# Crystal structure of $\eta^1$-benzoato-chloro-tris(1-pyrazolylmethane)-copper(II), $C_{17}H_{15}ClCuN_6O_2$

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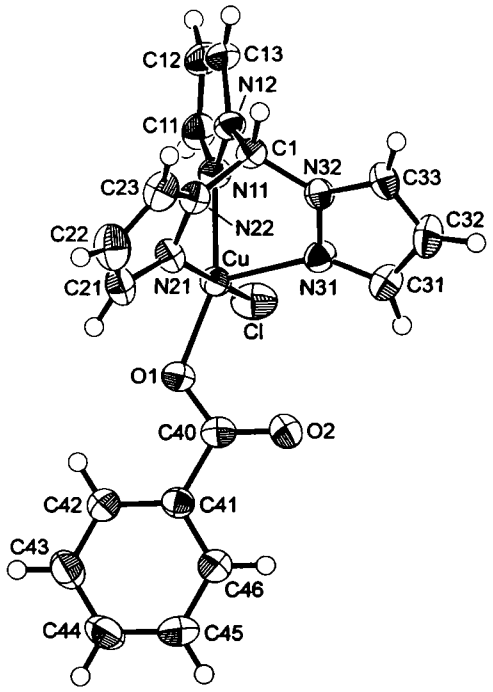


**Abstract**

$C_{17}H_{15}ClCuN_6O_2$, monoclinic, $P12_1/c1$ (No. 14), $a = 7.715(3)$ Å, $b = 14.382(2)$ Å, $c = 16.457(3)$ Å, $\beta = 99.95(2)°$, $V = 1798.6$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.041$, $wR_{ref}(F^2) = 0.110$, $T = 293$ K.

**Source of material**

The Cu(II) complex was prepared using the method reported in [1] in which (tris-pyrazolylmethane)$CuCl_2$ was reacted with an equimolar amount of sodium benzoate in methanol. Light blue crystals formed upon evaporation of the solvent

**Discussion**

The Cu atom exists in a five coordinate environment defined by a chloride, $d$(Cu—Cl) 2.2486(10) Å, O1 from a monodentate benzoate, $d$(Cu—O1, O2) 1.909(2) Å and 3.080(2) Å, and nitrogen atoms derived from the tridentate ligand. The coordination polyhedron is best described as been based on a distorted square pyramid. In this description the deviations of the Cl, O1, N11 & N21 atoms from their least-squares plane are 0.103(1) Å, –0.115(2) Å, –0.114(3) Å and 0.126(3) Å, respectively, and the Cu atom lies 0.2348(3) Å out of this plane in the direction of the N31 atom. The alternative description is one based on a trigonal bipyramid for which the Cl–Cu–N21 angle is 172.86(8)°. The Cu—N distances for the nitrogen atoms defining the basal plane of 2.033(3) Å and 2.069(3) Å are significantly shorter than apical $d$(Cu—N31) of 2.274(3) Å. In the crystal structure there are both C–H···$\pi$ and C–H···O interactions of note. The most significant C–H···$\pi$ contacts involve the C12-H atom which is orientated towards a cleft defined by translationally (along the $a$-axis) related N21–N22 and N31–N32 rings so that $d$(H···ring centroid of N31–N32) = 2.87 Å and the angle at H = 134°. The parameters involving the N21–N22 ring are 2.95 Å and 131°. The O2 atom forms two close contacts with a neighbouring molecule so that $d$(C1–H···O2$^i$) = 2.20 Å, $d$(C1···O2$^i$) = 3.102(4) A and the angle at H is 152°; symmetry operation $i$: 1–$x$, 1/2+$y$, –1/2–$z$. The other contact involves C13-H and has parameters associated with it of 2.47 Å, 3.155(5) Å and 131°, respectively. These complexes have been used in studies [2] of bioinorganic modelling of copper proteins such as hemocyanin in a related way to the tris-pyrazolylhydridoborate analogues [3] and the Cu-tacn (triazacyclononane) [4] compounds studied in [3,4].

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | blue block, size 0.16 × 0.21 × 0.24 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 13.89 cm$^{-1}$ |
| Diffractometer, scan mode: | Rigaku AFC6R, $\omega/2\theta$ |
| $2\theta_{max}$: | 55.2° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 4626, 4147 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 2780 |
| $N(param)_{refined}$: | 245 |
| Programs: | SIR92 [5], teXsan [6], SHELXL-97 [7], PLATON [8], DIBABS [9], ORTEPII [10] |

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

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1) | 4e | 0.5967 | –0.3626 | –0.2424 | 0.061(3) |
| H(11) | 4e | 0.9879 | –0.6051 | –0.3362 | 0.061 |
| H(12) | 4e | 1.1508 | –0.4649 | –0.2797 | 0.061 |
| H(13) | 4e | 0.9332 | –0.3570 | –0.2380 | 0.061 |
| H(21) | 4e | 0.2695 | –0.5075 | –0.5008 | 0.061 |
| H(22) | 4e | 0.1978 | –0.3406 | –0.4891 | 0.061 |
| H(23) | 4e | 0.3703 | –0.2865 | –0.3553 | 0.061 |
| H(31) | 4e | 0.3615 | –0.6710 | –0.1698 | 0.061 |
| H(32) | 4e | 0.3638 | –0.5543 | –0.0585 | 0.061 |
| H(33) | 4e | 0.4889 | –0.4099 | –0.1069 | 0.061 |
| H(42) | 4e | 0.2178 | –0.7146 | –0.5699 | 0.061 |
| H(43) | 4e | 0.0221 | –0.7806 | –0.6758 | 0.061 |
| H(44) | 4e | –0.1775 | –0.8889 | –0.6477 | 0.061 |
| H(45) | 4e | –0.1876 | –0.9277 | –0.5133 | 0.061 |
| H(46) | 4e | 0.004 | –0.8589 | –0.4065 | 0.061 |

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**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 | 4*e* | 0.54909(5) | −0.62112(3) | −0.35358(2) | 0.0332(2) | 0.0344(2) | 0.0327(2) | −0.0022(2) | 0.0046(1) | −0.0026(2) |
| Cl(1) | 4*e* | 0.7033(1) | −0.75242(6) | −0.32029(7) | 0.0491(5) | 0.0373(4) | 0.0727(7) | 0.0049(4) | 0.0051(4) | −0.0033(4) |
| O(1) | 4*e* | 0.3652(3) | −0.6789(2) | −0.4293(1) | 0.049(1) | 0.049(1) | 0.039(1) | −0.016(1) | −0.002(1) | 0.002(1) |
| O(2) | 4*e* | 0.2487(3) | −0.7561(2) | −0.3346(1) | 0.048(1) | 0.061(2) | 0.035(1) | −0.009(1) | 0.003(1) | 0.001(1) |
| N(11) | 4*e* | 0.7672(3) | −0.5431(2) | −0.3143(2) | 0.031(1) | 0.037(1) | 0.038(1) | −0.000(1) | 0.009(1) | −0.003(1) |
| N(12) | 4*e* | 0.7527(3) | −0.4577(2) | −0.2802(2) | 0.028(1) | 0.036(1) | 0.036(1) | −0.004(1) | 0.007(1) | −0.001(1) |
| N(21) | 4*e* | 0.4313(3) | −0.4959(2) | −0.3926(2) | 0.038(2) | 0.042(2) | 0.029(1) | 0.003(1) | 0.003(1) | −0.002(1) |
| N(22) | 4*e* | 0.4637(3) | −0.4195(2) | −0.3441(2) | 0.032(1) | 0.035(1) | 0.035(1) | 0.003(1) | 0.007(1) | 0.002(1) |
| N(31) | 4*e* | 0.4703(3) | −0.5750(2) | −0.2329(2) | 0.037(1) | 0.034(1) | 0.038(2) | −0.001(1) | 0.015(1) | −0.002(1) |
| N(32) | 4*e* | 0.5127(3) | −0.4860(2) | −0.2100(2) | 0.035(1) | 0.034(1) | 0.030(1) | 0.000(1) | 0.009(1) | −0.004(1) |
| C(1) | 4*e* | 0.5825(4) | −0.4250(2) | −0.2666(2) | 0.035(2) | 0.033(2) | 0.034(2) | −0.002(1) | 0.007(1) | 0.001(1) |
| C(11) | 4*e* | 0.9377(4) | −0.5529(3) | −0.3163(2) | 0.032(2) | 0.052(2) | 0.042(2) | 0.004(2) | 0.011(1) | 0.003(2) |
| C(12) | 4*e* | 1.0303(4) | −0.4747(3) | −0.2845(2) | 0.029(2) | 0.065(2) | 0.052(2) | −0.011(2) | 0.010(2) | 0.003(2) |
| C(13) | 4*e* | 0.9107(4) | −0.4155(3) | −0.2617(2) | 0.034(2) | 0.047(2) | 0.041(2) | −0.014(2) | 0.003(1) | 0.002(2) |
| C(21) | 4*e* | 0.3163(5) | −0.4690(3) | −0.4571(2) | 0.043(2) | 0.062(2) | 0.030(2) | 0.007(2) | 0.004(1) | 0.002(2) |
| C(22) | 4*e* | 0.2744(5) | −0.3756(3) | −0.4512(2) | 0.053(2) | 0.063(3) | 0.049(2) | 0.021(2) | 0.003(2) | 0.014(2) |
| C(23) | 4*e* | 0.3702(5) | −0.3459(3) | −0.3776(2) | 0.047(2) | 0.040(2) | 0.052(2) | 0.010(2) | 0.013(2) | 0.009(2) |
| C(31) | 4*e* | 0.4033(4) | −0.6105(2) | −0.1712(2) | 0.044(2) | 0.040(2) | 0.045(2) | 0.002(2) | 0.015(1) | 0.005(2) |
| C(32) | 4*e* | 0.4031(5) | −0.5454(3) | −0.1083(2) | 0.064(2) | 0.055(2) | 0.040(2) | 0.005(2) | 0.023(2) | 0.006(2) |
| C(33) | 4*e* | 0.4724(4) | −0.4663(2) | −0.1348(2) | 0.050(2) | 0.045(2) | 0.029(2) | 0.005(2) | 0.008(2) | −0.005(2) |
| C(40) | 4*e* | 0.2561(4) | −0.7358(2) | −0.4066(2) | 0.033(2) | 0.030(2) | 0.043(2) | 0.002(1) | 0.005(1) | −0.001(1) |
| C(41) | 4*e* | 0.1312(4) | −0.7797(2) | −0.4767(2) | 0.032(2) | 0.034(2) | 0.038(2) | 0.001(1) | 0.003(1) | −0.001(1) |
| C(42) | 4*e* | 0.1354(4) | −0.7573(3) | −0.5578(2) | 0.041(2) | 0.049(2) | 0.040(2) | −0.007(2) | 0.010(1) | −0.002(2) |
| C(43) | 4*e* | 0.0189(5) | −0.7973(3) | −0.6215(2) | 0.052(2) | 0.065(2) | 0.037(2) | −0.001(2) | 0.005(2) | −0.006(2) |
| C(44) | 4*e* | −0.1004(5) | −0.8612(3) | −0.6049(2) | 0.051(2) | 0.065(3) | 0.046(2) | −0.010(2) | −0.005(2) | −0.012(2) |
| C(45) | 4*e* | −0.1061(6) | −0.8843(4) | −0.5249(3) | 0.080(3) | 0.096(4) | 0.062(3) | −0.056(3) | −0.002(2) | 0.003(3) |
| C(46) | 4*e* | 0.0096(6) | −0.8431(3) | −0.4608(2) | 0.076(3) | 0.086(3) | 0.041(2) | −0.041(2) | −0.002(2) | 0.010(2) |

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