

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

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**Abstract.** The reaction of methylammonium nitrate and copper(II) nitrate pentahemihydrate in concentrated nitric acid yields the novel bis(monomethylammonium) tetranitratocuprate(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 nitratocuprate anion.

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

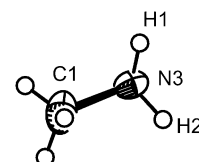
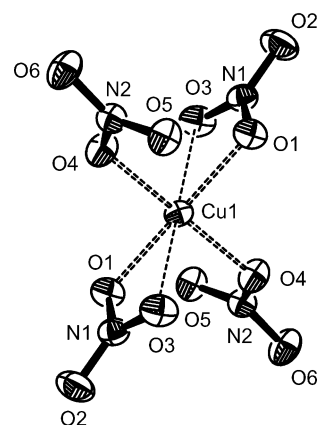
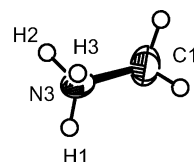
## Introduction

Water-free nitratocuprates(II) are a class of oxygen-rich compounds with potential applicability as pyrotechnic oxidizers [1, 2]. For monovalent cations, the cation:copper ratio can generally be 1:1 (compounds of the type  $\text{M}[\text{Cu}(\text{NO}_3)_3]$ , type 1), 2:1 ( $\text{M}_2[\text{Cu}(\text{NO}_3)_4]$ , type 2), 3:1 ( $\text{M}_3[\text{Cu}(\text{NO}_3)_4(\text{NO}_3)]$ , type 3) or 4:1 ( $\text{M}_4[\text{Cu}(\text{NO}_3)_4(\text{NO}_3)_2]$ , type 4). The few structurally characterized examples of nitratocuprates(II) include the following compounds; type 1:  $\text{M} = \text{NO}^+$  [3, 4]; type 2:  $\text{M} = \text{Na}^+$ ,  $\text{Ag}^+$  [4],  $\text{Cs}^+$  [5],  $\text{Ph}_4\text{As}^+$  [6, 7] and several complexes with cations containing large organic ligands [8–11]; type 3:  $\text{M} = \text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  [5]; type 4:  $\text{M} = \text{benzylammonium}$  [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 nitratocuprate(II) anion (types 3 and 4). The only exception so far are the corresponding sodium (type 2) and nitrosylium compounds (type 1). In this contribution, we present the synthesis and crystal structure of the novel bis(methylammonium) tetranitratocuprate(II),  $(\text{CH}_3\text{NH}_3)_2[\text{Cu}(\text{NO}_3)_4]$  (**1**). Methylammonium is the second lightest cation ( $M = 32.08$ ), which forms a type 2 nitratocuprate salt, characterized by single crystal X-ray diffraction.

## Results and Discussion

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



**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 the that of Cu1–O1. Thus the equatorial (almost) square plane is formed by each two 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  $\text{NO}[\text{Cu}(\text{NO}_3)_3]$  [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**

|           |           |           |           |
|-----------|-----------|-----------|-----------|
| Cu1–O1    | 1.967(1)  | N1–O2     | 1.221(2)  |
| Cu1–O3    | 2.527(1)  | N1–O3     | 1.245(2)  |
| Cu1–O4    | 1.958(1)  | N2–O4     | 1.296(1)  |
| C1–N3     | 1.468(2)  | N2–O5     | 1.224(2)  |
| N1–O1     | 1.293(2)  | N2–O6     | 1.239(2)  |
| N1–O1–Cu1 | 106.23(8) | N1–O3–Cu1 | 81.12(8)  |
| N2–O4–Cu1 | 117.74(8) | O3–Cu1–O4 | 92.73(4)  |
| O4–Cu1–O1 | 90.88(4)  | O1–Cu1–O3 | 124.15(4) |

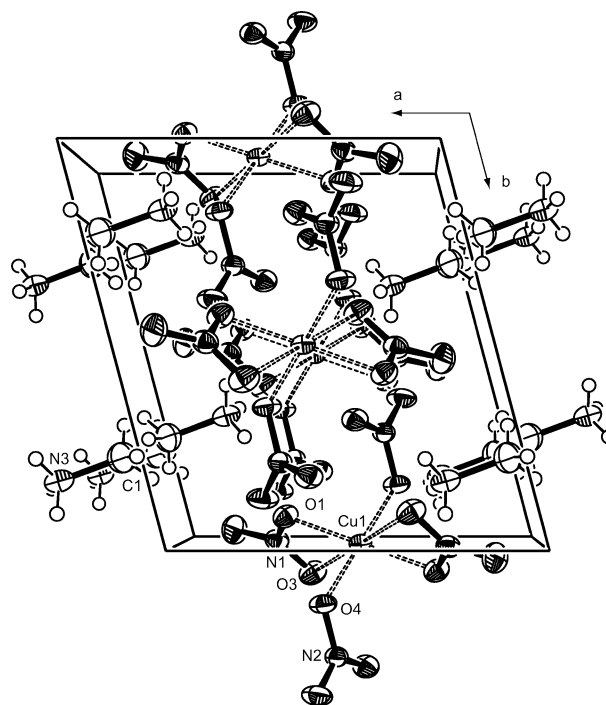
**Table 2** Hydrogen bonding in **1**

| $D\cdots H\cdots A$                        | $D\cdots H$ /Å | $H\cdots A$ /Å | $D\cdots A$ /Å | $D\cdots H\cdots A$ /° |
|--|----------------|----------------|----------------|------------------------|
| $\text{N3}-\text{H1}\cdots\text{O6}^i$     | 0.82(3)        | 2.26(3)        | 3.037(2)       | 158.(2)                |
| $\text{N3}-\text{H1}\cdots\text{O4}^i$     | 0.82(3)        | 2.48(3)        | 2.983(2)       | 121.(2)                |
| $\text{N3}-\text{H2}\cdots\text{O3}^{ii}$  | 0.87(2)        | 2.05(2)        | 2.914(2)       | 175.(2)                |
| $\text{N3}-\text{H3}\cdots\text{O6}^{iii}$ | 0.76(2)        | 2.19(2)        | 2.948(2)       | 171.(2)                |

Symmetry codes: (i)  $1-x, 0.5+y, 1.5-z$ ; (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  $\text{NMe}_2\text{H}_2^+$ ,  $\text{NMe}_3\text{H}^+$ ,  $\text{NMe}_4^+$ ,  $\text{NEt}_4^+$ ,  $\text{N}(\text{nPr})_4^+$  and  $\text{N}(\text{nBu})_4^+$  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  $\text{NO}_x$  gas. This was probably due to the formation of alkyl nitrate esters which exothermally decomposed.



**Fig. 2** View of the unit cell of **1** along [010]. Only selected atoms are labeled for clarity.

**Table 3** Crystal structure and refinement data of **1**

|  |  |
|--|--|
| empirical formula                            | $\text{C}_2\text{H}_{12}\text{N}_6\text{O}_{12}\text{Cu}$            |
| formula weight /g mol <sup>-1</sup>          | 375.72   |
| temperature /K                               | 200  |
| crystal size /mm                             | $0.35 \times 0.25 \times 0.1$  |
| crystal system                               | monoclinic   |
| space group                                  | $P2_1/c$   |
| $a$ /Å                                       | 8.4533(2)  |
| $b$ /Å                                       | 8.6922(2)  |
| $c$ /Å                                       | 9.3943(2)  |
| $\beta$ /°                                   | 104.82(0)  |
| $V$ /Å <sup>3</sup>                          | 667.3(4)   |
| $Z$  | 2  |
| $\rho_{\text{calc}}$ /g cm <sup>-3</sup>     | 1.8698   |
| $\mu$ /mm <sup>-1</sup>                      | 1.714  |
| $F(000)$                                     | 382  |
| $\theta$ range /°                            | 3.73–32.25   |
| index ranges                                 | $-12 \leq h \leq 12$<br>$-12 \leq k \leq 12$<br>$-14 \leq l \leq 13$ |
| reflections collected                        | 19343  |
| reflections unique                           | 2276 ( $R_{\text{int}} = 0.036$ )                                    |
| $R1$ (2 $\sigma$ )                           | 0.024  |
| $R1$ (all data)                              | 0.041  |
| $wR2$ (2 $\sigma$ )                          | 0.060  |
| $wR2$ (all data)                             | 0.067  |
| data/restraints/parameters                   | 2276/0/122   |
| GOOF on $F^2$                                | 1.013  |
| $\Delta\rho_{\text{max}}$ /e Å <sup>-3</sup> | 0.36   |
| $\Delta\rho_{\text{min}}$ /e Å <sup>-3</sup> | -0.32  |

## Experimental Section

### Synthesis

A solution of 3.46 g (52 mmol)  $\text{CH}_3\text{NH}_3 \cdot \text{HCl}$  in concentrated nitric acid (3 × 5 mL, 65 %  $\text{HNO}_3$ ) 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  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$  (17 mmol) were added. A few drops of nitric acid were added in order to dissolve the copper nitrate completely. During slow evaporation at 110 °C, greenish-blue single crystals of **1** 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 **1** in air after removal from the nitric acid. The crystals rapidly hydrolyse and melt in the crystal water.

**IR** (Diamond-ATR,  $\text{cm}^{-1}$ ): 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,  $\text{cm}^{-1}$ ): 2987 (23), 2329 (5), 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  $\text{Mo-K}\alpha$  radiation (wavelength  $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved using direct methods (SHELXS [14]) and refined by full-matrix least squares on  $F^2$ . (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 **1** have been deposited with the Cambridge Crystallographic Data Centre under the depository number 666736. 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)336-0333; email for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

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