Crystal structure of bis(η^1-benzoato)tris(1-pyrazolyl)methanecopper(II) hydrate, $C_{24}H_{22}CuN_6O_5$

B. Moubaraki[I], K. S. Murray[I] and E. R. T. Tiekink*,[II,I]

[I] Monash University, School of Chemistry, PO Box 23, Clayton, Victoria 3800, Australia
[II] The University of Adelaide, Department of Chemistry, Australia 5005

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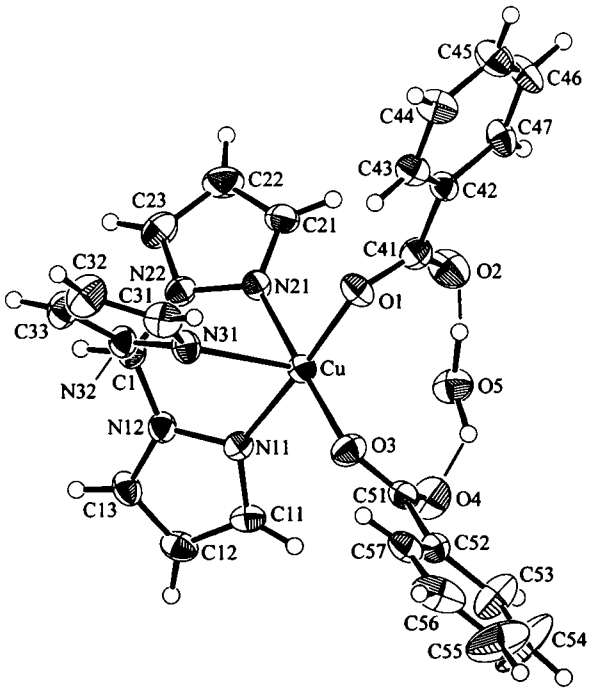

Abstract

$C_{24}H_{22}CuN_6O_5$, monoclinic, $P12_1/c1$ (No. 14), a = 12.344(7) Å, b = 12.465(4) Å, c = 17.053(3) Å, β = 110.81(2)°, V = 2452.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.057, $wR_{ref}(F^2)$ = 0.202, T = 293 K.

Source of material

The title complex was synthesised using (tris-pyrazolylmethane)$CuCl_2$ reacted with two mole equivalents of sodium benzoate in methanol-water solution. The crystals appeared upon evaporation of the solvent.

Discussion

The Cu atom exists within a N_3O_2 donor set that defines a square pyramidal geometry. The deviations of the O1, O3, N11 and N21 atoms from their least-squares plane are 0.014(5) Å, –0.016(5) Å, 0.054(9) Å and –0.13(1) Å, respectively. The Cu atom is effectively in the basal plane, lying 0.0018(9) Å out of the plane in the direction of the O1 atom. The respective d(Cu—N11) and d(Cu—N21) distances, i.e. those in the basal plane, of 2.026(4) Å and 2.065(4) Å are significantly shorter than d(Cu—N31) of 2.296(4) Å where the N31 atom occupies an apical position. The benzoate ligands are monodentate, forming d(Cu—O1) and d(Cu—O3) bond distances of 1.938(4) Å and 1.931(4) Å, respectively. The d(Cu···O2) and d(Cu···O4) separations of 3.096(5) Å and 3.173(5) Å, respectively are not indicative of significant bonding interactions. Indeed, the non-coordinating carbonyl atoms are linked to a solvate water molecule via hydrogen bonding interactions as illustrated in the Figure. The parameters associated with these interactions are d(O5–H1w···O2) of 1.82 Å, d(O5···O2) of 2.775(7) Å with the angle at H1w equal to 150°, and d(O5–H2w···O4) of 1.92 Å, d(O5···O4) of 2.758(8) Å with angle at H2w of 140°. The most important intermolecular interaction also involves the O5 water molecule. The O5 atom also forms an accepter interaction with the H atom bound to the bridgehead C1 atom of the tridentate ligand so that d(C1–H···O5^i) is 2.17 Å, d(C1···O5^i) is 3.114(7) Å and the angle at H is 160° for symmetry operation i: x, 1/2–y, –1/2+z. Despite being in close proximity to the coordination sphere of the copper centre, there is no significant interaction between these atoms as evidenced by the Cu···O5 separation of 3.554(5) Å. The structure of the title complex forms a part of a larger study of metal tris-pyrazolylmethane derivatives (Cu, Fe, Mn) used in bioinorganic model work. The benzoate coordination mode observed in the present structure is of relevance to recent bioinorganic modelling of non heme iron species using sterically hindered benzoates [1].

Table 1. Data collection and handling.

Crystal:	blue block, size 0.07 × 0.24 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.38 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC6R, $\omega/2\theta$
$2\theta_{max}$:	55.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6219, 5685
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2812
$N(param)_{refined}$:	326
Programs:	SHELXS-86 [2], teXsan [3], SHELXL-97 [4], PLATON [5], DIFABS [6], ORTEPII [7]

* Correspondence author (e-mail: chmtert@nus.edu.sg)
[I] Current address: National University of Singapore, Department of Chemistry, Singapore 117543

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1w)	4e	0.2299	0.1826	0.2923	0.083
H(2w)	4e	0.3679	0.2382	0.3412	0.083
H(1)	4e	0.2733	0.2009	-0.0772	0.066(4)
H(11)	4e	0.5376	0.2938	0.2131	0.066
H(12)	4e	0.5658	0.4100	0.1039	0.066
H(13)	4e	0.4303	0.3452	-0.0317	0.066
H(21)	4e	0.0642	0.0982	0.1156	0.066
H(22)	4e	-0.0689	0.1625	-0.0226	0.066
H(23)	4e	0.0563	0.2108	-0.1032	0.066
H(31)	4e	0.4046	-0.1580	0.0520	0.066
H(32)	4e	0.3434	-0.1605	-0.1024	0.066
H(33)	4e	0.2904	0.0247	-0.1508	0.066
H(43)	4e	0.2467	-0.2408	0.1865	0.066
H(44)	4e	0.1489	-0.3950	0.1932	0.066
H(45)	4e	0.0067	-0.3921	0.2530	0.066
H(46)	4e	-0.0369	-0.2344	0.3040	0.066
H(47)	4e	0.0613	-0.0800	0.2979	0.066
H(53)	4e	0.6818	0.1524	0.4681	0.066
H(54)	4e	0.8499	0.0791	0.5560	0.066
H(55)	4e	0.9244	-0.0709	0.5226	0.066
H(56)	4e	0.8400	-0.1449	0.3941	0.066
H(57)	4e	0.6743	-0.0697	0.2976	0.066

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	4e	0.35541(6)	0.08113(5)	0.16033(4)	0.0358(3)	0.0375(4)	0.0351(3)	-0.0018(3)	0.0124(3)	0.0024(3)
O(1)	4e	0.2889(3)	-0.0459(3)	0.1909(2)	0.048(2)	0.048(2)	0.057(2)	-0.002(2)	0.027(2)	0.010(2)
O(2)	4e	0.2010(4)	0.0412(4)	0.2662(3)	0.080(3)	0.045(3)	0.089(3)	-0.009(2)	0.045(3)	-0.010(3)
O(3)	4e	0.5041(4)	0.0487(3)	0.2447(2)	0.047(2)	0.053(3)	0.045(2)	-0.001(2)	0.005(2)	0.003(2)
O(4)	4e	0.5088(4)	0.1785(4)	0.3368(3)	0.065(3)	0.065(3)	0.067(3)	0.019(3)	0.021(2)	-0.006(3)
O(5)	4e	0.2851(4)	0.2486(4)	0.3041(3)	0.056(3)	0.053(3)	0.068(3)	0.000(2)	0.021(2)	-0.016(2)
N(11)	4e	0.4173(4)	0.2129(3)	0.1207(3)	0.038(3)	0.037(3)	0.037(2)	-0.001(2)	0.012(2)	-0.002(2)
N(12)	4e	0.3808(4)	0.2331(4)	0.0362(3)	0.048(3)	0.035(3)	0.037(2)	-0.004(2)	0.017(2)	0.002(2)
N(21)	4e	0.1959(4)	0.1265(4)	0.0755(3)	0.036(2)	0.039(3)	0.037(2)	0.002(2)	0.015(2)	0.003(2)
N(22)	4e	0.1906(4)	0.1657(4)	0.0004(3)	0.036(2)	0.041(3)	0.036(2)	0.004(2)	0.007(2)	0.003(2)
N(31)	4e	0.3701(4)	-0.0006(4)	0.0439(3)	0.048(3)	0.038(3)	0.040(3)	0.004(2)	0.020(2)	0.000(2)
N(32)	4e	0.3331(4)	0.0604(3)	-0.0264(3)	0.049(3)	0.039(3)	0.037(2)	-0.002(2)	0.020(2)	-0.005(2)
C(1)	4e	0.2940(5)	0.1683(4)	-0.0215(3)	0.043(3)	0.038(3)	0.034(3)	0.001(3)	0.013(2)	0.003(2)
C(11)	4e	0.4978(4)	0.2870(4)	0.1557(4)	0.033(3)	0.040(3)	0.053(3)	-0.001(2)	0.011(3)	-0.005(3)
C(12)	4e	0.5142(5)	0.3530(5)	0.0951(4)	0.048(4)	0.034(3)	0.067(4)	-0.007(3)	0.027(3)	-0.007(3)
C(13)	4e	0.4396(5)	0.3171(4)	0.0208(4)	0.063(4)	0.034(3)	0.048(3)	-0.006(3)	0.030(3)	0.002(3)
C(21)	4e	0.0869(5)	0.1221(5)	0.0721(4)	0.039(3)	0.051(4)	0.055(4)	-0.006(3)	0.019(3)	-0.005(3)
C(22)	4e	0.0114(5)	0.1578(6)	-0.0048(4)	0.032(3)	0.076(5)	0.067(4)	0.003(3)	0.007(3)	0.002(4)
C(23)	4e	0.0809(5)	0.1843(5)	-0.0487(4)	0.050(4)	0.057(4)	0.047(4)	0.010(3)	0.003(3)	0.004(3)
C(31)	4e	0.3791(5)	-0.0986(5)	0.0173(4)	0.052(4)	0.039(4)	0.068(4)	0.007(3)	0.025(3)	-0.007(3)
C(32)	4e	0.3456(6)	-0.1009(6)	-0.0691(4)	0.082(5)	0.053(5)	0.070(5)	0.008(4)	0.029(4)	-0.022(4)
C(33)	4e	0.3166(5)	0.0006(5)	-0.0956(4)	0.061(4)	0.060(4)	0.043(3)	0.004(3)	0.023(3)	-0.011(3)
C(41)	4e	0.2218(5)	-0.0414(5)	0.2334(4)	0.044(3)	0.044(3)	0.044(3)	0.003(3)	0.012(3)	-0.002(3)
C(42)	4e	0.1632(5)	-0.1438(4)	0.2405(3)	0.040(3)	0.035(3)	0.039(3)	-0.002(2)	0.016(2)	0.006(2)
C(43)	4e	0.1893(5)	-0.2391(5)	0.2101(4)	0.035(3)	0.043(3)	0.054(3)	0.008(3)	0.014(3)	0.008(3)
C(44)	4e	0.1313(5)	-0.3312(5)	0.2143(4)	0.053(4)	0.036(4)	0.083(5)	0.002(3)	0.028(4)	-0.001(3)
C(45)	4e	0.0460(6)	-0.3295(6)	0.2499(4)	0.069(4)	0.049(4)	0.078(5)	-0.009(4)	0.037(4)	0.008(4)
C(46)	4e	0.0204(6)	-0.2359(6)	0.2804(4)	0.066(4)	0.059(4)	0.080(5)	-0.005(4)	0.053(4)	0.006(4)
C(47)	4e	0.0787(5)	-0.1435(5)	0.2763(4)	0.061(4)	0.047(4)	0.052(4)	0.003(3)	0.034(3)	-0.001(3)
C(51)	4e	0.5485(5)	0.0978(5)	0.3148(4)	0.036(3)	0.049(4)	0.046(3)	-0.005(3)	0.017(3)	0.003(3)
C(52)	4e	0.6604(5)	0.0492(4)	0.3732(3)	0.042(3)	0.033(3)	0.040(3)	-0.001(2)	0.012(2)	0.005(2)
C(53)	4e	0.7133(7)	0.0928(6)	0.4514(4)	0.092(6)	0.060(5)	0.055(4)	0.009(4)	-0.006(4)	-0.007(4)
C(54)	4e	0.813(1)	0.0475(8)	0.5040(6)	0.15(1)	0.104(8)	0.067(6)	0.020(7)	-0.055(6)	-0.009(5)
C(55)	4e	0.8581(8)	-0.0403(8)	0.4841(7)	0.071(6)	0.089(7)	0.122(8)	0.007(5)	-0.042(6)	0.027(6)
C(56)	4e	0.8078(6)	-0.0839(6)	0.4084(6)	0.048(4)	0.047(4)	0.134(7)	0.014(4)	0.030(5)	0.036(5)
C(57)	4e	0.7082(5)	-0.0396(5)	0.3507(4)	0.047(4)	0.043(3)	0.061(4)	-0.005(3)	0.025(3)	0.010(3)

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