Leonard C. Pasqualini and Hubert Huppertz*

High-pressure synthesis of borate-nitrates: crystal structure of $M_3B_7O_{13}(NO_3)$ ($M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$)

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Abstract: The orthorhombic nitrate-boracites with the sum formula $M_3B_7O_{13}NO_3$ ($M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$) were synthesized in a Walker-type multianvil apparatus under high-pressure/high-temperature conditions of 6 GPa and 800 °C, respectively. The crystal structures of the five isotypic substances, which crystallize in the space group $Pca_2_1$, were determined via single-crystal X-ray diffraction and the structural features of the incorporated nitrate anions are discussed.

Keywords: boracite; borate-nitrate; crystal structure; high-pressure synthesis; late first-row transition metals

1 Introduction

The substance class of borate-nitrates shows, for the short age of the topic, a great variety of structurally different members. This variety, however, is unequally distributed, with the majority of borate-nitrates having lanthanide [1–9], alkali [10–14], or lead [15–17] cations for charge compensation. Only a few borate-nitrates feature transition metal cations [18, 19] and just one recently discovered example features an alkaline earth metal cation [20], which suggests that a wide spectrum of borate-nitrates has remained undiscovered. The presence of nitrates has been confirmed by Raman and IR spectroscopy for some borate-nitrates [4–8, 11, 12, 16, 17]. Even though most nitrates decompose at comparable low temperatures, some borate-nitrates show a thermal stability slightly above 450 °C [16, 17], and in the case of Co$_3$B$_7$O$_{13}$NO$_3$ even up to 770 °C.

The sum formula Mg$_3$B$_7$O$_{13}$Cl denotes the mineral Boracite, which lends its name to the substance class of boracites, which all share the structure of the anionic borate network, whereas the divalent cations and second anions are interchangeable by a wide variety of ions [22]. The oxidation state +2 of the cations in boracites is confirmed by magnetic measurements, as summarised by W. Schnelle and H. Schmid in a very detailed review [22]. While the majority of boracites feature a halide as second anion, some contain a chalcogenide (e.g. Mg$_3$B$_7$O$_{12.65}$S$_{0.85}$ [23]) or a hydroxyl group (e.g. Fe$_3$B$_7$O$_{14}$OH·1.5 H$_2$O [24]). In this work, we present the structures of five nitrate containing boracites (short: nitrate-boracites), with the sum formula $M_3B_7O_{13}NO_3$ ($M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$), which were synthesized with a high-pressure/high-temperature (HP/HT) set-up using a multianvil press. The existence of nitrate-boracites has been known for fifty years and their composition was confirmed with elemental analysis; however, a precise crystal structure determination was not reported until now due to the general tendency of (nitrate-)boracite crystals to be highly twinned [21]. The structural features of replacing halides with nitrates are of importance to understand this form of substitution and structurally compare these nitrate-boracites with their corresponding halide-boracites.

To discuss the structural features of the substitution of halide atoms by tetraatomic nitrate groups, the principal structure and the varying modifications of boracites are briefly summarized in the following. The high-temperature modification of boracite crystallizes in the cubic space group $F43c$. The low-temperature modifications exhibit different symmetries, ranging from orthorhombic (space group $Pca_2_1$; example: Ni$_3$B$_7$O$_{13}$Br [25]), monoclinic (Fe$_3$B$_7$O$_{13}$I; two transition phases in a narrow temperature range [26]), trigonal (space group $R3c$; example: Co$_3$B$_7$O$_{13}$Cl [27]) to tetragonal (space group $P$42$_1$2$_1$2; Cr$_3$B$_7$O$_{13}$Cl [28]) symmetry. The structure of the anionic borate network, which is also the main difference to the cubic high-temperature modification, is the same for all low-temperature modifications.

Cubic boracites consist of an anionic borate network, which forms channels along all the crystallographic axes.
in the cubic modification. The Fundamental Building Block (FBB) of this network, which is depicted in Figure 1, consists of seven (BO₄) tetrahedra, of which four are connected via one common vertex, which results in an elongation of the B–O bonds to the central oxygen atom. Each of the remaining three tetrahedra shares two oxygen atoms with this O(BO₃)₄ unit and connects it along the crystallographic axes with other such units. In Figure 2, the anionic substructure, consisting of those FBBs, can be seen. Inside the aforementioned channels, divalent metal cations M and monovalent anions X reside in an alternating pattern forming MO₄X₂ octahedra, with the oxygen atoms belonging to the anionic substructure, and XM₆ octahedra. As a result, the chains intersect at the X anions, as depicted in Figure 3.

The main difference between cubic (space group F43c) and orthorhombic boracites (Pca₂) is the change from the fourfold coordinated oxygen atom to a threefold coordinated oxygen atom and disconnecting one of the four distorted OBO₃ tetrahedra to form a trigonal planar (BO₃) unit. Except for this change to a (BO₃) unit, which is highlighted in Figure 1, the anionic substructure and channels remain structurally the same. While the M–X distances in the cubic boracites are equidistant, the metal cations are shifted towards one anion in orthorhombic boracites.

Figure 1: Top: O(BO₃)₄ tetrahedron (blue tetrahedra, left) and the resulting fundamental building block (FBB, right) with three connecting (BO₄) tetrahedra (yellow) and three connecting edges for three further FBBs (yellow lines) of cubic boracite. Bottom: Corresponding FBB of orthorhombic boracite. The ejection of one of the boron atoms to form a trigonal planar (BO₃) unit is highlighted.

Figure 2: Unit cell of cubic Cu₃B₇O₁₃Br [29] (left) and the structure of the orthorhombic Cu₃B₇O₁₃NO₃ (right). One FBB, which creates the borate network is highlighted in the middle of each structure.
boracites, which results in kinked chains with alternating long and short $M$–$X$ bond lengths [27].

2 Experimental section

2.1 Synthesis

The title compounds were synthesized by homogenizing and grinding $B_2O_3$ (99.9%, Strem Chemicals) and one of the respective hydrated nitrates (Co(NO$_3$)$_2$·6H$_2$O (99%, Merck), Ni(NO$_3$)$_2$·6H$_2$O (99%, Merck), Cu(NO$_3$)$_2$·3H$_2$O (≥ 98%, Sigma-Aldrich), Zn(NO$_3$)$_2$·6H$_2$O (99%, Sigma-Aldrich), Cd(NO$_3$)$_2$·4H$_2$O (99%, Sigma-Aldrich)) in a stoichiometric ratio of 7:6 in an agate mortar. The mixed reagents were encapsulated in Pt capsules, which were placed in α-BN (Henze Boron Nitride Products AG) crucibles with fitting lids of the same material. The experiments were carried out in 18/11 assemblies. All syntheses were performed via HP/HT methods using a Walker-type multianvil module within a 1000 t hydraulic press (Max Voggenreiter GmbH). The compression was carried out in a two step-process in a device consisting of six steel wedges and eight tungsten carbide cubes (Hawedia) as outer and inner anvils, respectively. Further details concerning this kind of setup are described in the literature [30–32].

The synthesis conditions were 6 GPa and 800 °C. Pressure was built up in 150 min, followed by heating to the desired temperature within 10 min. The temperature of the reaction mixture was held for 240 min and afterwards quenched to room temperature within a few minutes. Decompression to ambient conditions was performed within 450 min. The crystalline products were isolated from the beforehand cleaned Pt capsule for further characterization.

2.2 Phase identification and structure determination by X-ray diffraction

With the exception of Cd$_3$B$_7$O$_{13}$NO$_3$, all other products were not obtained in a phase pure manner, exhibiting one additional side product that was formed along with each respective nitrate-boracite. The formation of side products has previously been reported, yet most of the examples now known were published decades later [21]. Side products were identified on the basis of X-ray powder patterns.

All five samples were examined under a polarization Leica 125M microscope and suitable single-crystals were isolated and measured with a Bruker D8 Quest diffractometer equipped with a Photon 100 CMOS detector. The program WinGX-2018.1 [33] was used for the calculation of the structures, which were solved and refined with the implemented SHELXL-2014/4 [34] and SHELXL-2017/1 [35, 36] routines. The space group of all five substances could be determined as $Pca_2_1$ (no. 29) due to the systematic extinction conditions. The atom coordinates were standardized with the STRUCTURETIDY [37] routine from the PLATON [38] package. Due to the non-centrosymmetry of the space group, some structures were inverted with the command MOVE 1 1 1 to receive a Flack ($x$) parameter close to 0, as the standardized coordinates corresponded to the inverted twin domain. Except for the non-metal atoms of Co$_3$B$_7$O$_{13}$NO$_3$, for which the only single-crystal that could be isolated was very small, all atoms of all other structures could be refined anisotropically.

The anisotropic parameters of the oxygen atoms of the nitrate group were exceptionally large. When refining these atoms on split positions, the sums of the occupancy of the two parts equaled one within the deviation from one of the other atoms, when their occupancy was refined freely. Every oxygen atom had a very similar ratio of the split occupancies, which is why they were categorized into two groups and the sum of their occupancy was fixed to 1 with the SUMP 1.0 0.0001 1.0 2 1.0 3 command. This decreased the $U_{eq}$ values of the oxygen atoms significantly. An exception to this is again Co$_3$B$_7$O$_{13}$NO$_3$, in which every split position received its own occupancy distribution to achieve convergence of the refinement.

CSD-2190381 for Co$_3$B$_7$O$_{13}$NO$_3$, CSD-2190383 for Ni$_3$B$_7$O$_{13}$NO$_3$, CSD-2190385 for Cu$_3$B$_7$O$_{13}$NO$_3$, CSD-2190382 for Zn$_3$B$_7$O$_{13}$NO$_3$, and CSD-2190384 for Cd$_3$B$_7$O$_{13}$NO$_3$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
3 Results and discussion

3.1 Description of the products

With the exception of $\text{Cd}_3\text{B}_7\text{O}_{13}\text{NO}_3$, all the nitrate-boracites reported here exhibit a characteristic color, which makes them easily distinguishable from their side products. A summary of the description of the products is listed in Table 1. In Figure 4, photographs of the synthesized substances are provided.

<table>
<thead>
<tr>
<th>Nitrate-boracite</th>
<th>Side products</th>
<th>Substance</th>
<th>Color</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cd}_3\text{B}<em>7\text{O}</em>{13}\text{NO}_3$</td>
<td>Colorless</td>
<td>None</td>
<td>Colorless</td>
<td>[39]</td>
</tr>
<tr>
<td>$\text{Co}_3\text{B}<em>7\text{O}</em>{13}\text{NO}_3$</td>
<td>Purple-red</td>
<td>$\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$</td>
<td>Rose</td>
<td>[40]</td>
</tr>
<tr>
<td>$\text{Cu}_3\text{B}<em>7\text{O}</em>{13}\text{NO}_3$</td>
<td>Yellow</td>
<td>$\text{Cu(B}_3\text{O}_7)$</td>
<td>Blue</td>
<td>[41]</td>
</tr>
<tr>
<td>$\text{Ni}_3\text{B}<em>7\text{O}</em>{13}\text{NO}_3$</td>
<td>Red-orange</td>
<td>$\text{NiB}_3\text{O}_5(\text{OH})$</td>
<td>Turquoise</td>
<td>[42]</td>
</tr>
<tr>
<td>$\text{Zn}_3\text{B}<em>7\text{O}</em>{13}\text{NO}_3$</td>
<td>Pale yellow</td>
<td>$\beta\text{-Zn(B}_3\text{O}_5)$</td>
<td>Colorless</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4: Photographs of the synthesized boracites and their respective side products. All (side) products are directly labeled with their sum formula, as written in Table 1.
Table 2: Single-crystal data and structure refinement of M₅BₓO₁₃NO₃ (M = Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺).  

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>Co₅BₓO₁₃(NO₃)</th>
<th>Ni₅BₓO₁₃(NO₃)</th>
<th>Cu₅BₓO₁₃(NO₃)</th>
<th>Zn₅BₓO₁₃(NO₃)</th>
<th>Cd₅BₓO₁₃(NO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass, g mol⁻¹</td>
<td>522.5</td>
<td>521.8</td>
<td>536.4</td>
<td>541.8</td>
<td>682.9</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single-crystal diffractometer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiation/wavelength Å, Å</td>
<td>8.7560(6)</td>
<td>8.7144(4)</td>
<td>8.6621(3)</td>
<td>8.7469(9)</td>
<td>9.003(2)</td>
</tr>
<tr>
<td>a, Å</td>
<td>8.494(6)</td>
<td>8.4540(4)</td>
<td>8.4433(3)</td>
<td>8.5023(8)</td>
<td>8.815(2)</td>
</tr>
<tr>
<td>b, Å</td>
<td>12.020(2)</td>
<td>12.1453(5)</td>
<td>12.1028(4)</td>
<td>12.217(2)</td>
<td>12.590(2)</td>
</tr>
<tr>
<td>c, Å</td>
<td>907.5(2)</td>
<td>894.8(7)</td>
<td>885.2(5)</td>
<td>908.6(2)</td>
<td>999.2(2)</td>
</tr>
<tr>
<td>R, Å</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Crystal size, mm³</td>
<td>0.01 × 0.02 × 0.05</td>
<td>0.04 × 0.05 × 0.05</td>
<td>0.06 × 0.08 × 0.12</td>
<td>0.04 × 0.08 × 0.14</td>
<td>0.04 × 0.06 × 0.13</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>173(2)</td>
<td>209(2)</td>
<td>290(2)</td>
<td>280(2)</td>
<td>187(2)</td>
</tr>
<tr>
<td>Absorption coefficient, mm⁻¹</td>
<td>5.6</td>
<td>6.4</td>
<td>7.3</td>
<td>8.0</td>
<td>6.5</td>
</tr>
<tr>
<td>R(000), e</td>
<td>1004</td>
<td>1016</td>
<td>1028</td>
<td>1040</td>
<td>1256</td>
</tr>
<tr>
<td>θ, deg</td>
<td>3.34−31.42</td>
<td>3.35−39.42</td>
<td>2.41−41.30</td>
<td>2.40−38.05</td>
<td>2.31−39.45</td>
</tr>
<tr>
<td>Range in hkl</td>
<td>−12 ≤ h ≤ 12; −12 ≤ k ≤ 11; −16 ≤ l ≤ 17</td>
<td>−16 ≤ h ≤ 16; −15 ≤ k ≤ 15</td>
<td>−16 ≤ h ≤ 16; −15 ≤ k ≤ 15</td>
<td>−16 ≤ h ≤ 16; −15 ≤ k ≤ 15</td>
<td>−16 ≤ h ≤ 16; −15 ≤ k ≤ 15</td>
</tr>
<tr>
<td>Refl. Total/Independent</td>
<td>17426/2876</td>
<td>91887/5375</td>
<td>90873/5969</td>
<td>33072/4725</td>
<td>32044/5800</td>
</tr>
<tr>
<td>Rw/Ro</td>
<td>0.0650/0.0501</td>
<td>0.0621/0.0261</td>
<td>0.0571/0.0269</td>
<td>0.0247/0.0301</td>
<td>0.0223/0.0195</td>
</tr>
<tr>
<td>Refl. with I &gt; 2σ(I)</td>
<td>2280</td>
<td>4865</td>
<td>5228</td>
<td>4542</td>
<td>5511</td>
</tr>
<tr>
<td>Data/restr./ref. parameters</td>
<td>2876/2/141</td>
<td>5375/2/245</td>
<td>5969/2/245</td>
<td>4725/2/245</td>
<td>5800/2/245</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final R1/σ(R1)</td>
<td>0.0404/0.0709</td>
<td>0.0352/0.0935</td>
<td>0.0273/0.0586</td>
<td>0.0192/0.0436</td>
<td>0.0174/0.0402</td>
</tr>
<tr>
<td>Final R1/σ(R2) (all data)</td>
<td>0.0618/0.0748</td>
<td>0.0408/0.0960</td>
<td>0.0360/0.0612</td>
<td>0.0206/0.0441</td>
<td>0.0190/0.0408</td>
</tr>
<tr>
<td>x(Flack)</td>
<td>−0.01(2)</td>
<td>0.05(2)</td>
<td>0.02(1)</td>
<td>0.018(8)</td>
<td>−0.03(2)</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.066</td>
<td>1.086</td>
<td>1.021</td>
<td>1.056</td>
<td>1.083</td>
</tr>
<tr>
<td>Largest diff. peak/hole, e Å⁻³</td>
<td>0.70/−0.76</td>
<td>2.12/−1.65</td>
<td>0.82/−1.00</td>
<td>1.09/−0.49</td>
<td>1.33/−0.81</td>
</tr>
</tbody>
</table>

3.2 Crystal structures

All nitrate-borate crystals crystallize in the orthorhombic space group Pca₂ (no. 29), as a lot of transition metal halide boracites do in their low-temperature modification [25, 43–46]. The unit cell consists of four formula units (Z = 4) and the lattice parameters vary between a = 8.6621(3) to 8.7560(6), b = 8.4433(3) to 8.5023(8), and c = 12.0208(4) to 12.2168(11) Å, which results in V = 885.2(5) to 908.55(14) Å³ for the 3d transition metals, with Cu₅BₓO₁₃NO₃ being the smallest and Co₅BₓO₁₃NO₃ and Zn₅BₓO₁₃NO₃ being the largest. The lattice parameters of Cd₅BₓO₁₃NO₃ are 2.9–3.6% larger than those of Zn₅BₓO₁₃NO₃, which results in an increase of the cell volume of about 10%. A list containing details of the structure refinement based on the single-crystal data is found in Table 2. Bond valence sums (BVS) were calculated for all substances with the bond-length/bond-strength concept [47, 48] and a charge distribution was calculated using the charge distribution in solids (CHARDI) concept [49, 50]. For these calculations, the structures with anisotropically refined, unsplit nitrate oxygen atoms were used. Lists containing the atomic coordinates, displacement parameters, interatomic distances, angles, and charge calculations are given in the Supporting Information available online in Tables S1–S25.

The structural difference between the nitrate-borate crystals and the corresponding halide-boracites can be summarized in two points: the length difference between the a and b axes and the resulting deviance of the M–M and especially the N–N distances within the chains. As within all boracites [22], the bonding situation within the anionic boron network, which is depicted in Figures 1 and 2, is rather unaffected by the M and X species. Therefore, the focus of this study lies on the bonding situation of the nitrate anion.

As the monoatomic halide anion X is substituted by the tetraatomic nitrate group (NO₃)⁻, the nitrogen atom resides at the position of the X, with the three oxygen atoms binding to two of the six surrounding M atoms with varying bond lengths. To relate the halide-boracites with the nitrate-borate crystals, comparing the N–M distances or the corresponding coordination polyhedra helps to understand the structural features, even though those atoms are not directly bonded. In contrast to the orthorhombic low temperature halide-boracites, in which the axes a and b are nearly identical and the ratio c/a = √2, the two axes in the nitrate-borate crystals are significantly different, as can be seen in Table 2. The mean of c/a and c/b, however, equals √2 with a difference of less than 0.2%. 
CdNiCu channels, which are the vertices of one edge of the (NO3) octahedron, which are connected by one oxygen atom, are marked in orange and their lengths are given. The (NO3) groups resulting from the split oxygen positions are colored green and purple.

Especially O14 and O14A, which correspond to the longest octahedron. As already mentioned, every (NO3)M6 octahedron, as depicted in Figure 5. The longer this edge, the larger is the anisotropic displacement of the corresponding oxygen atom. As mentioned in the Experimental Section, the oxygen atoms were refined on split positions. Especially O14 and O14A, which correspond to the longest edge, are displaced up to 0.4 Å from one another (in Ni3B7O13NO3). A picture of this complex situation is shown in Figure 5. A summary of the split positions and the corresponding distances is given in Table 3. An exception from this heavy distortion is Cd3B7O13NO3, as the split positions of the oxygen atoms of the nitrate group are relatively close to each other, especially when considering the larger cell parameters, as the oxygen atoms of the nitrate group are nearly centered in the middle of the faces of the (NO3)Cd6 octahedron.

The already mentioned shift of the M cations towards one of the two opposing nitrate groups results in the M06 octahedra resembling rather a distorted monocapped square pyramid (5 + 1) than a stretched octahedron. The deviation of the (N–)O–M–O(–N) angle from 180° is a result of the cation M binding to one of the three oxygen atoms of the nitrate anion instead of the nitrogen atom directly, which resides on the position of the anion X of the related halide-boracites. The N–M–N angles are nearly identical to the X–M–X angles.

### 4 Conclusions

This publication confirms the existence of nitrate-boracites with late first-row transition metals and sheds light on their crystal structures, which were hitherto unknown. The comparison of the crystal structures of nitrate-boracites with those of the respective halide-boracites shows the variation in the structural features induced by the substitution of a monoatomic anion with a trigonal planar tetraatomic anion. This knowledge may now suggest other candidates for the substitution of halides with nitrates to expand the promising field of borate-nitrates.

### Table 3: N–N distances within the channels and the Osplit–Osplit distances plus the corresponding edge lengths (cel) of the (NO3)M6 octahedron.

<table>
<thead>
<tr>
<th></th>
<th>c axis</th>
<th>ab dia.</th>
<th>O14–O14A</th>
<th>cel</th>
<th>O15–O15A</th>
<th>cel</th>
<th>O16–O16A</th>
<th>cel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>6.101(9)</td>
<td>5.943(6)</td>
<td>0.41(4)</td>
<td>4.607(2)</td>
<td>0.14(3)</td>
<td>3.977(1)</td>
<td>0.29(3)</td>
<td>4.204(2)</td>
</tr>
<tr>
<td>Ni</td>
<td>6.073(9)</td>
<td>5.941(5)</td>
<td>0.41(2)</td>
<td>4.4195(8)</td>
<td>0.18(2)</td>
<td>3.9421(7)</td>
<td>0.28(1)</td>
<td>4.1858(8)</td>
</tr>
<tr>
<td>Cu</td>
<td>6.051(6)</td>
<td>5.856(3)</td>
<td>0.25(1)</td>
<td>4.3860(5)</td>
<td>0.22(1)</td>
<td>4.0047(4)</td>
<td>0.21(1)</td>
<td>4.1947(5)</td>
</tr>
<tr>
<td>Zn</td>
<td>6.109(4)</td>
<td>5.915(2)</td>
<td>0.262(5)</td>
<td>4.4707(5)</td>
<td>0.17(5)</td>
<td>3.9360(5)</td>
<td>0.17(9)</td>
<td>4.1725(4)</td>
</tr>
<tr>
<td>Cd</td>
<td>6.296(6)</td>
<td>6.020(3)</td>
<td>0.19(1)</td>
<td>4.5917(5)</td>
<td>0.20(1)</td>
<td>4.0981(6)</td>
<td>0.20(1)</td>
<td>4.3128(5)</td>
</tr>
</tbody>
</table>

Figure 5: View on a (NO3)Ni6 octahedron. The three edges of the octahedron, which are connected by one oxygen atom, are marked in orange and their lengths are given. The (NO3) groups resulting from the split oxygen positions are colored green and purple.
5 Supporting information

Additional crystal structure data is given as supplementary material available online (https://doi.org/10.1515/znb-2022-0106).

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References


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