Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$, a novel oxophosphate with a shchurovskyite-type topology: synthesis, structure, magnetic properties and crystal chemistry of rubidium copper phosphates

**Synopsis:** A novel compound, Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$, was synthesized by a hydrothermal method and characterized as the shchurovskyite-type structure, based upon a heteropolyhedral copper phosphate framework. Microscopic calculations are indicative of possible low-dimensional magnetic behavior, as they confirm weak magnetic coupling between the copper-based layers mediated by the Cu–Cu pairs.

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**Keywords:** hydrothermal synthesis; copper oxophosphate; shchurovskyite; single-crystal X-ray diffraction; IR spectroscopy; structural complexity; magnetic properties

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Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$, a novel oxophosphate with a shchurovskyite-type topology: synthesis, structure, magnetic properties and crystal chemistry of rubidium copper phosphates

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Single crystals of Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$ were synthesized by a hydrothermal method in the multicomponent system CuCl$_2$–Ca(OH)$_2$–RbCl–B$_2$O$_3$–Rb$_3$PO$_4$. The synthesis was carried out in the temperature range from 690 to 700 K and at the general pressure of 480–500 atm [1 atm = 101.325 kPa] from the mixture in the molar ratio 2CuO:CaO:Rb$_2$O:B$_2$O$_3$:P$_2$O$_5$. The crystals studied by single-crystal X-ray analysis were found to be monoclinic, space group C2, a = 16.8913 (4), b = 5.6406 (1), c = 8.3591 (3) Å, β = 93.919 (3)°, V = 794.57 (4) Å$^3$. The crystal structure of Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$ is similar to that of shchurovskyite and dmisokolovite and is based upon a heteropolyhedral open framework formed by polar layers of copper polyhedra linked via isolated PO$_4$ tetrahedra. The presence of well-isolated 2D heteropolyhedral layers in the title compound suggests low-dimensional magnetic behavior which is masked however by the fierce competition between multiple ferromagnetic and antiferromagnetic exchange interactions. At $T_C = 25$ K, Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$ reaches a magnetically ordered state with large residual magnetization.

1. Introduction

Alkaline phosphates with transition metals attract interest because of their broad technological applications as battery materials, sorbents, catalysts, ion-exchangers etc. (Cheetham et al., 1999; Maspoch et al., 2007; Williams et al., 2013; Whittingham, 2014; Yakubovich et al., 2016). Among these, copper pyrophosphates are of interest because of their magnetic structures of different dimensionalities (Shvanskaya et al., 2013; Mannasova et al., 2016).

Typically, the coordination environment of the Cu$^{2+}$ cation in oxygen compounds is a distorted octahedron (due to the Jahn–Teller effect) (Burns & Hawthorne, 1995a,b; Krivovichev, Filatov & Vergasova, 2013). However, the coordination number may be reduced to five or four, due to some local crystal-chemical requirements. For instance, the recently described crystal structure of (Rb,K)$_3$Cu$_3$(P$_2$O$_7$)$_2$ is characterized by the simultaneous presence of CuO$_6$ octahedra.
and CuO₅ pyramids (Krivovichev & Chernyat’eva, 2016).
Among minerals, natural copper arsenates shchurovskyyite,
K₂CaCu₁₃(AsO₄)O₂, and dmisokoloviite, K₆Cu₆Al(AsO₄)O₂,
found in sublimates of the Arsenatnaya fumarole (Tolbachik
volcano, Kamchatka, Russia), have three types of Cu²⁺ coor-
dination environments: CuO₆ octahedra, CuO₅ pyramids and
CuO₄ squares (Pekov et al., 2015, 2018). In the structures of
copper oxysalts CuO₅ polyhedra can build cationic motifs of
different dimensionalities (from isolated polyhedra to
heteropolyhedral frameworks). A classification of minerals
and inorganic compounds has been proposed based on the
polymerization of CuO₅ squares (Leonyuk et al., 1998, 2001).

Oxysalts with mineral-like structures containing ‘additional’
oxygen atoms and OH groups that can be described in terms
of anion-centered tetrahedra (Krivovichev & Filatov, 2001;
Krivovichev, Menté et al., 2013) as having anion-centered
[(OH)Me₃] triangles and [OME₅] tetrahedra (Me = Cu, Ni, Fe,
Zn etc.) attract interest due to their magnetic properties
controlled by the local structure of the oxygen-based copper
polycations (Aksenov et al., 2017; Yannnova et al., 2017;
Volkova & Marinin, 2017, 2018a,b).

In this paper we report on the hydrothermal synthesis,
single-crystal X-ray structure analysis and IR spectra of a
novel oxy [or oxo³]phosphate Rb₂CaCu₆(PO₄)₂O₂: we evaluate
the magnitude and sign-of-spin coupling between
magnetic Cu²⁺ ions and discuss the possible manifestation of
low-dimensional magnetic behavior of this compound. The
crystal-chemical features and structural complexity of rubi-
dium copper phosphates and related oxysalts are also
discussed.

2. Experimental

2.1. Synthesis and sample characterization

Single crystals of Rb₂CaCu₆(PO₄)₂O₂ were synthesized by a
hydrothermal method in the multicomponent system CuCl₂–
Ca(OH)₂–RbCl–B₂O₃–Rb₃PO₄. The synthesis was carried out
in the temperature range from 690 to 700 K and at the general
pressure of 480–500 atm [1 atm = 101,325 kPa] from the oxide
mixture in the molar ratio 2CuO:CaO:Rb₂O:CaO₂:P₂O₅. A
standard Cu-lined stainless steel autoclave of 16 ml capacity
was used. The coefficient of the autoclave filling was selected
so that the pressure was constant. The heating time was
20 days and corresponds to the full completion of the chemical
reaction. The product was then cooled to room temperature
over 24 h. The precipitate was separated by filtration, washed
several times with hot distilled water and finally dried at room
temperature for 12 h. The reaction products were small green
crystals of the new phase Rb₂CaCu₆(PO₄)₂O₂ (Fig. 1) in 15%
yield, light blue crystals of CaCu₃(PO₄)₂ and deep blue crystals
of CuBO₂. The crystals of Rb₂CaCu₆(PO₄)₂O₂ were selected
manually for further studies.

The elemental contents (Fig. S1, Table S1, in the supporting
information) of the selected crystals were determined by a
Jeol JSM6480LV scanning electron microscope equipped with
an INCA Wave 500 wavelength spectrometer. The conditions
of analysis were: accelerating voltage 20 kV, current 20 nA,
beam diameter 3 µm.

2.2. Vibrational spectroscopy

The IR spectrum of Rb₂CaCu₆(PO₄)₂O₂ was obtained using
an FSM 12011 FTIR spectrometer using the KBr disc tech-
nique in the wavenumber region from 4000 to 400 cm⁻¹. The
spectral resolution was about 2 cm⁻¹.

The IR absorption spectrum is shown in Fig. 2. The bands
in the region 1100–400 cm⁻¹ are due to phosphate units. Theo-
retical group analysis for the tetrahedral phosphate ion PO₄³⁻
in a local position with C₁ symmetry and C₂ factor group leads
to the following allowed IR vibrations: v₁ - 3A + 3B, v₂ - A +
B, v₄ - 3A + 3B and v₅ - 2A + 2B for each of the two
independent phosphorus sites. IR bands observed at 1109,
1060, 1036, 1002, 963 cm⁻¹ are assigned to the anti-
symmetric stretching v₁ modes of PO₄³⁻ units. The IR bands
at 950 and 925 cm⁻¹ are attributed to the phosphate ions v₄
symmetric stretching modes. The IR bands in the region 640–
470 cm⁻¹ are due to antisymmetric bending v₅ vibrations. The
bands at 452 and 418 cm⁻¹ are assigned to v₂ symmetric
bending vibrations. Because of the proximity and partial
overlapping of many vibrations, the observed number of

![Image](a.png)

Figure 1
A photograph of crystals of the Rb₂CaCu₆(PO₄)₂O₂ compound (a) and a
scanning electron microscopy image showing the crystal morphology (b).

![Image](b.png)

Figure 2
IR spectrum of Rb₂CaCu₆(PO₄)₂O₂ at room temperature.
Table 1
Experimental details Generated from cif.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
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<tr>
<td>Crystal data</td>
<td>CaCu6O18P₄Rb₂</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>1004.2</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, C2</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>16.9813 (4), 5.6406 (1), 8.3591 (3)</td>
</tr>
<tr>
<td>β (°)</td>
<td>93.919 (3)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>794.57 (4)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Radiation type</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71069</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>14.80</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.24 × 0.22 × 0.15</td>
</tr>
</tbody>
</table>

| Data collection | Xcalibur, Sapphire3 with high theta cut-off |
| Refinement | R[2θ > 2σ(F²)], wR(F²), S |
| No. of reflections | 5108 |
| No. of parameters | 153 |
| ΔRmax, Δθmax (e Å⁻³) | 1.21, -1.26 |
| Absolute structure | 0 of Friedel pairs used in the refinement [Section editor comment: No absolute structure parameter?]

Table 2
Selected interatomic distances (Å) for Rb₂Ca[Ca₆O₄(Po₄)₄] Should symmetry operations be given?

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
<th>Bond</th>
<th>Distance</th>
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</thead>
<tbody>
<tr>
<td>Rb—O9</td>
<td>2.814 (3)</td>
<td>Ca—O6</td>
<td>2.312 (3)</td>
</tr>
<tr>
<td>Rb—O1</td>
<td>2.876 (3)</td>
<td>Ca—O5</td>
<td>2.423 (3)</td>
</tr>
<tr>
<td>Rb—O6</td>
<td>2.940 (3)</td>
<td>Ca—O3</td>
<td>2.575 (3)</td>
</tr>
<tr>
<td>Rb—O7</td>
<td>3.074 (3)</td>
<td>Ca—O7</td>
<td>2.970 (4)</td>
</tr>
<tr>
<td>Rb—O1</td>
<td>3.133 (3)</td>
<td>Mean</td>
<td>2.570 (X)</td>
</tr>
<tr>
<td>Rb—O7</td>
<td>3.278 (4)</td>
<td>Cu—O7</td>
<td>1.397 (4)</td>
</tr>
<tr>
<td>Rb—O8</td>
<td>3.424 (3)</td>
<td>Cu—O4</td>
<td>1.907 (3)</td>
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<tr>
<td>Cu—O4</td>
<td>1.902 (2)</td>
<td>Cu—O5</td>
<td>2.146 (3)</td>
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<tr>
<td>Cu—O1</td>
<td>1.937 (3)</td>
<td>Cu—O4</td>
<td>2.253 (2)</td>
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<tr>
<td>Cu—O8</td>
<td>1.959 (3)</td>
<td>Mean</td>
<td>2.062 (X)</td>
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<tr>
<td>Cu—O9</td>
<td>2.075 (3)</td>
<td>Cu—O6†</td>
<td>2.297 (3)</td>
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<tr>
<td>Cu—O8</td>
<td>2.407 (3)</td>
<td>P1—O9</td>
<td>1.536 (2)</td>
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<tr>
<td>Mean</td>
<td>2.056 (X)</td>
<td>P1—O3</td>
<td>1.540 (3)</td>
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<tr>
<td>Cu—O4</td>
<td>1.913 (2)</td>
<td>P1—O8</td>
<td>1.544 (3)</td>
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<tr>
<td>Cu—O2</td>
<td>1.922 (3)</td>
<td>P1—O2</td>
<td>1.568 (3)</td>
</tr>
<tr>
<td>Mean</td>
<td>1.918 (X)</td>
<td>Mean</td>
<td>1.548 (X)</td>
</tr>
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<td>Cu—O6†</td>
<td>2.368 (3)</td>
<td>P2—O6</td>
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<td>Cu—O3</td>
<td>1.925 (3)</td>
<td>P2—O2</td>
<td>1.536 (3)</td>
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<td>Cu—O2</td>
<td>1.993 (3)</td>
<td>P2—O7</td>
<td>1.553 (3)</td>
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<tr>
<td>Cu—O5</td>
<td>2.473 (3)</td>
<td>P2—O5</td>
<td>1.557 (3)</td>
</tr>
<tr>
<td>Mean</td>
<td>2.131 (X)</td>
<td>Mean</td>
<td>1.541 (3)</td>
</tr>
</tbody>
</table>

† Not considered in the calculation of the average bond length, but has been included in the calculation of the bond-valence sums.

2.3. X-ray powder diffraction and single-crystal analysis

Powder X-ray diffraction data of Rb₂CaCu₆(PO₄)₄O₂ (Fig. S2) were collected with a Stoe-Stadi MP (Stoe & Cie Gmbh, Darmstadt, Germany) powder diffractometer equipped with a curved Ge(111) monochromator to provide strictly monochromatic Co Kα1 radiation, 40 kV, 35 mA. The data were acquired by successively covering the scanning region using a position-sensitive linear detector with 2θ or Δ(2θ) = 5° and a channel width of 0.02°.

A green unshaped grain of Rb₂CaCu₆(PO₄)₄O₂ (0.13 × 0.15 × 0.18 mm) was selected carefully under a polarizing microscope and used for single-crystal X-ray data collection. The single-crystal X-ray data were collected at room temperature on an Oxford Diffraction Xcalibur S diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a CCD detector using the ω scanning mode. Raw data were integrated and then scaled, merged and corrected for Lorentz–polarization effects using the CrysAlis package (Oxford Diffraction, 2009). The following unit-cell parameters have been obtained by the least-squares refinement: a = 16.8913 (4), b = 5.6406 (1), c = 8.3591 (3) Å, β = 93.919 (3)°, V = 794.57 (4) Å³. Space group C2 (No. 5) was chosen based on the reflection statistics and was confirmed by the successful refinement of the structure. The experimental details of the data collection and refinement results are listed in Table 1.

A structure model was produced by the ‘charge flipping’ method using the SUPERFLIP computer program (Palatinus & Chapuis, 2007). The structure determinations and refinements were carried out using the Jana2006 program package (Pettifore et al., 2006). Atomic scattering factors for neutral atoms together with anomalous dispersion corrections were taken from International Tables for Crystallography (Prince, 2006). Illustrations were produced with the Jana2006 program package in combination with the program DIAMOND (Brandenburg & Putz, 2005). Table S2 lists the fractional atomic coordinates, occupancy, site symmetries and equivalent atomic displacement parameters (Ueq). Anisotropic atomic displacement parameters (Uij) are presented in Table S3. Selected interatomic distances are given in Table 2.

Bond-valence sums (BVS, Table 3) were calculated using

\[ \text{BVS} = \sum \left( \frac{q_i q_j}{r_{ij}} \right) \]

where \(q_i\) and \(q_j\) are the charges of atoms i and j, respectively, and \(r_{ij}\) is the distance between them. The bond-valence summation (BVS) equation is used to calculate average bond lengths and distances. The bond-valence parameters for Cu²⁺—O bonds (Krivo et al., 2006) were used for the calculation of the average bond length, but has been included in the calculation of the bond-valence sums.

Table 3
Bond-valence calculation for Rb₂Ca[Ca₆O₄(Po₄)₄].

<table>
<thead>
<tr>
<th>Site</th>
<th>Rb</th>
<th>Cu1</th>
<th>Cu2</th>
<th>Cu3</th>
<th>Cu4</th>
<th>Ca</th>
<th>P1</th>
<th>P2</th>
<th>Σc/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.19+0.10</td>
<td>0.49</td>
<td>1.24</td>
<td>2.02</td>
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<td></td>
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<tr>
<td>O2</td>
<td>0.51+0.21</td>
<td>0.42+0.21</td>
<td>1.14</td>
<td>2.07</td>
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<tr>
<td>O3</td>
<td>0.31</td>
<td>0.19+0.21</td>
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<td>1.73</td>
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<tr>
<td>O4</td>
<td>0.54</td>
<td>0.52+0.21</td>
<td>0.53</td>
<td>2.09</td>
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<tr>
<td>O5</td>
<td>0.11+0.15</td>
<td>0.27+0.21</td>
<td>1.18</td>
<td>1.85</td>
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<tr>
<td>O6</td>
<td>0.16</td>
<td>0.03+0.15</td>
<td>0.50+0.21</td>
<td>1.31</td>
<td>1.94</td>
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<tr>
<td>O7</td>
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<td>0.54+0.21</td>
<td>0.39+0.21</td>
<td>1.19</td>
<td>1.97</td>
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<tr>
<td>O8</td>
<td>0.04</td>
<td>0.46+0.13</td>
<td>1.21</td>
<td>1.84</td>
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<tr>
<td>O9</td>
<td>0.23</td>
<td>0.33</td>
<td>0.20</td>
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<tr>
<td>Σc/a</td>
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<td>1.90</td>
<td>1.88</td>
<td>4.82</td>
<td>4.92</td>
<td></td>
</tr>
</tbody>
</table>

References

vichev, 2012a) and for other bonds (Rb—O, Ca—O and P—O) (Brown & Altermatt, 1985).

2.4. Theoretical study of magnetic properties

To examine the low-dimensional properties of Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$, we evaluated the magnitude and sign-of-spin coupling $J_{SS}$ between Cu$^{2+}$ ions within the 2D networks and between them (Fig. 3). For each Cu–Cu exchange-coupled pair, the exchange parameters $J$ were obtained from numerical calculations in terms of a microscopic many-electron superexchange model using a computational scheme (Mironov et al., 2003; Nikiforova et al., 2011; Zorina et al., 2013). In these calculations, the electronic structure and magnetic characteristics of the individual Cu$^{2+}$ ions located in the different copper sites are treated in terms of ligand-field (LF) calculations combined with the angular-overlap model (AOM) (Schaffer, 1968); the latter provides more consistent information on the orbital composition of the ground-state wavefunctions of Cu$^{2+}$ ions in the low-symmetry coordination polyhedra Cu$_6$O$_x$ [Fig. 4(a)]. The AOM parameters used for Cu$^{2+}$ ions are $e_π = 4000$ and $e_σ = 1000$ cm$^{-1}$ (at the reference metal–ligand distance $R_0 = 2.15$ Å); the radial dependence of these parameters is approximated by $e_π(R) = e_π(R_0)/(R/R_0)^{9}$ with $n = 4$. Furthermore, we used $B = 900$ and $C = 4000$ cm$^{-1}$ Racah parameters (for the 3$d^9$ charge-transfer state of copper ions) and $ζ = 650$ cm$^{-1}$ spin–orbit coupling constant. Exchange parameters $J$ were calculated for all actual Cu–Cu exchange-coupled pairs in the crystal structure of Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$, in which adjacent Cu$^{2+}$ ions are bridged by oxygen atoms and/or tetrahedral PO$_4$ phosphate groups [Figs. 4(b) and 4(c)]. It is noteworthy that the key elements of the superexchange theory are electron transfer parameters $t_{ij}$ which are one-electron matrix elements connecting magnetic 3$d$ orbitals on two exchange-coupled transition-metal centers A and B, $t_{ij} = |3d(A)|h|3d(B)|$: in fact, exchange parameters $J$ are very sensitive to the set of electron transfer parameters $t_{ij}$. In our calculations, these matrix elements are obtained from molecular orbital (MO) calculations in terms of the extended Hückel theory (EHT) using atomic EHT parameterization available from http://www.op.titech.ac.jp/lab/mori/EHTB/EHTB.htm [URL not found, please check]. More specifically, the EHT calculations were performed for clusters involving two adjacent copper atoms and their extended atomic surroundings involving bridging and terminal oxygen atoms and tetrahedral PO$_4$ groups; examples are shown in Fig. 3. The local structure of these clusters corresponds to the actual crystal structure of Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$. The electron transfer parameters $t_{ij}$ are derived by projection of the ten most 3$d$-rich molecular orbitals of the Cu(A)–Cu(B) pair onto purely atomic 3$d$ orbitals of two copper atoms A and B (Lee, 1989; Nikiforova et al., 2011; Zorina et al., 2013). The Cu(A)–Cu(B) charge-transfer energy is set to 65000 cm$^{-1}$ (8 eV); this approach has been previously applied to analyze the spin-coupling mechanism in 3$d$-based molecular magnets (Nikiforova et al., 2011).

2.5. Structural complexity calculation

The structural complexity of the crystal structures was measured using Shannon information per atom ($I_G$) and per reduced unit cell ($I_{G(total)}$):

$$I_G = -\sum_{i=1}^{k} p_i \log_2 p_i \text{ (bits per atom)}$$

$$I_{G(total)} = -v I_G = -v \sum_{i=1}^{k} p_i \log_2 p_i \text{ (bits per unit cell)}$$
where \( k \) is the number of different crystallographic orbits and \( p_i \) is the random-choice probability for an atom from the \( i \)th crystallographic orbit, that is

\[
p_i = \frac{m_i}{v}
\]

where \( m_i \) is the multiplicity of a crystallographic orbit relative to the reduced unit cell, and \( v \) is the number of atoms in the reduced unit cell (= number of vertices in the quotient graph) (Krivovichev, 2012b, 2013a). This approach was successfully used to characterize the complexity of minerals, zeolites and different types of inorganic compounds (Krivovichev, 2013b; Siidra et al., 2014; Grew et al., 2016; Hazen et al., 2017). Complexity parameters for the whole structure have been calculated using the software \textit{TOPOS} (Blatov et al., 2014).

### 3. Results

#### 3.1. Crystal structure

The crystal structure of Rb\(_2\)CaCu\(_6\)(PO\(_4\))\(_4\)O\(_2\) is similar to those of shchurovskiyite, K\(_2\)CaCu\(_6\)(AsO\(_4\))\(_4\)O\(_2\), and dmisokolovite, K\(_3\)Cu\(_5\)(AsO\(_4\))\(_4\)O\(_2\) (Table 4), and is based upon a heteropolyhedral open framework formed by polar Cu-based oxo layers linked via isolated PO\(_4\) tetrahedra (Fig. 5).

The layer is formed by CuO\(_n\) polyhedra of three types: square \((n = 4)\), square-pyramid \((n = 5)\) and octahedron \((n = 6)\). It is based upon rods of edge-sharing Cu2O\(_4\) squares and Cu3O\(_6\) octahedra [the Cu2···Cu3 distance is 2.775 (1) Å] extending along [010]. The Cu2O\(_4\) square has two long (2.968 Å) distances to the O6 atoms [comparable with that observed in the structure of shchurovskiyite (Pekov et al., 2015)], so the coordination environment of the Cu2 site can be considered as a Jahn–Teller-distorted (4+2)-tetragonal bipyramid [which is common for inorganic oxysalts (Burns & Hawthorne, 1995a,b; Krivovichev et al., 2013)].

### Table 4

<table>
<thead>
<tr>
<th>Copper site</th>
<th>( g_1 )</th>
<th>( g_2 )</th>
<th>( g_3 )</th>
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<tr>
<td>Cu1</td>
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<td>2.363</td>
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<td>Cu2</td>
<td>2.058</td>
<td>2.058</td>
<td>2.317</td>
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<td>Cu3</td>
<td>2.064</td>
<td>2.067</td>
<td>2.348</td>
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<tr>
<td>Cu4</td>
<td>1.997</td>
<td>2.219</td>
<td>2.331</td>
</tr>
</tbody>
</table>

3. Results

3.1. Crystal structure

The crystal structure of Rb\(_2\)CaCu\(_6\)(PO\(_4\))\(_4\)O\(_2\) is similar to those of shchurovskiyite, K\(_2\)CaCu\(_6\)(AsO\(_4\))\(_4\)O\(_2\), and dmisokolovite, K\(_3\)Cu\(_5\)(AsO\(_4\))\(_4\)O\(_2\) (Table 4), and is based upon a heteropolyhedral open framework formed by polar Cu-based oxo layers linked via isolated PO\(_4\) tetrahedra (Fig. 5).

The layer is formed by CuO\(_n\) polyhedra of three types: square \((n = 4)\), square-pyramid \((n = 5)\) and octahedron \((n = 6)\). It is based upon rods of edge-sharing Cu2O\(_4\) squares and Cu3O\(_6\) octahedra [the Cu2···Cu3 distance is 2.775 (1) Å] extending along [010]. The Cu2O\(_4\) square has two long (2.968 Å) distances to the O6 atoms [comparable with that observed in the structure of shchurovskiyite (Pekov et al., 2015)], so the coordination environment of the Cu2 site can be considered as a Jahn–Teller-distorted (4+2)-tetragonal bipyramid [which is common for inorganic oxysalts (Burns & Hawthorne, 1995a,b; Krivovichev et al., 2013)].

However, the bond-valence contribution of this bond is low [0.03 valence units (v.u.); Table 3], which allows us to treat the Cu2O\(_4\) polyhedron as a square with two long distances to the O6 atoms [comparable with that observed in the structure of shchurovskiyite (Pekov et al., 2015)], so the coordination environment of the Cu2 site can be considered as a Jahn–Teller-distorted (4+2)-tetragonal bipyramid [which is common for inorganic oxysalts (Burns & Hawthorne, 1995a,b; Krivovichev et al., 2013)].

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polyhedron as a planar square. Each rod is decorated by ‘additional’ CuO$_5$ and CuO$_4$ distorted square-pyramids [Fig. 5(a)]. Apical vertices of these pyramids are parallel to each other and elongated along [010], resulting in the non-centricosymmetric (polar) character of the layers. Adjacent rods are linked by sharing common vertices of the CuO$_5$ polyhedra.

In the crystal structures of Rb$_2$CaCu$_4$(PO$_4$)$_3$O$_2$ and shchurovskytie, Cu atoms form rather complex cationic 2D arrays (Pekov et al., 2015). Replacement of one Cu atom by Al in the crystal structure of dmisokolovite (Pekov et al., 2015) leads to another type of low-dimensional topology of Cu atoms [Fig. 5(b)].

Heteropolyhedral Cu-based layers are linked via isolated PO$_4$ tetrahedra forming a 3D framework with the composition [CuO$_5$(PO$_4$)$_3$]$^{3-}$, containing wide channels occupied by both alkaline (Rb$^+$) and alkaline-earth (Ca$^{2+}$) cations. The density of the framework (FD) is 25.17 Cu$^+$P atoms per 1 nm$^3$. Despite the fact that the ionic radius of rubidium ($r_{\text{Rb}^{\text{VII}}} = 1.56$ Å) is considerably larger than that of potassium ($r_{\text{K}^{\text{VII}}} = 1.46$ Å), the unit-cell volume of shchurovskytie-type compounds predominantly depends on the ionic radii of the tetrahedrally coordinated cations. Therefore, the unit-cell volume of Rb$_2$CaCu$_4$(PO$_4$)$_3$O$_2$ ($V = 794.57$ Å$^3$) is smaller than that of shchurovskytie K$_2$CaCu$_4$(AsO$_4$)$_3$O$_2$ ($V = 839.24$ Å$^3$).

The crystal structure of Rb$_2$CaCu$_4$(PO$_4$)$_3$O$_2$ contains two types of parallel channels extending along [010]. Channel I is delimited by four CuO$_4$ polyhedra and four PO$_4$ tetrahedra and has a distorted hexagonal cross section. The effective width (e.c.w.) of channel I, calculated (McCusker et al., 2003) by subtracting the ionic diameter of O$^{5-}$ (2.7 Å) from the shortest and longest O···O distances across the channel, is 2.6 × 5.7 Å (the O7–O7 and O8–O8 distances, respectively).

Channel I is filled by Rb atoms (Fig. S3a). Channel II is delimited by two CuO$_4$ polyhedra and two PO$_4$ tetrahedra and has a tetragonal cross section (e.c.w. = 0.9 × 1.3 Å, measured using the O5··O5 and O7··O7 distances). This channel is filled by Ca$^{2+}$ cations (Fig. S3b).

The crystal structures of Rb$_2$CaCu$_4$(PO$_4$)$_3$O$_2$, shchurovskytie, K$_2$CaCu$_4$(AsO$_4$)$_3$O$_2$, and dmisokolovite, K$_3$Cu$_5$Al(AsO$_4$)O$_2$, are characterized by the presence of ‘additional’ oxygen atoms and thus may be described in terms of anion-centered tetrahedra (Krivovichev & Filatov, 2001; Krivovichev et al., 2013 [two Krivovichev et al. 2013 references, please indicate which]). Within this approach, the crystal-chemical formula of the title compound can be written as (for $Z = 2$) Rb$_2$Ca[O$^{15}$Cu$_6$](PO$_4$)$_4$, where square brackets denote a structural unit formed by anion-centered tetrahedra (Roman numerals indicate the coordination number of the ‘additional’ oxygen atoms). The O4 atom is tetrahedrally coordinated by four Cu$^{2+}$ cations with the average (O4–Cu) distance of 1.912 Å. The (OCu$_4$) tetrahedra are linked via common Cu2··Cu3 edges forming a [O$_2$Cu$_6$]$^{8+}$ dimer [Fig. 6(a)]. The arrangement of isolated anion-centered dimers

![Figure 6](image_url)

Anion-centered [O$_2$Cu$_6$] dimer Distances in Å. Why are s.u.’s missing on distances? These numbers are too small and should be given in caption. (a) and general view of the crystal structure of Rb$_2$CaCu$_4$(PO$_4$)$_3$O$_2$ projected on (010) (b) and (001) (c).

![Figure 7](image_url)

Temperature dependence of d.c. magnetic susceptibility $\chi = M/B$ M/H in Rb$_2$CaCu$_4$(PO$_4$)$_3$O$_2$ taken at $H = 80$ kA m$^{-1}$ (1000 Oe) in the field-cooled mode. The inset represents the hysteresis loop taken at $T = 2$ K.
and PO₄ tetrahedra as well as Rb⁺ and Ca²⁺ cations is shown in Figs. 6(b) and 6(c).

3.2. Magnetic properties of Rb₂CaCu₆(PO₄)₄O₂: experiment

Magnetic properties of the collection of non-oriented tiny single crystals of Rb₂CaCu₆(PO₄)₄O₂ of total mass 3.73 mg were measured using the VSM option of the Physical Properties Measurements System PPMS (Quantum Design) 9 T. The temperature dependence of d.c. magnetic susceptibility \( \chi = M/H \) taken in the field-cooled regime at \( H = 80 \text{ kA m}^{-1} \) (1000 Oe) in the range 2–300 K is shown in Fig. 7. A sharp upturn in magnetization at \( T_C = 25 \text{ K} \) signals transition into a long-range-ordered state with spontaneous magnetic moment. This is confirmed by the sharp hysteresis loop taken at \( T = 2 \text{ K} \), as shown in the inset to Fig. 7. The residual magnetization equals \( M_R = 1.1 \mu_B \) per formula unit and the coercive force is 22.4 kA m\(^{-1}\), which places Rb₂CaCu₆(PO₄)₄O₂ beyond the range of magnetically soft materials.

![Figure 8](image)

(Upper panel) Representative ESR spectrum of Rb₂CaCu₆(PO₄)₄O₂ with the fitting curves as described in the text. The dashed lines show the individual Lorentzian fit components and the solid line is the sum of all three. (Lower panel) The temperature evolution of ESR spectra of Rb₂CaCu₆(PO₄)₄O₂. Inset: the temperature dependence of principal values of the \( g \)-tensor.

At elevated temperatures, the \( \chi(T) \) curve in Rb₂CaCu₆(PO₄)₄O₂ follows the Curie-Weiss law with inclusion of the temperature-independent term

\[
\chi = \chi_0 + \frac{C}{T - \Theta}.
\]

The fitting curve is shown by the dash in the main panel of Fig. 1 [Fig. 7]. The parameters of the fitting in the range 120–300 K are \( \chi_0 = -3.2 \times 10^{-4} \text{ emu mol}^{-1} \) [emu = electromagnetic unit?], Curie constant \( C = 1.74 \text{ emuK mol}^{-1} \) and Weiss temperature \( \Theta = -7.2 \text{ K} \) [delete minus sign?]. The value of the temperature-independent term is somewhat less than the summation of individual diamagnetic Pascal’s constants of constituent ions, equal to \(-3.8 \times 10^{-4} \text{ emu mol}^{-1} \) (Bain & Berry, 2008), which can be attributed to a paramagnetic van Vleck contribution of Cu²⁺ ions (Banks et al., 2009). The value of the effective magnetic moment

\[
\mu_{\text{eff}} = (8C)^{1/2}\mu_B
\]

is equal to 3.73 \( \mu_B \) which is to be compared with summation of the spin-only magnetic moments of six Cu²⁺ ions equal to 4.24 \( \mu_B \). The 10–20\% reduction of the effective magnetic moment is a standard feature of copper-based low-dimensional magnetic systems (Vasiliev et al., 2018). The low absolute value of the Weiss temperature, \( \Theta = -7.2 \text{ K} \), as compared with the magnetic ordering temperature, \( T_C = 25 \text{ K} \), signifies fierce competition between ferromagnetic and antiferromagnetic exchange interactions in the title compound.

3.3. Electron spin resonance: experiment

An electron spin resonance (ESR) study of a powder sample of Rb₂CaCu₆(PO₄)₄O₂ was performed using an X-band ESR spectrometer CMS 8400 (ADANI) (\( f \approx 9.4 \text{ GHz} \), \( B \leq 0.7 \text{ T} \) equipped with a low-temperature mount, operating in the range \( T = 6–300 \text{ K} \). The effective \( g \)-factors have been calculated with respect to a BDPA (a,g-bisdiphenyline-b-phenylallyl) reference sample with \( g_{\text{et}} = 2.00359 \). The main results are represented in Fig. 8. Typical ESR powder patterns of Rb₂CaCu₆(PO₄)₄O₂ in the paramagnetic phase are typical for Cu²⁺ ions with an anisotropic \( g \)-tensor. The amplitude of the signal increases monotonously upon cooling to 30 K, then

---

Table 5

<table>
<thead>
<tr>
<th>Cu-·-Cu pair</th>
<th>( A )</th>
<th>( J )</th>
<th>( J/A )</th>
</tr>
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<tbody>
<tr>
<td>Cu₁·-Cu₁’</td>
<td>−1.23</td>
<td>+0.28</td>
<td>−0.23</td>
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<tr>
<td>Cu₁·-Cu₂</td>
<td>−15.6</td>
<td>−3.9</td>
<td>0.25</td>
</tr>
<tr>
<td>Cu₁·-Cu₃</td>
<td>−13.9</td>
<td>−21.8</td>
<td>1.57</td>
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<td>0.53</td>
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<td>Cu₂·-Cu₄</td>
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</tr>
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<td>Cu₃·-Cu₄</td>
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<td>Cu₄·-Cu₄ (interlayer)</td>
<td>−0.235</td>
<td>−0.055</td>
<td>0.23</td>
</tr>
</tbody>
</table>

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\textbf{Acta Cryst. (2019). B75}

Sergey M. Aksenov et al. • Rb₂CaCu₆(PO₄)₄O₂
the signal degrades due to the onset of long-range magnetic order at $T_C = 25 \text{ K}$.

In order to evaluate the main ESR parameters the experimental spectra were fitted by the sum of three components corresponding to the principal values of the $g$-tensor using three Lorentzian profiles. A representative example of the line-shape analysis is given in the upper panel of Fig. 8 with the resolved resonance modes denoted by dashed lines and their sum shown by the solid line. The presence of three different components obviously indicates the reduced symmetry of the crystal environment as compared with cubic symmetry and is typical for Cu$^{2+}$ either in trigonally distorted octahedral, square-planar or square-pyramidal coordination (Krishna & Gupta, 1994). The principal $g$-values of the anisotropic $g$-tensor remain almost temperature independent over the whole temperature range investigated, with values $g_1 = 2.07 \pm 0.01$, $g_2 = 2.20 \pm 0.01$ and $g_3 = 2.31 \pm 0.01$ resulting in averaged $g_{av} = 2.20 \pm 0.02$, which is consistent with typical values for Cu$^{2+}$ ions in other copper oxides (Zakharov et al., 2014; Danilovich et al., 2019). Remarkably, the obtained experimental $g$-values agree quite well with the theoretically calculated ones listed in Table 4. Note, it is impossible to resolve the signals from different Cu sites since the experimental absorption line is relatively broad and overlapping in nature. The slight deviation of the $g$-factors from their high-temperature values is indicative of the development of internal fields upon approach to the long-range-ordered phase.

3.4. Magnetic properties of Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$: estimates of Cu–Cu exchange parameters

The presence of the 2D heteropolyhedral Cu-based layers in the crystal structure of Rb$_2$CaCu$_6$(PO$_4$)$_4$O$_2$ suggests low-dimensional magnetic properties of this compound (Takahashi, 1986). LF/AOM calculations indicate that Cu$^{2+}$ ions in the copper sites Cu(1–4) have one unpaired electron occupying a magnetic 3$d$ orbital of the $x^2-y^2$ type; the calculated components of the anisotropic $g$-tensor of the copper sites Cu(1–4) are listed in Table 5. These $g$-values are typical of Jahn–Teller Cu$^{2+}$ ions with the basic square-planar CuO$_4$ coordination in the equatorial plane (with four short Cu–O bonds) and more distant apical oxygen atoms.

Spin coupling between two unpaired electrons on $x^2-y^2$ magnetic orbitals centered on two Cu$^{2+}$ ions depends strongly on the character of the bridging groups and mutual spatial orientation of the two $x^2-y^2$ magnetic orbitals on the Cu$^{2+}$ (A) and Cu$^{2+}$ (B) ions (which is specified by orientation of the two CuO$_4$ square units). Coplanar orientation of neighboring CuO$_4$ squares favors dominant antiferromagnetic (AF) spin coupling, while non-coplanar orientation results in some ferromagnetic (F) superexchange pathways between half-

---

**Table 6**

<table>
<thead>
<tr>
<th>Mineral/compound</th>
<th>Space group</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (')</th>
<th>$V$ (Å$^3$)</th>
<th>FD</th>
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<td>C2</td>
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<td>K$_2$Ca(Cu$_5$O$_7$)F$_2$</td>
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<td>4</td>
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<td>Dmisokolovite†</td>
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<td>5.6406</td>
<td>8.3591</td>
<td>93.919</td>
<td>794.57</td>
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</table>

† Pekov et al. (2015).
Table 7  
Crystallographic data and complexity parameters for rubidium copper phosphates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Z</th>
<th>a (Å), α (%)</th>
<th>b (Å), β (%)</th>
<th>c (Å), γ (%)</th>
<th>V (Å³)</th>
<th>FD</th>
<th>v</th>
<th>I₀ (bits per atom)</th>
<th>I₀total (bits per unit cell)</th>
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<tr>
<td>Orthophosphates</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Henry et al. (2000); † Henry et al. (2010); ‡ Chaouche et al. (2010); †† Yakubovich et al. (2008); †§ Armstrong et al. (2011); † Williams et al. (2012); †∥ Badri et al. (2013); †‡ Yakubovich et al. (2016); †∫ Shvanskaya et al. (2012); †‡ Chernyayeva et al. (2019); †∥ Shvanskaya et al. (2013); † Williams et al. (2013); †¦ Krivovichev & Chernyat'eva (2016). † Because of the absence of crystal structure data, we are not able to calculate FD value and complexity parameters. Moreover, the reported chemical formula is not charge balanced.

filled x²-y² orbitals and other doubly occupied d orbitals. Given that in most of the Cu···Cu pairs in the crystal structure of Rb₂CaCu₃(P₃O₈)₂O₂ the CuO₄ units are non-coplanar, some competition between F and AF contributions might be expected, which would tend to reduce the overall magnitude of the exchange parameter J. More quantitatively, the AF versus F competition is measured by the ratio between the spin-independent (A) and spin-dependent (J) exchange parameters in the full spin Hamiltonian $H = -JS\cdot S_B$ resulting from the superexchange mechanism.

For the spin $S = 1/2$ of Cu²⁺ ions, the AF contributions are described by the J/(1/4 – S_A·S_B) spin Hamiltonian with the J/4 ratio; for the F contribution this ratio is negative. Thus, generally we have J/4 < 0. Therefore, the J/|A| ratio reflects the degree of the AF/F competition in the Cu···Cu pairs: the smaller the J/|A|, the stronger the F contributions, which dominate at J/|A| < 0. With this in mind, we calculated the A and J exchange parameters for all actual exchange-coupled pairs Cu···Cu in Rb₂CaCu₃(P₃O₈)₂O₂ (Table 6).

These data show that, except for the Cu₂–Cu₃ pairs (J/|A| = 3.76), the ratio J/|A| is considerably less than 4, thereby indicating strong F/AF competition in the exchange-coupled pairs. This is consistent with the non-coplanar orientation of the CuO₄ square units with short Cu–O bonds in most of the Cu···Cu pairs. It is also noteworthy that the small value of the spin-independent exchange parameter A necessarily implies a small spin-dependent (conventional) exchange parameter J owing to the relation J/|A| ≤ 4; in other words, a small A value indicates poor efficiency of the bridging groups as mediators of the spin coupling between two magnetic centers Cu²⁺(A) and Cu²⁺(B) (which manifests in small electron transfer

parameters $t_{ij}$). This situation occurs for the Cu₁···Cu¹’ pairs within the copper layer and for the Cu₄···Cu⁴’ pairs connecting two neighboring copper layers, in which a small parameter A combines with a low J/|A| ratio, ultimately resulting in very weak spin coupling (J = +0.28 and J = −0.05 cm⁻¹, respectively, Table 6). It is important to note that these pairs play a key role in the overall magnetic behavior of Rb₂CaCu₃(P₃O₈)₂O₂ as they determine magnetic connectivity within the copper layers (the Cu₁···Cu¹’ pair, weakly ferromagnetic spin coupling with J = +0.28 cm⁻¹) and magnetic coupling between the copper layers (the Cu₄···Cu⁴’ pair, weak AF spin coupling, J = −0.05 cm⁻¹). By contrast, the Cu₂···Cu₃ pairs in the rods composed of edge-sharing CuO₄ squares exhibit a moderately strong AF spin coupling (J = +0.28 cm⁻¹ and J = −0.05 cm⁻¹), respectively, Table 6).

4. Discussion

Rb₂CaCu₃(P₃O₈)₂O₂ belongs to the group of rubidium copper phosphates (Table 6) and is related to fluorophosphates...
RbCu₆(PO₂F₂)(PO₄)₂F₂ and Rb₂Cuₓ(PO₂F₂)ₓ(PO₄)₂F (sic) (Armstrong et al., 2011), which both possess structures based upon heteropolyhedral frameworks. The first compound consists of heteropolyhedral mixed copper phosphate layers linked via isolated PO₄ tetrahedra (O = O, F) [Fig. 9(a)]. Layers are formed by [Cu₆O₄F₆] trimers of face-sharing CuO₆ octahedra and PO₄ tetrahedra [Fig. 9(b)]. Armstrong et al. (2011) reported that the crystal structure of Rb₂Cuₓ(PO₂F₂)ₓ(PO₄)₂F is based upon infinite chains of CuO₆ square-based pyramids and CuO₄F₂ octahedra, which are linked by PO₄F₂ tetrahedra. Unfortunately, there is no further information concerning the crystal structure of this compound.

The chemical formula Rb₂Cuₓ(PO₂F₂)ₓ(PO₄)₂F is notably non-electroneutral, assuming a divalent state of Cu.

Except for Rb₂Cuₓ(H₂PO₄) (Chauouche et al., 2010) and Rb₂Cuₓ(PO₄)₂F₃ (Armstrong et al., 2011), all rubidium copper phosphates have microporous structures with low framework densities from 13.00 to 25.17 Cu+/M [Me = metal?]+/P atoms per 1 nm² (Table 6). Among these, the family of diphosphates with the general formula AₓCu₆(P₂O₇)₄Cl₄(TX₄) (where A = K⁺, Rb⁺, Cs⁺; T = P₂O₇, Cu²⁺, Pt²⁺, Pd²⁺, Au³⁺; X = O²⁻, OH⁻, Cl⁻, Br⁻) (Williams et al., 2013) (Fig. 10) is characterized by very low framework densities of ~13.1 (1). Their [Cu₆(P₂O₇)₄Cl₄]²⁻⁰ open frameworks contain large channels filled by alkaline earth? cations and tetrahedral or planar (TX₄) anions. [Table 7 not yet cited, please include a citation]

5. Conclusion

Single crystals of Rb₂CaCu₆(PO₄)₂O₂ were synthesized by a hydrothermal method. The crystal structure of Rb₂CaCu₆(PO₄)₂O₂ is similar to those of shchurovskite and dmskolovite and is based on a heteropolyhedral open framework formed by polar copper layers linked via isolated PO₄ tetrahedra. The results of our microscopic calculations in terms of a many-electron superexchange model are indicative of possible low-dimensional magnetic behavior of the title material, since they confirm weak magnetic coupling between the Cu-based layers mediated by the Cu₄−Cu₄ pairs (J = −0.05 cm⁻¹). However, the actual character of the low-dimensional magnetism (1D or 2D) is rather uncertain, owing to the presence of weak exchange interactions within the layers (i.e. weakly ferromagnetic Cu₁−Cu′ pairs, J = +0.28 cm⁻¹), which may destroy magnetic connectivity within the copper 2D network and thus tends to further reduce the efficiency dimensionality of the magnetic system. The calculated values of the principal components of the g-tensor nicely correspond to averaged values of g-factors defined experimentally. The low-dimensional magnetic behavior of the title compound is masked by the fierce competition between multiple ferromagnetic and antiferromagnetic exchange interactions. At T_C = 25 K, Rb₂CaCu₆(PO₄)₂O₂ reaches a magnetically ordered state with large residual magnetization M_R. Taking into account the even number of magnetic ions per formula unit one may presume the non-collinear magnetic structure exists at T < T_C, which is to be verified in neutron scattering measurements.

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