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Dicarboxylic Acid (Pyridine-2, 6-Dicarboxylato)-(Pyridine-2,6-Dicarboxylic Acid)-Copper(II) Monohydrate, Analyzed Using Electron Diffraction

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Abstract

The crystal of the title compound (a mononuclear copper(II) complex affording distorted octahedral geometry) was analyzed using electron diffraction for the first time. The crystal system and space group are orthorhombic and Pnna, and the lattice constants are $Z=4$, $a=7.94$ (10) Å, $b=11.06$ (7) Å, $c=17.09$ (6) Å, and $V=1501$ (22) Å^3, which was similar to orthorhombic and monohydrate crystal by X-ray diffraction reported previously. Besides merit of measurements using very small crystals like powder, electron diffraction may result in slight differences in positions of hydrogen atoms. However, similar results to X-ray diffraction could be obtained in this time. The Hirshfeld surface analysis based on electron diffraction exhibits that H···H contacts may account for the largest percentage of all intermolecular non-covalent interactions.

Keywords: Electron Diffraction; Copper(II) Complex; Hirshfeld Surface Analysis; Crystal Explorer; Re-Determination

Introduction

In principle, generally, what contributes to general X-ray diffraction is the distribution of electron clouds, and what contributes to electron diffraction is the electrostatic potential including the atomic nucleus. As a principle advantage, electron diffraction is thought to be able to more accurately determine the position of hydrogen nuclei than X-ray diffraction. The scattering amplitude of electrons is about 104 Times larger than that of X-rays, and the interaction between electrons and electrostatic potential is strong, so multiple scattering is likely to occur. Electrons have a wavelength 30 to 100 times shorter than X-rays, so de Broglie waves are short, making it easy to obtain information about reciprocal lattices. The measurable crystal size is different; in X-ray structural analysis, it is about a few millimeters, whereas in electron diffraction, it is possible to measure microcrystals from tens to hundreds of nanometers.
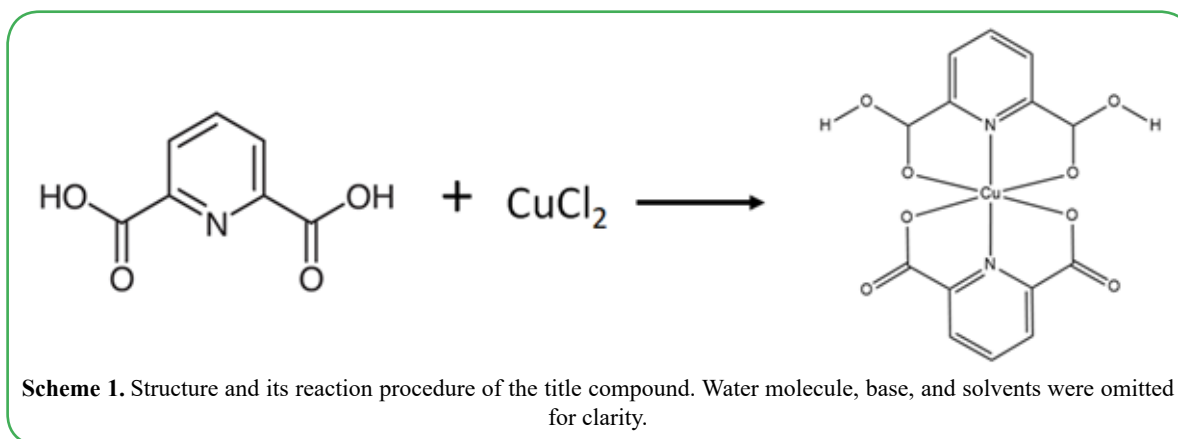
The compounds (Scheme 1) reported here have been reported many times before, including space group *P*c [1-5], *P*nna [1, 6-8], *P*2$_1$/c [9, 10]. Although they have various packing configurations depending on the space group and the number of crystalline water molecules, they commonly form a strong network through hydrogen bonding with water molecules. In addition, the Cu central metal has a d^9 electron configuration, and distorted due to the Jahn-Teller effect have also been observed [6]. The fact that X-ray crystallography has been carried out many times makes it an interesting compound and a reliable source of data. There are some general characteristic features of electron diffraction, which includes the possible to measure even small crystals like powder (about 10–100 nm) due to multiple scattering (cross section of electrons is about 104 to 105 times larger than that of X-ray) and short wavelength (wavelength of electrons is 30–100 times shorter than that of X-ray). Therefore, deviation to long bond lengths involving hydrogen atoms may be expected in principle [11].

Materials and Methods

A solution of pyridine-2,6-dicarboxylic acid (0.33 g, 2.0 mmol) in 10 mL of ethanol was slowly added dropwise to an aqueous (distilled water) solution of NaOH (0.17 g, 4.0 mmol) in 5 mL and continuously stirred for 15 minutes (0.25 hour) at about 300 K (namely room temperature). To this solution was slowly added dropwise a 20 mL of (EtOH : H$_2$O = 1 : 1; v/v) solution of copper(II) chloride dehydrate (0.17 g, 1.0 mmol) at the same temperature. After stirring the solution for 3 h before filtration, suitable single crystals for the measurement (both X-ray and electron diffraction) were obtained from the filtrate after about two weeks (Scheme 1).

Electron diffraction measurement was performed using a Rigaku XtaLAB Synergy-ED. The (precipitate or small single crystal) sample consisted of plate-like single crystal with the size of approximately 300 nm thickness was used for the data collection. The single data set was measured at 298.15 K (namely room temperature) with beam of a wavelength of 0.0251 Å. The initial structure was clearly solved with intrinsic phasing [12], revealing the expected molecular structure with most of all heavy atoms, and refined (first isotropically and next anisotropically) using a SHELXL program [13] in a program suit Olex2 [14]. Since all hydrogen atom-derived peaks were clearly observed in the differential Fourier map, hydrogen atoms were assigned to those peaks instead of riding model and refined respectively. The distance between each hydrogen atom and each adjacent non-hydrogen atom was restrained by DFIX command.

Scheme 1. Structure and its reaction procedure of the title compound. Water molecule, base, and solvents were omitted for clarity.

Crystallograhic data for $C_{14}H_{10}CuN_2O_9$ (M = 413.79 g/mol): T = 298.15 K, orthorhombic system, space group (No. 52) Pnna, a = 7.94 (10) Å, b = 11.06 (7) Å, c = 17.09 (6) Å, V = 1501 (22) Å3, Z = 4, D_{calc} = 1.831 g/cm³, 5648 measured reflections (0.238 ° <2Θ < 1.798 °), 1396 unique reflections (R_{int} = 0.1189, R_{sigma} = 0.1066) used in calculations of all data. The final value of R1 was 0.1491 (I > 2σ(I)) and the corresponding value of wR2 was 0.4213 (by using all data of reflections).
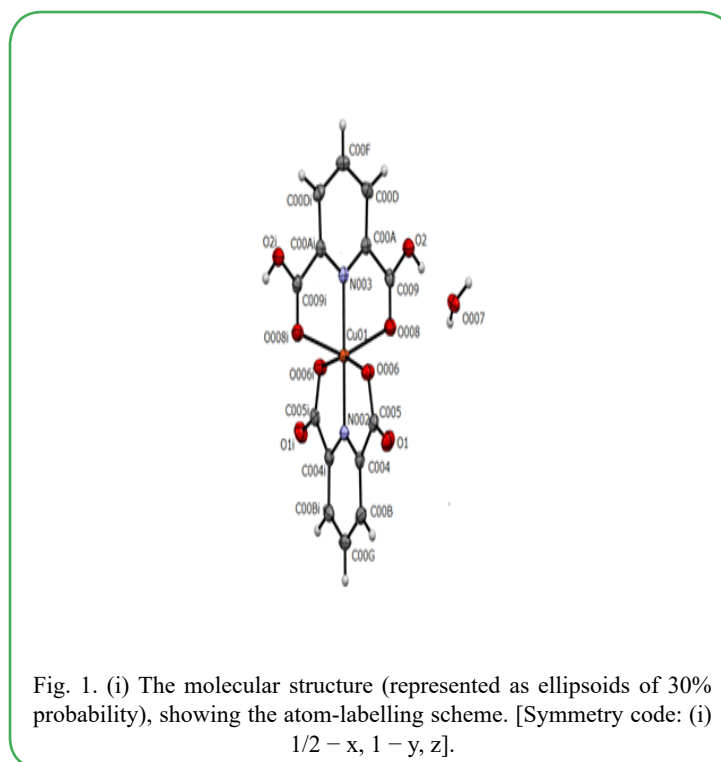
Detailed crystallographic data and structural results is given in CIF (supporting information).

Results

The crystallographic system and space group were orthorhombic and Pnna. As for the lattice constants, electron diffraction yielded Z=4, a=7.94 (10) Å, b=11.06 (7) Å, c=17.09 (6) Å, and V=1501 (22) Å³. Next, non-hydrogen hydrogen bond distances are C00G—H00G = 0.96 (2) Å, C00B—H00B = 0.98 (2) Å, O2—H2 = 1.03 (4) Å, C00F—H00F = 1.00 (2) Å, and C00D—H00D = 1.12 (2) Å by electron diffraction. The coordination bond distances are Cu01—N002 = 1.924 (10) Å, Cu—N003 = 2.034 (10) Å, Cu01—O006 = 2.013 (13) Å, and Cu01—O008 = 2.43 Å by electron diffraction (Fig. 1i). This time, however, we merely treated hydrogen atoms in similar way to refinement using X-ray diffraction except for original

positions of hydrogen atoms. Appropriate treatment for electron diffraction should be established in future. Furthermore, Hirshfeld surface analysis data of two data showed that these hydrogen-containing bonds tend to account for a slightly larger fraction of the total intermolecular interactions in the electron diffraction results. Currently, there are very few papers about electron diffraction structure analysis that is appropriate for comparison with X-ray results. In contract, X-ray diffraction [15] gave Z=4, a=7.883 (14) Å, b=10.980 (2) Å, c=16.985 (3) Å, and V=1470.28 (5) Å³. The corresponding non-hydrogen-hydrogen bond distances are 0.95 Å for C1—H1, 0.95 Å for C2—H2, 0.84 Å for O4—H4, 0.95 Å for C5—H5, and 0.95 Å for C6—H6. The coordination bond distances are shows 1.92 Å for Cu—N1, 2.01 Å for Cu—N2, 2.02 Å for Cu—O1, and 2.43 Å for Cu—O3. Non-hydrogen-hydrogen bond distances by electron diffraction are longer than by X-ray diffraction. The results obtained were similar between electron diffraction and X-ray diffraction with regard to the coordination bond distances.

In the crystal packing (Fig. 1ii), near molecules are non-covalently connected by two types O—H•••O intermolecular hydrogen bonds included H_2O molecules. As a result, the molecules are linked along the direction of the crystallographic b-axis. Similar features were also observed the related compounds [3-5].

Fig. 1. (i) The molecular structure (represented as ellipsoids of 30% probability), showing the atom-labelling scheme. [Symmetry code: (i) 1/2 − x, 1 − y, z].
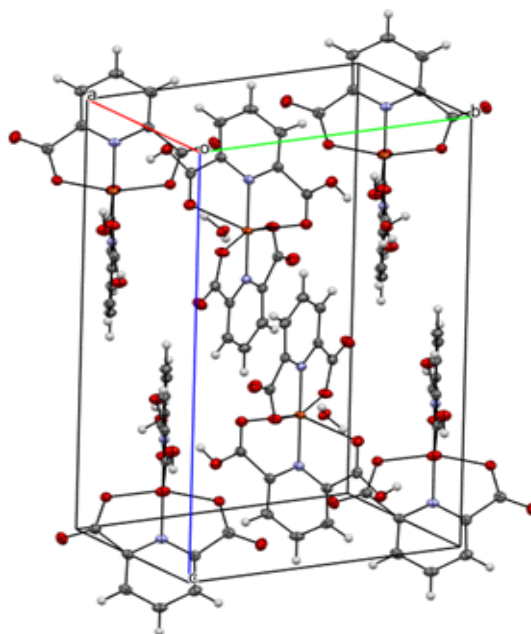
Fig. 1. (ii) The crystal packing of the title compound.

In X-ray diffraction [15], C1-H1 is 0.95 Å, while in electron diffraction it is 1.10(2) Å, and for O4-H4, 0.84 Å is 1.00(4) Å. It has become reasonable to constrain and analyze the distance by assuming it to be short. As a result, in the Hirshfeld surface analysis, the proportion of intermolecular interactions involving hydrogen among all intermolecular interactions was slightly larger in the electron diffraction results. This is thought to be due to the fact that electron diffraction can determine the positions of atoms more accurately than X-ray diffraction.

In order to visualize the intermolecular (hydrogen bonding) interactions in the crystal packing of this compound, the Hirshfeld surface analysis [16] was carried out with CrystalExplorer5 [17].

The fingerprint plot for this compound's crystal structure typically exhibits so-called 'wings′ features (Fig.2i). The percentage (values) contribution to the Hirshfeld surface area by close contacts with H atoms inside the surface (wrapping a molecule) and H atoms outside is 17.4% (Fig. 2ii), for O atoms inside such a surface and H atoms outside the surface and for H atoms inside this surface and O atoms outside it is 46.0% (Fig. 2iii), for C atoms inside the surface and H atoms outside it and for H atoms inside the Hirshfeld surface and C atoms outside it is 6.8% (Fig. 2iv), respectively. This analysis of the O•••H interaction apparantly indicates the close intermolecular contact involving H_2O molecules (di is 1.0 Å and de is 0.65 Å).
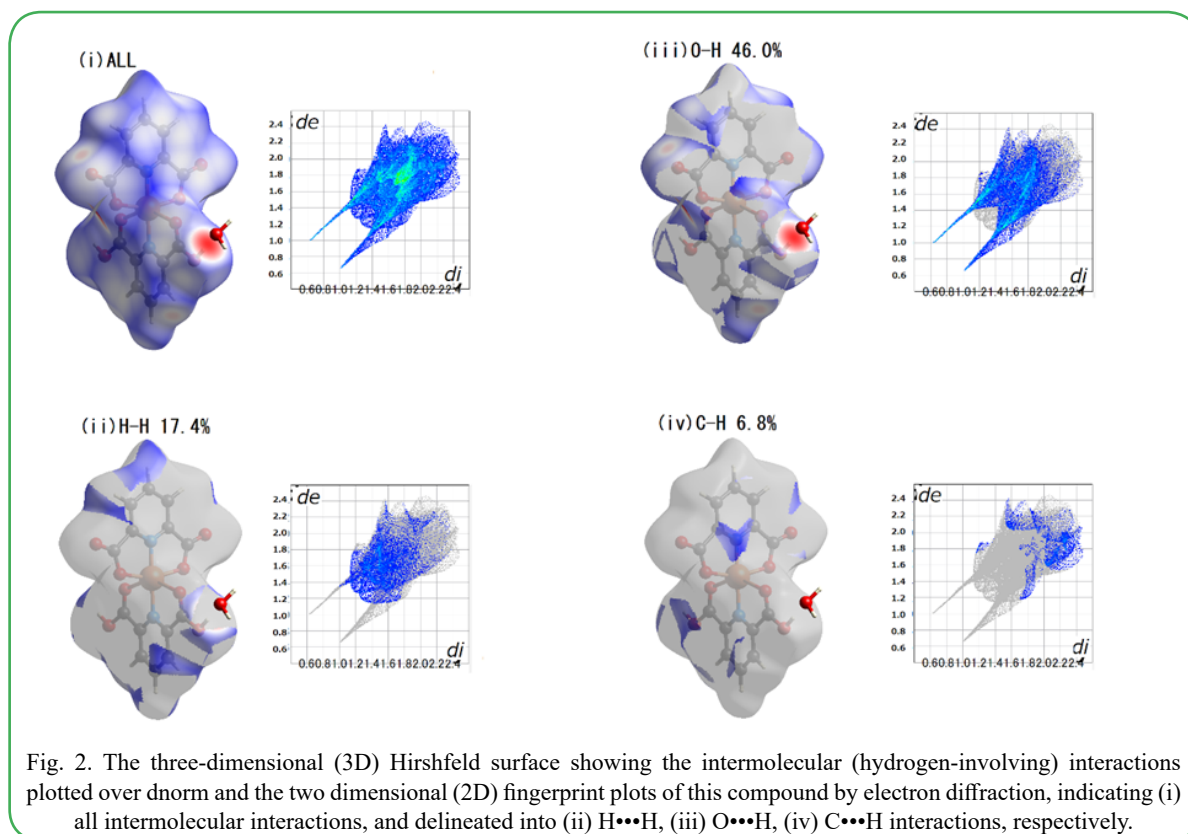

Fig. 2. The three-dimensional (3D) Hirshfeld surface showing the intermolecular (hydrogen-involving) interactions plotted over dnorm and the two dimensional (2D) fingerprint plots of this compound by electron diffraction, indicating (i) all intermolecular interactions, and delineated into (ii) H•••H, (iii) O•••H, (iv) C•••H interactions, respectively.

Discussion

The following findings were obtained regarding the differences between analysis using X-ray diffraction and electron diffraction. Basically, there is no significant difference in molecular size or intermolecular bond strength in the analysis results of X-ray diffraction and electron diffraction. Electron diffraction showed longer non-hydrogen bond lengths (reasonably refined and interpreted as such). The reason for this is that the electrostatic potential created by the atomic nucleus and electron cloud contributes to electron diffraction, and the distribution of the electron cloud contributes to X-rays. In other words, electron diffraction can more accurately determine the position of a hydrogen atom's nucleus. In turn, this will lead to a more accurate representation of the actual environment inside a crystal (like the complementary use of X-ray and neutron diffraction).

Conclusion

Crystal structure of the title compound was re-determined using electron diffraction to compare with the following X-ray diffraction. A search in the Cambridge Structural Database (CSD) [18] shows similar structures determined using X-ray diffraction. *P*nna monohydrate (RAZNAH [1], RAZNAH01 [6], RAZNAH02 [8]), *P*nna dehydrate (RAZNAH03 [7]), *P*c trihydrate (HPYRCU02 [1], HPYRCU03 [2]), $P2_1/c$ monohydrate+hydroxide (TEHFOD [10]), and $P2_1/c$ monohydrate+hydronium (FAYPUR[19]).

Due to these characteristics of electron diffraction, it is thought that it may play an important role in the following two points in particular. (1) Determination of accurate hydrogen position in the crystal. (2) Structure determination using fine crystals, which is in increasing demand. In the field of drug discovery, there are also expectations for determining the chirality of nanocrystal-sized drugs, and electron diffraction is expected to become even more popular in the future.

Competing interests: Authors report no conflict or competing interest.

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