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Structure determination of a novel metal-organic compound synthesized from aluminum and 2,5-pyridinedicarboxylic acid

Kenny Ståhl,^{a)} Bastian Brink, and Jonas Andersen

Department of Chemistry, Building 207, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

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The structure of $[Al_2(pydc)_2(\mu_2-OH)_2(H_2O)_2]_n$ ($pydc = 2,5$ -pyridinedicarboxylate) was successfully determined from powder X-ray diffraction data. The compound crystallizes in the triclinic system (space group $P\bar{1}$) with $a = 6.7813(1)$ Å, $b = 7.4944(1)$ Å, $c = 8.5013(1)$ Å, $\alpha = 95.256(1)^\circ$, $\beta = 102.478(1)^\circ$, $\gamma = 108.979(1)^\circ$. The structure consists of aluminum ions coordinating N and O in distorted octahedra, sharing an edge through two hydroxide ions. These dinuclear complexes are connected by $pydc$ ions, which at one end coordinate by nitrogen and oxygen and only by oxygen at the other end. The $pydc$ orientation is reversed in the neighboring $pydc$, forming double stranded chains interconnected by the aluminum dinuclear complexes in a ladder-like arrangement along $[001]$. © 2011 International Centre for Diffraction Data. [DOI: 10.1154/1.3659288]

Key words: aluminum, 2,5-pyridinedicarboxylic acid, hydrothermal synthesis, metal-organic framework, XRPD

I. INTRODUCTION

Studies of dicarboxylic acids and their reactions with various metals have led to novel materials, the so-called metal organic frameworks (MOFs). These compounds can form layered materials as well as microporous and macroporous three-dimensional structures. Increasing interest in MOF is connected with the possible applications in, e.g., gas storage, gas separation, drug delivery, ion exchange, and catalysis (Férey, 2008). In the investigation of functionalized materials based on the well-known MOFs, MIL-53 (Loiseau *et al.*, 2004) and MOF-5 (Li *et al.*, 1999) with benzene-1,4-dicarboxylate linkers, a new material was synthesized from 2,5-pyridinedicarboxylic acid (H_2pydc) and aluminum nitrate. This paper presents the synthesis and structure determination and refinement from X-ray powder diffraction data for a new aluminum 2,5-pyridinedicarboxylate compound, $[Al_2(pydc)_2(\mu_2-OH)_2(H_2O)_2]_n$.

II. EXPERIMENTAL

A. Synthesis

The synthesis of aluminum 2,5-pyridinedicarboxylate hydroxide dehydrate is carried out with 5.5 g aluminum nitrate nonahydrate (Sigma-Aldrich 98+ % ACS), 2.95 g 2,5-pyridinedicarboxylic acid (Aldrich, 98%) and 0.7 g sodium hydroxide (Fluka $\geq 97.0\%$) dissolved in 150 ml of water. The solution is transferred to a Teflon lined stainless steel autoclave and heated to $150^\circ C$ for 24 h. The solution is cooled and the crystals are separated by centrifugation and washed with water to neutral pH . The white crystals are finally dried in air at $102^\circ C$.

B. Data collection

The powder diffraction data were collected using a Huber G670 Guinier imaging plate camera, using $Cu K\alpha_1$

radiation. The samples were placed in a thin layer on scotch tape and rotated during data collection. Data were collected in transmission mode for 2 h in the range of 3 to 100° in steps of 0.005° in 2θ .

C. Structure determination and refinements

The pattern was indexed using the program ITO (Visser, 1969) and the crystal structure subsequently solved by EXPO (Altomare *et al.*, 1994; Altomare *et al.*, 1995). The structure was refined by WINPOW (a local variation of LHMP, Howard *et al.*, 1986). The Rietveld refinement was carried out by refining 80 parameters in a 2θ interval from 7° to 99° in steps of 0.005° in 2θ . A split pseudo-Voigt profile function was applied together with a Chebyshev background polynomial. All nonhydrogen

TABLE I. Crystallographic data and refinement summary of $[Al_2(pydc)_2(\mu_2-OH)_2(H_2O)_2]_\infty$.

Formula	$C_7H_6AlNO_6$
Formula mass (g/mol)	227.11
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	6.7813(1)
b (Å)	7.4944(1)
c (Å)	8.5013(1)
α ($^\circ$)	95.257(1)
β ($^\circ$)	102.478(1)
γ ($^\circ$)	108.979(1)
V (Å ³)	392.73(3)
Z	2
ρ (g/cm ³)	1.895
No. of parameters	80
R_{wp} (%)	5.77
GOF	3.14
R_p (%)	4.16
No. of Bragg reflections	791
R_B (%)	1.83

^{a)} Author to whom correspondence should be addressed. Electronic mail: kenny@kemi.dtu.dk

TABLE II. Fractional coordinates and thermal parameters of $[\text{Al}_2(\text{pydc})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]_\infty$.

Atom	x	y	z	$U_{\text{iso}}(\text{\AA}^2)$
Al1	0.2013(5)	0.1529(4)	0.5291(3)	0.0515(9)
C1	0.2500(8)	0.1244(8)	0.8971(6)	0.0206(5)
C2	0.2458(9)	0.1989(9)	1.0622(8)	0.0206(5)
C3	0.2225(8)	0.3740(8)	1.0812(7)	0.0206(5)
C4	0.2407(7)	0.4843(7)	0.9628(7)	0.0206(5)
C5	0.2313(9)	0.4219(10)	0.8040(8)	0.0206(5)
C6	0.2550(10)	0.0619(8)	1.1882(8)	0.0206(5)
C7	0.2512(9)	0.5323(8)	0.6600(7)	0.0206(5)
N1	0.2421(7)	0.2354(6)	0.7843(6)	0.0206(5)
O1	0.3082(5)	-0.0704(5)	1.1760(5)	0.0206(5)
O2	0.2212(6)	0.1511(5)	1.3129(4)	0.0206(5)
O3	0.2742(6)	0.6932(5)	0.6970(4)	0.0206(5)
O4	0.2571(5)	0.4251(5)	0.5405(4)	0.0206(5)
O5	0.8944(5)	0.1041(6)	0.4704(4)	0.0206(5)
O6	0.5202(5)	0.2048(4)	0.5903(4)	0.0206(5)
H1	0.2649	0.0035	0.8732	0.0380
H3	0.1935	0.4213	1.1784	0.0380
H4	0.2662	0.6175	0.9966	0.0380

coordinates were refined with thermal parameters coupled for the pydc and for the hydroxyl and water oxygens. The expected bond lengths of the pydc (Liang *et al.*, 2001) were used as restraints. Hydrogens of the pydc were added in calculated positions and allowed to ride on the corresponding carbon atom. The hydroxyl and water hydrogens could not be located. Some crystallographic data and a refinement summary are given in Table I, the resulting atomic parameters in Table II and the refinement profiles

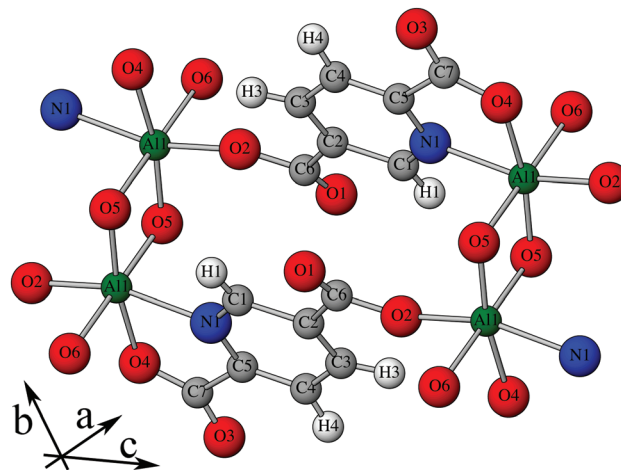


Figure 2. (Color) The molecular structure and atomic positions of $[\text{Al}_2(\text{pydc})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]_n$. Red: oxygen, blue: nitrogen, green: aluminum, grey: carbon, white: calculated hydrogen positions.

are shown in Figure 1. In addition, a CIF file is provided as supplemental data.

III. RESULTS AND DISCUSSION

Aluminum ions coordinate N and O in distorted octahedra sharing an edge through two hydroxide ions, as seen in Figure 2. These dinuclear complexes ($\text{Al-Al} = 2.844(6) \text{ \AA}$, Table III) are connected by pydc ions, that at one end is coordinating through N1 and O4 and at the other by O2. The pydc orientation is reversed in the neighboring pydc, forming double stranded chains interconnected by the aluminum dinuclear complexes in a ladder-like arrangement along $[001]$, as seen

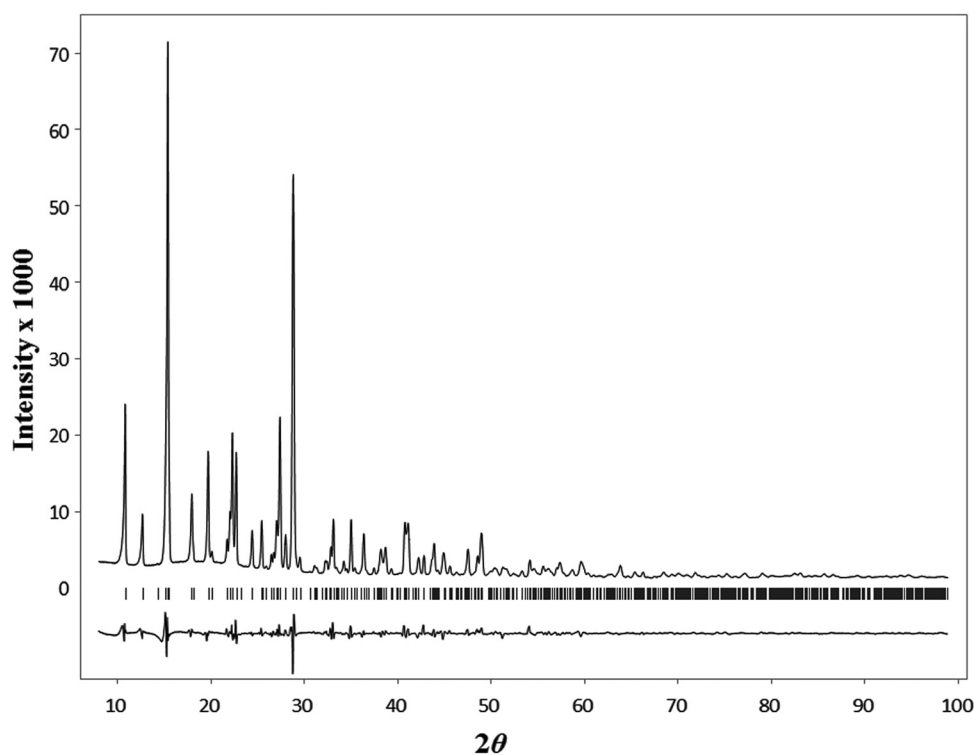


Figure 1. Rietveld refinement profile for $[\text{Al}_2(\text{pydc})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]_n$. The top pattern illustrates observed intensities, while the lower curve shows the difference from calculated intensities. Bragg positions are illustrated by short vertical bars.

TABLE III. Selected interatomic and tentative hydrogen bond distances in $[\text{Al}_2(\text{pydc})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]_n$.

Bond	Distance (Å)
Al1-O2 ^a	1.870 (5)
Al1-O4 ^b	1.940 (5)
Al1-O5 ^c	1.936 (4)
Al1-O5	1.821 (5)
Al1-O6	2.002 (4)
Al1-N1	2.145 (5)
O1---O6 ^d	2.539 (5)
O3---O5 ^e	2.542 (5)

^aSymmetry code: $1-x, y, 1-z$.

^bSymmetry code: $x, y, z-1$.

^cSymmetry code: $x-1, y, z$.

^dSymmetry code: $1-x, y, 2-z$.

^eSymmetry code: $1-x, 1-y, 1-z$.

in Figure 3. The ladders are tentatively connected by hydrogen bonds. Although the hydroxyl and water hydrogen positions could not be located in this study the O5 and O6 distances to the uncoordinated carboxylate O1 and O3 in the range 2.539(5) to 2.542(5) Å suggest reasonably strong hydrogen bonding (Table III). The crystal structure of $[\text{Al}_2(\text{pydc})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]_n$ is surprisingly similar to the structures of $[\text{Ni}_2(\text{Hdcp})_2(\mu_2\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2]_n$ (King *et al.*, 2004) and $[\text{Cu}_2(\text{Hdcp})_2(\mu_2\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2]_n$ (Hdcp = pyrazole-3,5-dicarboxylate) (Han and Ma, 2006) despite the difference in ring system of the organic linker and in cation charge. The charge difference is compensated for by exchanging one water by one hydroxyl ion per aluminum. The hydroxyl O5 thus shows a significantly shorter Al coordination distance than the water O6, 1.825(5) Å as compared with 2.005(4) Å, as also observed in MIL-53 (Loiseau *et al.*, 2004). Also the hydrogen bonding schemes will be different in that the additional water H and the protonated pyrazole N allow for more hydrogen bonds (King *et al.*, 2004; Han and Ma, 2006).

IV. CONCLUSION

The crystal structure of $[\text{Al}_2(\text{pydc})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]_\infty$ was successfully determined from X-ray powder diffraction data. The structure can be described as a parallel stacking of ladders, with ladder steps consisting of two edge-sharing aluminum octahedra connected by organic 2,5-pyridinedicarboxylate linkers forming a one-dimensional metal-organic network structure.

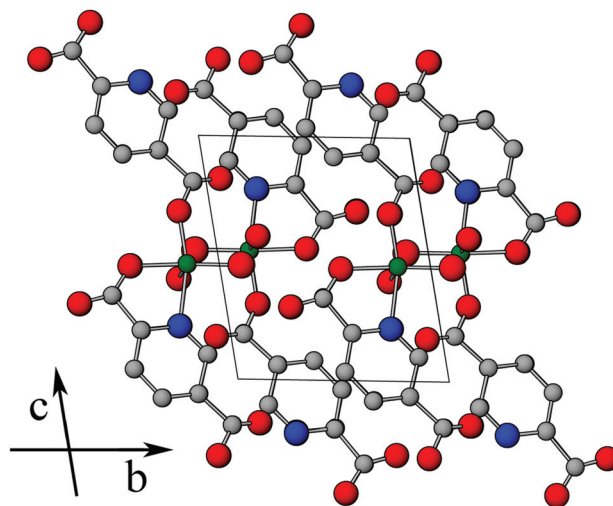


Figure 3. (Color) Packing of the unit cell of $[\text{Al}_2(\text{pydc})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]_n$ seen along the a axis. Red: oxygen, blue: nitrogen, green: aluminum, grey: carbon. Hydrogens are omitted for clarity.

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