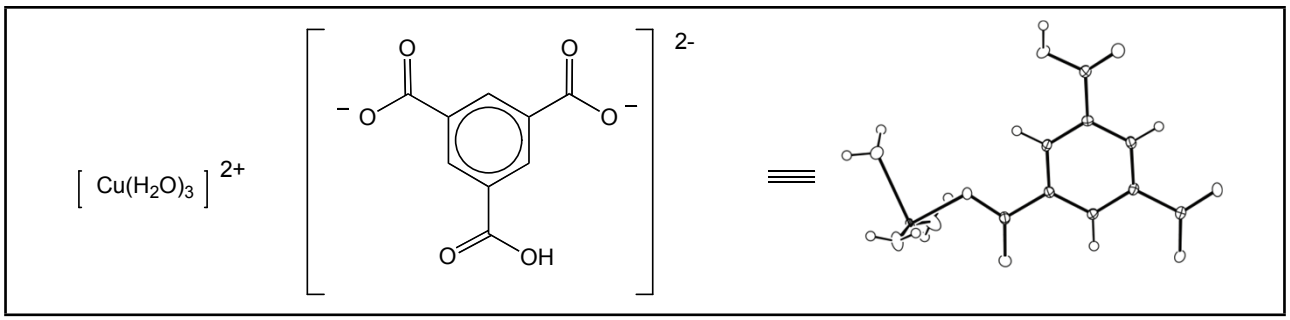
X-ray Structure Determination of Compound 99209



Compound CuBTC, $C_9H_{10}O_9Cu$, crystallizes in the monoclinic space group $P2_1/n$ (systematic absences 0k0: k=odd and h0l: h+l=odd) with a=6.7778(7)Å, b=18.8206(18)Å, c=8.5384(8)Å, β=92.471(4)°, V=1088.16(18)Å^3, Z=4, and d_{calc}=1.988 g/cm^3 . X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 143(1)K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 3562 frames were collected with a crystal to detector distance of 37.6 mm, rotation widths of 0.5° and exposures of 10 seconds:

scan type	2θ	ω	ϕ	χ	frames
ϕ	24.50	7.41	12.48	28.88	739
ω	-23.00	333.49	158.99	-70.01	69
ω	24.50	14.22	11.23	-20.60	202
ϕ	19.50	59.55	348.71	-26.26	739
ϕ	-15.50	258.48	8.28	19.46	739
ϕ	22.00	14.84	73.18	97.50	739
ϕ	9.50	3.52	27.06	96.28	103
ϕ	-23.00	316.70	79.62	98.89	232

Rotation frames were integrated using SAINT[i], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[ii] program package for further processing and structure solution. A total of 37602 reflections were measured over the ranges $2.16 \leq \theta \leq 27.53°$, $-8 \leq h \leq 8$, $-24 \leq k \leq 24$, $-11 \leq l \leq 11$ yielding 2488 unique reflections (Rint = 0.0170). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[iii] (minimum and maximum transmission 0.6410, 0.7456).

The structure was solved by direct methods (SHELXS-97[iv]). Refinement was by full-matrix least

squares based on F^2 using SHELXL-97.[v] All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0203P)^2 + 1.2057P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0194 and wR2=0.0526 for 2474 observed reflections for which $F > 4\sigma(F)$ and R1=0.0196 and wR2=0.0526 and GOF =1.112 for all 2488 unique, non-zero reflections and 173 variables.[vi] The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.442 and -0.383 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure 1. is an ORTEP[vii] representation of the molecule with 30% probability thermal ellipsoids displayed.

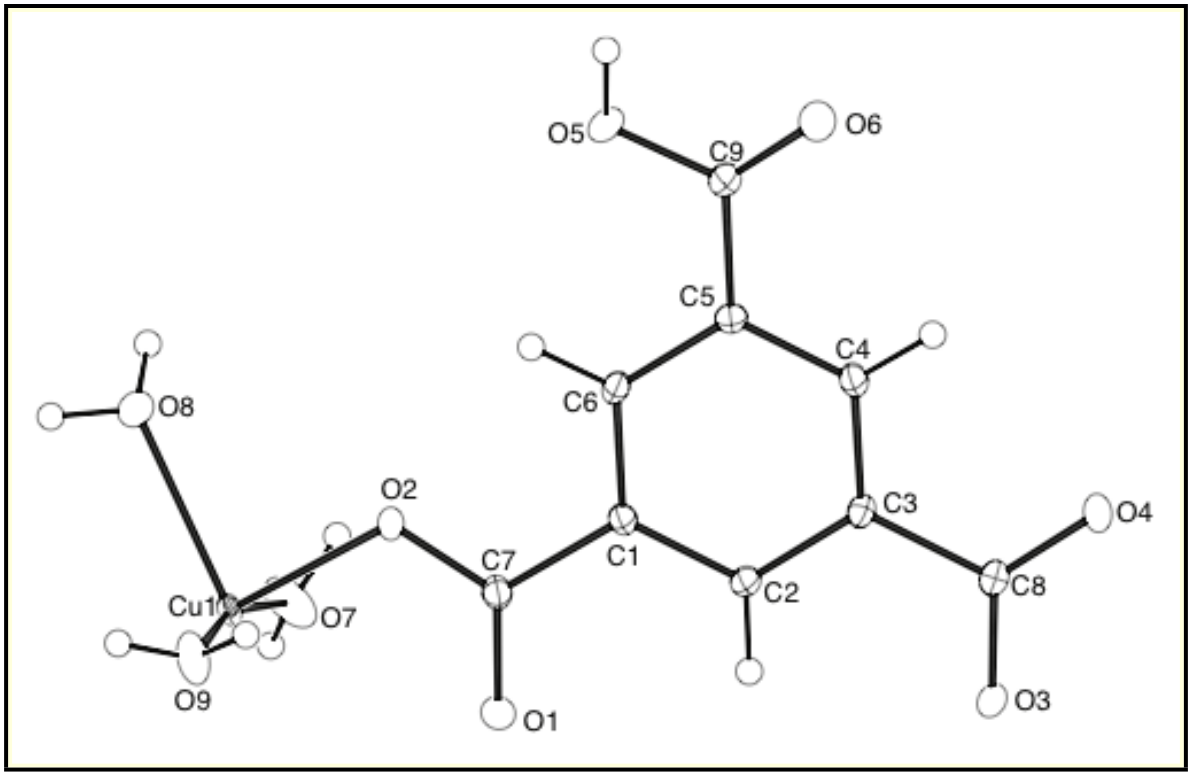


Figure 1. ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 99209

Empirical formula	$C_9H_{10}O_9Cu$
Formula weight	325.71
Temperature	143(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Cell constants:	
a	6.7778(7) Å
b	18.8206(18) Å
c	8.5384(8) Å
β	92.471(4)°
Volume	1088.16(18) $Å^3$
Z	4
Density (calculated)	1.988 Mg/m^3
Absorption coefficient	2.052 mm^{-1}
F(000)	660
Crystal size	0.30 x 0.22 x 0.12 mm^3
Theta range for data collection	2.16 to 27.53°
Index ranges	$-8 \leq h \leq 8$, $-24 \leq k \leq 24$, $-11 \leq l \leq 11$
Reflections collected	37602
Independent reflections	2488 [R(int) = 0.0170]
Completeness to theta = 27.53°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6410
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2488 / 0 / 173
Goodness-of-fit on F^2	1.112
Final R indices [I>2sigma(I)]	R1 = 0.0194, wR2 = 0.0526
R indices (all data)	R1 = 0.0196, wR2 = 0.0526
Largest diff. peak and hole	0.442 and -0.383 $e.Å^{-3}$

Table 2. Refined Positional Parameters for Compound 99209

Atom	x	y	z	U_{eq}, Å^2
Cu1	0.28800(3)	0.225703(9)	0.67920(2)	0.01069(6)
O1	0.21325(19)	0.37290(6)	0.76454(13)	0.0192(2)
O2	0.26282(17)	0.31014(6)	0.55002(12)	0.0138(2)
O3	0.20327(17)	0.63714(6)	0.70946(13)	0.0151(2)
O4	0.24091(17)	0.68863(6)	0.47757(13)	0.0162(2)
O5	0.30147(19)	0.41493(6)	0.04327(13)	0.0189(2)
O6	0.2329(2)	0.52871(7)	0.00008(14)	0.0289(3)
O7	0.55452(18)	0.25524(7)	0.75611(15)	0.0242(3)
O8	0.37653(18)	0.16942(6)	0.46243(13)	0.0199(2)
O9	-0.00047(17)	0.21053(6)	0.64473(15)	0.0197(2)
C1	0.2468(2)	0.43450(8)	0.52193(17)	0.0102(3)
C2	0.2392(2)	0.50185(8)	0.58888(16)	0.0103(3)
C3	0.2435(2)	0.56206(7)	0.49336(17)	0.0104(3)
C4	0.2545(2)	0.55462(8)	0.33173(17)	0.0120(3)
C5	0.2607(2)	0.48730(8)	0.26466(17)	0.0116(3)
C6	0.2579(2)	0.42732(7)	0.35995(17)	0.0112(3)
C7	0.2407(2)	0.36894(8)	0.62158(17)	0.0114(3)
C8	0.2295(2)	0.63497(8)	0.56335(17)	0.0110(3)
C9	0.2632(2)	0.48045(8)	0.09111(18)	0.0147(3)

$U_{eq}=1/3[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$

Table 3. Positional Parameters for Hydrogens in Compound 99209

Atom	x	y	z	U_{iso}, Å^2
H2	0.2227	0.5062	0.6970	0.020
H4	0.2529	0.5956	0.2684	0.020
H5	0.2807	0.4134	-0.0579	0.020
H6	0.2601	0.3809	0.3155	0.020
H7a	0.6262	0.2778	0.6934	0.020
H7b	0.6240	0.2451	0.8361	0.020
H8a	0.4841	0.1731	0.4159	0.020
H8b	0.3677	0.1242	0.4750	0.020
H9a	-0.0721	0.2388	0.5870	0.020
H9b	-0.0387	0.1703	0.6184	0.020

Table 4. Refined Thermal Parameters (U's) for Compound 99209

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	0.01629(10)	0.00668(10)	0.00906(10)	0.00188(6)	0.00016(7)	-0.00031(6)
O1	0.0358(7)	0.0129(5)	0.0092(5)	-0.0001(4)	0.0029(4)	-0.0023(5)
O2	0.0234(6)	0.0072(5)	0.0107(5)	0.0007(4)	0.0020(4)	0.0009(4)
O3	0.0251(6)	0.0093(5)	0.0111(5)	-0.0023(4)	0.0019(4)	-0.0008(4)
O4	0.0233(6)	0.0086(5)	0.0168(5)	0.0020(4)	0.0034(4)	0.0016(4)
O5	0.0354(7)	0.0130(5)	0.0082(5)	-0.0026(4)	-0.0003(4)	0.0040(5)
O6	0.0622(9)	0.0139(6)	0.0108(6)	0.0027(4)	0.0033(6)	0.0054(6)
O7	0.0200(6)	0.0308(7)	0.0211(6)	0.0110(5)	-0.0056(5)	-0.0088(5)
O8	0.0295(6)	0.0136(5)	0.0171(6)	-0.0023(4)	0.0076(5)	-0.0003(5)
O9	0.0185(6)	0.0122(5)	0.0281(6)	0.0052(5)	-0.0030(5)	-0.0015(4)
C1	0.0121(6)	0.0086(6)	0.0100(6)	0.0010(5)	0.0003(5)	0.0000(5)
C2	0.0122(6)	0.0097(6)	0.0090(6)	-0.0009(5)	0.0000(5)	-0.0003(5)
C3	0.0115(6)	0.0083(6)	0.0112(6)	-0.0014(5)	-0.0004(5)	-0.0002(5)
C4	0.0158(7)	0.0088(6)	0.0112(7)	0.0014(5)	0.0002(5)	-0.0003(5)
C5	0.0151(7)	0.0109(7)	0.0088(6)	-0.0004(5)	0.0007(5)	-0.0002(5)
C6	0.0146(7)	0.0079(6)	0.0111(6)	-0.0014(5)	0.0005(5)	0.0004(5)
C7	0.0136(6)	0.0093(6)	0.0112(6)	0.0006(5)	-0.0005(5)	-0.0011(5)
C8	0.0110(6)	0.0091(6)	0.0128(7)	-0.0011(5)	-0.0005(5)	0.0002(5)
C9	0.0217(7)	0.0111(7)	0.0113(7)	-0.0012(5)	0.0015(6)	-0.0012(6)

The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$

Table 5. Bond Distances in Compound 99209, Å

Cu1-O3#1	1.9184(11)	Cu1-O2	1.9377(11)	Cu1-O7	1.9751(12)
Cu1-O9	1.9852(12)	Cu1-O8	2.2368(11)	O1-C7	1.2448(18)
O2-C7	1.2762(18)	O3-C8	1.2684(18)	O3-Cu1#2	1.9184(11)
O4-C8	1.2520(18)	O5-C9	1.3282(18)	O6-C9	1.207(2)
C1-C2	1.3925(19)	C1-C6	1.395(2)	C1-C7	1.5003(19)
C2-C3	1.397(2)	C3-C4	1.392(2)	C3-C8	1.5012(19)
C4-C5	1.392(2)	C5-C6	1.392(2)	C5-C9	1.488(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y-1/2,-z+3/2 #2 -x+1/2,y+1/2,-z+3/2

Table 6. Bond Angles in Compound 99209, °

O3#1-Cu1-O2	174.07(5)	O3#1-Cu1-O7	94.10(5)	O2-Cu1-O7	90.88(5)
O3#1-Cu1-O9	87.57(5)	O2-Cu1-O9	88.37(5)	O7-Cu1-O9	166.06(6)
O3#1-Cu1-O8	89.71(4)	O2-Cu1-O8	86.42(4)	O7-Cu1-O8	97.72(5)
O9-Cu1-O8	96.13(5)	C7-O2-Cu1	116.61(9)	C8-O3-Cu1#2	120.85(10)
C2-C1-C6	119.98(13)	C2-C1-C7	120.89(13)	C6-C1-C7	119.12(13)
C1-C2-C3	119.78(13)	C4-C3-C2	120.02(13)	C4-C3-C8	119.57(13)
C2-C3-C8	120.37(13)	C5-C4-C3	120.22(13)	C4-C5-C6	119.76(13)
C4-C5-C9	119.36(13)	C6-C5-C9	120.85(13)	C5-C6-C1	120.24(13)
O1-C7-O2	123.16(13)	O1-C7-C1	121.06(13)	O2-C7-C1	115.78(13)
O4-C8-O3	124.35(13)	O4-C8-C3	119.86(13)	O3-C8-C3	115.79(13)
O6-C9-O5	122.05(14)	O6-C9-C5	124.53(14)	O5-C9-C5	113.41(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y-1/2,-z+3/2 #2 -x+1/2,y+1/2,-z+3/2

[i]Bruker (2009) SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

[ii]Bruker (2009) SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.

[iii]Sheldrick, G.M. (2007) SADABS. University of Gottingen, Germany.

[iv]Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

[v]Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

[vi]$R1 = \Sigma||F_o| - |F_c|| / \Sigma |F_o|$
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$
$GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$
where n = the number of reflections and p = the number of parameters refined.

[vii]"ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations". C.K. Johnson (1976) ORNL-5138.