Nonmetallic metal toward a pressure-induced bad-metal state in two-dimensional Cu$_3$LiRu$_2$O$_6$†

Bin Huang,† Ziyi Liu,† Yifeng Han,† Shuang Zhao,† Meixia Wu,† Corey E. Frank,† Martha Greenblatt,‖ Mark Croft,‖ Nicholas F. Quackenbush,‖ Sizhan Liu,‡ Trevor A. Tyson,‡ Lei Zhang,‡ Junliang Sun,‡ Pengfei Shan,‡ Jianhong Dai,‡ Xiaohui Yu,§ Jinguang Cheng § (∗§) and Man-Rong Li † (∗†)

The novel two-dimensional honeycomb layered Cu$_3$LiRu$_2$O$_6$ exhibits Pauli-like paramagnetic and Mott variable range hopping semiconduction behaviors, which contrast the large specific-heat Sommerfeld coefficient for metals, and indicate a possible spin-excitation induced nonmetallic metal. This nonmetallic feature can be significantly suppressed by pressure toward producing a bad-metal state, as reflected by the temperature-dependent resistivity response up to 35 GPa.

Materials based on delafossite modified structures have exhibited interesting physical properties and important applications, such as photocatalytic activity, thermoelectric behavior, use as transparent conductors, and in measurement-based quantum computation. The crystal structure of delafossite ABO$_3$ consists of two-dimensional (2D) edge-sharing BO$_6$ octahedral planes separated by intercalated linear-dumbbell A-cations. It can be modified to A$_2$BO$_3$ or A$_3$A'B$_2$O$_6$-types when intralayer disordering is introduced. Recently, exotic physical phenomena have been manifested in modified delafossites with 4d/5d transition metals at the B-site, particularly because of strong spin–orbit coupling (SOC) that coexists with other competing interactions and geometrical frustration inherent in the honeycomb layers. Mott and metal–insulator transitions have been reported in modestly frustrated A$_2$RuO$_3$ (A = Li, Na), while highly anisotropic Kitaev interactions rooted in the difference in electron configuration and SOC between Ru$^{4+}$ (4d$^1$, S = 1) and Ir$^{4+}$ (5d$^1$, S = 1/2) have been proposed in the iridates Na$_2$IrO$_3$ and Li$_2$IrO$_3$. Exotic low-energy excitations have been observed in the random Kitaev magnet Cu$_3$IrO$_3$. A quantum spin liquid state has, for the first time, been discovered in the quaternary 3R-delafossite A$_3$A'B$_2$O$_6$-type H$_2$LiIr$_2$O$_6$ which suggests that the electronic and magnetic properties of delafossite can be generally tuned by cationic substitution.

In the modified delafossite A$_3$A'B$_2$O$_6$, a higher degree of complication arises when two types of cations are ordered in the triangular layer, as in the quaternary 3R-delafossite A$_3$MB$_2$O$_6$. In comparison with ABO$_3$ delafossite, the lattice disorder in A$_3$MB$_2$O$_6$ disturbs the periodic potential and thus interferes with the electron waves, and makes the materials highly 2D in nature. This scenario can lead to dramatic changes in physical properties, as observed in ruthenate-based modified delafossites, implying that the electronic and magnetic properties of modified delafossites can be refined by substitution of the inter- and/or intra-layer cations, and are worthy of further exploration. In this work, we prepared a novel modified delafossite, Cu$_3$LiRu$_2$O$_6$, via a topoatomic soft chemistry synthesis from Li$_2$RuO$_3$ (Fig. S1, ESI†), and studied its crystal structure, magnetic response, specific heat, and pressure-dependent resistivity in detail.

The crystal structure determination of modified delafossite is challenging due to its complicated layer-stacking fault. Refinements of the synchrotron powder X-ray diffraction (SPXD) data of Cu$_3$LiRu$_2$O$_6$ were carried out in C2/m (no. 12, as in Ag$_2$LiRuO$_6$ and Ag$_2$LiMn$_2$O$_6$) and C2/c (no. 15, as in Cu$_2$LiIr$_2$O$_6$ and Cu$_3$RuO$_3$) respectively. An acceptable goodness of fit was observed in both cases, but the C2/m model gave better agreement overall (Fig. 1, $R_{wp}/R_p =$ 5.65/6.92%) than the C2/c (Fig. S2 [ESI†]), $R_{wp}/R_p =$ 6.82/9.43%) model.

Key Laboratory of Bioorganic and Synthetic Chemistry of Ministry of Education, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, P. R. China. E-mail: limanrong@mail.sysu.edu.cn
Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100871, P. R. China
Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey 08854, USA
Department of Physics and Astronomy, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey 08854, USA
Materials Measurement Science Division, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
Department of Physics, New Jersey Institute of Technology, Newark, New Jersey 07102, USA
College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China
School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, P. R. China
Songshan Lake Materials Laboratory, Dongguan 523808, P. R. China
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Therefore, the C2/m cell \((a = 5.2085(2) \ \text{Å}, \ b = 9.0236(2) \ \text{Å}, \ c = 6.0267(2) \ \text{Å}, \ \beta = 106.59(1)^\circ, \ V = 271.42(2) \ \text{Å}^3, \ z = 2)\) was used to describe the crystal structure of Cu3LiRu2O6. As can be seen in Fig. 1, an asymmetric broad feature (Warren-line shape)\(^{22}\) of the peaks appears around 8–11 degrees, which is characteristic of a 2D structural order with stacking faults in the \(c\) direction, as further corroborated by the streaked diffraction peaks in the selected-area electron diffraction (SAED) patterns (Fig. S3 (ESI))\(^{23}\). The detailed crystallographic parameters, bond valence sums (BVS) calculations, and octahedral distortion parameters \((\Delta)\) are listed in Tables S1 and S2 (ESI). Both BVS (Table S2, ESI)\(^{1}\) and X-ray absorption near-edge spectroscopy (XANES, Fig. S9 and S10, ESI)\(^{†}\) studies imply Ru\(^{4+}\) and Cu\(^{+}\) dominated valence in Cu3LiRu2O6.

Fig. 2 shows the magnetization curves of Cu3LiRu2O6 at different magnetic fields \((H_{\text{bulk}} = 0.1, 1, 5 \ \text{T})\). Unlike the strongly AFM \((T_N \sim 15 \ \text{K})\) spin coupling in Cu3LiIr2O6,\(^{16}\) no evidence for long-range magnetic order or spin freezing was detected down to 2 K in Cu3LiRu2O6; instead the susceptibility remains subtly increased.

The full-range susceptibility can be fitted by the equation \(\chi = \chi_0 + C/(T - \theta)\) with the temperature-independent contribution \(\chi_0\), the Curie–Weiss temperature \(\theta_{\text{CW}}\) and the Curie constant \(C\). A least-squares fit gives \(\chi_0 = 0.0039 \ \text{emu mol}^{-1} \ \text{Oe}^{-1}\), \(\theta_{\text{CW}} = -2.54 \ \text{K}\), and \(C = 0.028 \ \text{K} \ \text{emu} \ \text{mol}^{-1} \ \text{Oe}^{-1}\). From the value of \(C\), the resulting magnetic moment \(\mu_{\text{eff}}\) is 0.47 \(\mu_{\text{B}}\) in Cu3LiRu2O6 in a 0.1 T magnetic field, which is much smaller than the expected free-ion value of 2.83 \(\mu_{\text{B}}\) for Ru\(^{4+}\) (effective \(S = 1\)). It is the electron correlations among the electrons in the narrow \(\pi^*\) conduction band of t2g\(^{1}\) parentage that give rise to such a weak Curie–Weiss term in Cu3LiRu2O6, resembling those of LaNiO\(_3\),\(^{24}\) BaNbO\(_3\),\(^{25}\) and Sr\(_2\)V\(_2\)O\(_6\).\(^{26}\) Note that the molar magnetic susceptibility as a function of the magnetic field was investigated at 2 K, which veers away from a straight line, indicating the presence of ferromagnetic impurities in Cu3LiRu2O6 (inset of Fig. 2a). Thus, as the magnetic field is increased, the susceptibility of Cu3LiRu2O6 is slightly decreased and \(\mu_{\text{eff}}(0.49 \mu_{\text{B}}\text{ when } \mu_0 H = 1 \ \text{T}\) and 0.54 \(\mu_{\text{B}}\text{ when } \mu_0 H = 5 \ \text{T}\)\) is subtly increased.

The temperature dependence of resistivity \(\rho(T)\) under various pressures up to 11 GPa for Cu3LiRu2O6 polycrystalline sample. The inset shows In \(\rho\) versus \(T^{-1/4}\) plots for the \(\rho(T)\) data.

Fig. 3a displays the temperature dependence of specific heat, \(C(T)\), measured at 0 and 8 T. No obvious anomaly can be discerned in the studied temperature range 2–200 K, signaling the absence of a phase transition, in agreement with the magnetic susceptibility results. We found that the \(C(T)\) data in the measured temperature range can be well described by considering one Debye (\(\Theta_D = 287 \ \text{K}\)) and two Einstein modes (\(\Theta_{\text{E}1} = 113 \ \text{K}, \ \Theta_{\text{E}2} = 633 \ \text{K}\)) as illustrated...
by the dotted line. As can be seen, the application of an 8 T external magnetic field has a marginal effect and only modifies $C(T)$ slightly at low temperatures. The $C(T)$ data below 10 K are replotted in Fig. 3b in the form of $C/T$ versus $T^2$, and a linear model $C/T = \gamma + \beta T^2$ was applied to extract the linear specific-heat coefficient $\gamma$ and the Debye temperature $\Theta_D = (12\pi^2nR/5b)^{1/3}$, where $n = 12$ is the number of atoms in the formula unit, and $R = 8.3145$ J mol$^{-1}$ K$^{-1}$ is the ideal gas constant. Interestingly, we observe large linear specific-heat Sommerfeld coefficients $\gamma = 41.7(5)$ and $47.9(4)$ mJ mol$^{-1}$ K$^{-2}$ for 0 and 8 T, respectively, suggesting metallic behavior, which contradicts the VRH semiconducting resistivity behavior shown in Fig. 2b. Although the presence of magnetic Ru$^{4+}$ ions might give rise to a magnetic contribution to specific heat at low temperature, the observation of nearly temperature-independent magnetic susceptibility and the perfect overlap of ZFC/FC for $\chi(T)$ rules out the presence of localized moments and spin-liquid or spin-glass states. In this regard, Cu$_3$LiRu$_2$O$_6$ may belong to the novel family of nonmetallic metals, as reported for Lu$_2$Rh$_2$O$_7$ and FeCrAs, considering their common features.

Nonmetallic metals present three common features: a triangular magnetic lattice and a temperature-independent Pauli paramagnetic response, large Sommerfeld coefficient $\gamma$, and a gap in the density of states (negative slope of the $\rho(T)$ curve). The triangular motifs enable geometric magnetic frustration, which corresponds to the corner-sharing tetrahedral sublattice in the pyrochlore Lu$_2$Rh$_2$O$_7$, the distorted Kagome Cr-network in FeCrAs, and the honeycomb Ru-layer in Cu$_3$LiRu$_2$O$_6$. A hidden spin-liquid state or Hund’s metal behavior is proposed by researchers to explain the nonmetallic metal response in FeCrAs, while inelastic neutron scattering suggests that the high-energy itinerant-like spin excitation accounts for the nonmetallic resistivity in FeCrAs, as also proposed for Lu$_2$Rh$_2$O$_7$. Considering the similarity of the 4d-electron character between Ru and Rh, it is most likely spin excitation that is responsible for the nonmetallic metal behavior in Cu$_3$LiRu$_2$O$_6$, which requires further corroboration from spin dynamic measurements on large single crystals. Alternatively, the presence of a large amount of lattice disorders and grain boundaries can produce potentials which localize the charge carriers with an Anderson localization effect. Here, the Anderson localization scenario seems unlikely due to the absence of large magnetoresistance, or clean signals of non-Fermi-liquid behavior.

For materials with competing ground states, pressure is a powerful tool with which to refine the balance between SOC, Coulomb repulsion, and crystal field interactions for novel phenomena, as observed in layered ruthenates and iridates. Fig. 2b shows $\rho(T)$ measured up to 11 GPa for Cu$_3$LiRu$_2$O$_6$. The resistivity decreases gradually with increasing pressure over the whole temperature range. At RT, the resistivity is $\sim$10 times smaller (0.01(1) $\Omega$ cm) at 11 GPa than that (0.09(1) $\Omega$ cm) at 0 GPa. The resistivity is significantly reduced at lower temperatures and higher pressures, being three orders of magnitude smaller (1.62(1) $\Omega$ cm) at 11 GPa than that at 0 GPa ($\sim$3000 $\Omega$ cm) at 10 K. All observed resistivity behaviors can be well explained by Mott’s VRH mechanism, as shown in the inset to Fig. 2b, where the slope that reflects the Mott activation energy, $T_0$, decreases gradually with increasing pressure. The reduction in $T_0$ with pressure may be attributed to the intrinsic suppression of the band gap under pressure, in addition to an improvement in the grain connection for the studied polycrystalline sample. The schematic temperature-and pressure-dependent resistivity phase diagram is shown in Fig. 4. Apparently, the nonmetallic state in Cu$_3$LiRu$_2$O$_6$ can be strongly suppressed under pressure. However, a true metallic state cannot be achieved up to 35 GPa, the highest pressure in the present study, as shown in the inset to Fig. 4, where resistance ($R$) keeps decreasing at higher pressure (9–28 GPa) but starts to increase when the pressure is above 28 GPa, as discovered in other 4d/5d-transition metal oxides. The temperature-dependent $R$-$T$ plots in the higher-pressure region (inset to Fig. 4) cannot be well fitted or explained by any thermal activation model, indicating that the sample enters a conductive or a bad-metal state. Further investigations are needed to examine whether much higher pressures are required to drive Cu$_3$LiRu$_2$O$_6$ into a true metallic state.

In summary, we have prepared a new modified delafossite-type Cu$_3$LiRu$_2$O$_6$ via a soft topotactic reaction, and extensively characterized its crystal structure and physical properties.
Both magnetic susceptibility and specific heat measurements on Cu$_3$LiRu$_2$O$_6$ demonstrate strong electron correlations, giving temperature-independent Pauli-like paramagnetic behavior and a large Sommerfeld coefficient, γ. However, resistivity measurements show that Cu$_3$LiRu$_2$O$_6$ is insulating at room temperature and follows Mott variable range hopping semiconducting behavior to low temperature. The contradiction suggests that Cu$_3$LiRu$_2$O$_6$ is a nonmetallic metal, probably attributable to spin excitation. Temperature-dependent resistivity measurements up to 35 GPa reveal that the nonmetallic state in Cu$_3$LiRu$_2$O$_6$ can be significantly suppressed by pressure, indicating a possible distortion, as reflected by the differences between Cu$_3$LiRu$_2$O$_6$ radii, electron configuration of the constituent TM, and lattice parameters.

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Conflicts of interest
There are no conflicts to declare.

Notes and references
Supporting Information

Nonmetallic Metal toward Pressure-Induced Bad-Metal State in Two-Dimensional Cu$_3$LiRu$_2$O$_6$

Bin Huang,$^a$ Ziyi Liu,$^b$ Yifeng Han,$^a$ Shuang Zhao,$^a$ Meixia Wu,$^a$ Corey Frank,$^c$ Martha Greenblatt,$^c$ Mark Croft,$^d$ Nicholas F. Quackenbush,$^e$ Sizhan Liu,$^f$ Trevor A. Tyson,$^f$
Lei Zhang,$^g$ Junliang Sun,$^g$ Peifei Shan,$^{b,h}$ Jianhong Dai,$^b$ Xiaohui Yu,$^{b,h,i}$ Jinguang Cheng,$^{b,h,i,*}$ Man-Rong Li$^a,*$

a. Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, P. R. China.
b. Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China
c. Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey 08854, United States.
d. Department of Physics and Astronomy, Rutgers, the State University of New Jersey, 136 Frelinghuysen Road, Piscataway, New Jersey 08854, United States.
e. Materials Measurement Science Division, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States.
f. Department of Physics, New Jersey Institute of Technology, Newark, New Jersey 07102, United States.
g. College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China
h. School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, P. R. China
i. Songshan Lake Materials Laboratory, Dongguan 523808, P. R. China

Email: limanrong@mail.sysu.edu.cn; jgcheng@iphy.ac.cn
1. Method

Synthesis. The preparation of Cu$_3$LiRu$_2$O$_6$ is based on the following topotactic metathesis reaction (Fig. S1):

$$2 \text{Li}_2\text{RuO}_3 + 3 \text{CuCl} \rightarrow \text{Cu}_3\text{LiRu}_2\text{O}_6 + 3 \text{LiCl},$$

where the Li$_2$RuO$_3$ precursor was prepared from a mixture of Li$_2$CO$_3$ (Macklin, 99.99%) and RuO$_2$ (Macklin, 99.95%) with molar ratio of 1.05 : 1 (excess Li$_2$CO$_3$ was added to compensate for Li volatilization at high temperature). The mixture was pressed into a pellet and first heated to 923 K at a rate of 3.5 K/min, held for 48 h, and then to 1173 K at a rate of 4.2 K/min and kept for another 48 h in air without intermediate grinding. Finally, the furnace was cooled to 923 K at the rate of 0.8 K/min before naturally cooling to room temperature (RT). A mixture of CuCl (Alfa Aesar, 99.9%) and as-prepared Li$_2$RuO$_3$ with molar ratio between of 1 : 2.03 to 1: 3.0 was heated at 673 K (heating rate of 1-5 K/min) for 16 h in a quartz tube under vacuum and then cooled to RT at 1-5 K/min. The product was washed five times with ammonium hydroxide (NH$_4$OH, Aladdin, 28%) to remove excess CuCl and then washed twice with deionized water before being dried in an oven at 323 K. Part of the obtained powder was pressed into a dense tablet under 3 GPa of pressure at RT for physical properties measurements.

Chemical and Crystal Structure Characterizations. For phase and purity identification, powder X-ray diffraction (PXD) data were measured with a Rigaku (D-MAX 2200 VPC) instrument with a Cu-Kα radiation source ($\lambda = 1.5418$ Å).
Synchrotron powder X-ray diffraction (SPXD) data were collected at ambient conditions on beamline BL14B (\( \lambda = 0.69004 \, \text{Å} \)) at the Shanghai Synchrotron Radiation Facility (SSRF). The sample was loaded into a 0.5 mm glass capillary and the diffraction data were collected in spinning-mode. The Mythen1K detector system was used for high quality data acquisition, and the wavelength was obtained using an Al\(_2\)O\(_3\) (NIST 676a) standard. Detailed information about beamline BL14B1 has been referenced below.\(^1\)\(^2\) Diffraction data analysis and Rietveld refinement were performed with the Topas-Academic software package.\(^3\) An SDT Q600 (V20.9 Build 20) analyzer was used to perform thermogravimetric analysis (TGA).

Scanning electron microscope and energy disperse spectroscopy (SEM-EDS) were carried out on a Dual beam FIB (Helios nanolab G4 CX, FEI, USA) equipped with a SDD-EDS detector (AZtec X-Max 150, Oxford, UK). Selected area electron diffraction (SAED) was measured on a transmission electron microscope (TEM, JEM-2100) with an accelerating voltage of 200 kV. The X-ray absorption near edge spectroscopy (XANES) was performed at the Brookhaven National Synchrotron Light Source (NSLS-II) using double crystal monochromators with the Ru-L\(_2\), L\(_3\) edges being measured at the 8-BM, TES beamline (with Si-111 crystals) and the Cu-K edges being measured at 6-BM, BMM (with higher resolution, Si-311 crystals). The Cu-K edge data were collected in both the transmission and fluorescence mode with simultaneous standards. Cu-standards run at NSLS-I on beamline X19-A have also been included. Due to the low energy of the Ru-L edges the data was collected in the fluorescence mode with adjacently run standards.
Physical Properties Measurements. The temperature dependent resistivity for a sample of Cu$_3$LiRu$_2$O$_6$ under different pressures was measured with the palm cubic anvil cell (CAC) apparatus up to 11 GPa and diamond anvil cell (DAC) up to 35 GPa. A standard four-probe method was used for the resistivity measurements. Glycerol was employed as the pressure transmitting medium and the pressure values were estimated from the pressure-load calibration curve at RT. Details about the experimental setup for CAC can be found elsewhere.$^4$ Magnetic measurements were performed with a Quantum Design Magnetic Property Measurement System in the temperature range from T = 2 to 300 K. The susceptibility was measured in both field-cooled (FC) and zero-field-cooled (ZFC) modes at magnetic fields between 0.1 and 5 T. The specific heat of Cu$_3$LiRu$_2$O$_6$ was measured with two-tau relaxation method in a PPMS-9T. The sample mass is 2.35 mg and the sample coupling close to 100% has been maintained during the measurements.

2. Composition

The topotactic ion exchange reaction depends largely on experimental conditions such as the mass scale and the cooling rate. Cava et al. prepared Cu$_3$NaIr$_2$O$_6$ via a mixture of Na$_2$IrO$_3$ and CuCl (molar ratio of 1 : 3.1 with mass scale of 0.4 to 2 g) at 400 °C for 24 h in fused silica jacket, followed by oven cooling to RT,$^6$ while Tafti et al. performed the similar synthesis at 350 °C for 16 h (heating and cooling rate of 1 °C/min and mass scale of 0.15 to 0.3 g), but obtained the fully substituted product Cu$_2$IrO$_3$.$^7,^8$ In our case, the title compound can be prepared with a CuCl : Li$_2$RuO$_3$ ratio between 2.03 : 1 and 3
and a mass scale between 0.36 and 1 g at varied heating and cooling rates (1 °C/min - naturally furnace cooling). Attempts to increase the Cu⁺ substitution degree at higher temperatures were unsuccessful and resulted in decomposition (Fig. S4). SEM-EDS measurements were carried out on the as-made sample (hereafter the Li₂RuO₃/CuCl = 1/2.03 batch sample was used for the characterization unless specified) after phase examination by PXD, giving Cu : Ru ratio of 1.4(1):1 (Fig. S5), suggesting a compositional formula of Cu₃LiRu₂O₆ under charge balance. To further confirm the composition and oxygen content, TGA was conducted with a heating rate of 10 K/min from 300 to 873 K in a reducing atmosphere of 1% H₂/Ar gas mixture (Fig. S6). PXD pattern after TGA (Fig. S7) indicates that Cu₃LiRu₂O₆ was reduced to a mixture of Cu and Ru (Li is too light to be observed by PXD), corresponding to a weight (oxygen) loss percentage Δm/m about 19.19(1)%, which coincides well with the expected value (19.36%) of the nominal formula, Cu₃LiRu₂O₆. Had Li been fully replaced by Cu to form Cu₂RuO₃, the weight loss would be expected to be 17.4(1)%.

3. Crystal Structure

The atomic occupancies of Cu1 at 4h sites, Cu2 at 2d sites, O1 at 4i sites, and O2 at 8j sites were close to fully occupied within the standard deviation (no more than 1%) during the refinements, and thus fixed to be unit. The mixed (Li/Ru)1 and (Li/Ru)2 at 4g (0, y, 0) and 2a (0, 0, 0) sites were constrained to be fully occupied to ensure the overall Cu/Li/Ru ratio of 3/1/2 according to the SEM-EDS and TGA analyses. The final atomic occupancy was converged to Ru1/Li1 = 0.718/0.282(6) and Ru2/Li2 =
0.436/0.564(1), respectively. The crystal structure of Cu$_3$LiRu$_2$O$_6$ is shown in **Inset of Fig. 1**, where the Cu atoms are sandwiched between the edge-sharing (Li/Ru)$_1$O$_6$ and (Li/Ru)$_2$O$_6$ octahedral layers along [001] direction. The metal-metal distances between the centroid of octahedra vary from 2.994 to 3.034 Å. Each metal site is surrounded by six nearest metal neighbors in the octahedral layer, forming distorted 2D hexagonal network (**Fig. S8a**, where (Li/Ru)1 and (Li/Ru)2 were denoted as Ru1 and Ru2, respectively). The Ru1-centered hexagon (packed by three-neighboring Ru1 (3.034 Å, 2.994 Å × 2) and three-neighboring Ru2 (3.014 Å × 2, 2.995 Å)) is less regular than the Ru2-centered one (six Ru1 with Ru2-Ru1 of 3.014 Å × 4 and 2.995 Å × 2). The hexagonal network in the alternative Cu-layers displays similar (**Fig. S8b**) connections, where the Cu-Cu distance varies between 2.910 and 3.203 Å. Geometrically, the anisotropic Cu-Cu distance is correlated to the O-Cu-O bond angles, in which O1-Cu2-O1 is in linear dumbbell-arrangement (180.0(4)°), while that of O1-Cu2-O1 is bent to be 177.9(5)°.

**4. XANES**

XANES is a useful tool for locally probing the valence states at atomic sites in solids. The L$_{2,3}$ edges of 4d transition metals (TM) are dominated by intense “white line” (WL) features due to dipole transitions into final 4d states (see in **Fig. S9a**). One signature of increasing TM-valence states (decreasing d-count) is the chemical shift of the centrum of the WL-feature to higher energy. In **Fig. S9a** the chemical shift in Cu$_3$LiRu$_2$O$_6$ is very clearly lower than that of the Ru$^{5+}$ standard Sr$_2$YRuO$_6$ and is quite
comparable to that of the Ru$^{4+}$ standard Y$_2$CoRuO$_6$, supporting a Ru$^{4+}$ state in Cu$_3$LiRu$_2$O$_6$.

A second, more prominent, signature of TM-valence/d-configuration lies in the systematic evolution of the prominent bimodal A/B - the structure of the L$_{2,3}$ WL-features for octahedrally coordinated TM-O compounds as illustrated for 4d$^0$-4d$^4$ materials in Fig. S10a and b. This bimodal A (t$_{2g}$-hole related)/B (e$_g$-hole related) structure reflects the octahedral O-coordination ligand field (LF), splitting of the d-states, into a lower energy, 6-fold, t$_{2g}$ and higher energy, 4-fold, e$_g$ multiplets. This LF splitting is most clearly illustrated in the d$^0$ standard compound spectra shown in Fig. S10. The systematic filling of the t$_{2g}$ orbitals with increasing 4d-orbital-count (decreasing final state hole-count) clearly leads to a systematic decrease of the A-feature (t$_{2g}$-hole coupled) intensity (see Fig. S10) for a series of compounds spanning d$^0$-d$^4$. Referring to Fig. S9a the relative A-feature Ru-L$_{3,2}$ intensities of Cu$_3$LiRu$_2$O$_6$ are very substantially reduced below those of the Sr$_2$YRuO$_6$, d$^3$-Ru$^{5+}$ standard and are comparable to the Y$_2$CoRuO$_6$ d$^4$-Ru$^{4+}$ standard. Thus, the Ru-L$_{3,2}$ spectral feature structure of the Cu$_3$LiRu$_2$O$_6$ spectrum further supports the d$^4$-Ru$^{4+}$ configuration/valence in this compound.

The near edge features at the K-edges of 3d row transition-metal (TM(3d)) compounds are due to transitions from the 1s to 4p states, combined with a step feature for the continuum onset, multiple 4p features associated with different local ligand coordination, mixed 3d configurations, differing orbital orientations, and complicate near edge structure. Nevertheless, the systematic energy shifts in the TM(3d) K edges
and doping/chemical changes can serve as indicators of charge transfer.\textsuperscript{10,11} The Cu-K near edge of Cu\textsubscript{3}LiRu\textsubscript{2}O\textsubscript{6} was compared to various standard compound spectra in Fig. S9b. Both the structure and the chemical shifts of the near edge structure are sensitive to the valence and local atomic environment. Specifically, Fig. S9b displays Cu-K edge of a series of standard Cu compounds with varying formal valences and Cu-O coordination: Cu\textsuperscript{+}, Cu\textsubscript{2}O with linear 2-fold coordination;\textsuperscript{12} the \textasciitilde Cu\textsuperscript{2+} square planar coordinated CuO and the perovskite based La\textsubscript{2}CuO\textsubscript{4}.\textsuperscript{13} Before proceeding, it should be reiterated that the layered crystal structure of Cu\textsubscript{3}LiRu\textsubscript{2}O\textsubscript{6} involves: honeycomb hexagonal planes of edge sharing RuO\textsubscript{6} octahedra with a 6-coordinate Li in the center of the hexagon (Fig. S8a); a plane of linear O-Cu-O moieties is located between the honeycomb layers (seen in Fig. 1). The linear O-Cu-O sites are closely resembled the geometry in the Cu\textsuperscript{+} standard Cu\textsubscript{2}O. The striking similarity of the edge-onset spectrum of Cu\textsubscript{3}LiRu\textsubscript{2}O\textsubscript{6} to that of Cu\textsubscript{2}O (seen in Fig. S9b) is a solid confirmation of both the Cu\textsuperscript{+} state and the linear O-Cu-O structure in this material.
**SUPPLEMENTARY FIGURES**

**Fig. S1** Topotactic reaction of precursor Li$_2$RuO$_3$ and CuCl to form ruthium containing honeycomb delafossites Cu$_3$LiRu$_2$O$_6$
**Fig. S2** Rietveld refinement of the SPXD data for Cu$_3$LiRu$_2$O$_6$ in C2/c structure at RT.

**Fig. S3** SAED patterns in the [1T10] reciprocal lattice plane for Cu$_3$LiRu$_2$O$_6$. 
**Fig. S4** PXD patterns for Cu$_3$LiRu$_2$O$_6$ at different temperature.

**Fig. S5** SEM-EDS image of Cu$_3$LiRu$_2$O$_6$. 
Fig. S6 TGA result in 1% H$_2$/Ar from 300 to 873 K.

Fig. S7 PXD patterns for Cu$_3$LiRu$_2$O$_6$ after TGA in 1% H$_2$/Ar.
Fig. S8 The crystal structure of Cu$_3$LiRu$_2$O$_6$ from the refinements of SPXD (a) Hexagonal network of the (Ru/Li)$_1$ (denoted as Ru1) and (Ru/Li)$_2$ (denoted as Ru2) layer. (b) Hexagonal network of the Cu-layer alternatively stacked with the Li/Ru later along [001] direction.

Fig. S9 (a) comparison of the Ru-L$_3$ edge spectra for Cu$_3$LiRu$_2$O$_6$ to the Sr$_2$YRuO$_6$ and Y$_2$CoRuO$_6$ standards (lower left) along with the Ru-L$_2$ edge spectra for the same compounds (inset upper right). Note the A- and B-features related respectively to transitions into empty t$_{2g}$ and e$_g$ final states. (b) Cu-K edge of Cu$_3$LiRu$_2$O$_6$ compared to those of standard compounds: Cu$^{1+}$, Cu$_2$O; and ~Cu$^{2+}$, La$_2$CuO$_4$. 
Fig. S10 The systematic TM-L₃ (a) and L₂ (b) edge WL-feature variation with 4d-electron (hole) count from d⁰ to d⁴ (10 to 6).¹⁴⁻²² Note: the bimodal A/B structure corresponding to transitions into t₂g/e₈ final states respectively; and the systematic
decrease in A-feature spectral intensity (relative to the B-feature) with increasing \( t_{2g} \)-electron count (decreasing hole count). These spectra were mostly collected on NSLS beamline X19A in the total electron yield mode where the short sampling depth minimized self-absorption effects that are sizable in fluorescence mode measurements in this energy range.

SUPPLEMENTARY TABLES

Table S1. Structural parameters of \( \text{Cu}_3\text{LiRu}_2\text{O}_6 \). Refined from the SPXD data collected at RT.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ.</th>
<th>B(Å²)</th>
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<tr>
<td>Ru1</td>
<td>4g</td>
<td>0</td>
<td>0.332(1)</td>
<td>0</td>
<td>0.718(3)</td>
<td>0.84(13)</td>
</tr>
<tr>
<td>Li1</td>
<td>4g</td>
<td>0</td>
<td>0.332(1)</td>
<td>0</td>
<td>0.282(3)</td>
<td>0.84(13)</td>
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<tr>
<td>Ru2</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.436(6)</td>
<td>0.80(27)</td>
</tr>
<tr>
<td>Li2</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.564(6)</td>
<td>0.80(27)</td>
</tr>
<tr>
<td>Cu1</td>
<td>4h</td>
<td>1/2</td>
<td>0.322(1)</td>
<td>1/2</td>
<td>1</td>
<td>3.59(4)</td>
</tr>
<tr>
<td>Cu2</td>
<td>2d</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
<td>3.59(4)</td>
</tr>
<tr>
<td>O1</td>
<td>4i</td>
<td></td>
<td>0.427(4)</td>
<td>0</td>
<td>0.163(3)</td>
<td>1</td>
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<tr>
<td>O2</td>
<td>8j</td>
<td></td>
<td>0.416(3)</td>
<td>0.319(2)</td>
<td>0.168(2)</td>
<td>1</td>
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*Monoclinic, space group C2/m (No. 12), a = 5.2085(2) Å, b = 9.0236(2) Å, c = 6.0267(2) Å, β = 106.59(1)°, V = 271.42(2) Å³, Z = 2, Rw% = 5.65, Rp% = 6.92.

**Table S2.** Selected interatomic distances(Å), bond angles(°), and BVS of Cu₃LiRu₂O₆ at RT.

<table>
<thead>
<tr>
<th>MO₆/MO₂</th>
<th>Cu₃LiRu₂O₆</th>
<th>-O1</th>
<th>-O2</th>
<th>&lt;M-O&gt;</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Li/Ru)1</td>
<td>1.904(1) × 2</td>
<td>2.116(1) × 2</td>
<td>1.818(1) × 2</td>
<td>1.946(1)</td>
<td>3.846(1)</td>
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<tr>
<td>(Li/Ru)2</td>
<td>2.159(1) × 2</td>
<td>2.036(1) × 4</td>
<td>2.077(1)</td>
<td>2.029(1)</td>
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<tr>
<td>Cu1</td>
<td>1.925(1) × 2</td>
<td>1.925(1)</td>
<td>0.854(1)</td>
<td></td>
<td></td>
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<tr>
<td>Cu2</td>
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<td>1.957(1)</td>
<td>0.783(1)</td>
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<td></td>
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</tbody>
</table>

Δ(Li/Ru)₁ = 4.14 × 10⁻³; Δ(Li/Ru)₂ = 0.779 × 10⁻³

<table>
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<th>Angle</th>
<th>Value</th>
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<td>&lt;O-(Li/Ru)₁-O&gt;</td>
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<tr>
<td>&lt;O-(Li/Ru)₂-O&gt;</td>
<td></td>
</tr>
<tr>
<td>&lt;O-Cu-O&gt;</td>
<td></td>
</tr>
<tr>
<td>&lt;Li/Ru-O-Cu/Ru&gt;</td>
<td></td>
</tr>
<tr>
<td>O1-</td>
<td>O1-</td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
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<tr>
<td>(Li/Ru)1</td>
<td>74.4(4)</td>
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<td>O1</td>
<td>-O1</td>
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<td>(Li/Ru)2</td>
<td>180.0(4)</td>
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<td>O1</td>
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<td>72.9(3)</td>
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<td>(Li/Ru)1</td>
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<tr>
<td>81.1(3)</td>
<td>93.9(3)</td>
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<tr>
<td>(Li/Ru)2</td>
<td>-O2</td>
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<tr>
<td>93.9(3)</td>
<td>173.4(4)</td>
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<tr>
<td>-O2-</td>
<td>(Li/Ru)1</td>
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<tr>
<td>O1-</td>
<td>O1-</td>
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<tr>
<td>(Li/Ru)1</td>
<td>87.9(4)</td>
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<td>O1</td>
<td>-O2</td>
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<tr>
<td>(Li/Ru)2</td>
<td>83.5(3)</td>
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<tr>
<td>O2-</td>
<td>O2</td>
</tr>
<tr>
<td>-O2-</td>
<td>O2</td>
</tr>
<tr>
<td>(Li/Ru)1</td>
<td>-O2</td>
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</table>

References