Synthesis and Crystal Structure of \((\text{CH}_3\text{NH}_3)_2[\text{Cu(NO}_3)_4]\): a Rare Example of a Tetrarotacuprate(II) with a Light Cation of the Type \(M_2[\text{Cu(NO}_3)_4]\)

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Abstract. The reaction of methylammonium nitrate and copper(II) nitrate pentahemihydrate in concentrated nitric acid yields the novel bis(methylammonium) tetrarotacuprate(II). By evaporation of the nitric acid at elevated temperatures single crystals suitable for crystal structure analysis by X-ray diffraction were obtained. The crystal structure shows a clear Jahn-Teller distortion in the octahedral tetrarotacuprate anion.

Keywords: Coordination chemistry; Cuprates; Jahn-Teller distortion; Tetrarotacuprate(II); Crystal structures

Introduction

Water-free tetrarotacuprates(II) are a class of oxygen-rich compounds with potential applicability as pyrotechnic oxidizers [1, 2]. For monovalent cations, the cation:cupper ratio can generally be 1:1 (compounds of the type \(M[\text{Cu(NO}_3)_4]\), type 1), 2:1 (\(M_2[\text{Cu(NO}_3)_4]\), type 2), 3:1 (\(M_3[\text{Cu(NO}_3)_4]\), type 3) or 4:1 (\(M_4[\text{Cu(NO}_3)_4]\), type 4). The few structurally characterized examples of tetrarotacuprates(II) include the following compounds: type 1: \(M = \text{NO}^+\) [3, 4]; type 2: \(M = \text{Na}^+, \text{Ag}^+\) [4], \(\text{Cs}^+\) [5], \(\text{Ph}_4\text{As}^+\) [6, 7] and several complexes with cations containing large organic ligands [8–11]; type 3: \(M = \text{NH}_4^+, \text{K}^+, \text{Rb}^+\) [5]; type 4: \(M = \text{benzylammonium}\) [12].

From the above list, it is obvious that most light cations (atomic weight < approx. 100) generally prefer a co-crystallization of their nitrate and the tetrarotacuprate(II) anion (types 3 and 4). The only exception so far are the corresponding sodium (type 2) and nitrosylum compounds (type 1). In this contribution, we present the synthesis and crystal structure of the novel bis(methylammonium) tetrarotacuprate(II), \((\text{CH}_3\text{NH}_3)_2[\text{Cu(NO}_3)_4]\) (1). Methylammonium is the second lightest cation (\(M = 32.08\)), which forms a type 2 tetrarotacuprate salt, characterized by single crystal X-ray diffraction.

Results and Discussion

The crystal structure of 1 is shown in Figure 1. The \(\text{Cu}^{II}\) ion is coordinated by four nitrate ions. Two of them (N1) act as anisobidentate ligands [8, 13]. In this case, the

\begin{center}
\includegraphics[width=0.3\textwidth]{structure.png}
\end{center}

Fig. 1 Molecular structure of 1 in the crystal. Only selected hydrogen atoms are labeled for clarity.

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Cu1−O3 bond (2.527(1) Å) is significantly longer than Cu1−O1 (1.967(1) Å), which is due to Jan–Teller distortion. The bond length of the monodentate nitrate ligand (Cu1−O4) is similar (1.958(1) Å) to that of Cu1−O1. Thus the equatorial (almost) square plane is formed by each of O1 and O4 atoms, whereas the elongated axial positions of the octahedron are occupied by the two O3 atoms. The distorted octahedral coordination environment is similar to that of NO3Cu(NO3)2 [4]. In 1, one can differentiate three different categories of Cu−O distances; four short Cu−O bonds (Cu1−O1 and Cu1−O4) forming the square plane, two elongated axial Cu−O bonds (Cu1−O3) and two much longer Cu1−O5 distances (2.908(1) Å). In nitratocuprates(II) described as square planar complexes (e.g. [8, 12]), only two different categories of Cu−O distances are found. In the crystal structure of 1, hydrogen bonds are present and allow the assignment of the ammonium and the methyl group of the cation (see Table 2). The anions are bridged via these hydrogen bonds, which is probably the reason for the stability of this unusual type 2-tetranitratocuprate(II) with a light cation.

Table 1 Selected bond lengths /Å and angles /° of 1

<table>
<thead>
<tr>
<th></th>
<th>Cu1−O1</th>
<th>N1−O2</th>
<th>Cu1−O3</th>
<th>N1−O3</th>
<th>Cu1−O4</th>
<th>N2−O4</th>
<th>Cu1−O5</th>
<th>N2−O5</th>
<th>Cu1−O6</th>
<th>N3−O6</th>
<th>Cu1−O7</th>
<th>N3−O7</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond length /Å</td>
<td>1.967(1)</td>
<td>1.221(2)</td>
<td>2.527(1)</td>
<td>1.245(2)</td>
<td>1.958(1)</td>
<td>1.296(1)</td>
<td>1.468(2)</td>
<td>1.224(2)</td>
<td>1.293(2)</td>
<td>1.390(2)</td>
<td>106.23(8)</td>
<td></td>
</tr>
<tr>
<td>bond angle /°</td>
<td>81.12(8)</td>
<td>92.73(4)</td>
<td>117.74(8)</td>
<td>124.15(4)</td>
<td>106.23(8)</td>
<td>117.74(8)</td>
<td>124.15(4)</td>
<td>106.23(8)</td>
<td>117.74(8)</td>
<td>124.15(4)</td>
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</tbody>
</table>

Table 2 Hydrogen bonding in 1

| D−H−A /Å | 0.82(3) | 2.26(3) | 3.037(2) | 158.2(2) | 0.82(3) | 2.48(2) | 2.983(2) | 121.2(2) | 0.87(2) | 2.05(2) | 2.914(2) | 175.2(2) | 0.76(2) | 2.19(2) | 2.948(2) | 171.2(2) |
| D−H /Å  | 0.82(3) | 2.26(3) | 3.037(2) | 158.2(2) | 0.82(3) | 2.48(2) | 2.983(2) | 121.2(2) | 0.87(2) | 2.05(2) | 2.914(2) | 175.2(2) | 0.76(2) | 2.19(2) | 2.948(2) | 171.2(2) |

Symmetry codes: (i) x−1, 0.5+y, 1−z; (ii) x, 1.5−y, 0.5+z; (iii) 1−x, 1−y, 2−z

The packing of 1 along [010] is shown in Figure 2. It can be described as a packing of superposed tetranitratocuprate anions intercalated with staggered layers of methylammonium cations.

Compound 1 is the first alkylammonium nitratocuprate(II), which has been structurally characterized. The synthesis of several other alkylammonium nitrates has also been tried in this study, e.g. that of the NMMe₃H₃⁺*, NMMe₃H⁺, NMMe₃⁺, NEt₄⁺, N(nPr)₄⁺ and N(nBu)₄⁺ salts. However, in no other case, single crystals of the corresponding nitratocuprate could be obtained. In several cases, the reactions produced dark blue or dark green ionic liquids. In some cases, the hot reaction mixture reacted violently forming a brown solid and NO₃ gas. This was probably due to the formation of alkyl nitrate esters which exothermally decomposed.

**Experimental Section**

**Synthesis**

A solution of 3.46 g (52 mmol) CH₃NH₃·HCl in concentrated nitric acid (3×5 mL, 65% HNO₃) was evaporated (not to complete dryness) three times on an oil bath (110 °C) to remove any chloride.
To the residual solution, 4 g of Cu(NO₃)₂, 2.5 H₂O (17 mmol) were added. A few drops of nitric acid were added in order to dissolve the copper nitrate crystals. During slow evaporation at 110 °C, greenish-blue single crystals of I formed in the solution. They were removed from the liquid and used for X-ray diffraction. Attention has to be paid to the highly hygroscopic character of I in air after removal from the nitric acid. The crystals rapidly hydrolyze and melt in the crystal water.

IR (Diamond-ATR, cm⁻¹): 3539 (s), 3319 (vs), 3238 (sh), 2468 (w), 2344 (w), 2088 (vw), 1763 (w), 1732 (vw), 1609 (m), 1511 (sh), 1414 (vs), 1277 (vs), 1044 (m), 1017 (s), 939 (w), 874 (w), 800 (m), 759 (m), 715 (vw), 664 (m), 517 (m); Raman (25 °C, cm⁻¹): 2987 (23), 2329 (s), 1597 (23), 1526 (28), 1319 (21), 1047 (100), 986 (14), 765 (23), 714 (19), 462 (5), 294 (37).

X-Ray Crystallography

Data collection was performed with an Oxford Xcalibur diffractometer equipped with a CCD area detector, using Mo-Kα radiation (wavelength λ = 0.71073 Å). The structure was solved using direct methods (SHELXS [14]) and refined by full-matrix least-squares on F². (SHELXL [14]). All non-hydrogen atoms were refined anisotropically. The ORTEP plots of the figures show thermal ellipsoids at the 50% probability level. Crystallographic data for the structure of I have been deposited with the Cambridge Crystallographic Data Centre under the deposit number 666756. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: int. code + (1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

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References