Synthesis and Magnetic Properties of the KCu(IO₃)₃ Compound with [CuO₅]∞ Chains

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ABSTRACT: The new quaternary iodate KCu(IO₃)₃ has been prepared by hydrothermal synthesis. KCu(IO₃)₃ crystallizes in the monoclinic space group P2₁/n with unit cell parameters a = 9.8143(4) Å, b = 8.2265(4) Å, c = 10.8584(5) Å, β = 91.077(2)°, and z = 4. The crystals are light blue and translucent. There are three main building units making up the crystal structure: [KO₁₀] irregular polyhedra, [CuO₅] distorted octahedra, and [IO₃] trigonal pyramids. The Jahn–Teller elongated [CuO₅] octahedra connect to each other via corner sharing to form [CuO₅]∞ zigzag chains along [010]; the other building blocks separate these chains. The Raman modes can be divided into four groups; the lower two groups into mainly lattice modes involving K and Cu displacements and the upper two groups into mainly bending and stretching modes of [IO₃E], where E represents a lone pair of electron. At low temperatures, the magnetic susceptibility is characterized by a broad maximum centered at ~5.4 K, characteristic for antiferromagnetic short-range ordering. Long-range magnetic ordering at T_C = 1.32 K is clearly evidenced by a sharp anomaly in the heat capacity. The magnetic susceptibility can be very well described by a spin S = 1/2 antiferromagnetic Heisenberg chain with a nearest-neighbor spin exchange of ~8.9 K.

INTRODUCTION

Compounds comprising a p-element cation (L) such as Se⁴⁺, Te⁴⁺, or I⁺ with a sterically active lone electron pair (E) have been attracting increasing interest due to their rich chemistry, which can yield new compounds that often show low-dimensional physical properties. Other typical lone-pair elements, e.g., Pb²⁺ and Bi³⁺, often exhibit less steric activity and have higher coordination numbers. To tune physical properties such as geometric magnetic frustration, semiconducting properties, or second harmonic generation (SHG), the relation between structural characteristics and physical properties is of utmost importance.

Due to the volume occupied by the lone-pair electrons, the L-cations adopt one sided coordination, most often [LO₃] trigonal pyramids or [LO₄] see-saws. By including the lone pair, i.e., forming [LO₅E], the coordination polyhedron becomes a distorted tetrahedra or a trigonal bipyramid for [LO₅E]. It is common that the lone pairs help to open up the crystal structures, and such compounds are often layered with only weak van der Waal interactions between the layers, or they form three-dimensional framework structures comprising open voids where the lone pairs reside. When such compounds contain transition metals, they are very often arranged in the form of chains or layers.

Iodine in the oxidation state +5 adopts a distorted tetrahedral [IO₃E] coordination where the lone pairs help to open up the structure and increase the chances to form non-centrosymmetric crystal structures. Iodates have been mainly studied for their optical properties, and several are SHG active such as the oxides Bi₂(IO₄)(IO₃)₃, BiO(IO₃), and BaZr(IO₃)₆, as well as the oxohalides Bi₂Te(IO₃)OCl, Bi(IO₃)F₂, and Bi₂OF₃(IO₃)₆. Several iodate compounds containing an alkali metal have also proved to be SHG active, such as, e.g., A₂Bi₂O₁₅ (A = K or Rb⁺), A₂Au(IO₃)₄ (A = Na, Rb, Cs), KSB₃O₁₅, K₃Au(IO₃)₃, A₄Pt(IO₃)₆ (A = Na, K, Rb, Cs), K₅Ti(IO₃)₆ (A = Li, Na), and Na₂Sn(IO₃)₆. Some few compounds belonging to the A–M–I₅⁺ O system (M = transition metal) have been previously described. One such example is K₃M₂(IO₃)₄(H₂O)₂ (M²⁺ = Co²⁺, Mn²⁺, Zn²⁺, Mg²⁺) reported by Li et al.
In this study, the new compound KCu(IO₃)₃ is presented together with its magnetic and vibrational properties. KCu(IO₃)₃ has been characterized by Raman scattering, electron paramagnetic resonance (EPR), magnetic susceptibility and heat capacity measurements.

**Experimental Section**

Light blue orthorhombic single crystals of the new compound KCu(IO₃)₃ have been synthesized hydrothermally from 0.101 g (1 mmol) of CuF₂ (Aldrich, 99.9%) and 0.642 g (3 mmol) of KIO₃ (Alfa Aesar, 98%). The starting materials were mixed with 3 mL of deionized water in a 23 mL Teflon-lined autoclave. The autoclave was heated to 230 °C and maintained there for 72 h and subsequently cooled to room temperature with a cooling rate of ca 21 °C/h. The pH was ca 5 at the start of synthesis, and the size of the resulting crystals was mainly in the range 30–100 μm, with some crystals up to 250 μm in size. The synthesis product was rinsed in warm water and ethanol before drying. This treatment removed minor remnants of unreacted starting materials, mainly KIO₃. After this treatment, the yield was close to 100%. It was found that lowering the pH to ca 1 by the addition of HF resulted in smaller crystals and more unreacted starting materials and increasing the pH to above 10 by adding KOH did not result in the target phase at all. Smaller crystallites with less developed crystal faces were obtained if the plateau temperature or the dwell time at the plateau were reduced. In addition, a faster cooling rate resulted in less well-developed crystals.

The crystal structure of KCu(IO₃)₃ was solved from the single-crystal data collected on a Bruker D8 Venture diffractometer using a Mo Kα radiation; λ = 0.71073Å. The integration of the Bragg reflections and the absorption correction was done with software SAINT26 and SADABS,27 respectively, provided by the diffractometer manufacturer; additional absorption correction was done with the software Jana 2006.28 The structure was solved by dual space methods using the software SHELXT-2014/729 and re

**Results and Discussion**

**Crystal Structure of KCu(IO₃)₃.** Light blue translucent single crystals of KCu(IO₃)₃ crystallize in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 9.8143(4)$ Å, $b = 8.2265(4)$ Å, $c = 10.8584(5)$ Å, and $β = 91.077(2)^°$. Crystal structure data and refinement parameters are presented in Table 1. In the crystal structure, there is one crystallo-

### Table 1. Crystal Data and Refinement Parameters for KCu(IO₃)₃

| parameter                  | value                |
|----------------------------|----------------------|
| empirical formula          | KCu(IO₃)₃            |
| formula weight             | 627.34               |
| temperature (K)            | 293(2)               |
| wavelength (Å)             | 0.71073              |
| crystal system             | monoclinic           |
| space group                | $P2_1/n$             |
| $a$ (Å)                    | 9.8143(4)            |
| $b$ (Å)                    | 8.2265(4)            |
| $c$ (Å)                    | 10.8584(5)           |
| $β$ (°)                    | 91.077(2)°           |
| volume (Å³)                | 876.52(7)            |
| Z                          | 4                    |
| density calc (g/cm³)       | 4.754                |
| F(000)                     | 1116                 |
| crystal color              | light blue           |
| crystal habit              | orthorhombic         |
| crystal size (mm)          | 0.15 × 0.20 × 0.10   |
| theta range for data collection (°) | 2.77–73.41 |
| index ranges               | –19≤ h ≤ 19          |
|                         | –10 ≤ k ≤ 22         |
|                         | –19 ≤ l ≤ 19         |
| reflections collected      | 19650                |
| independent reflections    | 8323 [R(int) = 0.040] |
| data/restraints/parameters | 8323/0/128           |
| refinement method         | full-matrix least square refinement on F² |
| goodness-of-fit on F²     | 1.248                |
| final R indices            | $R_1 = 0.0362$       |
|                         | $\sum(w(Fo^2) - Fc^2)]/\sum(w(Fo^2))^{1/2} = 0.0943$ |
| R indices all data        | $R_1 = 0.0449$       |
|                         | $\sum(w(Fo^2) - Fc^2)]/\sum(w(Fo^2))^{1/2} = 0.0943$ |
| highest peak/deepest hole | 3.51/–2.61           |

The crystal structure of KCu(IO₃)₃ was solved from the single-crystal data collected on a Bruker D8 Venture diffractometer using a Mo Kα radiation and a Raman microscope (LabRam HR800, Horiba) at ambient conditions. Light polarization was chosen as parallel (xx) and crossed (xy) polarizations.

The temperature and magnetic field dependence of the magnetic susceptibilities was measured with a SQUID magnetometer (Quantum Design, MPMSX7) on a powder sample. Heat capacity measurements on a powder sample were performed in a physical property measurement system (Quantum Design, PPMS) equipped with a ⁴He closed-cycle refrigerator. The sample was mixed with Apiezon M vacuum grease to ensure thermal equilibration. The heat capacities of the calorimeter plate and the vacuum grease were determined in a preceding measurement and subsequently subtracted to obtain the total heat capacity of the sample. Electron spin resonance spectra were collected with a X-band spectrometer (Bruker, EMX control unit, EMXpremiumX bridge, ERC73 magnet) on the same sample on which magnetic susceptibility was taken from.

There are three main building units combined in the crystal structure: irregular [KO₁₀] polyhedra, Jahn–Teller distorted [CuO₆] octahedra, and [IO₃] trigonal pyramids. To deduce the coordination number for K⁺ in the structure, the operational definition by Brown30 was used where a ligand contributes at least 4% of the valence of the central cation. This
The maximum primary bond distance value is 3.3229 Å for K−O. There are ten K−O distances found in the range 2.678(2)−3.303(2) Å (Supporting Information). These oxygen atoms can then all be considered to belong to the primary coordination sphere around the K+ ions building the distorted [KO10] polyhedral displayed in Figure 1.

The Jahn-Teller distorted [CuO6] octahedra connect to each other via corner sharing to form [CuO5]∞ zigzag chains along [010] (Figures 2 and 3). The Cu−O distances are in the range 1.956(2)−2.236(4) Å, and the I−O bond distances are in the range 1.778(2)−1.95(3) Å;25 thus, they are comparable to the K−O, Cu−O, and I−O distances observed in the present compound KCu(IO3)3.

Several compounds have previously been described in the K+−M2+−I5+−O system. The metal (M2+) cations in the crystal structure of those metal iodates K2M(IO3)4(H2O)2 (M = Mn, Co, Zn, Mg) adopt octahedral coordination; the I5+ ions have a typical one-sided trigonal pyramid coordination and K+ has a coordination number of eight. The K−O bond distance for these compounds range between 2.70(1) and 3.20(1) Å, the M2+−O distances are in the range 2.018(9)−2.236(4) Å, and the I−O bond distances are in the range 1.782(9)−1.88(1) Å;25 thus, they are comparable to the K−O, Cu−O, and I−O distances observed in the present compound KCu(IO3)3.

Raman Scattering. Each 4e Wyckoff position of the P2₁/n (#14) monoclinic structure leads to 3Ag, 3Bg, 3Au, and 3Bu modes.36 The former two are Raman active, with Ag showing only diagonal and Bg showing only nondiagonal tensor elements. The latter two are IR active. As a sum, 42Ag + 42Bg = 84 Raman active modes may be observed in parallel and crossed polarizations, respectively.

In Figure 6, we show a representative room-temperature Raman spectrum in (xx) polarization, with x parallel to the crystallographic b axis. Approximately 40 modes are observed in this polarization, in good agreement with the expected number of modes. Some maxima are only resolved as shoulders of larger-intensity modes.

The frequency distribution of Raman modes can be separated into four groups, rationalized by the separation of high-frequency fundamental vibrational modes from the low-
frequency collective lattice modes as well as the differentiation given by binding strength and distortions of the structural constituents. Modes within the groups mainly share the linewidth and frequency splitting. The groups are proposed to distribute in the frequency ranges 40–180, 200–260, 270–480, and 650–850 cm⁻¹. A zoom into the low-frequency data in the inset shows that there exist characteristic frequency splittings. These are approximately 10, 20, and 7 cm⁻¹ for the first three groups. These frequency separations are attributed to the characteristic binding energies of the local coordinations involved in the vibrations and the Jahn–Teller distortions.

We attribute the lower two groups to mainly the lattice modes involving I, K, and Cu displacements and the upper two groups to mainly the bending and stretching modes of [IO₃E]. This is in agreement with previous phonon studies on M(IO₃)₂, with M = Ni, Mn, Co, and Zn and related compounds, as well as systematic tables of vibrational frequencies.

Especially [IO₃E] is expected to show phonon fingerprints as a function of coordination. IO₃ with an octahedral coordination leads to Raman bands at 750 cm⁻¹ with a shift of 15 cm⁻¹ to higher frequencies for a regular octahedron. Examples can be found in M((IO₃)₂) with M = Ni, Mn, Co, and Zn. With distortions up to a pyramidal IO₃⁻, further related modes exists with frequencies up to 800 cm⁻¹. These correspond to the symmetric and asymmetric stretching vibrations. In contrast, fundamental bending modes of IO₃ and [IO₃E] are expected in the frequency regime of group 3 modes. Corresponding literature values are in the range 300–450 cm⁻¹.

Thermal and Magnetic Properties of KCu(IO₃)₃. At low temperatures, the magnetic susceptibility of KCu(IO₃)₃ (Figure 7) is characterized by a broad maximum centered at ~5.4 K, characteristic for an antiferromagnetic short-range ordering in a low-dimensional magnetic system. At higher temperatures, the susceptibility follows an extended Curie–Weiss law (see the inset in Figure 7) according to

\[ \chi_{\text{mol}}(T) = \frac{C}{T - \theta_{\text{CW}}} + \chi_0 \]

with a Curie–Weiss temperature \( \theta_{\text{CW}} = -4.5(1) \) K, indicating a predominant antiferromagnetic spin-exchange interaction. The Curie–Weiss constant \( C \) is given by

\[ C = \frac{N_A g^2 \mu_B^2 S(S + 1)}{3k_B} \]

where \( N_A \) denotes Avogadro’s constant and \( k_B \) is the Boltzmann constant, \( \mu_B \) is the Bohr magneton, and \( g \) is the g-factor. For Cu²⁺ cations with a 3d⁹ electronic configuration, the spin \( S \) amounts to 1/2, \( \chi_0 \) takes care of a temperature-independent contribution to the magnetic susceptibility, which is a sum of diamagnetic contributions from the electrons in the closed shells and a van Vleck contribution. The diamagnetic contribution can be estimated from the respective elements in their appropriate oxidation state using the increments from Selwood’s table.38 They add up to \(-174 \times 10^{-6} \) cm³/mol. The van Vleck contribution for Cu²⁺ cations depends on the direction of the magnetic field with respect to the crystal axes, and it typically amounts to approximately \( 100 \times 10^{-6} \) cm³/mol.39 The fit of the inverse magnetic susceptibility data between 20 and 200 K resulted in a g-factor of \( g = 2.21(3) \), typical for Cu²⁺ powder samples, and a temperature-independent susceptibility contribution of \( \chi_0 = +85(2) \times 10^{-6} \) cm³/mol. The g-factor was independently determined from electron paramagnetic resonance (EPR) spectroscopy measurements on the same powder sample on which the susceptibility data were measured. Figure 8 displays the room-temperature EPR spectrum collected at a frequency of 9.4873 GHz. One observes a spectrum typical for a powder with Cu²⁺ entities in a Jahn–Teller elongated environment with g-factors \( g_1 > g_{12} \) where \( g_i \) denotes the gyromagnetic ratio with the magnetic

![Figure 6. Raman spectrum in (xx) polarization at \( T = 295 \) K with an axis break from 525 to 650 cm⁻¹. Bars highlight the grouping of the modes. The insets zoom into the data of the first and third group.](image)

![Figure 7. Molar magnetic susceptibility of KCu(IO₃)₃ (black circles). The red solid line represents a fit to the theoretical results of a spin \( S = 1/2 \) Heisenberg chain with a uniform antiferromagnetic nearest-neighbor spin exchange of 8.90(5) K with a g-factor of 2.204(2) and a temperature-independent contribution of 103(10) \( \times 10^{-6} \) cm³/mol. The inset displays the inverse molar susceptibility with a fit to an extended Curie–Weiss law for a spin \( S = 1/2 \), a g-factor of 2.21(3), a Curie–Weiss temperature, \( \theta_{\text{CW}} \), of ~4.5(1) K, and a paramagnetic temperature-independent contribution of 85(2) \( \times 10^{-6} \) cm³/mol.](image)

![Figure 8. X-band \( (\nu = 9.480 \) GHz) room-temperature EPR powder spectrum of KCu(IO₃)₃ (blue circles). The red solid line is a fit assuming an axial symmetry of the g-tensor, with the two principal values \( g_1 \) and \( g_{12} \).](image)
field aligned parallel to the z-axis and $g_{1,2}$ the g-factors perpendicular to the z-axis.\(^3\)

For the simplicity of simulation, we have assumed an axial symmetry, i.e., $g_1 = g_3 = g_L$ and a linewidth being independent of the orientation of the field with respect to the principal axes of the g-tensor. There are six different Cu-to-O distances in the primary coordination sphere around the Cu cations. They are grouped into four $\leq 1.993(3)$ Å and two $\geq 2.344(3)$ Å (Supporting Information).

Because of a rather large linewidth of about 120 Oe, further details of the spectrum could not be resolved and we used a program to fit the spectrum following the formalism given by Pilbrow.\(^44\)

The red solid line in Figure 8 displays a fit of the room-temperature powder EPR spectrum of KCu(IO\(_3\))\(_3\) with principal g-factors, $g_0 = 2.282(2)$ and $g_\perp = 2.163(2)$, implying a powder-averaged g-factor for the magnetic susceptibility of

$$g_{\text{pow}} = \sqrt{\frac{1}{3} (g_\parallel^2 + 2g_\perp^2)} = 2.203(3)$$

which is in good agreement with the g-factor determined from the susceptibility measurements.

The low-temperature magnetic susceptibility could be successfully fitted assuming a spin $S = 1/2$ Heisenberg chain with a uniform nearest-neighbor spin-exchange interaction, $J_{\text{intra}}$, described by the Hamiltonian

$$\mathcal{H} = J_{\text{intra}} \sum_i S_i S_{i+1}$$

The magnetic susceptibility of the $S = 1/2$ Heisenberg chain with an antiferromagnetic nearest-neighbor spin-exchange interaction has been calculated by transfer-matrix density-matrix renormalization group and Quantum Monte Carlo calculations to high precision. Johnston et al. encoded these data into a Padé approximant that has been used here to fit the experimental data.\(^5\) In the least-squares fits, we added again a temperature-independent susceptibility $\chi_0$ and varied the g-factor and the intrachain spin exchange $J_{\text{intra}}$. Figure 7 (main frame) displays the best fit, which was achieved by the following parameters: $g = 2.204(5)$, $J_{\text{intra}} = 8.90(5)$ K, and $\chi_0 = 100(12) \times 10^{-6}$ cm\(^3\)/mol.

The g-factor is in very good agreement with the EPR data, $\chi_0$ is consistent with the value obtained from the fit of the inverse susceptibility but somewhat larger than what might be expected from the estimate of the diamagnetic and van Vleck contribution for a Cu\(^{2+}\) cation in a distorted octahedral environment (see above).

Assuming a linear chain with $z = 2$ nearest neighbors, the Curie–Weiss temperature can be calculated according to

$$\theta_{\text{CW}} = -\frac{1}{3} S(S+1) J_{\text{intra}} = 4.45(3) \text{K}$$

(5)

matching well the value for $\theta_{\text{CW}}$ found from the fit of the magnetic susceptibility.

Due to interchain spin exchange, $J_{\text{inter}}$, long-range magnetic ordering sets in at $T_C = 1.32(2)$ K, as is clearly evidenced by a sharp anomaly in the heat capacity (Figure 9a (inset)). The interchain spin exchange can be estimated using the relation in eq 6.\(^46\)

$$J_{\text{inter}} = \frac{T_C}{1.28 \sqrt{\ln(SJ_{\text{intra}}/T_C)}} \approx 0.5 \text{ K}$$

(6)

Figure 9. (a) Magnetic contribution, $C_{\text{mag}}(T)/T$, to the heat capacity of KCu(IO\(_3\))\(_3\) (black circles). The red solid line represents the heat capacity of a spin $S = 1/2$ Heisenberg chain with a uniform antiferromagnetic nearest-neighbor spin exchange of 8.71(2) K. The inset displays the total heat capacity. The blue dashed line indicates the lattice contribution to the heat capacity, which has been subtracted from the total heat capacity. The lattice contribution was approximated by a polynomial, $C_{\text{latt}}(T) = \beta T^3 + \delta T^5$, with coefficients $\beta$ and $\delta$ given in the text. (b) Temperature dependence of the magnetic entropy obtained by integrating $C_{\text{mag}}(T)/T$ (black circles). The inset shows the magnetic entropy next to the Neel temperature marked by the vertical red arrow. About 12% of the magnetic entropy is recovered below the Neel temperature.

Above the sharp anomaly, short-range order magnetic contributions to the heat capacity generate a broad maximum centered at $\sim 4.5$ K. Toward higher temperatures, the lattice contribution to the heat capacity becomes dominant and the magnetic contributions are difficult to discern. The magnetic contribution to the heat capacity was analyzed assuming that the total heat capacity is a sum of a lattice contribution, $C_{\text{latt}}(T)$, which is approximated by a power series

$$C_{\text{latt}}(T) = \beta T^3 + \delta T^5$$

(7)

with adjustable coefficients $\beta$ and $\delta$ and a magnetic contribution, $C_{\text{chain}}$, which above $T_C$ was approximated by the heat capacity of a spin $S = 1/2$ Heisenberg chain with a uniform nearest-neighbor spin-exchange interaction, $C_{\text{chain}}(T)$. The total heat capacity was subsequently fitted to

$$C_{\text{tot}}(T) = C_{\text{chain}}(T) + \beta T^3 + \delta T^5$$

(8)

where the Padé approximation by Johnston et al.\(^45\) was used for $C_{\text{chain}}(T)$.

Figure 9a (inset) displays the fit of the total heat capacity between 2 and 20 K. The main frame in Figure 9a shows the magnetic contribution to the heat capacity, $C_{\text{chain}}(T)/T$, obtained after subtraction of the lattice contribution together with a fit to the Padé approximant for the $S = 1/2$ Heisenberg chain. The nearest-neighbor spin-exchange parameter obtained from this fit amounts to $J_{\text{intra}} = 8.71(9)$ K, in best agreement with the exchange parameter derived from the susceptibility data (see above).

The magnetic entropy released during magnetic short- and long-range order, shown in Figure 9b, was obtained by integrating $C_{\text{chain}}(T)/T$ versus $T$. The total entropy comes
close to $R \ln 2$ expected for the ordering of a spin $S = 1/2$ system. About 12% of the entropy is released by the long-range ordering below $T_C = 1.32$ K. The coefficient $\beta$ is related to the Debye temperature $\theta_{\text{Debye}}(T \to 0)$ via eq 9

$$\beta = n^2/S \pi^3 R^1/\theta_{\text{Debye}}^3$$

where $R$ is the molar gas constant and $n = 14$ is the number of atoms per formula unit. Using the fitted parameter for $\beta$, the Debye temperature becomes $\theta_{\text{Debye}}(0) = 225(1)$ K.

In summary, the magnetic properties of KCu(IO$_3$)$_3$ are well described by that of a spin $S = 1/2$ Heisenberg chain with antiferromagnetic nearest-neighbor spin-exchange interaction of $\sim 9$ K. The interchain spin exchange is about a factor of 20 smaller and drives KCu(IO$_3$)$_3$ to a long-range antiferromagnetic order below $\sim 1.3$ K. A linear chain magnetism may be suspected from the crystal structure featuring the Jahn–Teller elongated CuO$_6$ octahedra connected via corners. A closer inspection of the distortion geometry of the oxygen octahedra, however, reveals that the linear spin lattice more likely results from super–superexchange via a pair of oxygen atoms labeled O1, O3, O6, and O9 in Figure 10, respectively. With distances to superexchange via a pair of oxygen atoms labeled O1, O3, O6, and O9 in Figure 10, respectively. With distances

![Image](https://example.com/image.png)

Figure 10. Projection of a section of the crystal structure of KCu(IO$_3$)$_3$ along [302] showing Cu atoms in blue and O and I atoms in red and yellow, respectively. Only those oxygen atoms of the Jahn–Teller elongated CuO$_6$ octahedra that connects to the central Cu atom below 2 Å highlighting the putative super–superexchange spin exchange paths via oxygen pairs also coordinating the I$^+$ cations.

**CONCLUSIONS**

The new iodate, KCu(IO$_3$)$_3$, has been synthesized by employing a hydrothermal technique with CuF$_2$ and KIO$_3$ as starting compounds. Single-crystal X-ray diffraction data were used for the structure determination. The compound crystallizes in the centrosymmetric space group $P2_1/n$ with the unit cell parameters $a = 9.8143(4) \AA$, $b = 8.2265(4) \AA$, $c = 10.8584(5) \AA$, and $\beta = 91.077(2)^\circ$. The structure contains the Jahn–Teller elongated [CuO$_6$] octahedra that connects to each other via corner sharing to form isolated chains. Three types of [IO$_3$] triagonal pyramids connect to the octahedra via corner sharing. Dimers of edge-sharing [KO$_{10}$] distorted polyhedra are further linked to the chain via face sharing.

Using Raman scattering, a separation of phonon modes into groups with characteristic frequencies has been observed. Low and high frequencies are attributed to the collective lattice modes and high-frequency fundamental modes, respectively.

The observed total number of modes and their frequency fully support the given structure description.

The magnetic properties of KCu(IO$_3$)$_3$ are well-described by that of a linear spin $S = 1/2$ Heisenberg chain with an antiferromagnetic nearest-neighbor spin exchange interaction of $\sim 9$ K. The interchain spin exchange is smaller by about a factor of 20, causing a long-range antiferromagnetic order below $\sim 1.3$ K. The linear spin lattice appears to result from super–superexchange via two oxygen anions coordinating simultaneously to the Cu$^{2+}$ and the I$^+$ cations.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02064.

Atomic coordinates and equivalent anisotropic displacement parameters ($A^2$) for KCu(IO$_3$)$_3$ (Table S1); and selected bond lengths (Å) and angles (°) for KCu(IO$_3$)$_3$ (Table S2); bond valence sum calculations for KCu(IO$_3$)$_3$ (Table S3) (PDF)

Crystallographic data ( CIF)

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Notes

The authors declare no competing financial interest.

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