Electronic Supplementary Material (ESI) for CrystEngComm


Electronic Supporting Information

# Copper(II) complexes of 3- and 4-picolinehydroxamic acids: from mononuclear compounds to 1D- and 2D-coordination polymers

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***Supporting Information***

Table S1. Bond distances (Å) and angles (°) in **1**.

| | | | |
|---|---|---|---|
| Cu1—O1 | 1.9250 (13) | N1—C1 | 1.311 (3) |
| Cu1—O1$^{i}$ | 1.9250 (13) | N1—H1N | 0.86 (3) |
| Cu1—O2 | 1.9248 (14) | N2—C6 | 1.337 (3) |
| Cu1—O2$^{i}$ | 1.9248 (14) | N2—C5 | 1.341 (3) |
| Cu1—O3 | 2.8282 (18) | N2—H2N | 0.84 (3) |
| Cl1—O5 | 1.412 (10) | C1—C2 | 1.479 (3) |
| Cl1—O4B | 1.418 (9) | C2—C6 | 1.385 (3) |
| Cl1—O4 | 1.420 (10) | C2—C3 | 1.395 (3) |
| Cl1—O3 | 1.4356 (16) | C3—C4 | 1.391 (3) |
| Cl1—O5B | 1.449 (10) | C3—H3 | 0.9500 |
| Cl1—O6 | 1.453 (5) | C4—C5 | 1.383 (3) |
| Cl1—O6B | 1.473 (6) | C4—H4 | 0.9500 |
| O1—C1 | 1.272 (2) | C5—H5 | 0.9500 |
| O2—N1 | 1.373 (2) | C6—H6 | 0.9500 |
| O2—Cu1—O2$^{i}$ | 180.00 (5) | C1—N1—H1N | 125.5 (17) |
| O2—Cu1—O1 | 84.71 (6) | O2—N1—H1N | 115.6 (17) |
| O2$^{i}$—Cu1—O1 | 95.29 (6) | C6—N2—C5 | 122.90 (18) |
| O2—Cu1—O1$^{i}$ | 95.29 (6) | C6—N2—H2N | 118.2 (18) |
| O2$^{i}$—Cu1—O1$^{i}$ | 84.71 (6) | C5—N2—H2N | 118.6 (18) |
| O1—Cu1—O1$^{i}$ | 180.0 | O1—C1—N1 | 120.31 (17) |
| O2—Cu1—O3 | 88.05 (5) | O1—C1—C2 | 119.25 (17) |
| O2$^{i}$—Cu1—O3 | 91.95 (5) | N1—C1—C2 | 120.43 (17) |
| O1—Cu1—O3 | 92.39 (6) | C6—C2—C3 | 118.76 (18) |
| O1$^{i}$—Cu1—O3 | 87.61 (6) | C6—C2—C1 | 115.97 (17) |
| O5—Cl1—O4 | 111.2 (11) | C3—C2—C1 | 125.21 (18) |
| O5—Cl1—O3 | 113.0 (8) | C4—C3—C2 | 119.64 (19) |
| O4—Cl1—O3 | 107.1 (9) | C4—C3—H3 | 120.2 |
| O4B—Cl1—O5B | 107.8 (10) | C2—C3—H3 | 120.2 |

| | | | |
|---|---|---|---|
| O5—Cl1—O6 | 113.5 (5) | C5—C4—C3 | 119.30 (19) |
| O4—Cl1—O6 | 107.5 (5) | C5—C4—H4 | 120.3 |
| O3—Cl1—O6 | 104.0 (3) | C3—C4—H4 | 120.3 |
| O4B—Cl1—O6B | 108.6 (5) | N2—C5—C4 | 119.48 (18) |
| O5B—Cl1—O6B | 103.1 (6) | N2—C5—H5 | 120.3 |
| C1—O1—Cu1 | 109.79 (12) | C4—C5—H5 | 120.3 |
| N1—O2—Cu1 | 107.25 (10) | N2—C6—C2 | 119.91 (18) |
| Cl1—O3—Cu1 | 120.10 (10) | N2—C6—H6 | 120.0 |
| C1—N1—O2 | 117.72 (16) | C2—C6—H6 | 120.0 |
| O2—Cu1—O1—C1 | −4.25 (13) | Cu1—O1—C1—N1 | 4.3 (2) |
| $O2^{i}$—Cu1—O1—C1 | 175.75 (13) | Cu1—O1—C1—C2 | −176.03 (13) |
| O3—Cu1—O1—C1 | −92.07 (13) | O2—N1—C1—O1 | −1.5 (3) |
| O1—Cu1—O2—N1 | 3.42 (11) | O2—N1—C1—C2 | 178.89 (16) |
| $O1^{i}$—Cu1—O2—N1 | −176.58 (11) | O1—C1—C2—C6 | 14.5 (3) |
| O3—Cu1—O2—N1 | 95.99 (11) | N1—C1—C2—C6 | −165.83 (17) |
| O5—Cl1—O3—Cu1 | −165.3 (10) | O1—C1—C2—C3 | −162.50 (19) |
| O4B—Cl1—O3—Cu1 | −26.0 (9) | N1—C1—C2—C3 | 17.1 (3) |
| O4—Cl1—O3—Cu1 | −42.4 (8) | C6—C2—C3—C4 | 0.0 (3) |
| O5B—Cl1—O3—Cu1 | −147.0 (7) | C1—C2—C3—C4 | 176.98 (19) |
| O6—Cl1—O3—Cu1 | 71.2 (10) | C2—C3—C4—C5 | 0.1 (3) |
| O6B—Cl1—O3—Cu1 | 100.2 (11) | C6—N2—C5—C4 | −0.7 (3) |
| O2—Cu1—O3—Cl1 | 168.24 (12) | C3—C4—C5—N2 | 0.2 (3) |
| $O2^{i}$—Cu1—O3—Cl1 | −11.76 (12) | C5—N2—C6—C2 | 0.8 (3) |
| O1—Cu1—O3—Cl1 | −107.14 (11) | C3—C2—C6—N2 | −0.5 (3) |
| $O1^{i}$—Cu1—O3—Cl1 | 72.86 (11) | C1—C2—C6—N2 | −177.73 (17) |
| Cu1—O2—N1—C1 | −2.21 (19) | | |
| Symmetry codes: (i) $-x+1/2, -y+3/2, -z+1$. | | | |

Table S2. Bond distances (Å) and angles (°) in **4a**.

| | | | |
|---|---|---|---|
| Cu1—O2 | 1.9329 (15) | C2—C3 | 1.391 (3) |
| Cu1—O1 | 1.9469 (16) | C2—C6 | 1.394 (3) |
| Cu1—N4 | 1.9595 (18) | C3—C4 | 1.373 (3) |
| Cu1—N3 | 1.9721 (18) | C3—H3 | 0.9500 |
| Cu1—O2$^{i}$ | 2.5239 (16) | C4—H4 | 0.9500 |
| Cu1—Cu1$^{i}$ | 3.2239 (5) | C5—C6 | 1.374 (3) |
| Cl1—O4 | 1.4256 (17) | C5—H5 | 0.9500 |
| Cl1—O5 | 1.4347 (18) | C6—H6 | 0.9500 |
| Cl1—O3 | 1.4453 (17) | C11—C12 | 1.387 (3) |
| Cl1—O6 | 1.4651 (17) | C11—H11 | 0.9500 |
| Cl2—O10 | 1.4340 (18) | C12—C13 | 1.383 (3) |
| Cl2—O8 | 1.4357 (19) | C12—H12 | 0.9500 |
| Cl2—O7 | 1.4407 (18) | C13—C14 | 1.388 (3) |
| Cl2—O9 | 1.4605 (17) | C13—H13 | 0.9500 |
| O1—C1 | 1.274 (3) | C14—C15 | 1.384 (3) |
| O2—N1 | 1.366 (2) | C14—H14 | 0.9500 |
| N1—C1 | 1.314 (3) | C15—C16 | 1.482 (3) |
| N1—H1A | 0.86 (3) | C16—C17 | 1.384 (3) |
| N2—C5 | 1.339 (3) | C17—C18 | 1.391 (3) |
| N2—C4 | 1.340 (3) | C17—H17 | 0.9500 |
| N2—H2A | 0.84 (3) | C18—C19 | 1.381 (3) |
| N3—C11 | 1.343 (3) | C18—H18 | 0.9500 |
| N3—C15 | 1.353 (3) | C19—C20 | 1.385 (3) |
| N4—C20 | 1.345 (3) | C19—H19 | 0.9500 |
| N4—C16 | 1.352 (3) | C20—H20 | 0.9500 |
| C1—C2 | 1.486 (3) | | |
| O2—Cu1—O1 | 84.36 (6) | C3—C2—C1 | 122.8 (2) |
| O2—Cu1—N4 | 174.18 (7) | C6—C2—C1 | 117.7 (2) |
| O1—Cu1—N4 | 96.62 (7) | C4—C3—C2 | 119.1 (2) |

| | | | |
|---|---|---|---|
| O2—Cu1—N3 | 97.56 (7) | C4—C3—H3 | 120.4 |
| O1—Cu1—N3 | 167.82 (7) | C2—C3—H3 | 120.4 |
| N4—Cu1—N3 | 82.70 (7) | N2—C4—C3 | 119.7 (2) |
| O2—Cu1—O2$^{i}$ | 88.31 (6) | N2—C4—H4 | 120.1 |
| O1—Cu1—O2$^{i}$ | 100.66 (6) | C3—C4—H4 | 120.1 |
| N4—Cu1—O2$^{i}$ | 85.86 (6) | N2—C5—C6 | 119.6 (2) |
| N3—Cu1—O2$^{i}$ | 91.43 (6) | N2—C5—H5 | 120.2 |
| O2—Cu1—Cu1$^{i}$ | 51.49 (5) | C6—C5—H5 | 120.2 |
| O1—Cu1—Cu1$^{i}$ | 94.93 (5) | C5—C6—C2 | 119.1 (2) |
| N4—Cu1—Cu1$^{i}$ | 122.68 (5) | C5—C6—H6 | 120.4 |
| N3—Cu1—Cu1$^{i}$ | 95.64 (5) | C2—C6—H6 | 120.4 |
| O2$^{i}$—Cu1—Cu1$^{i}$ | 36.82 (3) | N3—C11—C12 | 121.9 (2) |
| O4—Cl1—O5 | 110.54 (12) | N3—C11—H11 | 119.0 |
| O4—Cl1—O3 | 110.99 (11) | C12—C11—H11 | 119.0 |
| O5—Cl1—O3 | 109.63 (11) | C13—C12—C11 | 118.4 (2) |
| O4—Cl1—O6 | 109.46 (11) | C13—C12—H12 | 120.8 |
| O5—Cl1—O6 | 108.75 (11) | C11—C12—H12 | 120.8 |
| O3—Cl1—O6 | 107.38 (10) | C12—C13—C14 | 120.0 (2) |
| O10—Cl2—O8 | 111.12 (12) | C12—C13—H13 | 120.0 |
| O10—Cl2—O7 | 109.70 (12) | C14—C13—H13 | 120.0 |
| O8—Cl2—O7 | 109.23 (11) | C15—C14—C13 | 118.8 (2) |
| O10—Cl2—O9 | 108.87 (11) | C15—C14—H14 | 120.6 |
| O8—Cl2—O9 | 109.45 (11) | C13—C14—H14 | 120.6 |
| O7—Cl2—O9 | 108.41 (11) | N3—C15—C14 | 121.2 (2) |
| C1—O1—Cu1 | 109.22 (13) | N3—C15—C16 | 114.50 (19) |
| N1—O2—Cu1 | 106.96 (12) | C14—C15—C16 | 124.2 (2) |
| C1—N1—O2 | 118.39 (18) | N4—C16—C17 | 121.6 (2) |
| C1—N1—H1A | 124 (2) | N4—C16—C15 | 114.10 (19) |
| O2—N1—H1A | 118 (2) | C17—C16—C15 | 124.3 (2) |

| | | | |
|---|---|---|---|
| C5—N2—C4 | 122.8 (2) | C16—C17—C18 | 118.5 (2) |
| C5—N2—H2A | 119.9 (18) | C16—C17—H17 | 120.7 |
| C4—N2—H2A | 117.3 (18) | C18—C17—H17 | 120.7 |
| C11—N3—C15 | 119.65 (19) | C19—C18—C17 | 119.8 (2) |
| C11—N3—Cu1 | 126.57 (15) | C19—C18—H18 | 120.1 |
| C15—N3—Cu1 | 113.70 (14) | C17—C18—H18 | 120.1 |
| C20—N4—C16 | 119.58 (19) | C18—C19—C20 | 118.8 (2) |
| C20—N4—Cu1 | 125.81 (16) | C18—C19—H19 | 120.6 |
| C16—N4—Cu1 | 114.54 (14) | C20—C19—H19 | 120.6 |
| O1—C1—N1 | 120.2 (2) | N4—C20—C19 | 121.6 (2) |
| O1—C1—C2 | 120.16 (19) | N4—C20—H20 | 119.2 |
| N1—C1—C2 | 119.7 (2) | C19—C20—H20 | 119.2 |
| C3—C2—C6 | 119.5 (2) | | |
| Symmetry codes: (i) $-x+1, -y+1, -z$. | | | |

Table S3. Hydrogen bonds parameters (Å, °) for **4a**.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1A···O9 | 0.86 (3) | 2.01 (3) | 2.869 (3) | 177 (3) |
| N2—H2A···O6$^{ii}$ | 0.84 (3) | 1.96 (3) | 2.771 (3) | 163 (3) |
| Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*−1. | | | | |

Table S4. Bond distances (Å) and angles (°) for **7**.

| | | | |
|---|---|---|---|
| Cu1—O2 | 1.908 (3) | C4—C12 | 1.402 (6) |
| Cu1—O1 | 1.969 (3) | C4—C5 | 1.442 (8) |
| Cu1—N2 | 1.997 (3) | C5—C6 | 1.338 (9) |
| Cu1—N1 | 1.999 (4) | C5—H5 | 0.9500 |
| Cu1—N3 | 2.265 (4) | C6—C7 | 1.426 (8) |
| Cl2—O5 | 1.405 (5) | C6—H6 | 0.9500 |
| Cl2—O4 | 1.414 (4) | C7—C8 | 1.408 (8) |
| Cl2—O3 | 1.423 (4) | C7—C11 | 1.415 (6) |
| Cl2—O6 | 1.425 (4) | C8—C9 | 1.364 (8) |
| O1—C15 | 1.283 (5) | C8—H8 | 0.9500 |
| O2—N4 | 1.361 (5) | C9—C10 | 1.399 (6) |
| N1—C1 | 1.329 (6) | C9—H9 | 0.9500 |
| N1—C12 | 1.365 (6) | C10—H10 | 0.9500 |
| N2—C10 | 1.328 (6) | C11—C12 | 1.424 (6) |
| N2—C11 | 1.349 (6) | C13—C18$^{i}$ | 1.389 (6) |
| N3—C14 | 1.329 (6) | C13—H13 | 0.9500 |
| N3—C13 | 1.335 (6) | C14—C16$^{i}$ | 1.390 (6) |
| N4—C15 | 1.309 (5) | C14—H14 | 0.9500 |
| N4—H4N | 0.8440 | C15—C16 | 1.484 (6) |
| C1—C2 | 1.406 (7) | C16—C17 | 1.382 (6) |
| C1—H1 | 0.9500 | C16—C14$^{ii}$ | 1.390 (6) |
| C2—C3 | 1.376 (8) | C17—C18 | 1.368 (7) |
| C2—H2 | 0.9500 | C17—H17 | 0.9500 |
| C3—C4 | 1.391 (8) | C18—C13$^{ii}$ | 1.389 (6) |
| C3—H3 | 0.9500 | C18—H18 | 0.9500 |
| O2—Cu1—O1 | 85.30 (12) | C6—C5—C4 | 122.1 (5) |
| O2—Cu1—N2 | 170.18 (13) | C6—C5—H5 | 119.0 |

| | | | |
|---|---|---|---|
| O1—Cu1—N2 | 95.18 (13) | C4—C5—H5 | 119.0 |
| O2—Cu1—N1 | 93.91 (14) | C5—C6—C7 | 121.2 (5) |
| O1—Cu1—N1 | 163.51 (13) | C5—C6—H6 | 119.4 |
| N2—Cu1—N1 | 82.84 (15) | C7—C6—H6 | 119.4 |
| O2—Cu1—N3 | 89.76 (13) | C8—C7—C11 | 116.8 (5) |
| O1—Cu1—N3 | 89.60 (13) | C8—C7—C6 | 124.9 (5) |
| N2—Cu1—N3 | 100.05 (13) | C11—C7—C6 | 118.4 (5) |
| N1—Cu1—N3 | 106.88 (14) | C9—C8—C7 | 119.5 (4) |
| O5—Cl2—O4 | 110.1 (4) | C9—C8—H8 | 120.3 |
| O5—Cl2—O3 | 108.1 (3) | C7—C8—H8 | 120.3 |
| O4—Cl2—O3 | 107.9 (3) | C8—C9—C10 | 120.2 (5) |
| O5—Cl2—O6 | 111.6 (3) | C8—C9—H9 | 119.9 |
| O4—Cl2—O6 | 107.5 (3) | C10—C9—H9 | 119.9 |
| O3—Cl2—O6 | 111.7 (3) | N2—C10—C9 | 121.7 (5) |
| C15—O1—Cu1 | 106.6 (3) | N2—C10—H10 | 119.1 |
| N4—O2—Cu1 | 105.0 (2) | C9—C10—H10 | 119.1 |
| C1—N1—C12 | 118.8 (4) | N2—C11—C7 | 122.8 (4) |
| C1—N1—Cu1 | 129.5 (3) | N2—C11—C12 | 117.1 (4) |
| C12—N1—Cu1 | 111.6 (3) | C7—C11—C12 | 120.1 (4) |
| C10—N2—C11 | 119.0 (4) | N1—C12—C4 | 123.3 (4) |
| C10—N2—Cu1 | 129.2 (3) | N1—C12—C11 | 116.3 (4) |
| C11—N2—Cu1 | 111.8 (3) | C4—C12—C11 | 120.4 (4) |
| C14—N3—C13 | 117.9 (4) | N3—C13—C18$^{i}$ | 122.3 (4) |
| C14—N3—Cu1 | 118.5 (3) | N3—C13—H13 | 118.8 |
| C13—N3—Cu1 | 120.9 (3) | C18$^{i}$—C13—H13 | 118.8 |
| C15—N4—O2 | 120.1 (3) | N3—C14—C16$^{i}$ | 123.2 (4) |
| C15—N4—H4N | 123.0 | N3—C14—H14 | 118.4 |
| O2—N4—H4N | 116.0 | C16$^{i}$—C14—H14 | 118.4 |
| N1—C1—C2 | 121.5 (5) | O1—C15—N4 | 119.5 (4) |

| | | | |
|---|---|---|---|
| N1—C1—H1 | 119.3 | O1—C15—C16 | 120.1 (4) |
| C2—C1—H1 | 119.3 | N4—C15—C16 | 120.3 (4) |
| C3—C2—C1 | 119.1 (5) | C17—C16—C14$^{ii}$ | 118.3 (4) |
| C3—C2—H2 | 120.4 | C17—C16—C15 | 119.3 (4) |
| C1—C2—H2 | 120.4 | C14$^{ii}$—C16—C15 | 122.3 (4) |
| C2—C3—C4 | 120.9 (5) | C18—C17—C16 | 118.7 (4) |
| C2—C3—H3 | 119.6 | C18—C17—H17 | 120.6 |
| C4—C3—H3 | 119.6 | C16—C17—H17 | 120.6 |
| C3—C4—C12 | 116.4 (5) | C17—C18—C13$^{ii}$ | 119.5 (4) |
| C3—C4—C5 | 125.9 (5) | C17—C18—H18 | 120.3 |
| C12—C4—C5 | 117.8 (5) | C13$^{ii}$—C18—H18 | 120.3 |
| Symmetry codes: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $x-1/2, -y+1/2, z-1/2$. | | | |

Table S5. Hydrogen bonds parameters (Å, °) for **7**.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H4N···O4$^{iii}$ | 0.84 | 2.06 | 2.907 (5) | 176 |
| Symmetry codes: (iii) *x*−1/2, −*y*+1/2, *z*+1/2. | | | | |

Table S6. Bond distances (Å) and angles (°) for **8**.

| | | | |
|---|---|---|---|
| Cu1—O1 | 1.926 (3) | C9—C10 | 1.382 (7) |
| Cu1—O2 | 1.939 (3) | C9—H9 | 0.9500 |
| Cu1—N1 | 1.998 (4) | C10—H10 | 0.9500 |
| Cu1—N2 | 2.002 (4) | C11—C12 | 1.393 (6) |
| Cu1—N3 | 2.329 (4) | C11—H11 | 0.9500 |
| Cu1B—O1B | 1.889 (3) | C12—C13 | 1.382 (7) |
| Cu1B—O2B | 1.966 (3) | C12—H12 | 0.9500 |
| Cu1B—N1B | 1.991 (4) | C13—C14 | 1.396 (7) |
| Cu1B—N2B | 2.007 (4) | C13—C16$^{i}$ | 1.486 (6) |
| Cu1B—N3B | 2.317 (4) | C14—C15 | 1.373 (6) |
| O1—N4 | 1.409 (5) | C14—H14 | 0.9500 |
| O2—C16 | 1.325 (6) | C15—H15 | 0.9500 |
| O3—H3O | 0.8650 | C16—C13$^{ii}$ | 1.486 (6) |
| O3—H3P | 0.8764 | O1B—N4B | 1.404 (5) |
| O4—H4O | 0.8596 | O2B—C16B | 1.322 (5) |
| O4—H4P | 0.8560 | N1B—C1B | 1.331 (6) |
| O5—H5O | 0.8808 | N1B—C5B | 1.354 (6) |
| O6—H6O | 0.8703 | N2B—C10B | 1.328 (6) |
| O6—H6P | 0.8591 | N2B—C6B | 1.350 (6) |
| O7—H7O | 0.8573 | N3B—C11B | 1.336 (6) |
| O8—H8O | 0.8592 | N3B—C15B | 1.348 (6) |
| O8—H8P | 0.8565 | N4B—C16B | 1.290 (6) |
| O9—H9O | 0.8587 | N4B—H4M | 0.8800 |
| O9—H9P | 0.8599 | C1B—C2B | 1.386 (6) |
| O10—H10O | 0.8576 | C1B—H1B | 0.9500 |
| O10—H10P | 0.8557 | C2B—C3B | 1.386 (7) |
| O11—H11O | 0.8787 | C2B—H2B | 0.9500 |
| O11—H11P | 0.8982 | C3B—C4B | 1.390 (7) |

| | | | |
|---|---|---|---|
| N1—C5 | 1.347 (6) | C3B—H3B | 0.9500 |
| N1—C1 | 1.353 (6) | C4B—C5B | 1.386 (7) |
| N2—C10 | 1.340 (6) | C4B—H4B | 0.9500 |
| N2—C6 | 1.353 (6) | C5B—C6B | 1.480 (7) |
| N3—C11 | 1.324 (6) | C6B—C7B | 1.392 (7) |
| N3—C15 | 1.342 (6) | C7B—C8B | 1.383 (8) |
| N4—C16 | 1.303 (6) | C7B—H7B | 0.9500 |
| N4—H4N | 0.8800 | C8B—C9B | 1.369 (8) |
| C1—C2 | 1.377 (6) | C8B—H8B | 0.9500 |
| C1—H1 | 0.9500 | C9B—C10B | 1.402 (7) |
| C2—C3 | 1.399 (7) | C9B—H9B | 0.9500 |
| C2—H2 | 0.9500 | C10B—H10B | 0.9500 |
| C3—C4 | 1.369 (6) | C11B—C12B | 1.378 (7) |
| C3—H3 | 0.9500 | C11B—H11B | 0.9500 |
| C4—C5 | 1.392 (6) | C12B—C13B | 1.393 (7) |
| C4—H4 | 0.9500 | C12B—H12B | 0.9500 |
| C5—C6 | 1.476 (6) | C13B—C14B | 1.397 (7) |
| C6—C7 | 1.395 (6) | C13B—C16B$^{iii}$ | 1.484 (6) |
| C7—C8 | 1.383 (7) | C14B—C15B | 1.383 (7) |
| C7—H7 | 0.9500 | C14B—H14B | 0.9500 |
| C8—C9 | 1.387 (7) | C15B—H15B | 0.9500 |
| C8—H8 | 0.9500 | C16B—C13B$^{iv}$ | 1.484 (6) |
| O1—Cu1—O2 | 84.18 (13) | C11—C12—H12 | 120.3 |
| O1—Cu1—N1 | 172.45 (15) | C12—C13—C14 | 117.4 (4) |
| O2—Cu1—N1 | 95.40 (14) | C12—C13—C16$^{i}$ | 120.8 (4) |
| O1—Cu1—N2 | 97.23 (14) | C14—C13—C16$^{i}$ | 121.8 (4) |
| O2—Cu1—N2 | 165.40 (14) | C15—C14—C13 | 118.9 (4) |
| N1—Cu1—N2 | 81.29 (15) | C15—C14—H14 | 120.6 |
| O1—Cu1—N3 | 92.89 (14) | C13—C14—H14 | 120.6 |

| | | | |
|---|---|---|---|
| O2—Cu1—N3 | 97.43 (13) | N3—C15—C14 | 124.3 (4) |
| N1—Cu1—N3 | 94.63 (14) | N3—C15—H15 | 117.9 |
| N2—Cu1—N3 | 97.01 (14) | C14—C15—H15 | 117.9 |
| O1B—Cu1B—O2B | 84.93 (13) | N4—C16—O2 | 124.5 (4) |
| O1B—Cu1B—N1B | 170.83 (15) | N4—C16—C13$^{ii}$ | 118.0 (4) |
| O2B—Cu1B—N1B | 96.74 (14) | O2—C16—C13$^{ii}$ | 117.5 (4) |
| O1B—Cu1B—N2B | 94.73 (15) | N4B—O1B—Cu1B | 109.9 (2) |
| O2B—Cu1B—N2B | 167.72 (15) | C16B—O2B—Cu1B | 105.1 (3) |
| N1B—Cu1B—N2B | 81.71 (16) | C1B—N1B—C5B | 119.1 (4) |
| O1B—Cu1B—N3B | 91.79 (14) | C1B—N1B—Cu1B | 126.4 (3) |
| O2B—Cu1B—N3B | 98.77 (13) | C5B—N1B—Cu1B | 114.5 (3) |
| N1B—Cu1B—N3B | 96.85 (15) | C10B—N2B—C6B | 120.2 (4) |
| N2B—Cu1B—N3B | 93.51 (15) | C10B—N2B—Cu1B | 125.8 (4) |
| N4—O1—Cu1 | 110.3 (2) | C6B—N2B—Cu1B | 114.0 (3) |
| C16—O2—Cu1 | 107.0 (3) | C11B—N3B—C15B | 116.9 (4) |
| H3O—O3—H3P | 102.6 | C11B—N3B—Cu1B | 121.6 (3) |
| H4O—O4—H4P | 102.5 | C15B—N3B—Cu1B | 120.7 (3) |
| H6O—O6—H6P | 105.1 | C16B—N4B—O1B | 113.4 (4) |
| H8O—O8—H8P | 111.0 | C16B—N4B—H4M | 123.3 |
| H9O—O9—H9P | 102.9 | O1B—N4B—H4M | 123.3 |
| H10O—O10—H10P | 106.5 | N1B—C1B—C2B | 123.1 (5) |
| H11O—O11—H11P | 107.2 | N1B—C1B—H1B | 118.5 |
| C5—N1—C1 | 118.7 (4) | C2B—C1B—H1B | 118.5 |
| C5—N1—Cu1 | 114.6 (3) | C3B—C2B—C1B | 117.9 (5) |
| C1—N1—Cu1 | 126.5 (3) | C3B—C2B—H2B | 121.0 |
| C10—N2—C6 | 118.9 (4) | C1B—C2B—H2B | 121.0 |
| C10—N2—Cu1 | 126.9 (3) | C2B—C3B—C4B | 119.5 (5) |
| C6—N2—Cu1 | 114.1 (3) | C2B—C3B—H3B | 120.2 |
| C11—N3—C15 | 116.5 (4) | C4B—C3B—H3B | 120.2 |

| | | | |
|---|---|---|---|
| C11—N3—Cu1 | 119.2 (3) | C5B—C4B—C3B | 119.0 (5) |
| C15—N3—Cu1 | 123.9 (3) | C5B—C4B—H4B | 120.5 |
| C16—N4—O1 | 112.0 (4) | C3B—C4B—H4B | 120.5 |
| C16—N4—H4N | 124.0 | N1B—C5B—C4B | 121.3 (4) |
| O1—N4—H4N | 124.0 | N1B—C5B—C6B | 114.7 (4) |
| N1—C1—C2 | 122.7 (4) | C4B—C5B—C6B | 124.0 (4) |
| N1—C1—H1 | 118.7 | N2B—C6B—C7B | 120.7 (5) |
| C2—C1—H1 | 118.7 | N2B—C6B—C5B | 114.9 (4) |
| C1—C2—C3 | 118.2 (4) | C7B—C6B—C5B | 124.4 (5) |
| C1—C2—H2 | 120.9 | C8B—C7B—C6B | 119.4 (5) |
| C3—C2—H2 | 120.9 | C8B—C7B—H7B | 120.3 |
| C4—C3—C2 | 119.4 (5) | C6B—C7B—H7B | 120.3 |
| C4—C3—H3 | 120.3 | C9B—C8B—C7B | 119.3 (5) |
| C2—C3—H3 | 120.3 | C9B—C8B—H8B | 120.4 |
| C3—C4—C5 | 119.6 (4) | C7B—C8B—H8B | 120.4 |
| C3—C4—H4 | 120.2 | C8B—C9B—C10B | 119.1 (5) |
| C5—C4—H4 | 120.2 | C8B—C9B—H9B | 120.5 |
| N1—C5—C4 | 121.4 (4) | C10B—C9B—H9B | 120.5 |
| N1—C5—C6 | 114.6 (4) | N2B—C10B—C9B | 121.4 (5) |
| C4—C5—C6 | 124.0 (4) | N2B—C10B—H10B | 119.3 |
| N2—C6—C7 | 121.5 (4) | C9B—C10B—H10B | 119.3 |
| N2—C6—C5 | 114.9 (4) | N3B—C11B—C12B | 123.8 (4) |
| C7—C6—C5 | 123.6 (4) | N3B—C11B—H11B | 118.1 |
| C8—C7—C6 | 118.5 (4) | C12B—C11B—H11B | 118.1 |
| C8—C7—H7 | 120.8 | C11B—C12B—C13B | 119.5 (4) |
| C6—C7—H7 | 120.8 | C11B—C12B—H12B | 120.2 |
| C7—C8—C9 | 120.2 (4) | C13B—C12B—H12B | 120.2 |
| C7—C8—H8 | 119.9 | C12B—C13B—C14B | 116.9 (4) |
| C9—C8—H8 | 119.9 | C12B—C13B—C16B$^{iii}$ | 122.4 (4) |

| | | | |
|---|---|---|---|
| C10—C9—C8 | 117.9 (4) | C14B—C13B—C16B$^{iii}$ | 120.7 (4) |
| C10—C9—H9 | 121.0 | C15B—C14B—C13B | 119.7 (5) |
| C8—C9—H9 | 121.0 | C15B—C14B—H14B | 120.1 |
| N2—C10—C9 | 123.0 (4) | C13B—C14B—H14B | 120.1 |
| N2—C10—H10 | 118.5 | N3B—C15B—C14B | 122.9 (5) |
| C9—C10—H10 | 118.5 | N3B—C15B—H15B | 118.5 |
| N3—C11—C12 | 123.6 (4) | C14B—C15B—H15B | 118.5 |
| N3—C11—H11 | 118.2 | N4B—C16B—O2B | 124.5 (4) |
| C12—C11—H11 | 118.2 | N4B—C16B—C13B$^{iv}$ | 115.6 (4) |
| C13—C12—C11 | 119.3 (4) | O2B—C16B—C13B$^{iv}$ | 119.9 (4) |
| C13—C12—H12 | 120.3 | | |

Symmetry codes: (i) −*x*, *y*+1/2, −*z*+1/2; (ii) −*x*, *y*−1/2, −*z*+1/2; (iii) −*x*+1, *y*+1/2, −*z*+1/2; (iv) −*x*+1, *y*−1/2, −*z*+1/2.

Table S7. Hydrogen bonds parameters (Å, °) for **8**.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3O···O1B$^{v}$ | 0.87 | 1.81 | 2.671 (5) | 175 |
| O3—H3O···N4B$^{v}$ | 0.87 | 2.56 | 3.312 (5) | 147 |
| O3—H3P···O3$^{v}$ | 0.88 | 1.84 | 2.721 (10) | 179 |
| O4—H4O···O3 | 0.86 | 1.89 | 2.750 (6) | 179 |
| O4—H4P···O2B | 0.86 | 2.01 | 2.868 (5) | 175 |
| O5—H5O···O2 | 0.88 | 1.99 | 2.863 (5) | 169 |
| O6—H6O···O5 | 0.87 | 1.95 | 2.758 (5) | 154 |
| O6—H6P···O1$^{vi}$ | 0.86 | 2.08 | 2.809 (5) | 142 |
| O7—H7O···O10$^{vii}$ | 0.86 | 2.12 | 2.974 (5) | 176 |
| O8—H8O···O5 | 0.86 | 1.90 | 2.758 (5) | 179 |
| O8—H8P···O7 | 0.86 | 1.95 | 2.789 (5) | 165 |
| O9—H9O···O8 | 0.86 | 1.92 | 2.783 (6) | 178 |
| O9—H9P···O4 | 0.86 | 1.93 | 2.763 (6) | 164 |
| O10—H10O···O3 | 0.86 | 2.58 | 3.092 (6) | 119 |
| O10—H10P···O7$^{viii}$ | 0.86 | 2.43 | 2.974 (5) | 122 |
| O11—H11O···O10$^{iii}$ | 0.88 | 2.30 | 2.97 (2) | 133 |
| O11—H11P···O9$^{iii}$ | 0.90 | 1.49 | 2.386 (18) | 176 |
| N4—H4N···O11$^{ix}$ | 0.88 | 1.79 | 2.558 (15) | 145 |
| N4—H4N···O9$^{i}$ | 0.88 | 2.47 | 3.098 (7) | 129 |
| N4B—H4M···O7$^{iii}$ | 0.88 | 2.07 | 2.766 (5) | 136 |

Symmetry codes: (v) $-x+1, -y+1, -z+1$; (vi) $-x, -y+1, -z$; (vii) $x, -y+1/2, z-1/2$; (viii) $x, -y+1/2, z+1/2$; (iii) $-x+1, y+1/2, -z+1/2$; (ix) $x-1, y, z$; (i) $-x, y+1/2, -z+1/2$.

Table S8. Bond distances (Å) and angles (°) in **9**.

| | | | |
|---|---|---|---|
| Cu1—O2 | 1.9238 (17) | C2—C6 | 1.385 (4) |
| Cu1—O1 | 1.9511 (18) | C2—C3 | 1.392 (4) |
| Cu1—N1 | 1.984 (2) | C3—C4$^{i}$ | 1.378 (3) |
| Cu1—O3 | 1.9938 (18) | C3—H3 | 0.9500 |
| Cu1—O4 | 2.3736 (19) | C4—C3$^{ii}$ | 1.378 (3) |
| Cl1—O6 | 1.409 (2) | C4—H4 | 0.9500 |
| Cl1—O5 | 1.418 (2) | C5—C6$^{ii}$ | 1.393 (3) |
| Cl1—O7 | 1.453 (2) | C5—H5 | 0.9500 |
| Cl1—O8 | 1.454 (2) | C6—C5$^{i}$ | 1.393 (3) |
| S1—O3 | 1.5362 (18) | C6—H6 | 0.9500 |
| S1—C9 | 1.781 (3) | C7—H7A | 0.9800 |
| S1—C10 | 1.781 (3) | C7—H7B | 0.9800 |
| S2—O4 | 1.508 (2) | C7—H7C | 0.9800 |
| S2—C8 | 1.779 (3) | C8—H8A | 0.9800 |
| S2—C7 | 1.780 (3) | C8—H8B | 0.9800 |
| O1—N2 | 1.377 (3) | C8—H8C | 0.9800 |
| O2—C1 | 1.275 (3) | C9—H9A | 0.9800 |
| N1—C5 | 1.343 (3) | C9—H9B | 0.9800 |
| N1—C4 | 1.344 (3) | C9—H9C | 0.9800 |
| N2—C1 | 1.307 (3) | C10—H10A | 0.9800 |
| N2—H2N | 0.86 (3) | C10—H10B | 0.9800 |
| C1—C2 | 1.488 (3) | C10—H10C | 0.9800 |
| O2—Cu1—O1 | 84.37 (7) | C3—C2—C1 | 115.1 (2) |
| O2—Cu1—N1 | 169.47 (8) | C4$^{i}$—C3—C2 | 119.1 (2) |
| O1—Cu1—N1 | 94.61 (8) | C4$^{i}$—C3—H3 | 120.4 |
| O2—Cu1—O3 | 89.26 (7) | C2—C3—H3 | 120.4 |
| O1—Cu1—O3 | 173.60 (7) | N1—C4—C3$^{ii}$ | 122.3 (2) |
| N1—Cu1—O3 | 91.55 (8) | N1—C4—H4 | 118.9 |

| | | | |
|---|---|---|---|
| O2—Cu1—O4 | 98.91 (8) | C3$^{ii}$—C4—H4 | 118.9 |
| O1—Cu1—O4 | 96.45 (7) | N1—C5—C6$^{ii}$ | 122.5 (2) |
| N1—Cu1—O4 | 91.62 (8) | N1—C5—H5 | 118.8 |
| O3—Cu1—O4 | 85.09 (7) | C6$^{ii}$—C5—H5 | 118.8 |
| O6—Cl1—O5 | 111.86 (18) | C2—C6—C5$^{i}$ | 118.4 (2) |
| O6—Cl1—O7 | 110.69 (14) | C2—C6—H6 | 120.8 |
| O5—Cl1—O7 | 110.28 (13) | C5$^{i}$—C6—H6 | 120.8 |
| O6—Cl1—O8 | 108.24 (17) | S2—C7—H7A | 109.5 |
| O5—Cl1—O8 | 107.77 (17) | S2—C7—H7B | 109.5 |
| O7—Cl1—O8 | 107.84 (14) | H7A—C7—H7B | 109.5 |
| O3—S1—C9 | 103.46 (12) | S2—C7—H7C | 109.5 |
| O3—S1—C10 | 105.18 (13) | H7A—C7—H7C | 109.5 |
| C9—S1—C10 | 98.15 (14) | H7B—C7—H7C | 109.5 |
| O4—S2—C8 | 107.43 (14) | S2—C8—H8A | 109.5 |
| O4—S2—C7 | 106.39 (15) | S2—C8—H8B | 109.5 |
| C8—S2—C7 | 97.71 (17) | H8A—C8—H8B | 109.5 |
| N2—O1—Cu1 | 106.32 (14) | S2—C8—H8C | 109.5 |
| C1—O2—Cu1 | 110.28 (15) | H8A—C8—H8C | 109.5 |
| S1—O3—Cu1 | 119.96 (10) | H8B—C8—H8C | 109.5 |
| S2—O4—Cu1 | 134.33 (11) | S1—C9—H9A | 109.5 |
| C5—N1—C4 | 118.7 (2) | S1—C9—H9B | 109.5 |
| C5—N1—Cu1 | 123.69 (17) | H9A—C9—H9B | 109.5 |
| C4—N1—Cu1 | 117.64 (17) | S1—C9—H9C | 109.5 |
| C1—N2—O1 | 118.3 (2) | H9A—C9—H9C | 109.5 |
| C1—N2—H2N | 127 (2) | H9B—C9—H9C | 109.5 |
| O1—N2—H2N | 115 (2) | S1—C10—H10A | 109.5 |
| O2—C1—N2 | 120.1 (2) | S1—C10—H10B | 109.5 |
| O2—C1—C2 | 118.3 (2) | H10A—C10—H10B | 109.5 |
| N2—C1—C2 | 121.6 (2) | S1—C10—H10C | 109.5 |

| | | | |
|---|---|---|---|
| C6—C2—C3 | 119.1 (2) | H10A—C10—H10C | 109.5 |
| C6—C2—C1 | 125.8 (2) | H10B—C10—H10C | 109.5 |

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*−1, *y*, *z*.

Table S9. Hydrogen bonds parameters (Å, °) for **9**.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2N···O7$^{iii}$ | 0.86 (3) | 2.03 (3) | 2.890 (3) | 177 (3) |
| Symmetry codes: (iii) *x*, *y*+1, *z*. | | | | |

Table S10. Bond distances (Å) and angles (°) in **10**.

| | | | |
|---|---|---|---|
| Cu1—O2 | 1.9293 (15) | N2—C4 | 1.349 (3) |
| Cu1—O3 | 1.9602 (16) | N2—Cu1$^{iii}$ | 1.9888 (18) |
| Cu1—O1 | 1.9664 (15) | C1—C2 | 1.479 (3) |
| Cu1—N2$^{i}$ | 1.9888 (18) | C2—C6 | 1.390 (3) |
| Cu1—O2$^{ii}$ | 2.4340 (16) | C2—C3 | 1.392 (3) |
| Cu1—O5 | 2.6693 (19) | C3—H3 | 0.9500 |
| Cu1—Cu1$^{ii}$ | 3.1435 (5) | C4—C5 | 1.379 (3) |
| Cl1—O8 | 1.427 (2) | C4—H4 | 0.9500 |
| Cl1—O6 | 1.432 (2) | C5—C6 | 1.384 (3) |
| Cl1—O5 | 1.4402 (19) | C5—H5 | 0.9500 |
| Cl1—O7 | 1.443 (2) | C6—H6 | 0.9500 |
| S1—O3 | 1.5358 (16) | C7—H7A | 0.9800 |
| S1—C7 | 1.778 (2) | C7—H7B | 0.9800 |
| S1—C8 | 1.782 (2) | C7—H7C | 0.9800 |
| S2—O4 | 1.5178 (18) | C8—H8A | 0.9800 |
| S2—C10 | 1.779 (3) | C8—H8B | 0.9800 |
| S2—C9 | 1.791 (3) | C8—H8C | 0.9800 |
| O1—C1 | 1.281 (3) | C9—H9A | 0.9800 |
| O2—N1 | 1.378 (2) | C9—H9B | 0.9800 |
| O2—Cu1$^{ii}$ | 2.4340 (16) | C9—H9C | 0.9800 |
| N1—C1 | 1.305 (3) | C10—H10A | 0.9800 |
| N1—H2N | 0.85 (3) | C10—H10B | 0.9800 |
| N2—C3 | 1.343 (3) | C10—H10C | 0.9800 |
| O2—Cu1—O3 | 89.34 (6) | C1—N1—H2N | 125.9 (18) |
| O2—Cu1—O1 | 83.52 (6) | O2—N1—H2N | 115.4 (18) |
| O3—Cu1—O1 | 169.87 (6) | C3—N2—C4 | 118.44 (19) |
| O2—Cu1—N2$^{i}$ | 179.30 (7) | C3—N2—Cu1$^{iii}$ | 121.97 (15) |
| O3—Cu1—N2$^{i}$ | 91.36 (7) | C4—N2—Cu1$^{iii}$ | 119.53 (15) |

| | | | |
|---|---|---|---|
| O1—Cu1—N2$^{i}$ | 95.79 (7) | O1—C1—N1 | 120.1 (2) |
| O2—Cu1—O2$^{ii}$ | 88.56 (6) | O1—C1—C2 | 119.79 (19) |
| O3—Cu1—O2$^{ii}$ | 92.66 (6) | N1—C1—C2 | 120.08 (19) |
| O1—Cu1—O2$^{ii}$ | 94.33 (6) | C6—C2—C3 | 118.6 (2) |
| N2$^{i}$—Cu1—O2$^{ii}$ | 91.43 (6) | C6—C2—C1 | 118.4 (2) |
| O2—Cu1—O5 | 86.15 (6) | C3—C2—C1 | 123.0 (2) |
| O3—Cu1—O5 | 87.24 (7) | N2—C3—C2 | 122.3 (2) |
| O1—Cu1—O5 | 85.12 (6) | N2—C3—H3 | 118.8 |
| N2$^{i}$—Cu1—O5 | 93.86 (7) | C2—C3—H3 | 118.8 |
| O2$^{ii}$—Cu1—O5 | 174.71 (6) | N2—C4—C5 | 122.4 (2) |
| O2—Cu1—Cu1$^{ii}$ | 50.72 (5) | N2—C4—H4 | 118.8 |
| O3—Cu1—Cu1$^{ii}$ | 91.65 (5) | C5—C4—H4 | 118.8 |
| O1—Cu1—Cu1$^{ii}$ | 89.38 (5) | C4—C5—C6 | 119.1 (2) |
| N2$^{i}$—Cu1—Cu1$^{ii}$ | 129.27 (5) | C4—C5—H5 | 120.4 |
| O2$^{ii}$—Cu1—Cu1$^{ii}$ | 37.85 (4) | C6—C5—H5 | 120.4 |
| O5—Cu1—Cu1$^{ii}$ | 136.86 (5) | C5—C6—C2 | 119.1 (2) |
| O2—Cu1—Cu1$^{i}$ | 148.50 (5) | C5—C6—H6 | 120.5 |
| O3—Cu1—Cu1$^{i}$ | 120.97 (5) | C2—C6—H6 | 120.5 |
| O1—Cu1—Cu1$^{i}$ | 65.28 (4) | S1—C7—H7A | 109.5 |
| N2$^{i}$—Cu1—Cu1$^{i}$ | 30.82 (5) | S1—C7—H7B | 109.5 |
| O2$^{ii}$—Cu1—Cu1$^{i}$ | 97.60 (4) | H7A—C7—H7B | 109.5 |
| O5—Cu1—Cu1$^{i}$ | 86.96 (4) | S1—C7—H7C | 109.5 |
| Cu1$^{ii}$—Cu1—Cu1$^{i}$ | 128.737 (13) | H7A—C7—H7C | 109.5 |
| O8—Cl1—O6 | 110.38 (13) | H7B—C7—H7C | 109.5 |
| O8—Cl1—O5 | 109.66 (12) | S1—C8—H8A | 109.5 |
| O6—Cl1—O5 | 109.50 (14) | S1—C8—H8B | 109.5 |
| O8—Cl1—O7 | 110.12 (14) | H8A—C8—H8B | 109.5 |
| O6—Cl1—O7 | 108.84 (13) | S1—C8—H8C | 109.5 |
| O5—Cl1—O7 | 108.31 (12) | H8A—C8—H8C | 109.5 |

| | | | |
|---|---|---|---|
| O3—S1—C7 | 102.49 (11) | H8B—C8—H8C | 109.5 |
| O3—S1—C8 | 103.84 (11) | S2—C9—H9A | 109.5 |
| C7—S1—C8 | 98.83 (12) | S2—C9—H9B | 109.5 |
| O4—S2—C10 | 106.35 (12) | H9A—C9—H9B | 109.5 |
| O4—S2—C9 | 105.67 (12) | S2—C9—H9C | 109.5 |
| C10—S2—C9 | 97.66 (13) | H9A—C9—H9C | 109.5 |
| C1—O1—Cu1 | 108.64 (14) | H9B—C9—H9C | 109.5 |
| N1—O2—Cu1 | 107.02 (12) | S2—C10—H10A | 109.5 |
| N1—O2—Cu1$^{ii}$ | 107.59 (12) | S2—C10—H10B | 109.5 |
| Cu1—O2—Cu1$^{ii}$ | 91.44 (6) | H10A—C10—H10B | 109.5 |
| S1—O3—Cu1 | 122.45 (10) | S2—C10—H10C | 109.5 |
| Cl1—O5—Cu1 | 131.81 (11) | H10A—C10—H10C | 109.5 |
| C1—N1—O2 | 117.88 (18) | H10B—C10—H10C | 109.5 |
| Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+1, *y*−1/2, −*z*+1/2. | | | |

Table S11. Hydrogen bonds parameters (Å, °) for **10**.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H2N···O4 | 0.85 (3) | 1.98 (3) | 2.752 (3) | 152 (3) |

Table S12. Bond distances (Å) and angles (°) in **11**.

| | | | |
|---|---|---|---|
| Cu1—O1 | 1.930 (2) | C3—H3 | 0.9500 |
| Cu1—O2 | 1.961 (2) | C4—C12 | 1.411 (5) |
| Cu1—N2 | 1.987 (3) | C4—C5 | 1.437 (5) |
| Cu1—N1 | 2.002 (3) | C5—C6 | 1.355 (6) |
| Cu1—N4$^{i}$ | 2.425 (3) | C5—H5 | 0.9500 |
| Cl1—O4 | 1.399 (3) | C6—C7 | 1.437 (5) |
| Cl1—O3 | 1.410 (3) | C6—H6 | 0.9500 |
| Cl1—O5 | 1.414 (4) | C7—C8 | 1.400 (6) |
| Cl1—O6 | 1.507 (4) | C7—C11 | 1.409 (5) |
| O1—N3 | 1.365 (4) | C8—C9 | 1.378 (6) |
| O2—C13 | 1.274 (4) | C8—H8 | 0.9500 |
| N1—C1 | 1.327 (5) | C9—C10 | 1.394 (5) |
| N1—C12 | 1.370 (4) | C9—H9 | 0.9500 |
| N2—C10 | 1.325 (5) | C10—H10 | 0.9500 |
| N2—C11 | 1.358 (5) | C11—C12 | 1.430 (5) |
| N3—C13 | 1.315 (4) | C13—C14 | 1.486 (5) |
| N3—H3A | 0.79 (4) | C14—C18 | 1.388 (5) |
| N4—C17 | 1.340 (4) | C14—C15 | 1.389 (5) |
| N4—C16 | 1.342 (5) | C15—C16 | 1.382 (5) |
| N4—Cu1$^{ii}$ | 2.425 (3) | C15—H15 | 0.9500 |
| C1—C2 | 1.408 (5) | C16—H16 | 0.9500 |
| C1—H1 | 0.9500 | C17—C18 | 1.383 (5) |
| C2—C3 | 1.373 (5) | C17—H17 | 0.9500 |
| C2—H2 | 0.9500 | C18—H18 | 0.9500 |
| C3—C4 | 1.399 (6) | | |
| O1—Cu1—O2 | 84.23 (10) | C6—C5—C4 | 121.6 (4) |
| O1—Cu1—N2 | 94.75 (11) | C6—C5—H5 | 119.2 |
| O2—Cu1—N2 | 170.88 (10) | C4—C5—H5 | 119.2 |

| | | | |
|---|---|---|---|
| O1—Cu1—N1 | 176.76 (11) | C5—C6—C7 | 121.6 (3) |
| O2—Cu1—N1 | 98.15 (10) | C5—C6—H6 | 119.2 |
| N2—Cu1—N1 | 83.25 (12) | C7—C6—H6 | 119.2 |
| O1—Cu1—N4$^{i}$ | 88.68 (10) | C8—C7—C11 | 116.9 (3) |
| O2—Cu1—N4$^{i}$ | 90.56 (10) | C8—C7—C6 | 125.3 (3) |
| N2—Cu1—N4$^{i}$ | 98.49 (10) | C11—C7—C6 | 117.8 (3) |
| N1—Cu1—N4$^{i}$ | 89.10 (10) | C9—C8—C7 | 120.0 (3) |
| O4—Cl1—O3 | 114.7 (2) | C9—C8—H8 | 120.0 |
| O4—Cl1—O5 | 113.6 (2) | C7—C8—H8 | 120.0 |
| O3—Cl1—O5 | 115.0 (2) | C8—C9—C10 | 119.2 (4) |
| O4—Cl1—O6 | 102.6 (3) | C8—C9—H9 | 120.4 |
| O3—Cl1—O6 | 106.2 (2) | C10—C9—H9 | 120.4 |
| O5—Cl1—O6 | 102.9 (3) | N2—C10—C9 | 122.5 (4) |
| N3—O1—Cu1 | 105.08 (19) | N2—C10—H10 | 118.8 |
| C13—O2—Cu1 | 107.4 (2) | C9—C10—H10 | 118.8 |
| C1—N1—C12 | 118.3 (3) | N2—C11—C7 | 122.8 (3) |
| C1—N1—Cu1 | 130.5 (2) | N2—C11—C12 | 116.6 (3) |
| C12—N1—Cu1 | 111.1 (2) | C7—C11—C12 | 120.6 (3) |
| C10—N2—C11 | 118.7 (3) | N1—C12—C4 | 123.1 (3) |
| C10—N2—Cu1 | 129.2 (3) | N1—C12—C11 | 116.5 (3) |
| C11—N2—Cu1 | 112.0 (2) | C4—C12—C11 | 120.4 (3) |
| C13—N3—O1 | 119.2 (3) | O2—C13—N3 | 119.5 (3) |
| C13—N3—H3A | 129 (3) | O2—C13—C14 | 120.4 (3) |
| O1—N3—H3A | 111 (3) | N3—C13—C14 | 120.2 (3) |
| C17—N4—C16 | 117.2 (3) | C18—C14—C15 | 118.2 (3) |
| C17—N4—Cu1$^{ii}$ | 121.9 (2) | C18—C14—C13 | 116.9 (3) |
| C16—N4—Cu1$^{ii}$ | 119.7 (2) | C15—C14—C13 | 125.0 (3) |
| N1—C1—C2 | 122.1 (3) | C16—C15—C14 | 118.8 (3) |
| N1—C1—H1 | 118.9 | C16—C15—H15 | 120.6 |

| | | | |
|---|---|---|---|
| C2—C1—H1 | 118.9 | C14—C15—H15 | 120.6 |
| C3—C2—C1 | 119.6 (4) | N4—C16—C15 | 123.5 (3) |
| C3—C2—H2 | 120.2 | N4—C16—H16 | 118.3 |
| C1—C2—H2 | 120.2 | C15—C16—H16 | 118.3 |
| C2—C3—C4 | 120.0 (3) | N4—C17—C18 | 123.2 (3) |
| C2—C3—H3 | 120.0 | N4—C17—H17 | 118.4 |
| C4—C3—H3 | 120.0 | C18—C17—H17 | 118.4 |
| C3—C4—C12 | 116.8 (3) | C17—C18—C14 | 119.1 (3) |
| C3—C4—C5 | 125.2 (4) | C17—C18—H18 | 120.4 |
| C12—C4—C5 | 117.9 (4) | C14—C18—H18 | 120.4 |
| Symmetry codes: (i) −*x*+1/2, *y*+1/2, *z*; (ii) −*x*+1/2, *y*−1/2, *z*. | | | |

Table S13. Hydrogen bonds parameters (Å, °) for **11**.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3A···O5$^{iii}$ | 0.79 (4) | 2.11 (4) | 2.844 (5) | 155 (4) |
| Symmetry codes: (iii) *x*−1/2, −*y*+1/2, −*z*+1. | | | | |

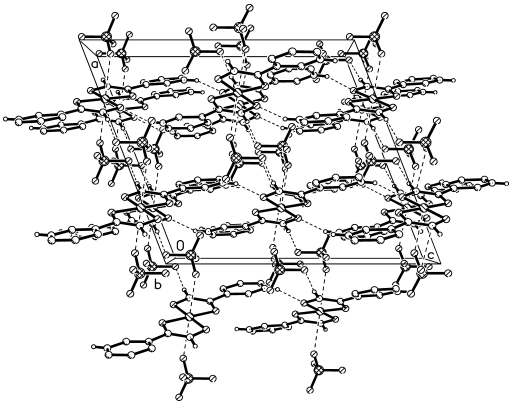

**Figure S1**. Unit cell in [Cu(**3-HPicHA**)$_2$($ClO_4$)$_2$] (**1**).

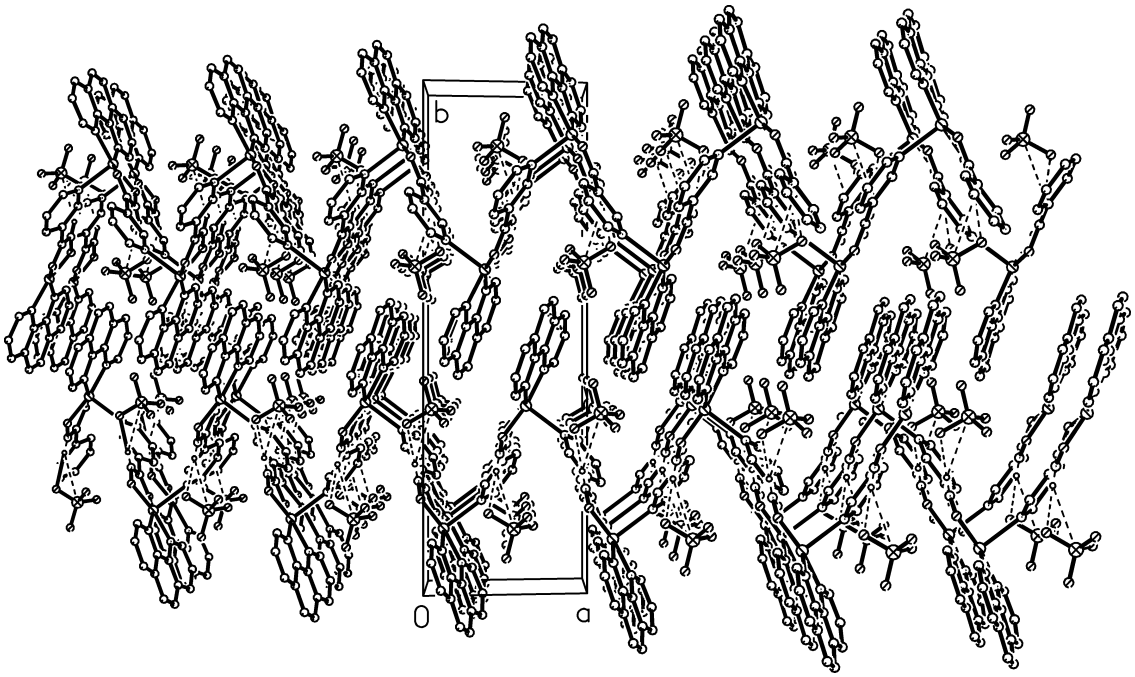


**Figure S2**. Packing diagram for *catena*-[Cu(**3-PicHA**)(**phen**)]$_n$($ClO_4$)$_n$ (**7**)

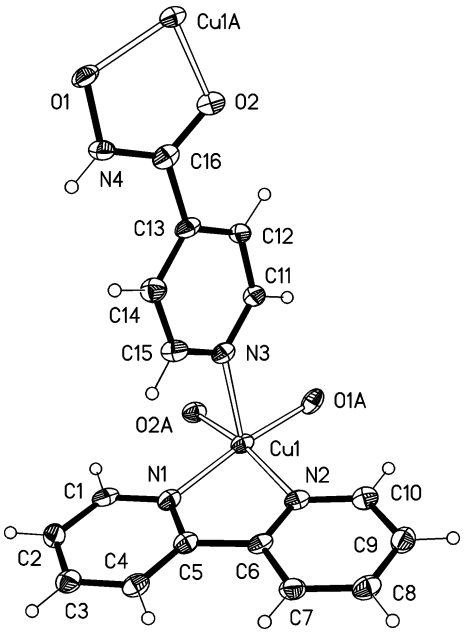


**Figure S3**. Structure of monomeric fragment of the coordination polymer *catena*-[Cu(**4-PicHA**)(**bpy**)]$_n$(OH)$_n$·3.25n$H_2O$ (**8**).

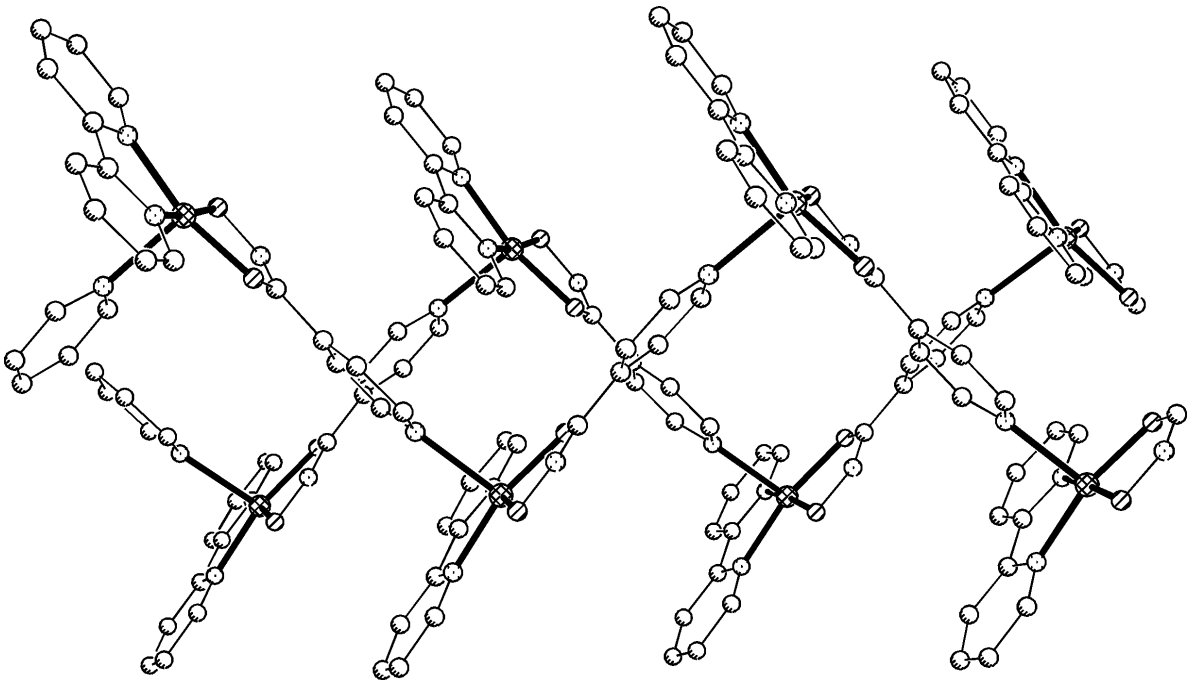

**Figure S4**. Mutual disposition of the polymeric chains conoformers in *catena*-[Cu(**4-PicHA**)(**bpy**)]$_n$(OH)$_n$·3.25n$H_2O$ (**8**).

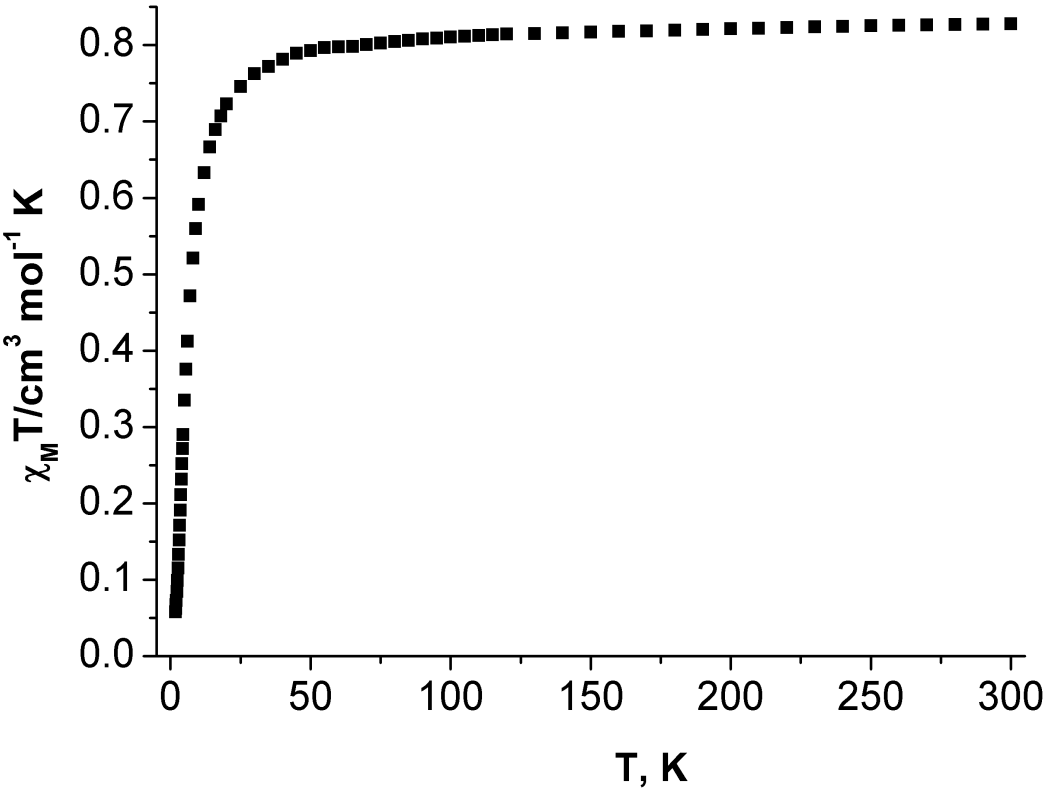


**Figure S5**. Temperature dependence of $\chi_M$T product for {Cu(**4-HPicHA**)(**bpy**)($ClO_4$)}$_2$]($ClO_4$)$_2$ (**4a**).

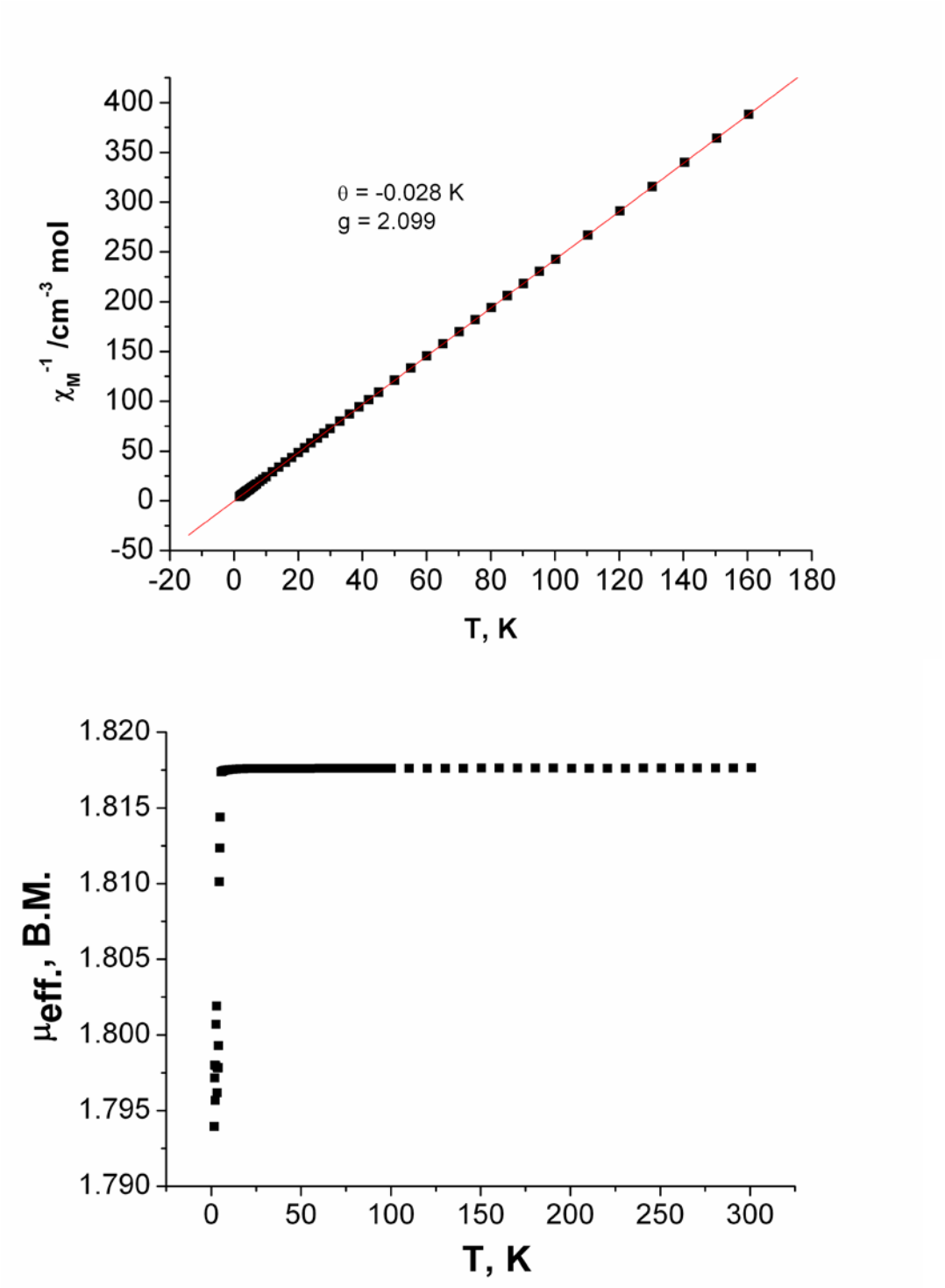


**Figure S6**. Temperature dependences of $\chi_M^{-1}$ (top) and effective magnetic moment per one copper(II) ion (bottom) for *catena*-[Cu(**3-PicHA**)(**phen**)]$_n$(ClO$_4$)$_n$ (**7**).

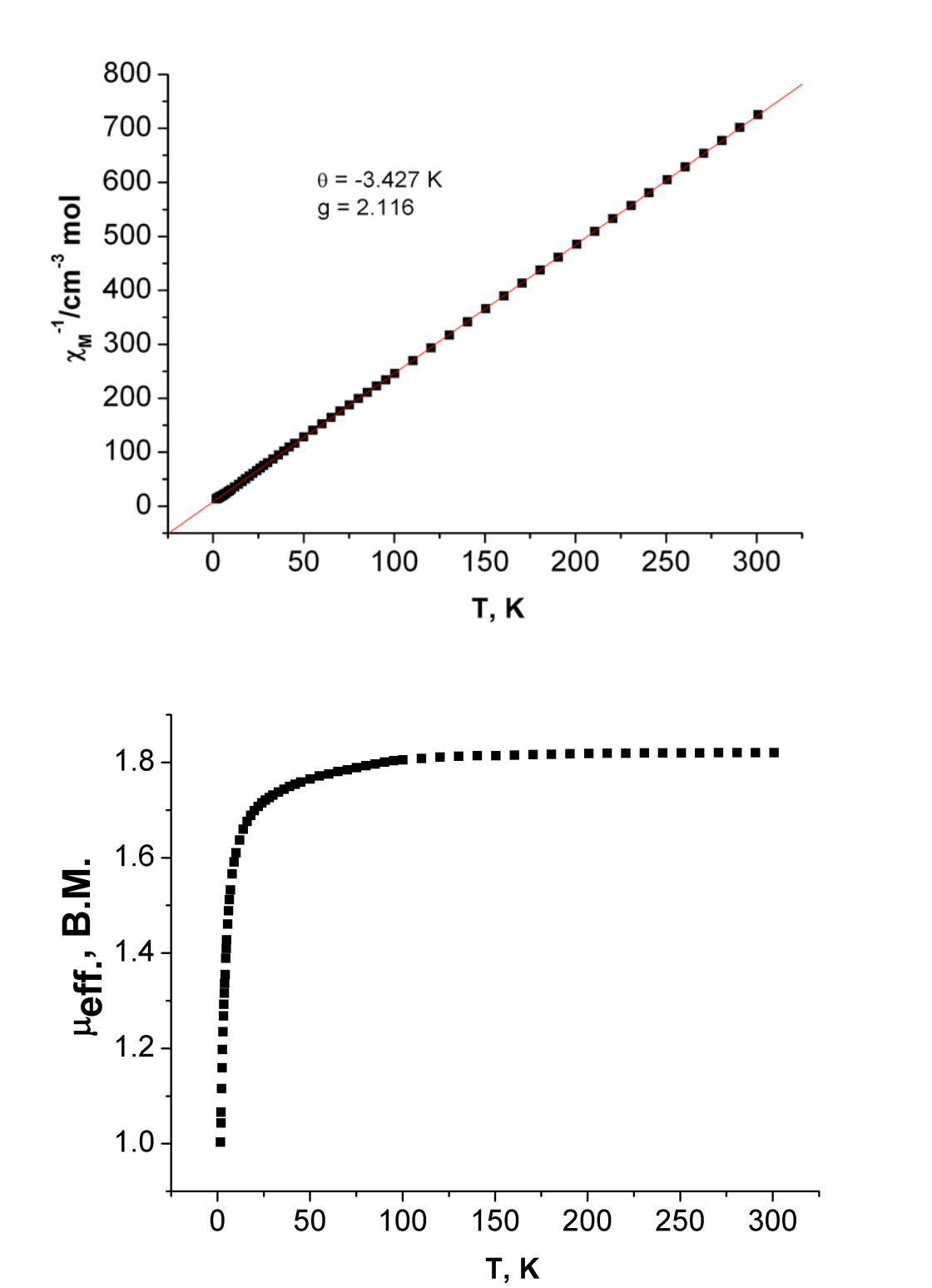


**Figure S7**. Temperature dependences of $\chi_M^{-1}$ (top) and effective magnetic moment per one copper(II) ion (bottom) for *catena*-[Cu(**4-PicHA**)(**bpy**)]$_n$(OH)$_n$·3.25n$H_2O$ (**8**).

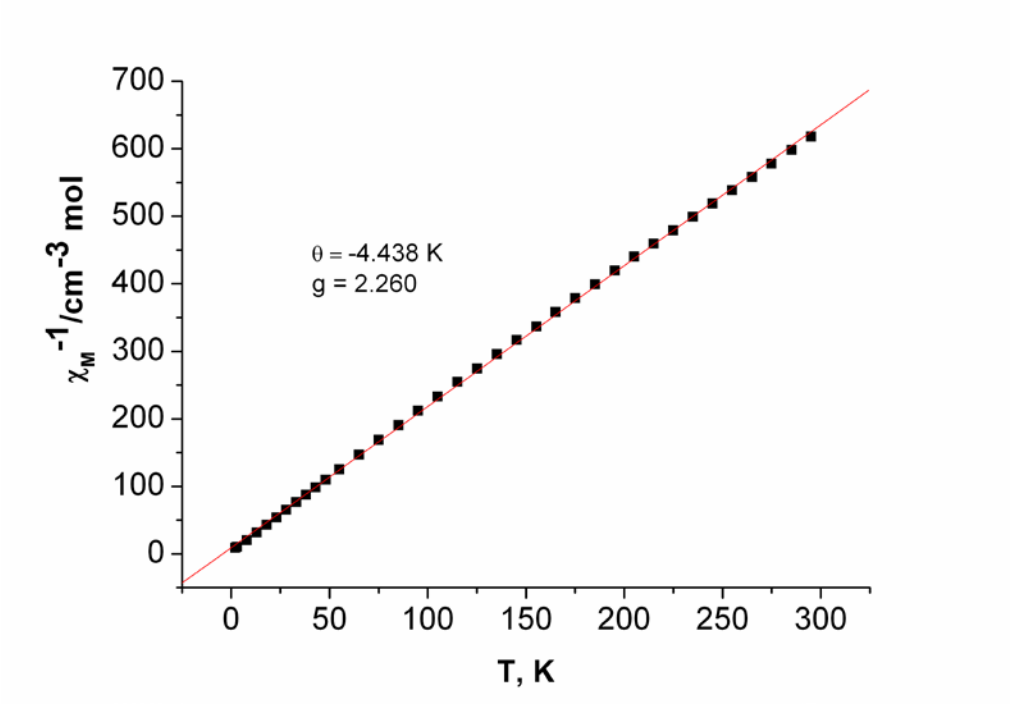


**Figure S8**. Temperature dependences of $\chi_M^{-1}$ for *catena*-[Cu(**4-PicHA**)$(DMSO)_2]_{2n}(ClO_4)_{2n}$ (**9**).

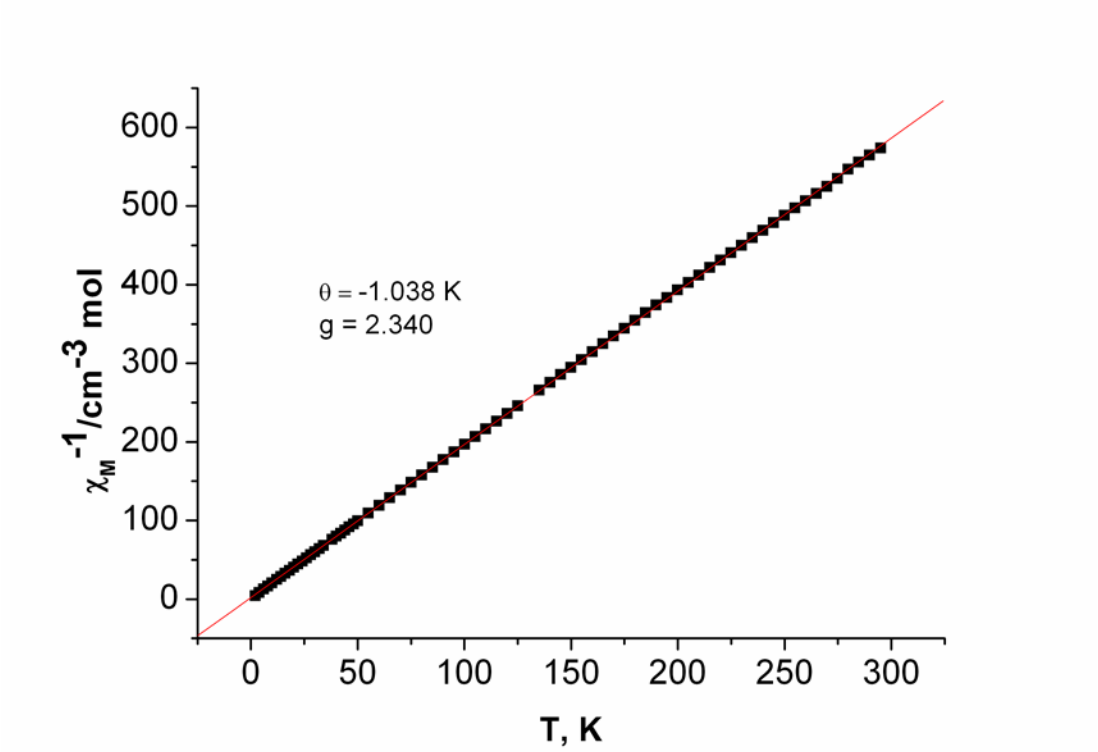


**Figure S9**. Temperature dependences of $\chi_M^{-1}$ for $[Cu(\mathbf{3\text{-}PicHA})(DMSO)(ClO_4)]_{nm}\cdot nmDMSO$ (**10**).

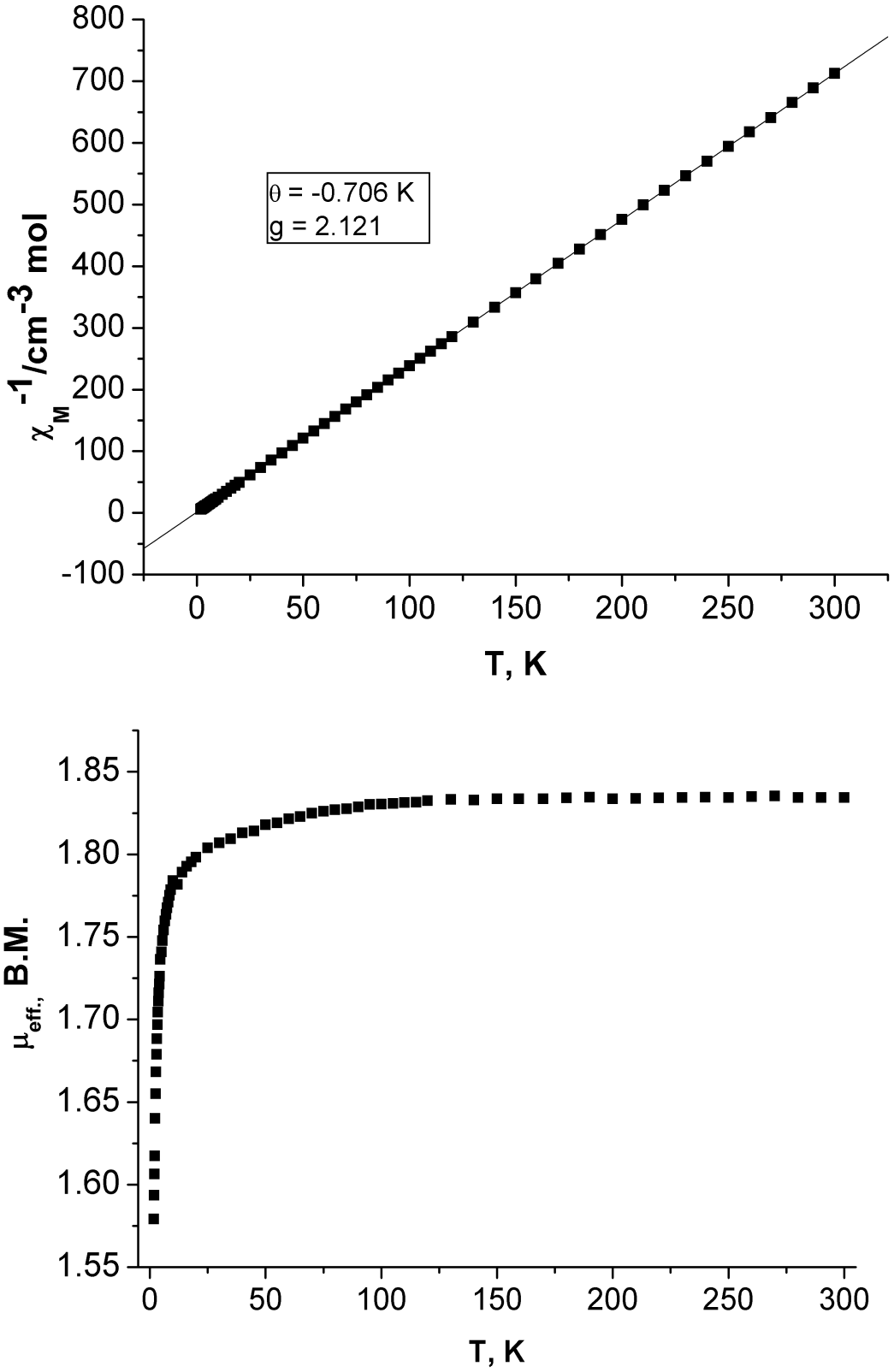


**Figure S10**. Temperature dependences of $\chi_M^{-1}$ (top) and effective magnetic moment per one copper(II) ion (bottom) for $[\{Cu(\textbf{4-PicHA})(\textbf{phen})\}_2]_n(ClO_4)_{2n}$ (**11**).