**SUPPLEMENTARY MATERIAL TO**

**Synthesis, Characterization, electrochemical studies and X-ray structures of Mixed–Ligand complexes of [Cu(phen)2(CH3COO)].2H2O(ClO4) and Cu(bipy)2(CH3COO)]H­2O(ClO4)**

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CCDC 1418811 and 1418812 are for [Cu(phen)2(CH3COO)].2H2O(ClO4) **(1)** and Cu(bipy)2(CH3COO)](ClO4)H­2O **(2)** respectively

Table S1. Crystal data and structure refinement for [Cu(phen)2(CH3COO)].2H2O(ClO4) **(1)**.

Identification code shelx

Empirical formula C26 H23 Cl Cu N4 O8

Formula weight 618.47

Temperature 100(2) K

Wavelength 0.71073 Å

Crystal system Monoclinic

Space group P n

Unit cell dimensions a = 9.3682(6) Å α = 90°.

b = 8.3029(5) Å β= 103.3014(18)°.

c = 16.8784(10) Å γ = 90°.

Volume 1277.64(14) Å3

Z 2

Density (calculated) 1.608 Mg/m3

Absorption coefficient 1.019 mm-1

F(000) 634

Crystal size 0.300 x 0.260 x 0.200 mm3

Theta range for data collection 2.292 to 30.570°.

Index ranges -13<=h<=13, -11<=k<=11, -23<=l<=24

Reflections collected 9896

Independent reflections 6312 [R(int) = 0.0196]

Completeness to theta = 25.500° 99.3 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7461 and 0.6516

Refinement method Full-matrix least-squares on F2

Data / restraints / parameters 6312 / 8 / 379

Goodness-of-fit on F2 1.070

Final R indices [I>2sigma(I)] R1 = 0.0325, wR2 = 0.0772

R indices (all data) R1 = 0.0377, wR2 = 0.0802

Absolute structure parameter 0.521(12)

Extinction coefficient n/a

Largest diff. peak and hole 0.601 and -0.278 e.Å-3

Table S2. Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103)

for [Cu(phen)2(CH3COO)].2H2O(ClO4) **(1)**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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x y z U(eq)

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Cu 2292(1) 4985(1) 6297(1) 14(1)

O(1) 1792(2) 2888(2) 6743(1) 18(1)

O(2) 2670(2) 2136(3) 5695(1) 22(1)

N(1) 2082(3) 6422(3) 7371(2) 15(1)

N(2) 4366(4) 4921(3) 6963(2) 15(1)

N(3) 2796(3) 6505(3) 5453(2) 15(1)

N(4) 267(3) 5241(3) 5589(2) 15(1)

C(11A) 2151(4) 1802(3) 6284(2) 17(1)

C(12A) 1924(5) 80(3) 6503(3) 29(1)

C(1) 936(4) 7070(4) 7596(2) 19(1)

C(2) 1063(4) 7973(4) 8309(2) 23(1)

C(3) 2437(4) 8247(4) 8792(2) 23(1)

C(4) 3674(4) 7578(4) 8582(2) 19(1)

C(5) 5144(4) 7732(4) 9065(2) 23(1)

C(6) 6279(4) 6974(4) 8862(2) 22(1)

C(7) 6068(3) 5989(4) 8148(2) 18(1)

C(8) 7201(3) 5104(4) 7933(2) 20(1)

C(9) 6889(3) 4130(4) 7262(2) 22(1)

C(10) 5447(3) 4077(4) 6778(2) 20(1)

C(11) 4643(3) 5846(3) 7643(2) 15(1)

C(12) 3432(3) 6649(3) 7864(2) 16(1)

C(13) 4077(3) 7101(3) 5387(2) 18(1)

C(14) 4234(4) 8132(4) 4763(2) 21(1)

C(15) 3011(4) 8568(4) 4175(2) 20(1)

C(16) 1629(3) 7948(3) 4217(2) 16(1)

C(17) 288(4) 8283(3) 3629(2) 19(1)

C(18) -1007(4) 7639(4) 3702(2) 19(1)

C(19) -1082(3) 6602(3) 4370(2) 16(1)

C(20) -2379(3) 5868(3) 4481(2) 18(1)

C(21) -2324(3) 4854(4) 5123(2) 18(1)

C(22) -970(3) 4551(4) 5672(2) 19(1)

C(23) 215(3) 6243(3) 4946(2) 14(1)

C(24) 1589(3) 6920(3) 4871(2) 14(1)

Cl(1) 7284(1) -404(1) 6606(1) 23(1)

O(3) 7603(3) 803(4) 6059(2) 41(1)

O(4) 7490(3) -1975(3) 6296(2) 38(1)

O(5) 5799(3) -209(3) 6682(2) 36(1)

O(6) 8281(3) -210(3) 7390(2) 36(1)

O(1W) 4978(3) 2019(3) 4944(2) 31(1)

O(2W) 176(3) 2583(4) 7910(2) 33(1)

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Table S3. Bond lengths [Å] and angles [°] for [Cu(phen)2(CH3COO)].2H2O(ClO4) **(1)**.

|  |  |
| --- | --- |
| Cu-O(1) | 1.995(2) |
| Cu-N(4) | 2.007(3) |
| Cu-N(2) | 2.009(3) |
| Cu-N(3) | 2.038(2) |
| Cu-N(1) | 2.217(3) |
| O(1)-C(11A) | 1.282(4) |
| O(2)-C(11A) | 1.236(4) |
| N(1)-C(1) | 1.332(4) |
| N(1)-C(12) | 1.357(4) |
| N(2)-C(10) | 1.327(4) |
| N(2)-C(11) | 1.356(4) |
| N(3)-C(13) | 1.327(4) |
| N(3)-C(24) | 1.361(4) |
| N(4)-C(22) | 1.329(4) |
| N(4)-C(23) | 1.359(4) |
| C(11A)-C(12A) | 1.504(4) |
| C(12A)-H(12A) | 0.9800 |
| C(12A)-H(12B) | 0.9800 |
| C(12A)-H(12C) | 0.9800 |
| C(1)-C(2) | 1.400(5) |
| C(1)-H(1A) | 0.9500 |
| C(2)-C(3) | 1.375(5) |
| C(2)-H(2A) | 0.9500 |
| C(3)-C(4) | 1.403(4) |
| C(3)-H(3A) | 0.9500 |
| C(4)-C(12) | 1.410(4) |
| C(4)-C(5) | 1.436(5) |
| C(5)-C(6) | 1.346(5) |
| C(5)-H(5A) | 0.9500 |
| C(6)-C(7) | 1.432(4) |
| C(6)-H(6A) | 0.9500 |
| C(7)-C(8) | 1.406(4) |
| C(7)-C(11) | 1.414(4) |
| C(8)-C(9) | 1.367(5) |
| C(8)-H(8A) | 0.9500 |
| C(9)-C(10) | 1.409(4) |
| C(9)-H(9A) | 0.9500 |
| C(10)-H(10A) | 0.9500 |
| C(11)-C(12) | 1.437(4) |
| C(13)-C(14) | 1.392(4) |
| C(13)-H(13A) | 0.9500 |
| C(14)-C(15) | 1.381(5) |
| C(14)-H(14A) | 0.9500 |
| C(15)-C(16) | 1.410(4) |
| C(15)-H(15A) | 0.9500 |
| C(16)-C(24) | 1.402(4) |
| C(16)-C(17) | 1.437(4) |
| C(17)-C(18) | 1.356(4) |
| C(17)-H(17A) | 0.9500 |
| C(18)-C(19) | 1.434(4) |
| C(18)-H(18A) | 0.9500 |
| C(19)-C(23) | 1.403(4) |
| C(19)-C(20) | 1.410(4) |
| C(20)-C(21) | 1.364(5) |
| C(20)-H(20A) | 0.9500 |
| C(21)-C(22) | 1.411(4) |
| C(21)-H(21A) | 0.9500 |
| C(22)-H(22A) | 0.9500 |
| C(23)-C(24) | 1.437(4) |
| Cl(1)-O(4) | 1.434(2) |
| Cl(1)-O(5) | 1.436(3) |
| Cl(1)-O(3) | 1.439(3) |
| Cl(1)-O(6) | 1.442(3) |
| O(1W)-H(1W1) | 0.85(2) |
| O(1W)-H(1W2) | 0.84(2) |
| O(2W)-H(2W1) | 0.84(2) |
| O(2W)-H(2W2) | 0.83(2) |
| O(1)-Cu-N(4) | 92.60(10) |
| O(1)-Cu-N(2) | 92.65(10) |
| N(4)-Cu-N(2) | 174.75(12) |
| O(1)-Cu-N(3) | 156.38(9) |
| N(4)-Cu-N(3) | 81.81(11) |
| N(2)-Cu-N(3) | 93.33(11) |
| O(1)-Cu-N(1) | 95.09(9) |
| N(4)-Cu-N(1) | 100.38(11) |
| N(2)-Cu-N(1) | 79.22(11) |
| N(3)-Cu-N(1) | 108.48(9) |
| C(11A)-O(1)-Cu | 105.61(19) |
| C(1)-N(1)-C(12) | 118.0(3) |
| C(1)-N(1)-Cu | 132.8(2) |
| C(12)-N(1)-Cu | 109.27(19) |
| C(10)-N(2)-C(11) | 119.4(3) |
| C(10)-N(2)-Cu | 125.1(2) |
| C(11)-N(2)-Cu | 115.5(2) |
| C(13)-N(3)-C(24) | 117.5(3) |
| C(13)-N(3)-Cu | 130.5(2) |
| C(24)-N(3)-Cu | 112.00(19) |
| C(22)-N(4)-C(23) | 118.5(3) |
| C(22)-N(4)-Cu | 128.3(2) |
| C(23)-N(4)-Cu | 113.3(2) |
| O(2)-C(11A)-O(1) | 122.3(3) |
| O(2)-C(11A)-C(12A) | 121.0(3) |
| O(1)-C(11A)-C(12A) | 116.6(3) |
| C(11A)-C(12A)-H(12A) | 109.5 |
| C(11A)-C(12A)-H(12B) | 109.5 |
| H(12A)-C(12A)-H(12B) | 109.5 |
| C(11A)-C(12A)-H(12C) | 109.5 |
| H(12A)-C(12A)-H(12C) | 109.5 |
| H(12B)-C(12A)-H(12C) | 109.5 |
| N(1)-C(1)-C(2) | 123.1(3) |
| N(1)-C(1)-H(1A) | 118.5 |
| C(2)-C(1)-H(1A) | 118.5 |
| C(3)-C(2)-C(1) | 118.8(3) |
| C(3)-C(2)-H(2A) | 120.6 |
| C(1)-C(2)-H(2A) | 120.6 |
| C(2)-C(3)-C(4) | 119.9(3) |
| C(2)-C(3)-H(3A) | 120.0 |
| C(4)-C(3)-H(3A) | 120.0 |
| C(3)-C(4)-C(12) | 117.1(3) |
| C(3)-C(4)-C(5) | 124.1(3) |
| C(12)-C(4)-C(5) | 118.7(3) |
| C(6)-C(5)-C(4) | 121.7(3) |
| C(6)-C(5)-H(5A) | 119.2 |
| C(4)-C(5)-H(5A) | 119.2 |
| C(5)-C(6)-C(7) | 121.1(3) |
| C(5)-C(6)-H(6A) | 119.5 |
| C(7)-C(6)-H(6A) | 119.5 |
| C(8)-C(7)-C(11) | 117.7(3) |
| C(8)-C(7)-C(6) | 123.4(3) |
| C(11)-C(7)-C(6) | 118.9(3) |
| C(9)-C(8)-C(7) | 119.5(3) |
| C(9)-C(8)-H(8A) | 120.2 |
| C(7)-C(8)-H(8A) | 120.2 |
| C(8)-C(9)-C(10) | 119.5(3) |
| C(8)-C(9)-H(9A) | 120.2 |
| C(10)-C(9)-H(9A) | 120.2 |
| N(2)-C(10)-C(9) | 121.9(3) |
| N(2)-C(10)-H(10A) | 119.0 |
| C(9)-C(10)-H(10A) | 119.0 |
| N(2)-C(11)-C(7) | 121.9(3) |
| N(2)-C(11)-C(12) | 118.2(3) |
| C(7)-C(11)-C(12) | 119.8(3) |
| N(1)-C(12)-C(4) | 123.0(3) |
| N(1)-C(12)-C(11) | 117.2(3) |
| C(4)-C(12)-C(11) | 119.7(3) |
| N(3)-C(13)-C(14) | 123.3(3) |
| N(3)-C(13)-H(13A) | 118.4 |
| C(14)-C(13)-H(13A) | 118.4 |
| C(15)-C(14)-C(13) | 119.4(3) |
| C(15)-C(14)-H(14A) | 120.3 |
| C(13)-C(14)-H(14A) | 120.3 |
| C(14)-C(15)-C(16) | 119.2(3) |
| C(14)-C(15)-H(15A) | 120.4 |
| C(16)-C(15)-H(15A) | 120.4 |
| C(24)-C(16)-C(15) | 116.9(3) |
| C(24)-C(16)-C(17) | 118.9(3) |
| C(15)-C(16)-C(17) | 124.2(3) |
| C(18)-C(17)-C(16) | 121.3(3) |
| C(18)-C(17)-H(17A) | 119.3 |
| C(16)-C(17)-H(17A) | 119.3 |
| C(17)-C(18)-C(19) | 121.0(3) |
| C(17)-C(18)-H(18A) | 119.5 |
| C(19)-C(18)-H(18A) | 119.5 |
| C(23)-C(19)-C(20) | 116.8(3) |
| C(23)-C(19)-C(18) | 118.8(3) |
| C(20)-C(19)-C(18) | 124.4(3) |
| C(21)-C(20)-C(19) | 119.8(3) |
| C(21)-C(20)-H(20A) | 120.1 |
| C(19)-C(20)-H(20A) | 120.1 |
| C(20)-C(21)-C(22) | 119.7(3) |
| C(20)-C(21)-H(21A) | 120.1 |
| C(22)-C(21)-H(21A) | 120.1 |
| N(4)-C(22)-C(21) | 121.9(3) |
| N(4)-C(22)-H(22A) | 119.1 |
| C(21)-C(22)-H(22A) | 119.1 |
| N(4)-C(23)-C(19) | 123.3(3) |
| N(4)-C(23)-C(24) | 116.3(3) |
| C(19)-C(23)-C(24) | 120.4(3) |
| N(3)-C(24)-C(16) | 123.7(3) |
| N(3)-C(24)-C(23) | 116.7(3) |
| C(16)-C(24)-C(23) | 119.6(3) |
| O(4)-Cl(1)-O(5) | 110.43(17) |
| O(4)-Cl(1)-O(3) | 109.61(19) |
| O(5)-Cl(1)-O(3) | 109.10(17) |
| O(4)-Cl(1)-O(6) | 108.83(16) |
| O(5)-Cl(1)-O(6) | 109.93(19) |
| O(3)-Cl(1)-O(6) | 108.92(19) |
| H(1W1)-O(1W)-H(1W2) | 101(3) |
| H(2W1)-O(2W)-H(2W2) | 104(3) |

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Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (Å2x 103) for [Cu(phen)2(CH3COO)].2H2O(ClO4) **(1)**. The anisotropic displacement factor exponent takes the form: -2p2[ h2a\*2U11 + ... + 2 h k a\* b\* U12 ]

|  |
| --- |
| U11 U22 U33 U23 U13 U12 |
|  |
| Cu 12(1) 16(1) 13(1) 2(1) 2(1) 0(1) |
| O(1) 21(1) 15(1) 19(1) 2(1) 5(1) 0(1) |
| O(2) 20(1) 29(1) 18(1) 2(1) 5(1) 2(1) |
| N(1) 16(1) 15(1) 15(1) 2(1) 3(1) 0(1) |
| N(2) 14(1) 17(1) 12(1) 2(1) 0(1) 1(1) |
| N(3) 14(1) 13(1) 16(1) -1(1) 4(1) -1(1) |
| N(4) 14(1) 16(1) 15(1) 1(1) 5(1) 0(1) |
| C(11A) 16(1) 18(1) 14(1) 1(1) -1(1) 0(1) |
| C(12A) 40(2) 17(1) 30(2) 1(1) 11(2) 0(1) |
| C(1) 21(2) 19(1) 18(2) 5(1) 5(1) 3(1) |
| C(2) 28(2) 22(1) 22(2) 3(1) 12(1) 7(1) |
| C(3) 33(2) 19(1) 17(2) 0(1) 8(1) 5(1) |
| C(4) 27(2) 14(1) 15(1) 3(1) 3(1) 0(1) |
| C(5) 32(2) 18(1) 15(1) -1(1) -2(1) -3(1) |
| C(6) 24(2) 20(1) 17(2) 3(1) -5(1) -4(1) |
| C(7) 17(2) 19(1) 16(1) 3(1) 0(1) -4(1) |
| C(8) 13(1) 26(2) 21(2) 7(1) 0(1) -1(1) |
| C(9) 15(1) 30(2) 23(2) 6(1) 5(1) 3(1) |
| C(10) 16(1) 25(2) 19(2) 1(1) 5(1) 1(1) |
| C(11) 16(1) 14(1) 15(1) 4(1) 2(1) -2(1) |
| C(12) 17(1) 13(1) 16(1) 2(1) 2(1) -1(1) |
| C(13) 14(1) 20(1) 21(2) -1(1) 4(1) -2(1) |
| C(14) 20(2) 21(1) 23(2) -1(1) 9(1) -6(1) |
| C(15) 27(2) 17(1) 19(2) 1(1) 11(1) -4(1) |
| C(16) 21(2) 13(1) 14(1) -2(1) 4(1) 0(1) |
| C(17) 25(2) 16(1) 15(1) 2(1) 1(1) 3(1) |
| C(18) 20(2) 19(1) 16(2) 1(1) -2(1) 2(1) |
| C(19) 14(1) 17(1) 16(1) -3(1) 0(1) 1(1) |
| C(20) 13(1) 20(1) 21(2) -5(1) 1(1) 2(1) |
| C(21) 12(1) 22(2) 22(2) -4(1) 6(1) -2(1) |
| C(22) 17(2) 19(1) 20(2) 2(1) 4(1) -1(1) |
| C(23) 14(1) 13(1) 13(1) -1(1) 2(1) 0(1) |
| C(24) 17(1) 12(1) 14(1) -2(1) 3(1) -1(1) |
| Cl(1) 19(1) 24(1) 24(1) -6(1) -2(1) 2(1) |
| O(3) 37(2) 47(2) 37(2) 12(1) 4(1) -1(1) |
| O(4) 29(2) 30(1) 50(2) -16(1) -5(1) 8(1) |
| O(5) 22(1) 41(2) 44(2) -5(1) 7(1) 6(1) |
| O(6) 33(2) 41(2) 26(1) -9(1) -10(1) 3(1) |
| O(1W) 30(1) 36(1) 27(1) 2(1) 10(1) -5(1) |
| O(2W) 22(1) 50(2) 27(1) -6(1) 8(1) -8(1) |

Table S5. Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å2x 103)

for [Cu(phen)2(CH3COO)].2H2O(ClO4) **(1)**.

|  |
| --- |
| x y z U(eq) |
|  |
| H(12A) 2737 -580 6410 43 |
| H(12B) 998 -318 6165 43 |
| H(12C) 1890 16 7078 43 |
| H(1A) -14 6910 7256 23 |
| H(2A) 216 8390 8456 27 |
| H(3A) 2548 8889 9269 27 |
| H(5A) 5319 8385 9540 27 |
| H(6A) 7237 7095 9199 27 |
| H(8A) 8177 5183 8251 24 |
| H(9A) 7639 3494 7124 27 |
| H(10A) 5244 3417 6305 24 |
| H(13A) 4930 6810 5787 22 |
| H(14A) 5175 8533 4742 25 |
| H(15A) 3099 9276 3747 24 |
| H(17A) 309 8969 3182 23 |
| H(18A) -1876 7879 3303 23 |
| H(20A) -3288 6078 4110 22 |
| H(21A) -3194 4355 5201 22 |
| H(22A) -942 3834 6114 23 |
| H(1W1) 5680(50) 1460(70) 5220(40) 110(30) |
| H(1W2) 4270(50) 1700(70) 5130(40) 100(20) |
| H(2W1) 690(50) 2550(60) 7560(30) 59(17) |
| H(2W2) -330(50) 1760(40) 7830(30) 50(15) |

Table S6. Torsion angles [°] for[Cu(phen)2(CH3COO)].2H2O(ClO4) **(1)**.

|  |  |
| --- | --- |
| Cu-O(1)-C(11A)-O(2) | -1.0(4) |
| Cu-O(1)-C(11A)-C(12A) | 178.4(3) |
| C(12)-N(1)-C(1)-C(2) | 0.4(4) |
| Cu-N(1)-C(1)-C(2) | -178.8(2) |
| N(1)-C(1)-C(2)-C(3) | 1.8(5) |
| C(1)-C(2)-C(3)-C(4) | -2.2(5) |
| C(2)-C(3)-C(4)-C(12) | 0.5(4) |
| C(2)-C(3)-C(4)-C(5) | -177.0(3) |
| C(3)-C(4)-C(5)-C(6) | 175.4(3) |
| C(12)-C(4)-C(5)-C(6) | -2.1(5) |
| C(4)-C(5)-C(6)-C(7) | 0.5(5) |
| C(5)-C(6)-C(7)-C(8) | -176.5(3) |
| C(5)-C(6)-C(7)-C(11) | 1.4(4) |
| C(11)-C(7)-C(8)-C(9) | -1.2(4) |
| C(6)-C(7)-C(8)-C(9) | 176.7(3) |
| C(7)-C(8)-C(9)-C(10) | 2.5(5) |
| C(11)-N(2)-C(10)-C(9) | -1.0(5) |
| Cu-N(2)-C(10)-C(9) | 178.0(2) |
| C(8)-C(9)-C(10)-N(2) | -1.5(5) |
| C(10)-N(2)-C(11)-C(7) | 2.4(4) |
| Cu-N(2)-C(11)-C(7) | -176.6(2) |
| C(10)-N(2)-C(11)-C(12) | -175.3(3) |
| Cu-N(2)-C(11)-C(12) | 5.7(3) |
| C(8)-C(7)-C(11)-N(2) | -1.3(4) |
| C(6)-C(7)-C(11)-N(2) | -179.3(3) |
| C(8)-C(7)-C(11)-C(12) | 176.3(3) |
| C(6)-C(7)-C(11)-C(12) | -1.7(4) |
| C(1)-N(1)-C(12)-C(4) | -2.2(4) |
| Cu-N(1)-C(12)-C(4) | 177.2(2) |
| C(1)-N(1)-C(12)-C(11) | 175.6(2) |
| Cu-N(1)-C(12)-C(11) | -5.0(3) |
| C(3)-C(4)-C(12)-N(1) | 1.7(4) |
| C(5)-C(4)-C(12)-N(1) | 179.4(3) |
| C(3)-C(4)-C(12)-C(11) | -176.0(3) |
| C(5)-C(4)-C(12)-C(11) | 1.7(4) |
| N(2)-C(11)-C(12)-N(1) | 0.0(4) |
| C(7)-C(11)-C(12)-N(1) | -177.7(3) |
| N(2)-C(11)-C(12)-C(4) | 177.9(3) |
| C(7)-C(11)-C(12)-C(4) | 0.2(4) |
| C(24)-N(3)-C(13)-C(14) | 0.7(4) |
| Cu-N(3)-C(13)-C(14) | 179.7(2) |
| N(3)-C(13)-C(14)-C(15) | -0.2(5) |
| C(13)-C(14)-C(15)-C(16) | -0.4(4) |
| C(14)-C(15)-C(16)-C(24) | 0.5(4) |
| C(14)-C(15)-C(16)-C(17) | -178.4(3) |
| C(24)-C(16)-C(17)-C(18) | 0.7(4) |
| C(15)-C(16)-C(17)-C(18) | 179.5(3) |
| C(16)-C(17)-C(18)-C(19) | 0.2(5) |
| C(17)-C(18)-C(19)-C(23) | -0.9(4) |
| C(17)-C(18)-C(19)-C(20) | -179.0(3) |
| C(23)-C(19)-C(20)-C(21) | -0.5(4) |
| C(18)-C(19)-C(20)-C(21) | 177.7(3) |
| C(19)-C(20)-C(21)-C(22) | 0.1(4) |
| C(23)-N(4)-C(22)-C(21) | -1.2(5) |
| Cu-N(4)-C(22)-C(21) | 179.8(2) |
| C(20)-C(21)-C(22)-N(4) | 0.7(5) |
| C(22)-N(4)-C(23)-C(19) | 0.8(4) |
| Cu-N(4)-C(23)-C(19) | 180.0(2) |
| C(22)-N(4)-C(23)-C(24) | -178.2(3) |
| Cu-N(4)-C(23)-C(24) | 0.9(3) |
| C(20)-C(19)-C(23)-N(4) | 0.0(4) |
| C(18)-C(19)-C(23)-N(4) | -178.3(3) |
| C(20)-C(19)-C(23)-C(24) | 179.0(3) |
| C(18)-C(19)-C(23)-C(24) | 0.7(4) |
| C(13)-N(3)-C(24)-C(16) | -0.6(4) |
| Cu-N(3)-C(24)-C(16) | -179.8(2) |
| C(13)-N(3)-C(24)-C(23) | 179.1(2) |
| Cu-N(3)-C(24)-C(23) | 0.0(3) |
| C(15)-C(16)-C(24)-N(3) | 0.1(4) |
| C(17)-C(16)-C(24)-N(3) | 179.0(3) |
| C(15)-C(16)-C(24)-C(23) | -179.7(3) |
| C(17)-C(16)-C(24)-C(23) | -0.8(4) |
| N(4)-C(23)-C(24)-N(3) | -0.6(4) |
| C(19)-C(23)-C(24)-N(3) | -179.7(3) |
| N(4)-C(23)-C(24)-C(16) | 179.2(3) |
| C(19)-C(23)-C(24)-C(16) | 0.1(4) |

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Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for [Cu(phen)2(CH3COO)].2H2O(ClO4) **(1)** [Å and °].

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
| C(2)-H(2A)...O(6)#1 | 0.95 | 2.53 | 3.101(4) | 119.2 |
| C(2)-H(2A)...O(1W)#2 | 0.95 | 2.59 | 3.153(4) | 117.9 |
| C(9)-H(9A)...O(2W)#3 | 0.95 | 2.56 | 3.283(4) | 133.5 |
| C(10)-H(10A)...O(2) | 0.95 | 2.62 | 3.243(4) | 123.6 |
| C(10)-H(10A)...O(1W) | 0.95 | 2.53 | 3.474(4) | 169.7 |
| C(13)-H(13A)...N(2) | 0.95 | 2.68 | 3.177(4) | 113.5 |
| C(13)-H(13A)...O(4)#4 | 0.95 | 2.56 | 3.302(4) | 135.0 |
| C(21)-H(21A)...O(1W)#5 | 0.95 | 2.56 | 3.416(4) | 150.5 |
| C(22)-H(22A)...O(1) | 0.95 | 2.66 | 3.118(4) | 110.4 |
| O(1W)-H(1W1)...O(3) | 0.85(2) | 2.09(3) | 2.912(4) | 162(7) |
| O(1W)-H(1W2)...O(2) | 0.84(2) | 1.98(4) | 2.747(4) | 151(6) |
| O(2W)-H(2W1)...O(1) | 0.84(2) | 1.93(2) | 2.758(3) | 169(5) |
| O(2W)-H(2W2)...O(6)#5 | 0.83(2) | 2.11(3) | 2.930(4) | 170(5) |

Symmetry transformations used to generate equivalent atoms:

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

#4 x,y+1,z #5 x-1,y,z

Table S8. Crystal data and structure refinement for Cu(bipy)2(CH3COO)](ClO4)H­2O **(2)**.

|  |  |  |
| --- | --- | --- |
| Identification code | shelxl |  |
| Empirical formula | C22 H21 Cl Cu N4 O7 |  |
| Formula weight | 552.42 |  |
| Temperature | 100(2) K |  |
| Wavelength | 0.71073 Å |  |
| Crystal system | Triclinic |  |
| Space group | P-1 |  |
| Unit cell dimensions | a = 8.2822(4) Å | α= 78.729(2)°. |
|  | b = 9.4748(4) Å | β= 82.881(2)°. |
|  | c = 14.7992(6) Å | γ = 85.092(2)°. |
| Volume | 1127.90(9) Å3 |  |
| Z | 2 |  |
| Density (calculated) | 1.627 Mg/m3 |  |
| Absorption coefficient | 1.140 mm-1 |  |
| F(000) | 566 |  |
| Crystal size | 0.500 x 0.240 x 0.200 mm3 |  |
| Theta range for data collection | 2.20 to 30.58°. |  |
| Index ranges | -11<=h<=11, -13<=k<=13, -21<=l<=21 |  |
| Reflections collected | 58024 |  |
| Independent reflections | 6914 [R(int) = 0.0421] |  |
| Completeness to theta = 25.50° | 100.0 % |  |
| Absorption correction | Semi-empirical from equivalents |  |
| Max. and min. transmission | 0.7461 and 0.6323 |  |
| Refinement method | Full-matrix least-squares on F2 |  |
| Data / restraints / parameters | 6914 / 68 / 339 |  |
| Goodness-of-fit on F2 | 1.083 |  |
| Final R indices [I>2sigma(I)] | R1 = 0.0357, wR2 = 0.0776 |  |
| R indices (all data) | R1 = 0.0451, wR2 = 0.0814 |  |
| Largest diff. peak and hole | 0.563 and -0.384 e.Å-3 |  |
|  |  |  |

Table S9. Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103)

for Cu(bipy)2(CH3COO)](ClO4)H­2O **(2)**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | x | y | z | U(eq) |
| Cu | 5317(1) | 4840(1) | 7450(1) | 14(1) |
| Cl(1) | 339(1) | -375(1) | 7208(1) | 21(1) |
| O(11) | 1427(2) | -1065(2) | 6565(1) | 36(1) |
| O(12) | 1148(2) | 775(2) | 7437(1) | 42(1) |
| O(13) | -1104(2) | 209(2) | 6787(1) | 37(1) |
| O(14) | -83(3) | -1404(2) | 8035(1) | 45(1) |
| O(11A) | 1276(12) | -797(13) | 6409(5) | 36(1) |
| O(12A) | 717(15) | 1053(5) | 7273(9) | 42(1) |
| O(13A) | -1371(3) | -383(14) | 7122(9) | 37(1) |
| O(14A) | 729(17) | -1368(10) | 8029(5) | 45(1) |
| O(1) | 3129(1) | 5531(1) | 7058(1) | 17(1) |
| O(2) | 2394(2) | 4246(2) | 8442(1) | 30(1) |
| O(1W) | 2286(2) | 1305(2) | 9032(1) | 30(1) |
| N(1) | 5532(2) | 3434(1) | 6597(1) | 14(1) |
| N(2) | 6868(2) | 5964(2) | 6279(1) | 15(1) |
| N(3) | 6693(2) | 3667(2) | 8423(1) | 14(1) |
| N(4) | 5323(2) | 6280(1) | 8251(1) | 15(1) |
| C(1) | 4781(2) | 2193(2) | 6797(1) | 17(1) |
| C(2) | 4932(2) | 1227(2) | 6197(1) | 20(1) |
| C(3) | 5892(2) | 1568(2) | 5356(1) | 20(1) |
| C(4) | 6635(2) | 2865(2) | 5133(1) | 18(1) |
| C(5) | 6430(2) | 3790(2) | 5766(1) | 14(1) |
| C(6) | 7155(2) | 5214(2) | 5584(1) | 15(1) |
| C(7) | 8065(2) | 5748(2) | 4752(1) | 21(1) |
| C(8) | 8725(2) | 7078(2) | 4645(1) | 24(1) |
| C(9) | 8442(2) | 7847(2) | 5356(1) | 22(1) |
| C(10) | 7498(2) | 7254(2) | 6161(1) | 18(1) |
| C(11) | 7313(2) | 2299(2) | 8480(1) | 17(1) |
| C(12) | 8199(2) | 1609(2) | 9190(1) | 20(1) |
| C(13) | 8469(2) | 2359(2) | 9867(1) | 21(1) |
| C(14) | 7840(2) | 3776(2) | 9816(1) | 17(1) |
| C(15) | 6958(2) | 4400(2) | 9084(1) | 14(1) |
| C(16) | 6249(2) | 5903(2) | 8955(1) | 14(1) |
| C(17) | 6513(2) | 6878(2) | 9502(1) | 18(1) |
| C(18) | 5791(2) | 8266(2) | 9313(1) | 20(1) |
| C(19) | 4814(2) | 8637(2) | 8598(1) | 20(1) |
| C(20) | 4604(2) | 7613(2) | 8078(1) | 18(1) |
| C(11A) | 2049(2) | 5009(2) | 7699(1) | 18(1) |
| C(12A) | 301(2) | 5339(3) | 7513(2) | 32(1) |

Table S10. Bond lengths [Å] and angles [°] for Cu(bipy)2(CH3COO)](ClO4)H­2O **(2)**.

|  |  |
| --- | --- |
| Cu-N(4) | 1.9750(14) |
| Cu-O(1) | 1.9896(12) |
| Cu-N(1) | 1.9899(13) |
| Cu-N(3) | 2.0422(14) |
| Cu-N(2) | 2.1786(14) |
| Cl(1)-O(13) | 1.4341(11) |
| Cl(1)-O(14) | 1.4343(11) |
| Cl(1)-O(13A) | 1.4378(12) |
| Cl(1)-O(11A) | 1.4367(12) |
| Cl(1)-O(14A) | 1.4377(12) |
| Cl(1)-O(11) | 1.4404(11) |
| Cl(1)-O(12A) | 1.4382(12) |
| Cl(1)-O(12) | 1.4416(11) |
| O(1)-C(11A) | 1.275(2) |
| O(2)-C(11A) | 1.244(2) |
| O(1W)-H(1W1) | 0.88(3) |
| O(1W)-H(1W2) | 0.87(3) |
| N(1)-C(1) | 1.341(2) |
| N(1)-C(5) | 1.354(2) |
| N(2)-C(10) | 1.342(2) |
| N(2)-C(6) | 1.347(2) |
| N(3)-C(11) | 1.343(2) |
| N(3)-C(15) | 1.353(2) |
| N(4)-C(20) | 1.341(2) |
| N(4)-C(16) | 1.345(2) |
| C(1)-C(2) | 1.383(2) |
| C(1)-H(1A) | 0.9500 |
| C(2)-C(3) | 1.387(2) |
| C(2)-H(2A) | 0.9500 |
| C(3)-C(4) | 1.385(2) |
| C(3)-H(3A) | 0.9500 |
| C(4)-C(5) | 1.391(2) |
| C(4)-H(4A) | 0.9500 |
| C(5)-C(6) | 1.487(2) |
| C(6)-C(7) | 1.390(2) |
| C(7)-C(8) | 1.390(2) |
| C(7)-H(7A) | 0.9500 |
| C(8)-C(9) | 1.379(3) |
| C(8)-H(8A) | 0.9500 |
| C(9)-C(10) | 1.389(2) |
| C(9)-H(9A) | 0.9500 |
| C(10)-H(10A) | 0.9500 |
| C(11)-C(12) | 1.383(2) |
| C(11)-H(11A) | 0.9500 |
| C(12)-C(13) | 1.385(3) |
| C(12)-H(12A) | 0.9500 |
| C(13)-C(14) | 1.389(2) |
| C(13)-H(13A) | 0.9500 |
| C(14)-C(15) | 1.389(2) |
| C(14)-H(14A) | 0.9500 |
| C(15)-C(16) | 1.479(2) |
| C(16)-C(17) | 1.389(2) |
| C(17)-C(18) | 1.388(2) |
| C(17)-H(17A) | 0.9500 |
| C(18)-C(19) | 1.385(3) |
| C(18)-H(18A) | 0.9500 |
| C(19)-C(20) | 1.384(2) |
| C(19)-H(19A) | 0.9500 |
| C(20)-H(20A) | 0.9500 |
| C(11A)-C(12A) | 1.502(3) |
| C(12A)-H(12B) | 0.9800 |
| C(12A)-H(12C) | 0.9800 |
| C(12A)-H(12D) | 0.9800 |
| N(4)-Cu-O(1) | 94.13(5) |
| N(4)-Cu-N(1) | 174.48(6) |
| O(1)-Cu-N(1) | 89.80(5) |
| N(4)-Cu-N(3) | 81.11(5) |
| O(1)-Cu-N(3) | 149.08(5) |

|  |  |
| --- | --- |
| N(1)-Cu-N(3) | 97.46(5) |
| N(4)-Cu-N(2) | 96.31(5) |
| O(1)-Cu-N(2) | 100.18(5) |
| N(1)-Cu-N(2) | 79.16(5) |
| N(3)-Cu-N(2) | 110.70(5) |
| O(13)-Cl(1)-O(14) | 110.03(7) |
| O(13)-Cl(1)-O(13A) | 28.3(5) |
| O(14)-Cl(1)-O(13A) | 82.3(5) |
| O(13)-Cl(1)-O(11A) | 98.3(5) |
| O(14)-Cl(1)-O(11A) | 121.6(5) |
| O(13A)-Cl(1)-O(11A) | 109.54(9) |
| O(13)-Cl(1)-O(14A) | 137.1(5) |
| O(14)-Cl(1)-O(14A) | 27.2(5) |
| O(13A)-Cl(1)-O(14A) | 109.44(9) |
| O(11A)-Cl(1)-O(14A) | 109.55(9) |
| O(13)-Cl(1)-O(11) | 109.48(7) |
| O(14)-Cl(1)-O(11) | 109.59(7) |
| O(13A)-Cl(1)-O(11) | 115.8(5) |
| O(11A)-Cl(1)-O(11) | 13.4(5) |
| O(14A)-Cl(1)-O(11) | 96.2(5) |
| O(13)-Cl(1)-O(12A) | 90.1(5) |
| O(14)-Cl(1)-O(12A) | 119.9(5) |
| O(13A)-Cl(1)-O(12A) | 109.40(9) |
| O(11A)-Cl(1)-O(12A) | 109.49(9) |
| O(14A)-Cl(1)-O(12A) | 109.41(9) |
| O(11)-Cl(1)-O(12A) | 115.7(6) |
| O(13)-Cl(1)-O(12) | 109.43(7) |
| O(14)-Cl(1)-O(12) | 109.40(7) |
| O(13A)-Cl(1)-O(12) | 126.4(5) |
| O(11A)-Cl(1)-O(12) | 107.2(6) |
| O(14A)-Cl(1)-O(12) | 93.0(5) |
| O(11)-Cl(1)-O(12) | 108.89(7) |
| O(12A)-Cl(1)-O(12) | 19.4(5) |
| C(11A)-O(1)-Cu | 108.47(10) |
| H(1W1)-O(1W)-H(1W2) | 104(3) |
| C(1)-N(1)-C(5) | 119.38(14) |
| C(1)-N(1)-Cu | 122.99(11) |
| C(5)-N(1)-Cu | 117.58(11) |
| C(10)-N(2)-C(6) | 118.56(14) |
| C(10)-N(2)-Cu | 129.68(12) |
| C(6)-N(2)-Cu | 111.73(10) |
| C(11)-N(3)-C(15) | 118.58(14) |
| C(11)-N(3)-Cu | 128.08(11) |
| C(15)-N(3)-Cu | 113.33(10) |
| C(20)-N(4)-C(16) | 119.89(14) |
| C(20)-N(4)-Cu | 124.14(11) |
| C(16)-N(4)-Cu | 115.65(11) |
| N(1)-C(1)-C(2) | 122.50(15) |
| N(1)-C(1)-H(1A) | 118.7 |
| C(2)-C(1)-H(1A) | 118.7 |
| C(1)-C(2)-C(3) | 118.26(16) |
| C(1)-C(2)-H(2A) | 120.9 |
| C(3)-C(2)-H(2A) | 120.9 |
| C(4)-C(3)-C(2) | 119.69(16) |
| C(4)-C(3)-H(3A) | 120.2 |
| C(2)-C(3)-H(3A) | 120.2 |
| C(3)-C(4)-C(5) | 119.12(15) |
| C(3)-C(4)-H(4A) | 120.4 |
| C(5)-C(4)-H(4A) | 120.4 |
| N(1)-C(5)-C(4) | 120.99(15) |
| N(1)-C(5)-C(6) | 115.88(14) |
| C(4)-C(5)-C(6) | 123.14(14) |
| N(2)-C(6)-C(7) | 121.88(15) |
| N(2)-C(6)-C(5) | 115.60(14) |
| C(7)-C(6)-C(5) | 122.52(15) |
| C(8)-C(7)-C(6) | 118.81(16) |
| C(8)-C(7)-H(7A) | 120.6 |
| C(6)-C(7)-H(7A) | 120.6 |
| C(9)-C(8)-C(7) | 119.55(16) |
| C(9)-C(8)-H(8A) | 120.2 |
| C(7)-C(8)-H(8A) | 120.2 |
| C(8)-C(9)-C(10) | 118.28(16) |
| C(8)-C(9)-H(9A) | 120.9 |
| C(10)-C(9)-H(9A) | 120.9 |
| N(2)-C(10)-C(9) | 122.90(16) |
| N(2)-C(10)-H(10A) | 118.6 |
| C(9)-C(10)-H(10A) | 118.6 |
| N(3)-C(11)-C(12) | 122.60(16) |
| N(3)-C(11)-H(11A) | 118.7 |
| C(12)-C(11)-H(11A) | 118.7 |
| C(11)-C(12)-C(13) | 118.76(16) |
| C(11)-C(12)-H(12A) | 120.6 |
| C(13)-C(12)-H(12A) | 120.6 |
| C(12)-C(13)-C(14) | 119.31(15) |
| C(12)-C(13)-H(13A) | 120.3 |
| C(14)-C(13)-H(13A) | 120.3 |
| C(15)-C(14)-C(13) | 118.80(16) |
| C(15)-C(14)-H(14A) | 120.6 |
| C(13)-C(14)-H(14A) | 120.6 |
| N(3)-C(15)-C(14) | 121.94(15) |
| N(3)-C(15)-C(16) | 114.66(13) |
| C(14)-C(15)-C(16) | 123.40(14) |
| N(4)-C(16)-C(17) | 121.39(15) |
| N(4)-C(16)-C(15) | 114.87(14) |
| C(17)-C(16)-C(15) | 123.74(14) |
| C(18)-C(17)-C(16) | 118.68(15) |
| C(18)-C(17)-H(17A) | 120.7 |
| C(16)-C(17)-H(17A) | 120.7 |
| C(19)-C(18)-C(17) | 119.57(16) |
| C(19)-C(18)-H(18A) | 120.2 |
| C(17)-C(18)-H(18A) | 120.2 |
| C(20)-C(19)-C(18) | 118.79(16) |
| C(20)-C(19)-H(19A) | 120.6 |
| C(18)-C(19)-H(19A) | 120.6 |
| N(4)-C(20)-C(19) | 121.67(16) |
| N(4)-C(20)-H(20A) | 119.2 |
| C(19)-C(20)-H(20A) | 119.2 |
| O(2)-C(11A)-O(1) | 122.79(16) |
| O(2)-C(11A)-C(12A) | 120.44(16) |
| O(1)-C(11A)-C(12A) | 116.76(15) |
| C(11A)-C(12A)-H(12B) | 109.5 |
| C(11A)-C(12A)-H(12C) | 109.5 |
| H(12B)-C(12A)-H(12C) | 109.5 |
| C(11A)-C(12A)-H(12D) | 109.5 |
| H(12B)-C(12A)-H(12D) | 109.5 |
| H(12C)-C(12A)-H(12D) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters (Å2x 103) for Cu(bipy)2(CH3COO)](ClO4)H­2O **(2)**. The anisotropic displacement factor exponent takes the form: -2π2[ h2a\*2U11 + ... + 2 h k a\* b\* U12 ]

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | U11 | U22 | U33 | U23 | U13 | U12 |
| Cu | 15(1) | 13(1) | 14(1) | -4(1) | -3(1) | 1(1) |
| Cl(1) | 24(1) | 22(1) | 17(1) | -2(1) | -4(1) | -5(1) |
| O(11) | 36(1) | 43(1) | 29(1) | -11(1) | 1(1) | 5(1) |
| O(12) | 58(1) | 53(1) | 25(1) | -12(1) | -6(1) | -36(1) |
| O(13) | 31(1) | 34(1) | 49(1) | -14(1) | -18(1) | 9(1) |
| O(14) | 64(2) | 39(1) | 25(1) | 7(1) | 5(1) | -14(1) |
| O(11A) | 36(1) | 43(1) | 29(1) | -11(1) | 1(1) | 5(1) |
| O(12A) | 58(1) | 53(1) | 25(1) | -12(1) | -6(1) | -36(1) |
| O(13A) | 31(1) | 34(1) | 49(1) | -14(1) | -18(1) | 9(1) |
| O(14A) | 64(2) | 39(1) | 25(1) | 7(1) | 5(1) | -14(1) |
| O(1) | 15(1) | 20(1) | 14(1) | -2(1) | -1(1) | 0(1) |
| O(2) | 42(1) | 30(1) | 18(1) | 6(1) | -10(1) | -16(1) |
| O(1W) | 36(1) | 25(1) | 32(1) | -10(1) | -14(1) | 6(1) |
| N(1) | 13(1) | 14(1) | 14(1) | -3(1) | -2(1) | -2(1) |
| N(2) | 14(1) | 15(1) | 17(1) | -3(1) | -4(1) | -1(1) |
| N(3) | 14(1) | 14(1) | 15(1) | -3(1) | -1(1) | -1(1) |
| N(4) | 16(1) | 13(1) | 15(1) | -3(1) | -2(1) | 1(1) |
| C(1) | 18(1) | 17(1) | 16(1) | -2(1) | 0(1) | -4(1) |
| C(2) | 23(1) | 17(1) | 21(1) | -5(1) | -2(1) | -6(1) |
| C(3) | 25(1) | 20(1) | 18(1) | -8(1) | -3(1) | -3(1) |
| C(4) | 19(1) | 19(1) | 15(1) | -4(1) | -1(1) | -2(1) |
| C(5) | 13(1) | 15(1) | 14(1) | -3(1) | -3(1) | -1(1) |
| C(6) | 14(1) | 14(1) | 16(1) | -1(1) | -4(1) | -1(1) |
| C(7) | 26(1) | 19(1) | 17(1) | -2(1) | -1(1) | -3(1) |
| C(8) | 27(1) | 22(1) | 21(1) | 4(1) | 0(1) | -6(1) |
| C(9) | 22(1) | 17(1) | 25(1) | 2(1) | -7(1) | -5(1) |
| C(10) | 19(1) | 16(1) | 22(1) | -3(1) | -6(1) | -3(1) |
| C(11) | 17(1) | 14(1) | 20(1) | -4(1) | -1(1) | 1(1) |
| C(12) | 19(1) | 16(1) | 25(1) | -1(1) | -2(1) | 3(1) |
| C(13) | 19(1) | 22(1) | 19(1) | 2(1) | -4(1) | 2(1) |
| C(14) | 18(1) | 20(1) | 14(1) | -2(1) | -3(1) | -1(1) |
| C(15) | 12(1) | 14(1) | 14(1) | -2(1) | 1(1) | -2(1) |
| C(16) | 14(1) | 13(1) | 14(1) | -2(1) | 1(1) | -1(1) |
| C(17) | 19(1) | 19(1) | 16(1) | -5(1) | -3(1) | -2(1) |
| C(18) | 23(1) | 18(1) | 21(1) | -9(1) | 0(1) | -3(1) |
| C(19) | 24(1) | 13(1) | 22(1) | -4(1) | 1(1) | 1(1) |
| C(20) | 19(1) | 17(1) | 19(1) | -2(1) | -3(1) | 2(1) |
| C(11A) | 19(1) | 19(1) | 15(1) | -5(1) | -2(1) | -4(1) |
| C(12A) | 16(1) | 49(1) | 30(1) | -6(1) | 2(1) | -4(1) |

Table S12. Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å2x 103)

for Cu(bipy)2(CH3COO)](ClO4)H­2O **(2)**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | x | y | z | U(eq) |
| H(1W1) | 2220(40) | 2250(30) | 8850(20) | 47(8) |
| H(1W2) | 1760(40) | 990(30) | 8640(20) | 50(8) |
| H(1A) | 4121 | 1970 | 7372 | 21 |
| H(2A) | 4392 | 353 | 6356 | 24 |
| H(3A) | 6039 | 914 | 4937 | 24 |
| H(4A) | 7276 | 3119 | 4554 | 21 |
| H(7A) | 8232 | 5212 | 4265 | 25 |
| H(8A) | 9368 | 7455 | 4087 | 29 |
| H(9A) | 8880 | 8759 | 5296 | 26 |
| H(10A) | 7290 | 7785 | 6650 | 22 |
| H(11A) | 7136 | 1786 | 8014 | 20 |
| H(12A) | 8616 | 638 | 9214 | 24 |
| H(13A) | 9077 | 1909 | 10361 | 25 |
| H(14A) | 8010 | 4308 | 10273 | 21 |
| H(17A) | 7174 | 6602 | 9996 | 21 |
| H(18A) | 5966 | 8956 | 9672 | 24 |
| H(19A) | 4296 | 9577 | 8466 | 24 |
| H(20A) | 3935 | 7861 | 7587 | 22 |
| H(12B) | -304 | 5767 | 8016 | 48 |
| H(12C) | -184 | 4446 | 7477 | 48 |
| H(12D) | 250 | 6019 | 6925 | 48 |

Table S13. Torsion angles [°] for Cu(bipy)2(CH3COO)](ClO4)H­2O **(2)**.

|  |  |
| --- | --- |
| N(4)-Cu-O(1)-C(11A) | -80.21(11) |
| N(1)-Cu-O(1)-C(11A) | 103.66(11) |
| N(3)-Cu-O(1)-C(11A) | -0.64(17) |
| N(2)-Cu-O(1)-C(11A) | -177.38(11) |
| N(4)-Cu-N(1)-C(1) | 146.8(5) |
| O(1)-Cu-N(1)-C(1) | -77.67(13) |
| N(3)-Cu-N(1)-C(1) | 72.18(13) |
| N(2)-Cu-N(1)-C(1) | -178.07(14) |
| N(4)-Cu-N(1)-C(5) | -35.8(6) |
| O(1)-Cu-N(1)-C(5) | 99.69(12) |
| N(3)-Cu-N(1)-C(5) | -110.45(12) |
| N(2)-Cu-N(1)-C(5) | -0.71(11) |
| N(4)-Cu-N(2)-C(10) | -3.57(15) |
| O(1)-Cu-N(2)-C(10) | 91.79(14) |
| N(1)-Cu-N(2)-C(10) | 179.62(15) |
| N(3)-Cu-N(2)-C(10) | -86.42(15) |
| N(4)-Cu-N(2)-C(6) | 178.41(11) |
| O(1)-Cu-N(2)-C(6) | -86.23(11) |
| N(1)-Cu-N(2)-C(6) | 1.60(11) |
| N(3)-Cu-N(2)-C(6) | 95.56(11) |
| N(4)-Cu-N(3)-C(11) | 177.52(15) |
| O(1)-Cu-N(3)-C(11) | 94.37(16) |
| N(1)-Cu-N(3)-C(11) | -7.87(14) |
| N(2)-Cu-N(3)-C(11) | -89.06(14) |
| N(4)-Cu-N(3)-C(15) | -1.45(11) |
| O(1)-Cu-N(3)-C(15) | -84.60(14) |
| N(1)-Cu-N(3)-C(15) | 173.16(11) |
| N(2)-Cu-N(3)-C(15) | 91.97(11) |
| O(1)-Cu-N(4)-C(20) | -32.56(14) |
| N(1)-Cu-N(4)-C(20) | 102.8(6) |
| N(3)-Cu-N(4)-C(20) | 178.20(14) |
| N(2)-Cu-N(4)-C(20) | 68.17(14) |
| O(1)-Cu-N(4)-C(16) | 153.98(11) |
| N(1)-Cu-N(4)-C(16) | -70.7(6) |
| N(3)-Cu-N(4)-C(16) | 4.74(11) |
| N(2)-Cu-N(4)-C(16) | -105.29(12) |
| C(5)-N(1)-C(1)-C(2) | 2.3(2) |
| Cu-N(1)-C(1)-C(2) | 179.64(13) |
| N(1)-C(1)-C(2)-C(3) | -0.3(3) |
| C(1)-C(2)-C(3)-C(4) | -1.5(3) |
| C(2)-C(3)-C(4)-C(5) | 1.4(3) |
| C(1)-N(1)-C(5)-C(4) | -2.5(2) |
| Cu-N(1)-C(5)-C(4) | -179.92(12) |
| C(1)-N(1)-C(5)-C(6) | 177.23(14) |
| Cu-N(1)-C(5)-C(6) | -0.23(18) |
| C(3)-C(4)-C(5)-N(1) | 0.6(2) |
| C(3)-C(4)-C(5)-C(6) | -179.03(15) |
| C(10)-N(2)-C(6)-C(7) | -0.7(2) |
| Cu-N(2)-C(6)-C(7) | 177.53(13) |
| C(10)-N(2)-C(6)-C(5) | 179.57(14) |
| Cu-N(2)-C(6)-C(5) | -2.16(17) |
| N(1)-C(5)-C(6)-N(2) | 1.7(2) |
| C(4)-C(5)-C(6)-N(2) | -178.62(15) |
| N(1)-C(5)-C(6)-C(7) | -177.99(15) |
| C(4)-C(5)-C(6)-C(7) | 1.7(2) |
| N(2)-C(6)-C(7)-C(8) | 1.5(3) |
| C(5)-C(6)-C(7)-C(8) | -178.83(16) |
| C(6)-C(7)-C(8)-C(9) | -1.2(3) |
| C(7)-C(8)-C(9)-C(10) | 0.1(3) |
| C(6)-N(2)-C(10)-C(9) | -0.4(2) |
| Cu-N(2)-C(10)-C(9) | -178.28(12) |
| C(8)-C(9)-C(10)-N(2) | 0.7(3) |
| C(15)-N(3)-C(11)-C(12) | 0.5(2) |
| Cu-N(3)-C(11)-C(12) | -178.40(12) |
| N(3)-C(11)-C(12)-C(13) | -0.5(3) |
| C(11)-C(12)-C(13)-C(14) | 0.2(3) |
| C(12)-C(13)-C(14)-C(15) | -0.1(3) |
| C(11)-N(3)-C(15)-C(14) | -0.4(2) |
| Cu-N(3)-C(15)-C(14) | 178.70(12) |
| C(11)-N(3)-C(15)-C(16) | 179.18(14) |
| Cu-N(3)-C(15)-C(16) | -1.74(16) |
| C(13)-C(14)-C(15)-N(3) | 0.2(2) |
| C(13)-C(14)-C(15)-C(16) | -179.35(15) |
| C(20)-N(4)-C(16)-C(17) | -1.4(2) |
| Cu-N(4)-C(16)-C(17) | 172.32(12) |
| C(20)-N(4)-C(16)-C(15) | 179.25(14) |
| Cu-N(4)-C(16)-C(15) | -6.99(17) |
| N(3)-C(15)-C(16)-N(4) | 5.7(2) |
| C(14)-C(15)-C(16)-N(4) | -174.74(15) |
| N(3)-C(15)-C(16)-C(17) | -173.58(15) |
| C(14)-C(15)-C(16)-C(17) | 6.0(2) |
| N(4)-C(16)-C(17)-C(18) | 0.3(2) |
| C(15)-C(16)-C(17)-C(18) | 179.59(15) |
| C(16)-C(17)-C(18)-C(19) | 0.9(3) |
| C(17)-C(18)-C(19)-C(20) | -1.0(3) |
| C(16)-N(4)-C(20)-C(19) | 1.3(2) |
| Cu-N(4)-C(20)-C(19) | -171.91(13) |
| C(18)-C(19)-C(20)-N(4) | 0.0(3) |
| Cu-O(1)-C(11A)-O(2) | 2.4(2) |
| Cu-O(1)-C(11A)-C(12A) | -176.70(14) |

Symmetry transformations used to generate equivalent atoms:

Table S14. Hydrogen bonds for Cu(bipy)2(CH3COO)](ClO4)H­2O **(2)** [Å and °].

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
| O(1W)-H(1W1)...O(2) | 0.88(3) | 1.88(3) | 2.758(2) | 172(3) |
| O(1W)-H(1W2)...O(12) | 0.87(3) | 1.97(3) | 2.793(2) | 158(3) |
| O(1W)-H(1W2)...O(12A) | 0.87(3) | 2.29(3) | 3.107(11) | 156(3) |

Symmetry transformations used to generate equivalent atoms: