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Chapter 6

CASE STUDIES ON CRYSTAL STRUCTURE DETERMINATION INVOLVING H ATOMS

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ABSTRACT

In view of recent structural chemistry with X-ray crystallography, hydrogen bonds in terminal H-O (phenol) group or H-O-H (D-O-D) (water) must be important, though it may be difficult to locate their hydrogen atoms appropriately only by geometrical calculations without the guide of electron density (D-map). In this short essay, we summarized some case studies on crystal structure determination involving hydrogen atoms by comparing final results temperature factors and CIF check with a PLATON program of refinement after locating according to D-map and geometrical calculations. (1) Phenol –OH groups in organic molecules; (2) isolated crystalline water (hydrogen bonded each other); (3) and (4) crystalline water of isotope (D_2O). In this short essay, we summarized some case studies on crystal structure determination involving hydrogen atoms by comparing final results temperature factors and CIF check with a PLATON program of refinement after locating according to D-map and geometrical calculations. (1) C14H12N2O3 phenol –OH groups in organic molecules; (2) C26H28Cu2N6O10 isolated crystalline water (hydrogen bonded each other); (3) and (4) C36H80Co2Cu3N24O4 crystalline water of isotope (D_2O).

INTRODUCTION

Recent progress of X-ray as well as neutron crystallography makes it important to obtain accurate information of hydrogen atoms apparently. Indeed, IUCr monographs on crystallography have published several volumes about hydrogen bonds [1, 2]. Particularly, many tools of X-ray crystallography for small molecules make it possible to determine their

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structures quickly and easily (of course, as general routine analyses without difficult structures or serious problems in view of crystallography) if suitable single crystals are obtained. Therefore, the purpose of structural determination of compounds or chemical significance of researches becomes more important nowadays. Some practical books for beginners to lead convenient usage of X-ray analyses [3, 4]. However, skillful measurements or careful refinements using SHELXL [5] sometimes result in "Alert" after checking CIF by a PLATON program. In this short essay, we summarize difficult or failed examples of crystal structure determination for small molecules in our chemical laboratory and added technical comments explanation based on practical experience as a crystallographer.

Herein, we summarized some examples of comparison of locating hydrogen atoms (D-map vs geometrical calculations) and results of refinement, which may be important structural (inorganic) chemistry [6]. (1) *C14H12N2O3* phenol –OH groups in organic molecules; (2) *C26H28Cu2N6O10* isolated crystalline water (hydrogen bonded each other); (3) and (4) *C36H80Co2Cu3N24O4* crystalline water of isotope (D_2O). The H/D isotope effect sometimes results in novel polymorphism [7]. However, not only technical aspects of refinement but also fundamental aspects [8] in crystallography may be concerned with this problem.

EXPERIMENTAL SECTION

Preparations

Single crystals of *C14H12N2O3* [9], *C26H28Cu2N6O10* [10], and *C36H80Co2 Cu3N24O4* [11] served X-ray analysis were prepared according to the literature.

X-Ray Crystallography

Red prismatic (*C14H12N2O3*), green prismatic (*C26H28Cu2N6O10*) and blue plate-like (*C36H80Co2Cu3N24O4*), single crystals were glued on top of a glass fiber and coated with a thin layer of epoxy resin to measure the diffraction data. Intensity data were collected on a Bruker APEX2 CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data analysis was carried out with a SAINT program package. The structures were solved by direct methods with a SHELXS-97 [12] and expanded by Fourier techniques and refined by full-matrix least-squares methods based on F^2 using the program SHELXL-97 [12]. An empirical absorption correction was applied by a program SADABS. All non-hydrogen atoms were readily located and refined by anisotropic thermal parameters. All hydrogen atoms except for hydroxyl groups in methanol molecules were located at geometrically calculated positions and refined using riding models.

RESULTS AND DISCUSSION

For all cases, comments, crystallographic data, residual density, anisotropic temperature factors, isotropic temperature factors taken from CIF, and alerts about hydrogen atoms by PLATON for [calc] or [D-map] are described.

Case 1. C14H12N2O3

This case is classified into addition of terminal hydrogen atoms connected to oxygen atom (phenol group) of an organic compound. The hydrogen atoms could be located based on both the difference Fourier electron density map (D-map) and geometrical calculations (calc). Refinement gave rise to geometrical parameters O2-H2 = 0.8400 (constrained), C7-O2-H2 = 109.5 by calc, while O2-H2 = 0.92(2) (refined), C7-O2-H2 = 103.6(14) by D-map. The latter has longer O2-H2 bond distance and smaller C7-O2-H2 angles than the former. The C7-O2 bond distance and R1, wR2, and S values are almost identical nevertheless of the methods.

[Calc]

Crystallographic data for *C14H12N2O3*. $C_{14}H_{12}N_2O_3$, T = 173 K, crystal size 0.13 mm × 0.17 mm × 0.22 mm, M_w = 256.26, orthorhombic, space group Pbcn (#284), a = 10.5560(17)Å, b = 12.944(2) Å, c = 18.025(3) Å, V = 2462.9(7) $Å^3$, Z = 8, D_{calc} = 1.382 g/cm^3, F(000) = 1072, R_1 = 0.0443, wR_2 = 0.1493 (2810 reflections), S = 1.091. (where $R_1 = \Sigma ||F_o|-|F_c||/ \Sigma |F_o|$. $R_w = (\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

_REFINE_DIFF_DENSITY_MAX 0.288
_REFINE_DIFF_DENSITY_MIN -0.244
_REFINE_DIFF_DENSITY_RMS 0.063

C7 C 1.20726(13) 0.32013(11) 0.22369(8) 0.0319(3) UANI 1 1 D ...
O2 O 1.27787(12) 0.24855(8) 0.25840(6) 0.0466(3) UANI 1 1 D ...
H2 H 1.3356 0.2778 0.2826 0.070 UISO 1 1 CALC R . .

C7 0.0341(7) 0.0300(7) 0.0317(7) 0.0040(5) -0.0004(6) 0.0041(6)
O2 0.0536(7) 0.0350(6) 0.0510(7) 0.0027(5) -0.0231(5) 0.0055(5)

PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms 1

[D-map]

Crystallographic data for C14H12N2O3. $C_{14}H_{12}N_2O_3$, *T* = 173 K, crystal size 0.13 mm × 0.17 mm × 0.22 mm, M_w = 256.26, orthorhombic, space group *Pbcn* (#284), *a* = 10.5560(17)Å, *b* = 12.944(2) Å, *c* = 18.025(3) Å, *V* = 2462.9(7) $Å^3$, *Z* = 8, D_{calc} = 1.382 g/cm^3, F(000) = 1072, R_1 = 0.0440, wR_2 = 0.1484 (2810 reflections), *S* = 1.085. (where $R_1 = \Sigma ||F_o|-|F_c||/ \Sigma |F_o|$. $R_w = (\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

_REFINE_DIFF_DENSITY_MAX 0.284
_REFINE_DIFF_DENSITY_MIN -0.242
_REFINE_DIFF_DENSITY_RMS 0.062

O2 O 1.27799(12) 0.24854(8) 0.25847(7) 0.0463(3) Uani 1 1 d ...
C7 C 1.20725(13) 0.32015(10) 0.22370(8) 0.0320(3) Uani 1 1 d ...
H2 H 1.338(2) 0.2871(17) 0.2834(13) 0.073(6) Uiso 1 1 d ...

O2 0.0535(7) 0.0345(6) 0.0509(7) 0.0028(5) -0.0225(6) 0.0054(5)
C7 0.0340(7) 0.0302(7) 0.0317(7) 0.0040(5) -0.0004(6) 0.0041(6)

PLAT420_ALERT_2_B D-H Without Acceptor O2 - H2 ... ?

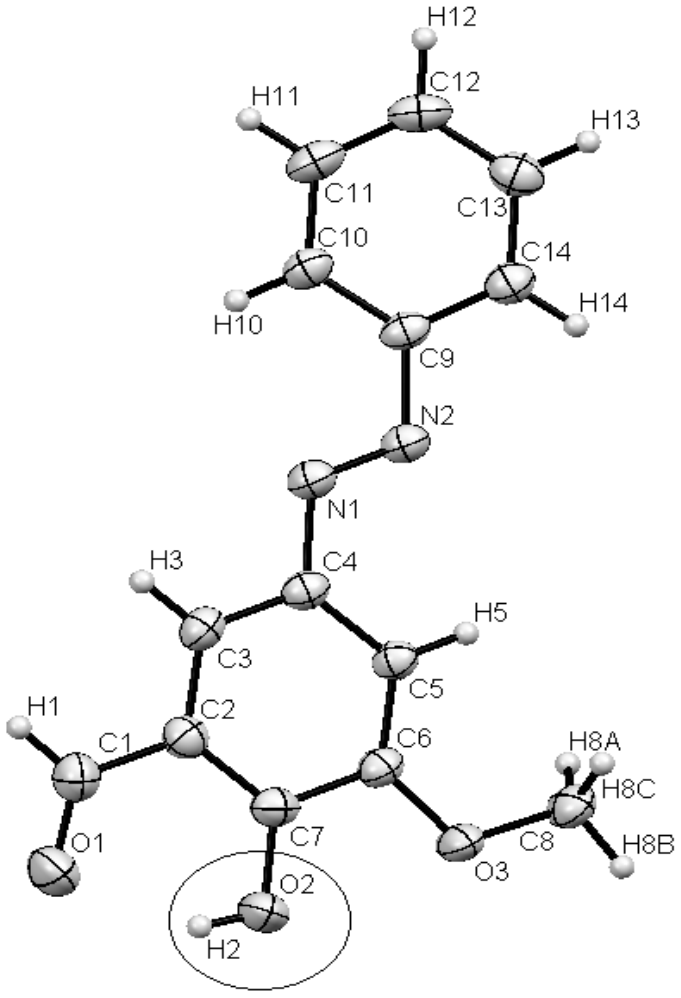

Figure 1. An ORTEP drawing of C14H12N2O3 showing the atom-labeling scheme Displacement ellipsoids are drawn at the 50 % probability level. Selected bond distances (Å) and angles (˚): [calc] C7-O2 = 1.3438(16), O2-H2 = 0.8400, C7-O2-H2 = 109.5; [D-map] C7-O2 = 1.3452(17), O2-H2 = 0.92(2), C7-O2-H2 = 103.6(14).

Case 2. C26H28Cu2N6O10

This case is classified into addition of hydrogen atoms connected to oxygen atom (crystalline water) of a metal complex. Because hydrogen atoms of crystalline water molecules could not be added by calculation, no hydrogen atoms are introduced in the regimented model and many alerts concerning to oxygen atoms emerged. Refinement based on a model added hydrogen atoms based on D-map resulted in small R1, wR2, and S values with abnormal geometries such as H4A-O4-H4B = 110(9) and H5A-O5-H5B = 92(8) regardless of fix instruction by ".ins file" of Shelxl.

[Calc]

H atoms of crystalline water could not be located by geometrical calculation.

Crystallographic data for C26H28Cu2N6O10. $C_{26}H_{28}Cu_2N_6O_{10}$, T = 173 K, crystal size 0.15 mm × 0.30 mm × 0.33 mm, M_w = 711.62, orthorhombic, space group $C222_1$ (#109), a = 11.8029(13) Å, b = 14.6462(16) Å, c = 16.8978(18) Å, V = 2921.1(5) Å^3, Z = 4, D_{calc} = 1.618 g/cm^3, F(000) = 1456, R_1 = 0.0654, wR_2 = 0.1733 (3215 reflections), S = 1.300. (where $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $R_w = (\Sigma w(|F_o|-|F_c|)^2 /\Sigma w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

_REFINE_DIFF_DENSITY_MAX 0.770
_REFINE_DIFF_DENSITY_MIN -1.093
_REFINE_DIFF_DENSITY_RMS 0.173

O4 O 0.7926(4) 0.9955(4) 0.5835(4) 0.0334(13) Uani 1 1 d ...
O5 O -0.0047(5) 0.9578(5) 0.6655(4) 0.0423(16) Uani 1 1 d ...

O4 0.021(2) 0.038(3) 0.042(3) -0.005(3) 0.005(2) -0.002(2)
O5 0.021(3) 0.047(4) 0.059(4) -0.021(3) 0.005(3) -0.005(3)

PLAT306_ALERT_2_A Isolated Oxygen Atom (H-atoms Missing ?) O4
PLAT306_ALERT_2_A Isolated Oxygen Atom (H-atoms Missing ?) O5
PLAT430_ALERT_2_B Short Inter D...A Contact O4 .. O5 .. 2.82 Ang.
PLAT430_ALERT_2_B Short Inter D...A Contact O4 .. O4 .. 2.83 Ang.
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing) ... ?
PLAT430_ALERT_2_C Short Inter D...A Contact O5 .. O5 .. 2.86 Ang.
REFLT03_ALERT_4_G Please check that the estimate of the number of Friedel pairs is correct. If it is not, please give the correct count in the
_publ_section_exptl_refinement section of the submitted CIF.
From the CIF: _diffrn_reflns_theta_max 27.55
From the CIF: _reflns_number_total 3215
Count of symmetry unique reflns 1887
Completeness (_total/calc) 170.38%
TEST3: Check Friedels for noncentro structure
Estimate of Friedel pairs measured 1328
Fraction of Friedel pairs measured 0.704
Are heavy atom types Z>Si present yes

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 28.17
PLAT158_ALERT_4_G The Input Unitcell is NOT Standard/Reduced ..... ?

[D-map]

Crystallographic data for C26H28Cu2N6O10. $C_{26}H_{28}Cu_2N_6O_{10}$, T = 173 K, crystal size 0.15 mm × 0.30 mm ×0.33 mm, M_w = 711.62, orthorhombic, space group $C222_1$ (#109), a = 11.8029(13) Å, b = 14.6462(16) Å, c = 16.8978(18) Å, V = 2921.1(5) Å^3, Z = 4, D_{calc} = 1.618 g/cm^3, F(000) = 1456, R_1 = 0.0539, wR_2 = 0.1512 (3215 reflections), S = 1.136. (where $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $R_w = (\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

_REFINE_DIFF_DENSITY_MAX 0.693
_REFINE_DIFF_DENSITY_MIN -1.034
_REFINE_DIFF_DENSITY_RMS 0.157

O4 O 0.2074(4) 0.0041(4) 0.4169(3) 0.0329(11) Uani 1 1 d D . .
H4A H 0.255(5) 0.050(4) 0.406(4) 0.03(2) Uiso 1 1 d D . .
H4B H 0.167(9) -0.010(8) 0.374(4) 0.09(4) Uiso 1 1 d D . .
O5 O 1.0050(5) 0.0409(4) 0.3348(4) 0.0411(14) Uani 1 1 d D . .
H5A H 0.964(4) 0.076(4) 0.368(3) 0.016(15) Uiso 1 1 d D . .
H5B H 1.019(8) 0.089(4) 0.303(5) 0.06(3) Uiso 1 1 d D . .

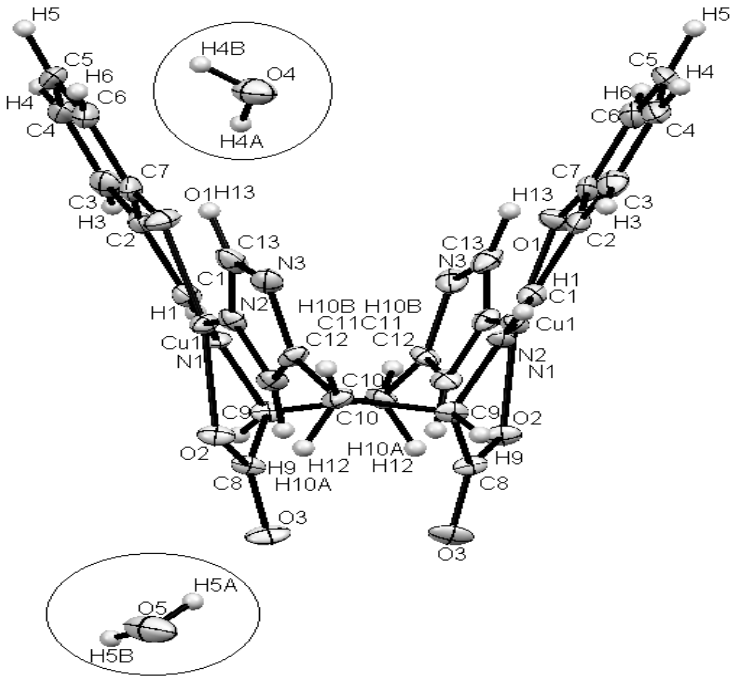

Figure 2. An ORTEP drawing of *C26H28Cu2N6O10* showing the atom-labeling scheme Displacement ellipsoids are drawn at the 50 % probability level. Selected bond distances (Å) and angles (˚): [D-map] O4-H4A = 0.898(10), O4-H4B = 0.897(10) , O5-H5A = 0.900(10) , O5-H5B = 0.898(10), H4A-O4-H4B = 110(9), H5A-O5-H5B = 92(8).

O4 0.021(2) 0.038(3) 0.040(3) -0.004(2) 0.003(2) -0.003(2)
O5 0.023(2) 0.044(3) 0.056(4) -0.020(3) 0.008(2) -0.004(2)

PLAT417_ALERT_2_B Short Inter D-H..H-D H5B .. H5B .. 1.85 Ang.
PLAT223_ALERT_4_C Large Solvent/Anion H Ueq(max)/Ueq(min) ... 3.7 Ratio
PLAT245_ALERT_2_C U(iso) H5A Smaller than U(eq) O5 by ... 0.025 AngSq
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 4
<.INS FIlE>
DFIX 0.9 0.01 O5 H5A
DFIX 0.9 0.01 O5 H5B
DFIX 0.9 0.01 O4 H4A
DFIX 0.9 0.01 O4 H4B

Case 3. C36H80Co2Cu3N24O4 (at 100 K)

This case is classified into addition of D atoms connected to oxygen atom (crystalline water D_2O) of a metal complex (a poor quality crystal). Since the numbers of alerts of this sample cooled up to 100 K are more than that of the same one at 296 K (see case 4), some problems has happened during cooling. Hydrogen atoms of both crystalline water molecules could not be added by calculation, while only one of the two water molecules could be added even based on D-map. It indicated quite high R1, wR2, and S values, introducing hydrogen atoms resulted in slight decreasing of them.

[Calc]

Crystallographic data for C36H80Co2Cu3N24O4 (100 K). $C_{36}H_{80}Co_2Cu_3N_{24}O_4$, T = 100 K, crystal size 0.09 mm × 0.19 mm × 0.20 mm, M_w = 1221.72, orthorhombic, space group *P -1* (#2), a = 9.968(5) Å, b = 11.912(6) Å, c = 11.984(6) Å, α = 78.105(5) °, β = 82.513(5) °, γ = 88.914(6) °, V = 1380.6(11) Å^3, Z = 1, D_{calc} = 1.469 g/cm^3, F(000) = 637, R_1 = 0.1615, wR_2 = 0.5377 (5608 reflections), S = 4.387. (where $R_1 = \Sigma ||F_o|-|F_c|| / \Sigma |F_o|$. $R_w = (\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

_REFINE_DIFF_DENSITY_MAX 6.163
_REFINE_DIFF_DENSITY_MIN -6.171
_REFINE_DIFF_DENSITY_RMS 0.647

O1 O 0.2649(13) 0.6723(13) 0.4938(12) 0.034(3) Uani 1 1 d ...
O2 O 0.2048(13) 0.6953(16) 0.2673(13) 0.047(4) Uani 1 1 d ...

O1 0.021(6) 0.050(8) 0.044(8) -0.034(6) -0.010(6) 0.008(6)
O2 0.017(6) 0.091(12) 0.050(9) -0.050(9) -0.014(6) 0.018(7)

DIFMN02_ALERT_2_A THE MINIMUM DIFFERENCE DENSITY IS < -0.1*ZMAX*2.00
_REFINE_DIFF_DENSITY_MIN GIVEN = -6.171

TEST VALUE = -5.800
DIFMX01_ALERT_2_A The maximum difference density is > 0.1*ZMAX*2.00
_REFINE_DIFF_DENSITY_MAX GIVEN = 6.163
TEST VALUE = 5.800
RFACR01_ALERT_3_A The value of the weighted R factor is > 0.45
WEIGHTED R FACTOR GIVEN 0.538
PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full Low 0.896
PLAT084_ALERT_2_A High wR2 Value 0.54
PLAT097_ALERT_2_A Large Reported Max. (Positive) Residual Density 6.16 eA-3
PLAT098_ALERT_2_A Large Reported Min. (Negative) Residual Density -6.17 eA-3
PLAT213_ALERT_2_A Atom Cu1 has ADP max/min Ratio ..... 12.2 prola
PLAT213_ALERT_2_A Atom Co1 has ADP max/min Ratio ..... 6.1 prola
PLAT306_ALERT_2_A Isolated Oxygen Atom (H-atoms Missing ?) O1
PLAT306_ALERT_2_A Isolated Oxygen Atom (H-atoms Missing ?) O2
GOODF01_ALERT_2_B The least squares goodness of fit parameter lies
outside the range 0.60 <> 4.00
Goodness of fit given = 4.387
RFACG01_ALERT_3_B The value of the R factor is > 0.15
R FACTOR GIVEN 0.162
PLAT082_ALERT_2_B High R1 Value 0.16
PLAT087_ALERT_2_B Unsatisfactory S value (Too High) 4.39
PLAT213_ALERT_2_B Atom Cu2 has ADP max/min Ratio ..... 4.7 prola
PLAT213_ALERT_2_B Atom Co2 has ADP max/min Ratio ..... 4.7 prola
PLAT250_ALERT_2_B Large U3/U1 Ratio for Average U(i,j) Tensor 5.7
PLAT430_ALERT_2_B Short Inter D...A Contact O1 .. O2 .. 2.81 Ang.
PLAT430_ALERT_2_B Short Inter D...A Contact O2 .. N6 .. 2.87 Ang.
DIFMN03_ALERT_1_C The minimum difference density is < -0.1*ZMAX*0.75
The relevant atom site should be identified.
DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 33
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms 9

[D-map]

Crystallographic data for C36H80Co2Cu3N24O4. $C_{36}H_{80}Co_2Cu_3N_{24}O_4$, T = 100 K, crystal size 0.09 mm × 0.19 mm × 0.20 mm, M_w = 1221.72, orthorhombic, space group *P -1* (#2), a = 9.968(5) Å, b = 11.912(6) Å, c = 11.984(6) Å, α = 78.105(5) °, β = 82.513(5) °, γ = 88.914(6) °, V = 1380.6(11) Å^3, Z = 1, D_{calc} = 1.469 g/cm^3, F(000) = 637, R_1 = 0.1613, wR_2 = 0.5374 (5608 reflections), S = 4.386. (where $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $R_w = (\Sigma w(|F_o|-|F_c|)^2 /\Sigma w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

_REFINE_DIFF_DENSITY_MAX 6.180
_REFINE_DIFF_DENSITY_MIN -6.178
_REFINE_DIFF_DENSITY_RMS 0.645

O1 O 0.2647(13) 0.6723(13) 0.4936(12) 0.033(3) Uani 1 1 d D . .
O2 O 0.2050(13) 0.6948(16) 0.2676(13) 0.047(4) Uani 1 1 d ...
H1A H 0.321(9) 0.731(6) 0.492(9) -0.02(2) Uiso 1 1 d DU ...
H1B H 0.249(9) 0.666(7) 0.423(3) -0.034(16) Uiso 1 1 d DU ...

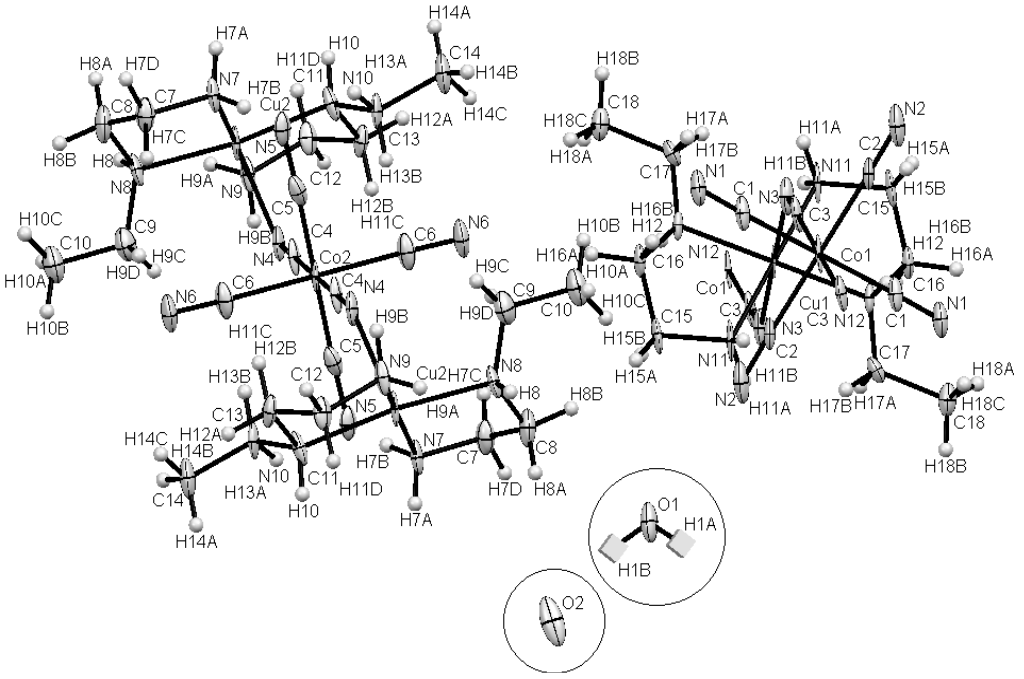

Figure 3. An ORTEP drawing of *C36H80Co2Cu3N24O4* showing the atom-labeling scheme Displacement ellipsoids are drawn at the 50 % probability level. Selected bond distances (Å) and angles (˚): [D-map] O1 - H1A = 0.900(12) , O1 - H1B = 0.900(12), H1A - O1 - H1B = 112(9).

O1 0.022(6) 0.046(8) 0.043(8) -0.034(6) -0.011(6) 0.005(6)
O2 0.016(6) 0.090(12) 0.051(9) -0.050(9) -0.013(6) 0.018(7)

<.INS FIlE>
DFIX 0.9 0.01 O1 H1A
DFIX 0.9 0.01 O1 H1B

DIFMN02_ALERT_2_A The minimum difference density is < -0.1*ZMAX*2.00
_REFINE_DIFF_DENSITY_MIN GIVEN = -6.178
TEST VALUE = -5.800
DIFMX01_ALERT_2_A The maximum difference density is > 0.1*ZMAX*2.00
_REFINE_DIFF_DENSITY_MAX GIVEN = 6.180
TEST VALUE = 5.800
RFACR01_ALERT_3_A The value of the weighted R factor is > 0.45
WEIGHTED R FACTOR GIVEN 0.537
PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full Low 0.896
PLAT084_ALERT_2_A High wR2 Value 0.54
PLAT097_ALERT_2_A Large Reported Max. (Positive) Residual Density 6.18 eA-3

PLAT098_ALERT_2_A Large Reported Min. (Negative) Residual Density -6.18 eA-3
PLAT213_ALERT_2_A Atom Cu1 has ADP max/min Ratio ..... 13.5 prola
PLAT213_ALERT_2_A Atom Co1 has ADP max/min Ratio ..... 6.0 prola
PLAT306_ALERT_2_A Isolated Oxygen Atom (H-atoms Missing ?) O2
PLAT417_ALERT_2_A Short Inter D-H..H-D H1A .. H8 .. 1.71 Ang.
GOODF01_ALERT_2_B The least squares goodness of fit parameter lies
outside the range 0.60 <> 4.00
Goodness of fit given = 4.386
RFACG01_ALERT_3_B The value of the R factor is > 0.15
R FACTOR GIVEN 0.161
PLAT082_ALERT_2_B High R1 Value 0.16
PLAT087_ALERT_2_B Unsatisfactory S value (Too High) 4.39
PLAT213_ALERT_2_B Atom Cu2 has ADP max/min Ratio ..... 4.7 prola
PLAT213_ALERT_2_B Atom Co2 has ADP max/min Ratio ..... 4.7 prola
PLAT250_ALERT_2_B Large U3/U1 Ratio for Average U(i,j) Tensor 5.7
PLAT417_ALERT_2_B Short Inter D-H..H-D H1A .. H9A .. 1.81 Ang.
DIFMN03_ALERT_1_C The minimum difference density is < -0.1*ZMAX*0.75
The relevant atom site should be identified.
DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT430_ALERT_2_C Short Inter D...A Contact O2 .. N6 .. 2.88 Ang.
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 3
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 35
PLAT004_ALERT_5_G Info: Polymeric Structure Found with Dimension. 3
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms 9

Case 4. C36H80Co2Cu3N24O4(296 K)

The identical data of “case 3” measured at 296 K. Hydrogen atoms of both crystalline water molecules could not be added by calculation, while only one of the two water molecules could be added even based on D-map. The results of D-map showed quite small R1, wR2, and S values, while the results of calc exhibited an alert of short O1-O2 distance due to absence of hydrogen atoms.

[Calc]

Crystallographic data for C36H80Co2Cu3N24O4 (296 K). $C_{36}H_{80}Co_2Cu_3N_{24}O_4$, T = 296 K, crystal size 0.09 mm × 0.19 mm × 0.20 mm, M_w = 1221.72, orthorhombic, space group *P -1* (＃2), a = 9.965(3) Å, b = 11.970(4) Å, c = 12.047(4) Å, α = 78.122(4) °, β = 82.740(4) °, γ = 88.952(4) °, V = 1394.8(8) Å^3, Z = 1, D_{calc} = 1.454 g/cm^3, F(000) = 629, R_1 = 0.0411, wR_2 = 0.1229 (6093 reflections), S = 1.055. (where $R_1 = \Sigma ||F_o|-|F_c|| / \Sigma |F_o|$. $R_w = (\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

_REFINE_DIFF_DENSITY_MAX 1.138
_REFINE_DIFF_DENSITY_MIN -0.800
_REFINE_DIFF_DENSITY_RMS 0.096

O1 O 0.2626(3) 0.6659(3) 0.4999(3) 0.0768(9) Uani 1 1 d ...
O2 O 0.2067(4) 0.6998(5) 0.2714(4) 0.1117(15) Uani 1 1 d ...

O1 0.0630(19) 0.091(2) 0.083(3) -0.0268(19) -0.0190(17) 0.0018(16)
O2 0.076(2) 0.176(4) 0.083(3) -0.028(3) -0.010(2) 0.022(3)

PLAT306_ALERT_2_A Isolated Oxygen Atom (H-atoms Missing ?) O1
PLAT306_ALERT_2_A Isolated Oxygen Atom (H-atoms Missing ?) O2
PLAT430_ALERT_2_B Short Inter D...A Contact O1 .. O2 .. 2.82 Ang.
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low 0.972
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT430_ALERT_2_C Short Inter D...A Contact O2 .. N6 .. 2.89 Ang.
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms 9
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00400 Deg.

[D-map]

Crystallographic data for C36H80Co2Cu3N24O4. $C_{36}H_{80}Co_2Cu_3N_{24}O_4$, T = 296 K, crystal size 0.09 mm × 0.19 mm × 0.20 mm, M_w = 1221.72, orthorhombic, space group *P -1* (＃2), a = 9.965(3) Å, b = 11.970(4) Å, c = 12.047(4) Å, α = 78.122(4) °, β = 82.740(4) °, γ = 88.952(4) °, V = 1394.8(8) Å^3, Z = 1, D_{calc} = 1.454 g/cm^3, F(000) = 629, R_1 = 0.0406, wR_2 = 0.1200 (6093 reflections), S = 1.055. (where $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $R_w = (\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2)^{1/2}$, $w = 1/(\sigma^2(F_o) + (0.1P)^2)$, $P = (F_{o2} + 2F_{c2})/3$).

_REFINE_DIFF_DENSITY_MAX 1.146
_REFINE_DIFF_DENSITY_MIN -0.800
_REFINE_DIFF_DENSITY_RMS 0.093

O1 O 0.2636(3) 0.6646(3) 0.5009(4) 0.0776(9) Uani 1 1 d D ...
O2 O 0.2069(4) 0.6994(4) 0.2712(4) 0.1121(15) Uani 1 1 d ...
H1A H 0.187(4) 0.693(6) 0.532(6) 0.14(3) Uiso 1 1 d D ...
H1B H 0.252(6) 0.693(5) 0.4276(18) 0.11(2) Uiso 1 1 d D ...

O1 0.063(2) 0.097(2) 0.079(3) -0.026(2) -0.0185(18) 0.0048(18)
O2 0.076(2) 0.178(4) 0.082(3) -0.028(3) -0.011(2) 0.023(3)

<.INS FIlE>
BIND O1 H1A
BIND O1 H1B
DFIX 0.9 0.01 O1 H1A
DFIX 0.9 0.01 O1 H1B

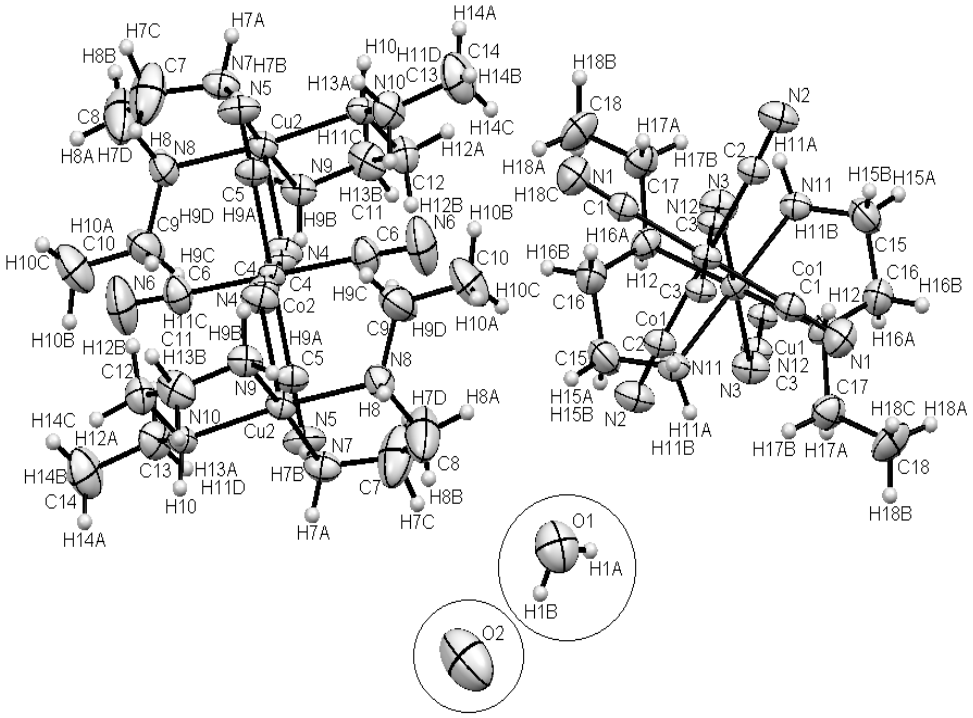

Figure 4. An ORTEP drawing of *C36H80Co2Cu3N24O4(296 K)* showing the atom-labeling scheme Displacement ellipsoids are drawn at the 50 % probability level. Selected bond distances (Å) and angles (˚): [D-map] O1 - H1A = 0.898(10) , O1 - H1B = 0.900(10), H1A - O1 - H1B = 96(6).

PLAT306_ALERT_2_A Isolated Oxygen Atom (H-atoms Missing ?) O2
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low 0.972
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ?
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.6 Ratio
PLAT430_ALERT_2_C Short Inter D...A Contact O2 .. N6 .. 2.90 Ang.
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 3
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms 9
PLAT154_ALERT_1_G The su’s on the Cell Angles are Equal ..... 0.00400 Deg.
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 2

CONCLUSION

In summary, we have exhibited some cases of introducing hydrogen atoms of terminal or isolated oxygen atoms. Normally, they are typical cases which are difficultly introducing hydrogen atoms by geometrical calculations without careful consideration (for example, expected hydrogen bond networks). Actually, phenol groups of organic molecules, whose structures are stable, little differences between calc and D-map are observed for good quality crystals. However,indroducing hydrogen atoms of crystalline water sometimes was

sometimes failed and ascribed to significant effects on the R1, wR2, and S values after refiment.

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