  are the only ones with intensity that increases with decreasing Q, and therefore they correspond to the magnetic modes observed in these data. For simplicity,  $f(Q)^2$  is not included in the labels of the figure panels.



**Figure 4.** (a) Variable-temperature infrared spectra of Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> along with the base temperature absorption difference spectrum  $\Delta(\alpha) = \alpha(20 \text{ K}) - \alpha(300 \text{ K})$  in the upper portion of the panel. (b) Oscillator strength of representative peaks from panel (a) as a function of temperature. Unless indicated, the error bars are on the order of the symbol size.

strength of the 29, 72, and 85 meV features is not conserved over the 20–300 K temperature range. This suggests that these structures cannot be attributed only to phonons. We instead propose that the 72 and 85 meV features have a magnetic component, as their energy scales are in excellent agreement with the magnetic excitations observed in the INS data. The absorption difference  $\Delta(\alpha) = \alpha(20 \text{ K}) - \alpha(300 \text{ K})$ , plotted at the top of Figure 4a, quantifies the magnetic portion of the spectrum and again provides evidence that oscillator strength is not conserved. While the behavior of the 29 meV feature is also in line with expectations for a superimposed phonon and magnetic excitation, there are no magnetic features revealed by inelastic neutron scattering in the vicinity. We note that this energy scale is consistent with an  $S_{tot} = 3/2$  magnetic excitation associated with isolated  $S_{tot} = 1/2$  Ru dimers,<sup>25</sup> which could exist at a very low concentration level in Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> due to crystalline defects. There are no signatures of other magnetic features in the infrared spectra up to energies of 100 meV.

**High-Temperature Magnetic Susceptibility.** With the energy scales now established for the two lowest-lying magnetic excitations in  $Ba_3CeRu_2O_{9}$ , we turn to magnetic susceptibility data to try and determine if antiferromagnetic superexchange between Ru ions or zero-field splitting within a metal-metal bonding scheme generates the nonmagnetic dimer ground state in  $Ba_3CeRu_2O_9$ . The expected energy scale for the spin gap from the spectroscopy measurements is rather large, which we verified by collecting additional

susceptibility data up to 600 K and finding that  $\chi T$  shows significant temperature-dependence over the entire range investigated (see the Supporting Information). The simplest scenario to consider in the single ion case is antiferromagnetic superexchange J between S = 1 Heisenberg moments. The Tdependence of the magnetic susceptibility can be derived from the van Vleck formula<sup>1</sup> and is given by

$$\chi_{\rm dimer} = \frac{N_{\rm A} \mu_{\rm B}^2 g^2}{k_{\rm B} T} \left( \frac{2x^2 + 10x^6}{1 + 3x^2 + 5x^6} \right) \tag{4}$$

where  $x = e^{-J/k_BT}$ . The nonmagnetic spin-singlet state is separated from the two lowest-lying magnetic excitations by energies of  $\Delta_0 = 2J$  ( $S_{tot} = 1$  level) and 6J ( $S_{tot} = 2$  level), respectively. This model was previously considered in ref 22, where the authors commented that it could not provide a good description of the temperature-dependence of the susceptibility. We verified this conclusion here by first attempting to fit our own susceptibility data to this model. This result is presented in the Supporting Information, where we show that this model can only be used to fit the data with an unphysical set of parameters. Our spectroscopy measurements are also not consistent with this simple Heisenberg model, as it cannot explain the presence of the two closely spaced magnetic excitations.

We note that the local moment, spin-only susceptibility model may not be appropriate for low-spin Ru<sup>4+</sup> in an octahedral environment due to the probable first-order orbital angular momentum contribution to its electronic ground state and its large spin orbit coupling constant  $\lambda$  on the order of 1000 K.<sup>39</sup> Therefore, the susceptibility may be better-described by a Hamiltonian that includes both  $\lambda L \cdot S$  and exchange terms instead. While no analytical expression can be derived for the susceptibility in this case, the temperature dependence can be calculated through exact diagonalization of the Hamiltonian, and this has been explored elsewhere.<sup>39</sup> Interestingly, comparable values for  $\lambda$  and J can generate a susceptibility curve with a broad maximum similar to that observed in the Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> data, but a fit to this numerical model is beyond the scope of this work. Instead, we considered a simple model that is an extension of the Heisenberg superexchange case described above, where ZFS of the  $S_{tot} = 1$  excited manifold is now permitted and provides a natural explanation for the two magnetic excitations we observe. The fitting results for this model with energy levels consistent with our spectroscopy measurements are presented in the Supporting Information. We find that this revised model also fails to provide an adequate description of the data with a complete set of physical parameters.

The second scenario is that ZFS within a molecular orbital picture leads to the nonmagnetic dimer ground state in Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub>. This explanation seems more plausible, as compared to the local moment models described above, due to the extremely short Ru–Ru intradimer distance in Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> and experimental evidence that molecular orbital formation occurs in the isostructural materials Ba<sub>3</sub>MRu<sub>2</sub>O<sub>9</sub> (M = In, Lu, Y)<sup>25</sup> with slightly longer intradimer Ru–Ru distances. Face-sharing octahedral architecture promotes  $\sigma$ -bonding of  $3z^2-r^2$  orbitals and  $\pi$ -bonding of a linear combination of the remaining d-orbitals,<sup>40–42</sup> which produces the molecular orbital scheme shown in Figure 5.

When there are eight valence electrons per Ru dimer, this metal-metal bonding scenario leads to an  $S_{tot} = 1$  electronic



Figure 5. Molecular orbital diagrams for  $Ba_3CeRu_2O_9$  corresponding to (a) the electronic ground state and (b) the first electronic excited state.

ground state with no orbital degree of freedom and a  $S_{tot} = 0$  first excited-state multiplet,<sup>26</sup> as illustrated in Figure 5a and b, respectively. An axial zero-field splitting D > 0 can lift the 3-fold degeneracy of the  $S_{tot} = 1$  manifold, leading to a  $S_{tot} = 1$ ,  $S_{tot}^z = 0$  singlet with a spin gap D to an excited doublet  $S_{tot} = 1$ ,  $S_{tot}^z = \pm 1$ , and in Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> this splitting can arise from the combined effects of spin—orbit coupling, the trigonal elongation of the Ru<sub>2</sub>O<sub>9</sub> complex, and the octahedral off-centering of the Ru ions.

However, this molecular orbital model cannot explain the presence of two magnetic modes in the INS data, so some modifications need to be considered before attempting to fit the susceptibility data. Although a nonzero *E* could split the excited doublet  $S_{tot} = 1$ ,  $S_{tot}^z = \pm 1$  into two singlets, our neutron powder diffraction results provide no evidence for a nonaxial distortion of the Ru<sub>2</sub>O<sub>9</sub> complex in Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> over a wide temperature range, and therefore this possibility can be ruled out. The second mode may simply represent a low-lying intermultiplet transition, and this is what we will assume here. The fitting functions for the magnetic susceptibility then become the following:

$$\chi_{\parallel} = \frac{2N_{\rm A}\mu_{\rm B}^2 g_{\parallel}^2}{k_{\rm B}T} \left( \frac{{\rm e}^{-D/k_{\rm B}T}}{1+2{\rm e}^{-D/k_{\rm B}T}+{\rm e}^{-\Delta/k_{\rm B}T}} \right)$$
(5)

and

$$\chi_{\perp} = \frac{2N_{\rm A}\mu_{\rm B}^2 g_{\perp}^2}{D} \left( \frac{1 - e^{-D/k_{\rm B}T}}{1 + 2e^{-D/k_{\rm B}T} + e^{-\Delta/k_{\rm B}T}} \right)$$
(6)

where  $\Delta$  is the energy gap between the  $S_{\text{tot}} = 1$ ,  $S_{\text{tot}}^z = 0$  ground state, and the  $S_{\text{tot}} = 0$  excited state and  $g_{\parallel}$  and  $g_{\perp}$  are the components of the *g*-tensor parallel and perpendicular to the *c*axis, respectively, for the  $S_{\text{tot}} = 1$ ,  $S_{\text{tot}}^z = \pm 1$  doublet.<sup>43</sup> The order of the  $S_{\text{tot}} = 1$ ,  $S_{\text{tot}}^z = \pm 1$ , and  $S_{\text{tot}} = 0$  modes in the excitation spectrum depends on the relative strength of *D* and  $\Delta$ , so there are two parameter sets that are consistent with the mode energies determined from the spectroscopy measurements: D = 85 meV,  $\Delta = 72$  meV or D = 72 meV,  $\Delta = 85$  meV. The energy level schemes for these two models are presented in Figure 6a and d, respectively.

We tested the validity of these two models by fitting our susceptibility data to the following expression:

$$\chi = \chi_0 + \frac{C_1}{T - \theta_1} + \frac{C_2}{T - \theta_2} + \chi_{\text{dimer}2}$$
(7)

with

$$\chi_{\rm dimer2} = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp} \tag{8}$$



**Figure 6.** (a) Energy level diagram for an  $S_{tot} = 1$  molecular orbital model with D = 85 meV and  $\Delta = 72$  meV. (b) Magnetic susceptibility of Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> plotted as open symbols with the best fit to the model described in (a) superimposed as a solid curve. (c) A rescaled version of panel (b) that highlights the fit quality in the high-temperature regime. The agreement between the data and the fit is excellent. (d) The energy level diagram for a competing  $S_{tot} = 1$  molecular orbital model with D = 72 meV and  $\Delta = 85$  meV. (e) The temperature-dependence of the magnetic susceptibility for Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> is shown again here with the best fit to the competing model described in (d) that yields realistic parameters superimposed on the data as a solid curve. (f) A rescaled version of panel (e) that highlights the poor fit quality for this model in the high-temperature regime.

where  $\chi_0$  is a *T*-independent contribution. Upon careful visual inspection of the full-T dependence of the magnetic susceptibility, two different Curie-Weiss regimes are apparent. These contributions were accounted for with the  $C_1$ ,  $\theta_1$  and  $C_2$ ,  $\theta_2$  terms. We find a superior fit, shown in Figure 6b and c, for the model with D = 85 meV. The other parameters returned by this fit are as follows:  $g_{\parallel} = 2.97(1)$ ,  $g_{\perp} = 1.070(5)$ ,  $C_1 =$ 0.046(1) emu-K/mol-FU,  $\theta_1 = -103(3)$  K,  $C_2 = 0.00299(3)$ emu-K/mol-FU,  $\theta_2 = -0.23(2)$  K, and  $\chi_0 = -1.7(7) \times 10^{-5}$ emu/mol-FU. On the basis of the fitted values of  $\theta_1$  and  $\theta_2$ , we attribute the first Curie-Weiss term to a ~2.3(1)% 9R-BaRuO<sub>3</sub> impurity and the second Curie-Weiss term to crystalline defects in  $Ba_2CeRu_2O_9$  that generate ~0.8(1)% isolated  $S_{tot} = 1/2$  Ru dimers. This impurity fraction estimate is in good agreement with our neutron powder diffraction results, while possible evidence for a small amount of  $S_{tot} = 1/2$  Ru dimers was also found in our infrared spectroscopy data. Furthermore, these Curie-Weiss parameters are consistent with the low-T susceptibility fitting described above, as the term associated with the defects dominates in the 2-20 K temperature range. On the other hand, our initial attempts at fitting the data with the D = 72 meV model resulted in an extremely large value for  $C_1$  (i.e., ~0.33 emu-K/mol-FU) that is inconsistent with the lack of intrinsic paramagnetism or extremely small impurity content of our sample. Therefore, we fixed  $C_1$  to the realistic value obtained from the fit to the D =85 meV model and present the fitting result in Figure 6e and f, which shows that the fit quality in this case is clearly inferior.

The excellent agreement between the susceptibility data and the D = 85 meV molecular orbital model indicates that metal metal bonding is extremely important in Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> and the nonmagnetic dimer ground state arises from a large, positive zero-field splitting D of the  $S_{tot} = 1$  multiplet. We note that ZFS is proportional to  $\lambda^2$  and inversely proportional to the energy difference between the ground-state multiplet and excited multiplets.<sup>1</sup> Therefore, this intriguing result may be explained by a spin molecular orbital coupling for the Ru dimers<sup>44</sup> that is enhanced relative to the Ru single ion spinorbit coupling and the presence of low-lying excited-state multiplets with an energy scale on the order of 10–100 meV. The low-lying excited-state multiplets can arise in molecular magnets<sup>25,45</sup> due to a delicate competition between spin polarization (i.e., Hund's coupling) promoting high-spin electronic ground states and intersite orbital hopping favoring metal-metal bonding and hence low-spin electronic ground states.<sup>26,46,47</sup> We note that the magnitude of the ZFS for Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> is even greater than the largest values of ~30–35 meV previously reported for members of the binuclear Ru paddlewheel family.<sup>16,17,19</sup> Molecular magnets based on wellseparated face-sharing octahedra are therefore excellent candidates for exhibiting SMM properties at high temperatures.

In the search for new SMMs with face-sharing octahedral units, important qualitative criteria include intramolecular bond lengths comparable to or smaller than the nearestneighbor distance in the corresponding elemental metal to promote molecular orbital formation and the realization of  $S_{tot}$ > 1/2 electronic ground states. For the specific case of the 6Hperovskites where the molecular orbital scheme is known, careful consideration should be given to the iridates Ba<sub>3</sub>MIr<sub>2</sub>O<sub>9</sub> where M is a divalent cation and therefore there are eight valence electrons per Ir dimer,<sup>48,49</sup> as they seem to meet these general criteria. Other intriguing candidates are based on the 12-L perovskite structure, 50-52 which consists of trimers of face-sharing metal-oxygen octahedra. Recent work has emphasized the importance of metal-metal bonding in some of these compounds,  $^{53,54}$  and the known molecular orbital scheme<sup>51</sup> also supports  $S_{tot} > 1/2$  electronic ground states for several different valence electron counts.

## CONCLUSIONS

We synthesized polycrystalline Ba<sub>3</sub>CeRu<sub>2</sub>O<sub>9</sub> and investigated its magnetic properties with a combination of magnetometry, neutron scattering, and infrared spectroscopy measurements.

Our neutron powder diffraction results indicate that the hexagonal P6<sub>3</sub>/mmc crystal structure and the extremely short Ru-Ru intradimer distance persist down to 0.3 K, while we find no evidence for long-range magnetic order or intrinsic paramagnetism down to low temperatures due to dimer ground states that are nonmagnetic. Inelastic neutron scattering and infrared spectroscopy reveal a large spin gap to the lowest-lying magnetic excitation. Subsequent susceptibility modeling shows that the nonmagnetic dimer states likely arise from a metal-metal bonding scheme with an extremely large, positive zero-field splitting (i.e., D > 0) of the  $S_{tot} = 1$ electronic ground state. Although the positive D ensures that  $Ba_3CeRu_2O_9$  is not a SMM, it is intriguing that the magnitude of the ZFS is exceptionally high and even greater than reported previously for members of the well-studied family of binuclear Ru paddlewheel compounds with metal-metal bonding, including  $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$  (Me = CH<sub>3</sub>),<sup>55,5</sup>  $\operatorname{Ru}_2(\operatorname{but})_4^2\operatorname{Cl}$  (but = butyrate),<sup>57</sup> and others.<sup>16-19</sup> Our work therefore suggests that a systematic study of materials based on isolated metal clusters may yield SMMs with exceptionally high blocking temperatures.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b03389.

Crystallographic data for  $Ba_3CeRu_2O_9$  at T = 0.3 K (CIF)

Crystallographic data for  $Ba_3CeRu_2O_9$  at T = 100 K (CIF)

Crystallographic data for  $Ba_3CeRu_2O_9$  at T = 300 K (CIF)

Additional magnetic susceptibility results and analysis (PDF)

## AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: aczelaa@ornl.gov

#### ORCID <sup>®</sup>

Alexander I. Kolesnikov: 0000-0003-1940-4649 Jinguang Cheng: 0000-0002-4969-1960 Janice L. Musfeldt: 0000-0002-6241-823X Adam A. Aczel: 0000-0003-1964-1943

#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We appreciate useful discussions with S. A. J. Kimber and C. Eichstaedt. Research at the University of Tennessee is supported by the National Science Foundation, Division of Materials Research, under award NSF-DMR 1350002 (HDZ) and the Department of Energy, Office of Basic Energy Sciences, Materials Science Division, under award DE-FG02-01ER45885 (J.L.M.). J.C. is supported by the MOST, NSFC, and CAS through projects with Grant nos. 2018YFA0305700, 11874400, and QYZDB-SSW-SLH013. A portion of this research used resources at the High Flux Isotope Reactor and the Spallation Neutron Source, which are DOE Office of Science User Facilities operated by Oak Ridge National Laboratory.

# REFERENCES

(1) Boca, R. Zero Field Splitting in Metal Complexes. *Coord. Chem. Rev.* 2004, 248, 757–815.

(2) Schulte, K. A.; Vignesh, K. R.; Dunbar, K. R. Effects of Coordination Sphere on Unusually Large Zero Field Splitting and Slow Magnetic Relaxation in Trigonally Symmetric Molecules. *Chem. Sci.* **2018**, *9*, 9018–9026.

(3) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. Single Molecule Magnets. *MRS Bull.* **2000**, *25*, 66–71.

(4) Woodruff, D. N.; Winpenny, R. E. P.; Layfield, R. A. Lanthanide Single-Molecule Magnets. *Chem. Rev.* **2013**, *113*, 5110–5148.

(5) Layfield, R. A. Organometallic Single-Molecule Magnets. Organometallics 2014, 33, 1084–1099.

(6) Craig, G. A.; Murrie, M. 3d Single-Ion Magnets. Chem. Soc. Rev. 2015, 44, 2135–2147.

(7) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. Magnetic Bistability in a Metal-Ion Cluster. *Nature* **1993**, *365*, 141–143.

(8) Murugesu, M.; Habrych, M.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. Single-Molecule Magnets: A  $Mn_{25}$  Complex With a Record S = 51/2 Spin for a Molecular Species. J. Am. Chem. Soc. 2004, 126, 4766–4767.

(9) Milios, C. J.; Vinslava, A.; Wernsdorfer, W.; Moggach, S.; Parsons, S.; Perlepes, S. P.; Christou, G.; Brechin, E. K. A Record Anisotropy Barrier for a Single-Molecule Magnet. *J. Am. Chem. Soc.* **2007**, *129*, 2754–2755.

(10) Waldmann, O. A Criterion for the Anisotropy Barrier in Single-Molecule Magnets. *Inorg. Chem.* **2007**, *46*, 10035–10037.

(11) Ruiz, E.; Cirera, J.; Cano, J.; Alvarez, S.; Loose, C.; Kortus, J. Can Large Magnetic Anisotropy and High Spin Really Coexist? *Chem. Commun.* **2008**, 52–54.

(12) Neese, F.; Pantazis, D. A. What is Not Required to Make a Single Molecule Magnet. *Faraday Discuss.* **2011**, *148*, 229–238.

(13) AlDamen, M. A.; Clemente-Juan, J. M.; Coronado, E.; Marti-Gastaldo, C.; Gaita-Arino, A. Mononuclear Lanthanide Single-Molecule Magnets Based on Polyoxometalates. *J. Am. Chem. Soc.* 2008, 130, 8874–8875.

(14) Martinez-Lillo, J.; Mastropietro, T. F.; Lhotel, E.; Paulsen, C.; Cano, J.; De Munno, G.; Faus, J.; Lloret, F.; Julve, M.; Nellutla, S.; Krzystek, J. Highly Anisotropic Rhenium(IV) Complexes: New Examples of Mononuclear Single-Molecule Magnets. *J. Am. Chem. Soc.* **2013**, *135*, 13737–13748.

(15) Guo, F.-S.; Day, B. M.; Chen, Y.-C.; Tong, M.-L.; Mansikkamaki, A.; Layfield, R. A. Magnetic Hysteresis up to 80 K in a Dysprosium Metallocene Single-Molecule Magnet. *Science* **2018**, *362*, 1400–1403.

(16) Miyasaka, H.; Clerac, R.; Campos-Fernandez, C. S.; Dunbar, K. R. The First Crystal Structure of a One-Dimensional Chain of Linked  $Ru^{II} = Ru^{II}Units.$  *J. Chem. Soc., Dalton Trans.* **2001**, 858–861.

(17) Furukawa, S.; Ohba, M.; Kitagawa, S. Rational Synthesis of a Two-Dimensional Honeycomb Structure Based on a Paramagnetic Paddlewheel Diruthenium Complex. *Chem. Commun.* 2005, 865–867.
(18) Chen, W.-Z.; Cotton, F. A.; Dalal, N. S.; Murillo, C. A.;

Ramsey, C. M.; Ren, T.; Wang, X. Proof of Large Positive Zero-Field Splitting in a Ru<sub>2</sub><sup>5+</sup> Paddlewheel. *J. Am. Chem. Soc.* **2005**, *127*, 12691–12696.

(19) Miyasaka, H.; Motokawa, N.; Matsunaga, S.; Yamashita, M.; Sugimoto, K.; Mori, T.; Toyota, N.; Dunbar, K. R. Control of Charge Transfer in a Series of  $Ru_2^{I,II}/TCNQ$  Two-Dimensional Networks by Tuning the Electron Affinity of TCNQ Units: A Route to Synergistic Magnetic/Conducting Materials. J. Am. Chem. Soc. **2010**, 132, 1532– 1544.

(20) Darriet, J.; Drillon, M.; Villeneuve, G.; Hagenmuller, P. Interactions Magnétiques dans des Groupements Binucléaires du Ruthénium + V. J. Solid State Chem. **1976**, *19*, 213–220.

(21) Darriet, J.; Soubeyroux, J. L.; Murani, A. P. Neutron Inelastic Scattering Study of Exchange Interactions in a Ruthenium V Dimer Ba<sub>3</sub>CaRu<sub>2</sub>O<sub>9</sub>. *J. Phys. Chem. Solids* **1983**, *44*, 269–272.

(22) Doi, Y.; Wakeshima, M.; Hinatsu, Y.; Tobo, A.; Ohoyama, K.; Yamaguchi, Y. Crystal Structures and Magnetic Properties of the 6H- Perovskites Ba<sub>3</sub>LnRu<sub>2</sub>O<sub>9</sub> (Ln = Ce, Pr, and Tb). *J. Mater. Chem.* **2001**, *11*, 3135–3140.

(23) Doi, Y.; Matsuhira, K.; Hinatsu, Y. Crystal Structures and Magnetic Properties of 6H-Perovskites  $Ba_3MRu_2O_9$  (M = Y, In, La, Sm, Eu, and Lu). J. Solid State Chem. **2002**, 165, 317–323.

(24) Senn, M. S.; Kimber, S. A. J.; Arevalo Lopez, A. M.; Hill, A. H.; Attfield, J. P. Spin Orders and Lattice Distortions of Geometrically Frustrated 6H-Perovskites  $Ba_3B'Ru_2O_9$  (B' = La<sup>3+</sup>Nd,<sup>3+</sup> and Y)<sup>3+</sup>. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 134402.

(25) Ziat, D.; Aczel, A. A.; Sinclair, R.; Chen, Q.; Zhou, H. D.; Williams, T. J.; Stone, M. B.; Verrier, A.; Quilliam, J. A. Frustrated Spin-1/2 Molecular Magnetism in the Mixed-Valence Antiferromagnets  $Ba_3MRu_2O_9$  (M = In, Y, Lu). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *95*, 184424.

(26) Cavigliasso, G.; Stranger, R. Density Functional Investigation of Metal-Metal Interactions in  $d^4d^4$  Face-Shared  $[M_2Cl_9]^{3-}$  (M = Mn, Tc, Re) Systems. *Inorg. Chem.* **2004**, *43*, 2368–2378.

(27) Streltsov, S. V.; Khomskii, D. I. Orbital Physics in Transition Metal Compounds: New Trends. *Phys.-Usp.* **2017**, *60*, 1121–1146.

(28) Stitzer, K. E.; Smith, M. D.; Gemmill, W. R.; zur Loye, H.-C. Novel Mixed-Valent (V/VI) Triple Perovskite Ruthenates: Observation of a Complex Low-Temperature Structural and Magnetic Transition. J. Am. Chem. Soc. 2002, 124, 13877–13885.

(29) Beran, P.; Ivanov, S. A.; Nordblad, P.; Middey, S.; Nag, A.; Sarma, D. D.; Ray, S.; Mathieu, R. Neutron Powder Diffraction study of  $Ba_3ZnRu_{2-x}Ir_xO_9$  (x = 0,1,2) with 6H-Type Perovskite Structure. Solid State Sci. **2015**, 50, 58–64.

(30) Rijssenbeek, J. T.; Huang, Q.; Erwin, R. W.; Zandbergen, H. W.; Cava, R. J. The Crystal Structure of  $Ba_3CuRu_2O_9$  and Comparison to  $Ba_3MRu_2O_9$  (M = In, Co, Ni, and Fe). J. Solid State Chem. **1999**, 146, 65–72.

(31) Granroth, G. E.; Kolesnikov, A. I.; Sherline, T. E.; Clancy, J. P.; Ross, K. A.; Ruff, J. P. C.; Gaulin, B. D.; Nagler, S. E. SEQUOIA: A Newly Operating Chopper Spectrometer at the SNS. *J. Physics: Conference Series* **2010**, *251*, 012058.

(32) O'Neal, K. R.; Patete, J. M.; Chen, P.; Holinsworth, B. S.; Smith, J. M.; Lee, N.; Cheong, S.-W.; Wong, S. S.; Marques, C.; Aronson, M. C.; Musfeldt, J. L. Size-Dependent Vibronic Coupling in Alpha-Fe<sub>2</sub>O<sub>3</sub>. J. Chem. Phys. **2014**, 141, 044710.

(33) Wooten, F. *Optical Properties of Solids*; Academic Press: New York, 1972.

(34) Shlyk, L.; Kryukov, S.; Durairaj, V.; Parkin, S.; Cao, G.; De Long, L. E. Magnetic and Electronic Properties of a  $Ba_3InRu_2O_9$  Single Crystal. J. Magn. Magn. Mater. **2007**, 319, 64–68.

(35) Shepard, M.; McCall, S.; Cao, G.; Crow, J. E. Thermodynamic Properties of Perovskite ARuO<sub>3</sub> (A = Ca, Sr, and Ba) Single Crystals. *J. Appl. Phys.* **1997**, *81*, 4978–4980.

(36) Yuan, S. J.; Butrouna, K.; Terzic, J.; Zheng, H.; Aswartham, S.; DeLong, L. E.; Ye, F.; Schlottmann, P.; Cao, G. Ground-State Tuning of Metal-Insulator Transition by Compositional Variations in  $BaIr_{1-x}Ru_xO_3$  ( $0 \le x \ 1 \le$ ). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, 93, 165136.

(37) Aczel, A. A.; Granroth, G. E.; MacDougall, G. J.; Buyers, W. J. L.; Abernathy, D. L.; Samolyuk, G. D.; Stocks, G. M.; Nagler, S. E. Quantum Oscillations of Nitrogen Atoms in Uranium Nitride. *Nat. Commun.* **2012**, *3*, 1124.

(38) Lin, J. Y. Y.; Aczel, A. A.; Abernathy, D. L.; Nagler, S. E.; Buyers, W. J. L.; Granroth, G. E. Using Monte Carlo Ray Tracing Simulations to Model the Quantum Harmonic Oscillator Modes Observed in Uranium Nitride. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89*, 144302.

(39) Drillon, M.; Padel, L.; Bernier, J.-C. Effects of Spin-Orbit Coupling and Exchange in BaRuO<sub>3</sub>. *J. Chem. Soc., Faraday Trans.* 2 **1979**, 75, 1193–1198.

(40) Kugel, K. I.; Khomskii, D. I.; Sboychakov, A. O.; Streltsov, S. V. Spin-orbital Interaction for Face-sharing Octahedra: Realization of a Highly Symmetric SU(4) Model. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *91*, 155125.

(41) Khomskii, D. I.; Kugel, K. I.; Sboychakov, A. O.; Streltsov, S. V. Role of Local Geometry in the Spin and Orbital Structure of Transition Metal Compounds. *J. Exp. Theor. Phys.* **2016**, *122*, 484–498.

(42) Liddle, S. T. Molecular Metal-Metal Bonds: Compounds, Synthesis, Properties; Wiley-VCH: New York, 2015.

(43) Paduan-Filho, A.; Chirico, R. D.; Joung, K. O.; Carlin, R. L. Field-Induced Magnetic Ordering in Uniaxial Nickel Systems: A Second Example. J. Chem. Phys. **1981**, 74, 4103–4105.

(44) Khosla, A. L.; Jacko, A. C.; Merino, J.; Powell, B. J. Spin-Orbit Coupling and Strong Electronic Correlations in Cyclic Molecules. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *95*, 115109.

(45) O'Neal, K. R.; Liu, Z.; Miller, J. S.; Fishman, R. S.; Musfeldt, J. L. Pressure-Driven High-to-Low Spin Transition in the Bimetallic Quantum Magnet  $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$ . Phys. Rev. B: Condens. Matter Mater. Phys. **2014**, 90, 104301.

(46) Streltsov, S. V.; Khomskii, D. I. Covalent Bonds Against Magnetism in Transition Metal Compounds. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 10491–10496.

(47) Harland, M.; Poteryaev, A. I.; Streltsov, S. V.; Lichtenstein, A. I. Electronic Correlations and Competing Orders in Multiorbital Dimers: A Cluster DMFT Study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2019**, *99*, 045115.

(48) Nag, N.; Middey, S.; Bhowal, S.; Panda, S. K.; Mathieu, R.; Orain, J. C.; Bert, F.; Mendels, P.; Freeman, P. G.; Mansson, M.; Ronnow, H. M.; Telling, M.; Biswas, P. K.; Sheptyakov, D.; Kaushik, S. D.; Siruguri, V.; Meneghini, C.; Sarma, D. D.; Dasgupta, I.; Ray, S. Origin of the Spin-Orbital Liquid State in a Nearly J = 0 Iridate BaZ<sub>3</sub>nIr<sub>2</sub>O<sub>9</sub>. *Phys. Rev. Lett.* **2016**, *116*, 097205.

(49) Nag, A.; Bhowal, S.; Bert, F.; Hillier, A. D.; Itoh, M.; Carlomagno, I.; Meneghini, C.; Sarkar, T.; Mathieu, R.; Dasgupta, I.; Ray, S. Ba<sub>3</sub>MIr<sub>2</sub>O<sub>9</sub> Hexagonal Perovskites in the Light of Spin-orbit Coupling and Local Structural Distortions. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2018**, *97*, 064408.

(50) Gore, J. G.; Battle, P. D. Structural and Electronic Properties of the Compounds  $Ba_4Ir_3MO_{12}$  (M = Li, Na, Mg, Y, Lu, Zr, and Ce). J. Mater. Chem. **1996**, 6, 201–206.

(51) Shimoda, Y.; Doi, Y.; Wakeshima, M.; Hinatsu, Y. Synthesis and Magnetic Properties of 12-L Perovskites  $Ba_4LnIr_3O_{12}$  (*Ln* = lanthanides). *J. Solid State Chem.* **2009**, *182*, 2873–2879.

(52) Shimoda, Y.; Doi, Y.; Wakeshima, M.; Hinatsu, Y. Magnetic and Electrical Properties of Quadruple Perovskites with 12 Layer Structures  $Ba_4LnM_3O_{12}$  (Ln = rare earths; M R= u, Ir): The Role of Metal-Metal Bonding in Perovskite-related Oxides. J. Solid State Chem. 2010, 183, 1962–1969.

(53) Nguyen, L. T.; Halloran, T.; Xie, W.; Kong, T.; Broholm, C.; Cava, R. J. Geometrically Frustrated Trimer-based Mott Insulator. *Phys. Rev. Mater.* **2018**, *2*, 054414.

(54) Nguyen, L. T.; Cava, R. J. Trimer-based Spin Liquid Candidate Ba<sub>4</sub>NbIr<sub>3</sub>O<sub>12</sub>. *Phys. Rev. Mater.* **2019**, *3*, 014412.

(55) Liao, Y.; Shum, W. W.; Miller, J. S. Synthesis and Magnetic Properties of 3-D  $[Ru_2^{I/III}(O_2CMe)_4]_3[M^{III}(CN)_6]$  (M = Cr, Fe, Co). J. Am. Chem. Soc. **2002**, 124, 9336–9337.

(56) Brinzari, T. V.; Chen, P.; Tung, L.-C.; Kim, Y.; Smirnov, D.; Singleton, J.; Miller, J. S.; Musfeldt, J. L. Magnetoelastic Coupling in  $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$ . Phys. Rev. B: Condens. Matter Mater. Phys. 2012, 86, 214411.

(57) Telser, J.; Drago, R. S. Re-investigation of the Electronic and Magnetic Properties of Ruthenium Butyrate Chloride. *Inorg. Chem.* **1984**, *23*, 3114–3120.