Synthesis and Characterization of a New Infinite 1D Polyoxomolybdate Polymer Further Connected *via* Cu(I) Nicotinate Subunits

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Single crystals of $Cu(C_6H_4NO_2)(C_6H_5NO_2)(H_2O)_2[Mo_2O_6]_n$ were grown hydrothermally and characterized by X-ray diffraction and elemental analysis. This compound shows a new $^1_\infty\{Mo_2O_8\}^{4-}$ infinite polymer chain, which is connected *via* copper(I) nicotinate subunits, forming an overall 3D network.

Key words: Polyoxomolybdate, MoO Polymer, Copper Complex, Nicotinic Acid, Hydrothermal Synthesis

Introduction

Polyoxomolybdates form an interesting class of inorganic materials, which exhibit a wide range of intriguing architectures [1]. They also have a great potential for applications based on their interesting physical behavior, *e. g.* in catalysis, for electrical conduction, optical response, and magnetism [2]. Many of these organic-inorganic hybrid molybdates are synthesized in the presence of organic ligands under hydrothermal conditions and exhibit multidimensionional structures [3–5]. Furthermore, polymeric structures based on infinite chains of oxomolybdate polyhedra have been reported as dimolybdate, trimolybdate, tetramolybdate and octamolybdate systems, which form the large majority [6]. Occasionally pentamolybdate and heptamolybdate systems have also been observed [7]. A special class of polymeric structures is the family of the "metal-coordination polymers" which have attracted considerable interest as novel materials with unusual chemical and physical properties [8]. These metal-coordination polymers incorporating oligomeric clusters based on polyoxomolybdates are especially noteworthy [9–11] because of their special physical features due to the combination of molybdate anions with supplementary transition metal ions [12, 13]. Thus, one-dimensional molybdenum oxide chains could be easily bridged by including a metal-ligand subunit into a higher-dimensional solid [14]. Such 3D frameworks of oxide chains and transition metal complexes are known in the literature [15–17]. Here we present a new and to our best knowledge unknown type of Mo-1D chain, which is bridged by copper nicotinate subunits.

Results and Discussion

The title compound $Cu(C_6H_4NO_2)(C_6H_5NO_2)$-$(H_2O)_2[Mo_2O_6]_n$ (**1**) was synthesized under hydrothermal conditions by reacting molybdenum trioxide, copper(II) sulfate and nicotinic acid in water, under similar conditions as described by Lu *et al.* [15]. The red crystals obtained were investigated by single-crystal X-ray diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molybdenum ions, one copper(I) ion and two nicotinate ligands in the asymmetric unit (one deprotonated and one not). The structure of **1** is built from a $^1_\infty\{Mo_2O_8\}^{4-}$ anion ladder (which is constructed by MoO_6 units) connected *via* the acid function of the copper(I) nicotinate complexes to the next $^1_\infty\{Mo_2O_8\}^{4-}$ ladder (Fig. 1). The construction of the MoO ladder can also be represented by using the Niggli form of the formula $\{MoO_{3/3}O_{3/1}\}$, showing that one of the oxygen atoms is shared with the next $\{MoO_{3/3}O_{3/1}\}$ unit to build an edge-connected coordination.

The novel 1D polyoxomolybdate chain displays an average Mo–O distance of 2.141(6) Å for the bridging oxygen atoms (O7 and O8), an average distance of 1.706(2) Å for the terminal oxygen atoms (O5, O6, O9, O10) and an average distance of 2.236(5) Å for the oxygen atoms of the carboxylate group (O3, O4). Table 1 shows a selection of the most important bonds

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Mo1–O4	2.220(6)
Mo1–O5	1.688(7)
Mo1–O6	1.711(6)
Mo1–O7	1.975(5)
Mo1–O8	2.308(6)
Mo2–O3	2.253(6)
Mo2–O7	2.277(6)
Mo2–O9	1.732(6)
Mo2–O10	1.695(7)
Cu1–N1	1.903(7)
Cu1–N2	1.924(8)
Cu1–O9	2.225(6)

Table 1. Selected bond lengths (Å) for **1** with estimated standard deviations in parentheses.

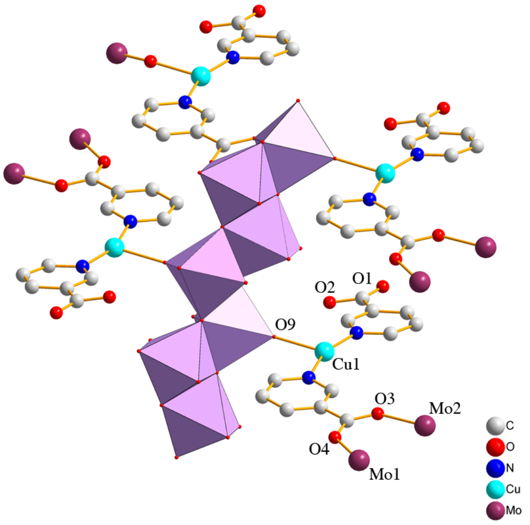

Fig. 1. The edge-sharing coordination polyhedra of the 1D Mo-O polymer of **1**.

and angles. The central MoO_6 unit has a slightly distorted octahedral configuration.

The copper(I) ion is also coordinated to O9 (O9–Cu1 2.22(5) Å) and possesses an approximate trigonal-planar coordination. The reduction of Cu(II) to Cu(I) ions with pyridine-like compounds under hydrothermal conditions is known in the literature [18], and a similar reduction process may have occurred also for the reaction performed herein. The pyridine rings of the nicotinate molecules are stacked in a columnar fashion allowing for π-π interactions (3.219 Å) and forming in total a 3D network. In the x direction, the channel system is clearly visible. In these channels two disordered water molecules are located (Fig. 2). Hydrogen bonds can be observed between O2 and water atom O101 (2.69 Å), as well as between O101 and O10 (2.94 Å) and also between water atoms O102 and O101 (2.96 Å). Due to the disorder of O101 and O102 it is difficult to give more detailed information about the length of these hydrogen bonds.

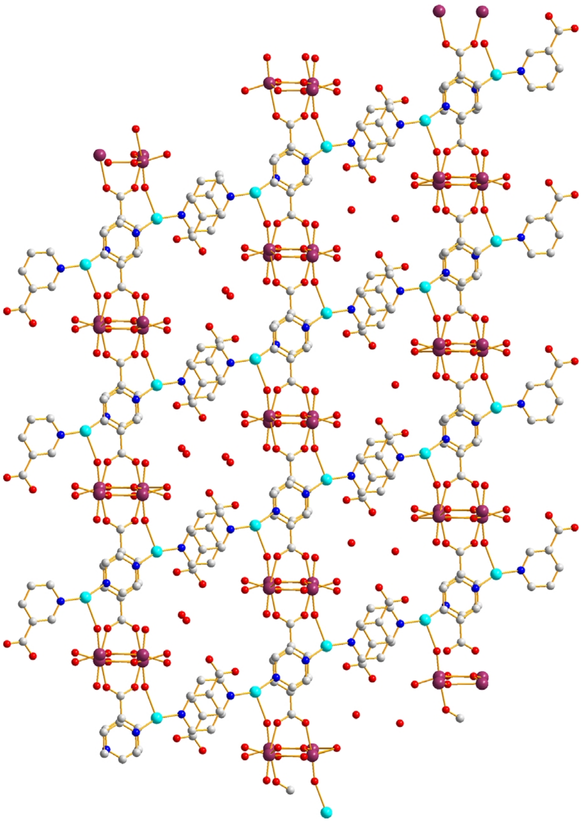

Fig. 2. View of the crystal structure of **1** along the crystallographic x direction.

Experimental Section

All reagents were of commercial origin and were used as received. The reactions were performed under hydrothermal conditions in air.

*$Cu(C_6H_4NO_2)(C_6H_5NO_2)(H_2O)_2[Mo_2O_6]_n$ (**1**)*

A mixture of MoO_3 (0.048 g, 0.33 mmol), nicotinic acid (0.1 g, 0.81 mmol), $CuSO_4$ (0.11 g, 0.69 mmol) and H_2O (10 mL) was taken into a 25 mL Teflon-lined stainless-steel autoclave and kept for 5 d at 170 °C. After slow cooling to r. t. red crystals within a blue solution had formed. The red crystals were washed with water and dried in air. One crystal was selected for single-crystal X-ray diffraction. The composition of the bulk material was confirmed by powder X-ray diffraction and elemental analysis. – $C_{12}H_{13}CuMo_2N_2O_{12}$ (632.66): calcd. C 22.78, Mo 30.33, Cu 10.04; found C 22.21, Mo 30.28, Cu 9.68.

X-Ray structure determination

Powder X-ray diffraction (PXRD) data were recorded using a Bruker ASX D8 Advance powder diffractometer

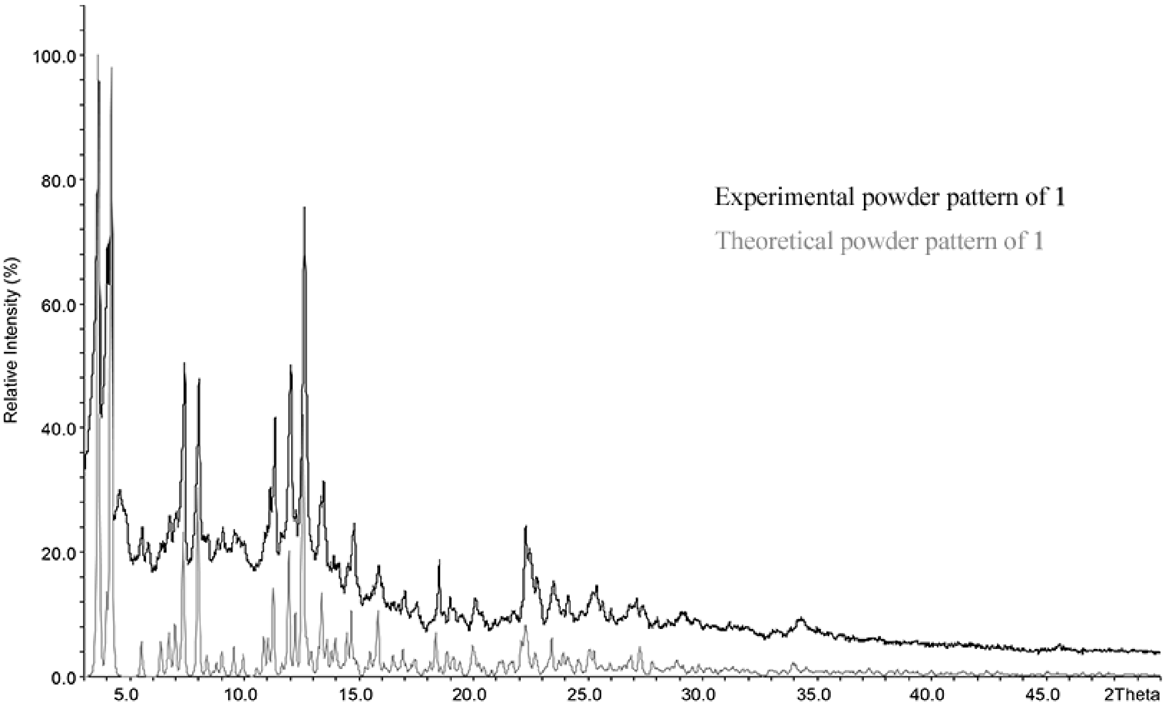

Fig. 3. Experimental powder pattern of the sample in comparison to the theoretical powder pattern of **1** as based on the single-crystal structure determination.

Table 2. Crystal structure data for **1**.

Formula	$C_{12}H_{13}CuMo_2N_2O_{12}$
M_r	632.66
Crystal size, mm^3	$0.1 \times 0.05 \times 0.01$
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	7.4257(15)
b, Å	11.127(2)
c, Å	12.328(3)
α, deg	113.27(3)
β, deg	95.01(3)
γ, deg	90.86(3)
V, Å^3	930.83
Z	2
D_{calcd}, g cm^{-3}	2.26
μ (MoK_α), cm^{-1}	2.5
$F(000)$, e	606
hkl range	$\pm 10, -15 \rightarrow +13, +16$
Refl. measd. / unique	13061 / 4860
Param. refined	256
$R(F)$ $[I \geq 2\sigma(I)]$ / $wR(F^2)^a$ (all refl.)	0.046 / 0.083
GoF $(F^2)^a$	0.603
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.73 / −0.85

with MoK_α radiation (λ = 0.71073 Å). Lattice parameters of the bulk material of **1** according to the LEBAIL fit: a = 7.426(6), b = 11.127(9), c = 12.328(9) Å, α = 113.267(2), β = 95.014(2), γ = 90.86(3)°. The reflections of the powder pattern can be assigned to compound **1** (Fig. 3).

The single-crystal measurements were carried out on a Stoe IPDS-II diffractometer with a MoK_α sealed tube at r. t. The structure was solved by Direct Methods and refined in anisotropic approximation using the SHELX suite of prgrams [19]. Both disordered free water molecules O101 and O102 were treated isotropically. Hydrogen atoms were constrained by a rigid model. In the final step of the single-crystal refinement, lattice parameters derived from the LEBAIL fit were used. The crystal data and numbers pertinent to data collection and structure refinement for **1** are provided in Table 2.

CCDC 801655 contains 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.

Supporting Information

Additional powder X-ray diffraction data of the bulk material of **1** with indexing of the unit cell is available as Supporting Information (online only).

Acknowledgement

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Supporting Information

Synthesis and Characterization of a New Infinite 1D Polyoxomolybdate Polymer Further Connected *via* Cu(I) Nicotinate Subunits

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PXRD of the bulk material of **1** with indexing of the unit cell.

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Phase name                                  Structure
   R-Bragg                                     9.841
   Spacegroup                                  P1̅
   Scale                                       0.000017(23)
   Cell Mass                                   1255.260
   Cell Volume (Å^3)                           930.8(12)
   Wt% - Rietveld                              100.000
   Crystallite Size
      Cry size Lorentzian (nm)                 84.7(56)
      Cry size Gaussian (nm)                   600(2900)
   Strain
      Strain G                                 0.939(3)
   Crystal Linear Absorption Coeff. (1/cm)     27.906(4)
   Crystal Density (g/cm^3)                    2.2395(3)
```

Lattice parameters

a (Å)	7.4256(6)
b (Å)	11.127(9)
c (Å)	12.328(9)
alpha (°)	113.267(2)
beta (°)	95.014(2)
gamma (°)	90.86(3)

Site	Np	x	y	z	Atom	Occ	Beq
C7	2	0.33390	0.60960	0.09110	C	1	1.99
H7	2	0.39150	0.67910	0.15700	H	1	2.369
C10	2	0.15850	0.53400	-0.09890	C	1	1.974
H10	2	0.09940	0.54950	-0.16200	H	1	2.369
C1	2	0.66260	0.40690	0.40870	C	1	2.527
H1	2	0.61810	0.31990	0.36790	H	1	3
C2	2	0.70670	0.61820	0.41700	C	1	3
H2	2	0.69380	0.67810	0.38110	H	1	3.632
C3	2	0.79820	0.66090	0.52980	C	1	3.395
H3	2	0.84110	0.74840	0.56960	H	1	4.027
C4	2	0.82460	0.57440	0.58140	C	1	3.474
H4	2	0.88860	0.60090	0.65660	H	1	4.185
C5	2	0.75440	0.44310	0.52050	C	1	2.763
C8	2	0.25670	0.38640	-0.00890	C	1	1.99
H8	2	0.26380	0.30130	-0.01170	H	1	2.369
C9	2	0.16220	0.40360	-0.10230	C	1	2.29
H9	2	0.10240	0.33280	-0.16590	H	1	2.763
C6	2	0.78100	0.34780	0.57840	C	1	4.185
O5	2	0.09220	-0.14730	-0.27090	O	1	2.511
O6	2	0.07670	0.10750	-0.14280	O	1	2.069
O10	2	0.41180	0.09190	0.27020	O	1	2.298
O9	2	0.44020	0.23530	0.14010	O	1	1.863
O1	2	0.87500	0.37360	0.67200	O	1	6.317
O2	2	0.68860	0.23470	0.51990	O	1	5.211

O101	2	0.77600	0.05870	0.61550	O	1	19.5
O102	2	0.73300	0.89640	0.35700	O	1	42.64
C12	2	0.24330	-0.22670	0.00350	C	1	1.382
C11	2	0.24250	-0.36450	-0.00220	C	1	1.476
N1	2	0.63440	0.49330	0.35570	N	1	2.337
N2	2	0.33990	0.48610	0.08710	N	1	2.006
O7	2	0.36810	-0.00880	-0.07650	O	1	1.492
O8	2	0.13550	0.06030	0.07720	O	1	1.713
O4	2	0.14540	-0.21120	-0.08020	O	1	1.855
O3	2	0.34150	-0.14010	0.08640	O	1	1.65
Cu1	2	0.4725(25)	0.4760(14)	0.2209(11)	Cu	1	2.613
Mo2	2	0.3973(17)	0.0800(10)	0.1356(10)	Mo	1	1.206
Mo1	2	0.0919(18)	-0.0416(11)	-0.1279(12)	Mo	1	1.283