



# Copper(II) perrhenate $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$ : Synthesis from isopropanol and $\text{CuReO}_4$ , structure and properties



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## ABSTRACT

The crystal structure of  $\text{Cu}^+\text{Re}^{7+}\text{O}_4$  is capable of a quasi-reversible incorporation of  $\text{C}_3\text{H}_7\text{OH}$  molecules. A room-temperature reaction between  $\text{CuReO}_4$  and  $\text{C}_3\text{H}_7\text{OH}$  under oxidizing conditions leads to the formation of a novel metal-organic hybrid compound  $\text{Cu}^{2+}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$ . Upon heating under reducing conditions, this compound transforms back into  $\text{CuReO}_4$ , albeit with  $\text{ReO}_2$  and metallic Cu as by-products. The crystal structure of  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  solved from single-crystal X-ray diffraction (*Pbca*,  $a = 10.005(3)$  Å,  $b = 7.833(2)$  Å, and  $c = 19.180(5)$  Å) reveals layers of corner-sharing  $\text{CuO}_6$ -octahedra and  $\text{ReO}_4$ -tetrahedra, whereas isopropyl groups are attached to both sides of these layers, thus providing additional connections within the layers through hydrogen bonds.  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  is paramagnetic down to 4 K because the spatial arrangement of the  $\text{Cu}^{2+}$  half-filled orbitals prevents magnetic superexchange. The paramagnetic effective moment of  $2.0(1) \mu_B$  is slightly above the spin-only value and typical for  $\text{Cu}^{2+}$  ions.

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## 1. Introduction

The persistent interest of material scientists in hybrid compounds combining organic and inorganic parts pertains to the high flexibility of such systems and broad opportunities for chemical combinations in materials. The perrhenate-ion  $\text{ReO}_4^-$  is known as a powerful complexing agent in aqueous and non-aqueous media [1]. More than 100 structures containing perrhenate-ions coordinated to transition-metal centers have been reported [2]. The combination of perrhenate ions with 3d transition metals can be beneficial for catalytic, magnetic, optical and redox properties. For example, heteropolymetallic complexes containing  $\text{ReO}_4^-$  and  $\text{Ti}^{4+}$  are capable of catalytic oxidation of sulfides [3].

Perrhenates of group 11 metals (Cu, Ag) are insulators with optical excitations lying in the range of visible light, which renders these compounds promising materials for photocatalytic and photovoltaic applications. The preparation of hybrid organic–inorganic compounds based on  $\text{AReO}_4$  perrhenates is a natural strategy to tune the band gap and improve functional properties of

simple perrhenates. Several compounds of this type were prepared by a hydrothermal synthesis from binary oxides mixed with an organic component [4,5]. For example,  $\text{Cu}(\text{bpy})\text{ReO}_4$  and  $\text{Cu}(\text{bpy})_2\text{ReO}_4 \cdot 0.5\text{H}_2\text{O}$  ( $\text{bpy} = 4,4'$ -bipyridine) solids can be reversibly transformed at quite low temperatures and simultaneously change their color, thus evidencing a drastic change in the band gap [4]. Remarkably, most of these compounds feature non-magnetic  $\text{Cu}^+$ , similar to pure  $\text{CuReO}_4$ , which is diamagnetic [6].

Here, we explore a different synthetic strategy that involves a direct reaction between the parent compound  $\text{CuReO}_4$  and isopropanol, one of simplest organic species.  $\text{CuReO}_4$  adopts its own structure type [6] and represents a three-dimensional framework of corner-sharing  $\text{CuO}_4^-$  and  $\text{ReO}_4^-$  tetrahedra similar to some silicon oxide and aluminosilicate structures. Its structure is subjected to the Loewenstein-rule [7]: each  $\text{ReO}_4^-$  (or  $\text{CuO}_4^-$ ) tetrahedron is surrounded by 4  $\text{CuO}_4^-$  (or  $\text{ReO}_4^-$ ) tetrahedra; tetrahedra with central ions of the same charge are never bounded with each other. Along the *c*-axis the structure exhibits fourfold double chains known from Narsarsukite [8] and beside these chains there are also 6-, 8- and 10-fold spirally twisted rings of the coordination polyhedra in the structure [6]. Large channels with an average diameter of 3.1 Å along the *c*-axis may facilitate the reaction of  $\text{CuReO}_4$  with small molecules. Indeed, we find that isopropanol readily enters the  $\text{CuReO}_4$  structure and triggers a drastic

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structural transformation accompanied by an oxidation of  $\text{Cu}^+$  toward  $\text{Cu}^{2+}$ . Despite its redox nature, this transformation is *quasi-reversible*. In the following, we report the synthesis, crystal structure, thermal stability, and magnetic properties of the new hybrid compound  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  obtained via a reaction of  $\text{CuReO}_4$  with isopropanol in the presence of oxygen.

## 2. Experimental

### 2.1. Synthesis

Single crystals and powder of  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  were prepared at room temperature via reaction between  $\text{CuReO}_4$  and dried isopropanol (99.7%, VWR) in dry oxygen atmosphere over 2 days, according to the reaction scheme:  $2\text{CuReO}_4 + 2\text{C}_3\text{H}_7\text{OH} \rightarrow \text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2 + \text{Cu}$ . Some amount of crystalline copper (I) oxide was also registered by X-ray powder diffraction. We observed that the presence of oxygen significantly accelerates the formation of the novel compound: without  $\text{O}_2$   $\text{CuReO}_4$  remains still a majority product after one week reaction time.

The parent compound  $\text{CuReO}_4$  was synthesized in a sealed silica tube at 500 °C using  $\text{Cu}_2\text{O}$  (Alfa Aesar, 99.9%) and  $\text{Re}_2\text{O}_7$  (Alfa Aesar, 99.9%), according to the procedure described in [6]. Phase analysis and the determination of cell parameters were carried out using X-ray powder diffraction with a STOE STADI P diffractometer ( $\text{Cu-K}\alpha_1$ -radiation,  $\lambda = 1.54059 \text{ \AA}$ ) in steps of  $0.02^\circ$  for  $2\theta$  from  $3$  to  $90^\circ$  in transmission mode. Phase composition of bulk polycrystalline samples was confirmed by the Rietveld refinement based on all available reflections using the program FullProf within the software package WinPLOTR [9].

### 2.2. Thermal and mass-spectrometric analysis

Thermal stability of  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  and mass-spectra of gaseous products during the sample decomposition were studied in the temperature range from 20 °C to 400 °C in an STA 449 (Netzsch, Selb, Germany). Experiments were carried out in alumina crucibles in an Ar atmosphere with the heating rate of 10 °C/min.

### 2.3. Structural characterization

Single-crystal X-ray diffraction studies of  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  were performed using the Xcalibur system from Oxford Diffraction and the software packages SHELXS [10], SHELXL [11] and X-STEP32 [12]. A combined empirical absorption correction with frame scaling was applied for measurements at ambient conditions, using the SCALE3 ABSPACK command in CrysAlisRed [13].

Hydrogen atoms bound to carbon and oxygen were located at their idealized positions using appropriate HFIX instructions in SHELXL and included in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacement parameters ( $U_{\text{iso}}$ ) fixed, respectively, at 1.2 or 1.5 times  $U_{\text{eq}}$  of the carbon atom to which they are attached, and at 1.07 times  $U_{\text{eq}}$  of the oxygen atom of the hydroxyl group.

### 2.4. Magnetization measurements

Magnetic properties of powdered  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  sample were studied with a superconducting quantum interference device (SQUID) from Quantum Design. Measurements were performed upon heating in zero-field-cooling (ZFC) and field-cooling (FC) mode in the temperature range from 4 to 350 K and with an applied field strength of 500 G.

## 3. Results

### 3.1. Crystal structure

Dried product of the reaction between  $\text{CuReO}_4$  and isopropanol is a multiphase mixture containing light-green single crystals of copper(II) diisopropanolperhenate  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  and the brown powder containing metallic copper and copper oxides. Mechanical separation of  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  crystals from the residual mixture allowed us to obtain the metal-organic copper(II) perhenate as a single-phase product. According to the single-crystal X-ray diffraction, it crystallizes in the orthorhombic space group *Pbca* with the lattice parameters listed in Table 1.

The structure of  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  can be described as a sequence of “inorganic” and “organic” layers along the *c*-axis, see Fig. 1 and Tables 1–3. The “inorganic” layers in the *ab*-plane consist of corner-sharing  $\text{CuO}_6$ -octahedra and  $\text{ReO}_4$ -tetrahedra (Fig. 2), forming 8-member-rings of four  $\text{ReO}_4$ - and four  $\text{CuO}_6$ -polyhedra. These layers are separated by the isopropyl groups. The  $\text{Re}^{7+}\text{O}_4$ -tetrahedra are nearly regular with the average Re–O-distance of 1.709 Å, which is similar to the Re–O bond lengths of 1.704 Å measured in  $\text{Cu}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$  [14]. In contrast, the  $\text{CuO}_6$  polyhedra are strongly distorted, with four short Cu–O-bonds of 1.93–1.95 Å in the equatorial plane, and two longer Cu–O-bonds of 2.50 Å in the axial positions (Table 3). This pronounced planar anisotropy of the local environment is a clear signature of the Jahn–Teller cation  $\text{Cu}^{2+}$  confirming that the incorporation of isopropanol into  $\text{CuReO}_4$  is accompanied by an oxidation of the  $\text{Cu}^+$

**Table 1**  
Crystal structure data of  $\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$  from single crystal XRD.

Chemical formula	$\text{Cu}(\text{C}_3\text{H}_7\text{OH})_2(\text{ReO}_4)_2$
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature [K]	293
Lattice parameters <i>a</i> , <i>b</i> , <i>c</i> [Å]	10.005(3), 7.833(2), 19.180(5)
<i>V</i> [Å <sup>3</sup> ]	1503.1 (5)
<i>Z</i>	8
Calculated density [g/cm <sup>3</sup> ]	3.023
Crystal form, color	prism, light-green
Crystal size (mm)	0.03 × 0.03 × 0.01
Data collection	Goniometer KM4/Xcalibur, detector:
Diffractometer	Sapphire2 (large Be window)
Data collection method	Ω-scans
Radiation type	Mo-Kα
<i>F</i> (000)	1244
Absorption correction	Analytical [13]
Absorption coefficient [mm <sup>-1</sup> ]	17.51
θ-range of data collection [°]	2.94–26.33
<i>hkl</i> range	−12 ≤ <i>h</i> ≤ 12, −9 ≤ <i>k</i> ≤ 9, −23 ≤ <i>l</i> ≤ 22
Reflections	
Measured	7115
Independent	1510
Observed [ <i>I</i> > 2 <i>s</i> ( <i>I</i> )]	795
<i>R</i> <sub>int</sub>	0.088
Completeness [%]	98.7
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
No. of reflections parameters	1510
restraints	87
	0
Goodness-of-Fit	0.80
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	
[ <i>I</i> > 2σ( <i>I</i> )]	0.036, 0.034
All	0.130, 0.043
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> [e/Å <sup>-3</sup> ]	0.94, −1.02

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