Synthesis, Characterization and Biological Activity of Novel Cu(II) Complexes of 6-Methyl-2-Oxo-1,2-Dihydroquinoline-3-Carbaldehyde-4n-Substituted Thiosemicarbazones

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Figure S1. Cyclic voltammograms for H:Li (top) and H:Li3 (bottom), both at a concentration of $2.00 \times 10^{-3}$ M, in [NBu][BF$_4$] 0.2 M in DMSO at a platinum disc working electrode ($d = 0.5$ mm) and at a scan rate of 0.2 V.s$^{-1}$. The arrows indicate the cathodic initial scan direction.
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A crystal of compound 2 was mounted on a Bruker APEXII diffractometer for the unit cell, space group determination and data collection and cooled using a cold nitrogen stream to 110(2)K.

Data were corrected for Lorentz and polarization factors with the data reduction software SAINT [1] and, empirically, for absorption using the SADABS program [2].

The cell constants were refined by least-squares, at the end of the data collection, using 5250 reflections (θmax ≤ 61.06 °). The centrosymmetric choice for the space group (P-1) was confirmed by the successful refinement. The data were collected using ω scans, in steps of 0.5 °. For each of the 1440 collected frames counting time was 20 sec.

The structure was solved by direct methods [3] and refined by full matrix least-squares [4] (the function minimized being Σ[w(Fo^2 -(1/k) Fc^2)^2]).

The least-squares refinement was carried out using anisotropic displacement parameters for all non-hydrogen atoms. The contribution of hydrogen atoms, in their calculated positions, was included in the refinement using a riding model (B(H) = a × B(bonded) (Å^2), with a = 1.3 for the methyl groups and a = 1.2 for the remaining ones). The hydrogen atoms bonded to the coordinated water molecules were found from a Fourier Difference map and refined without constraints.

The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature. All calculations were carried out by using the WINGX [5], SHELX [3] ORTEP [6] and MERCURY [7] programs.

More details of the data collection parameters, coordinates, ADPs and molecular geometry are listed in the deposited cif file.

References
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| **Table S1. Crystal data and structure refinement for 2.** |
|----------------------------------------------------------|
| **Empirical formula** | C₁₃H₁₈CuN₆O₉S |
| **Formula weight** | 497.93 |
| **Temperature** | 110(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal system** | Triclinic |
| **Space group** | P - 1 |
| **Unit cell dimensions** |  
| a | 8.146(3) Å | \( \alpha = 93.59(4)^\circ \) |
| b | 10.159(3) Å | \( \beta = 92.39(4)^\circ \) |
| c | 12.635(4) Å | \( \gamma = 112.15(4)^\circ \) |
| **Volume** | 964.2(6) Å³ |
| **Z** | 2 |
| **Density (calculated)** | 1.715 Mg/m³ |
| **Absorption coefficient** | 1.303 mm⁻¹ |
| **F(000)** | 510 |
| **Theta range for data collection** | 1.619 - 25.249° |
| **Index ranges** | \(-9 \leq h \leq 9, -12 \leq k \leq 12, -15 \leq l \leq 15\) |
| **Reflections collected** | 6853 |
| **Independent reflections** | 3485 \([R_{int} = 0.0395]\) |
| **Completeness to theta = 25.242°** | 99.60% |
| **Refinement method** | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 3485 / 0 / 287 |
| **Goodness-of-fit on F²** | 1.055 |
| **Final R indices [I > 2σ(I)]** | R₁ = 0.0560, wR₂ = 0.1434 |
| **R indices (all data)** | R₁ = 0.0713, wR₂ = 0.1588 |
| **Extinction coefficient** | n/a |
Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^4$) for 2. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|       | x    | y    | z    | $U(\text{eq})$ |
|-------|------|------|------|---------------|
| Cu(1) | 9806(1) | 5898(1) | 7698(1) | 20(1)         |
| S(1)  | 8405(1) | 5445(1) | 6050(1) | 23(1)         |
| OW1   | 9883(5)  | 4023(3) | 7677(3) | 33(1)         |
| OW2   | 7559(5)  | 5261(4) | 8750(3) | 31(1)         |
| O(1)  | 11324(4) | 6400(3) | 9012(2) | 23(1)         |
| O(51) | 5670(4)  | 6615(3) | 10307(3) | 32(1)       |
| O(52) | 6065(4)  | 5746(4) | 11774(2) | 36(1)       |
| O(53) | 8304(4)  | 6793(3) | 10845(3) | 32(1)       |
| O(61) | 11510(4) | 7615(3) | 14157(2) | 31(1)       |
| O(62) | 10619(4) | 9073(3) | 13359(2) | 27(1)       |
| O(63) | 12082(5) | 9712(3) | 14910(3) | 36(1)       |
| N(1)  | 12711(5) | 7581(4) | 10540(3) | 22(1)       |
| N(2)  | 10030(4) | 7897(3) | 7631(3)  | 18(1)       |
| N(3)  | 9251(5)  | 8180(4) | 6741(3)  | 21(1)       |
| N(4)  | 7811(5)  | 7517(4) | 5115(3)  | 23(1)       |
| N(5)  | 6670(5)  | 6386(4) | 10984(3) | 25(1)       |
| N(6)  | 11408(5) | 8796(4) | 14144(3) | 24(1)       |
| C(1)  | 10799(5) | 8947(4) | 8340(3)  | 20(1)       |
| C(2)  | 11714(5) | 8860(4) | 9325(3)  | 20(1)       |
| C(3)  | 12448(5) | 10060(5) | 10016(3) | 22(1)       |
| C(4)  | 13373(5) | 10062(5) | 10990(3) | 20(1)       |
| C(5)  | 14200(6) | 11295(5) | 11705(3) | 24(1)       |
| C(6)  | 15094(6) | 11246(5) | 12645(3) | 27(1)       |
| C(7)  | 15146(6) | 9926(5)  | 12881(3) | 28(1)       |
| C(8)  | 14380(6) | 8708(5)  | 12210(3) | 26(1)       |
| C(9)  | 13485(5) | 8772(4)  | 11249(3) | 21(1)       |
| C(10) | 11892(5) | 7547(4)  | 9582(3)  | 20(1)       |
| C(11) | 15979(6) | 12566(5) | 13403(4) | 33(1)       |
| C(12) | 8480(5)  | 7137(4)  | 5957(3)  | 19(1)       |
Table S3. Anisotropic displacement parameters ($\AA^2 \times 10^3$) for 2. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^2 U_{11} + ... + 2hk a \times b \times U_{12}]$.

|    | U11  | U22  | U33  | U23  | U13  | U12  |
|----|------|------|------|------|------|------|
| Cu(1) | 31(1) | 14(1) | 14(1) | -1(1) | -8(1) | 10(1) |
| S(1)   | 36(1) | 15(1) | 18(1) | -3(1) | -9(1) | 10(1) |
| OW1    | 27(2) | 21(2) | 24(2) | -9(1) | -25(2) | 22(2) |
| OW2    | 39(2) | 33(2) | 19(2) | -3(2) | -1(1) | 12(2) |
| O(1)   | 31(2) | 13(1) | 23(2) | -1(1) | -12(1) | 10(1) |
| O(51)  | 39(2) | 32(2) | 28(2) | 6(1) | -9(1) | 18(2) |
| O(52)  | 44(2) | 45(2) | 16(2) | 4(1) | -3(1) | 15(2) |
| O(53)  | 32(2) | 34(2) | 29(2) | 4(1) | -5(1) | 13(1) |
| O(61)  | 51(2) | 17(2) | 26(2) | -1(1) | -13(1) | 16(1) |
| O(62)  | 43(2) | 20(2) | 20(2) | -2(1) | -14(1) | 14(1) |
| O(63)  | 60(2) | 26(2) | 24(2) | -9(1) | -20(2) | 22(2) |
| N(1)   | 31(2) | 20(2) | 16(2) | 1(1) | -7(1) | 12(2) |
| N(2)   | 26(2) | 19(2) | 11(2) | 2(1) | -5(1) | 11(1) |
| N(3)   | 37(2) | 14(2) | 14(2) | -1(1) | -11(1) | 12(2) |
| N(4)   | 33(2) | 19(2) | 15(2) | -1(1) | -10(1) | 11(2) |
| N(5)   | 34(2) | 20(2) | 21(2) | -3(2) | -2(2) | 12(2) |
| N(6)   | 33(2) | 19(2) | 18(2) | -2(1) | -7(2) | 9(2) |
| C(1)   | 32(2) | 21(2) | 13(2) | 4(2) | -3(2) | 17(2) |
| C(2)   | 23(2) | 21(2) | 13(2) | 1(2) | -4(2) | 7(2) |
| C(3)   | 27(2) | 24(2) | 15(2) | 1(2) | -4(2) | 12(2) |
| C(4)   | 22(2) | 25(2) | 13(2) | 1(2) | -5(2) | 7(2) |
| C(5)   | 29(2) | 25(2) | 16(2) | -2(2) | -5(2) | 10(2) |
| C(6)   | 28(2) | 33(2) | 16(2) | -6(2) | -5(2) | 10(2) |
| C(7)   | 32(2) | 38(3) | 14(2) | 1(2) | -7(2) | 14(2) |
| C(8)   | 33(2) | 29(2) | 17(2) | 1(2) | -7(2) | 14(2) |
| C(9)   | 25(2) | 25(2) | 12(2) | 2(2) | -3(2) | 10(2) |
| C(10)  | 25(2) | 22(2) | 11(2) | 3(2) | -2(2) | 8(2) |
| C(11)  | 37(3) | 33(3) | 23(2) | -11(2) | -13(2) | 10(2) |
| C(12)  | 24(2) | 18(2) | 15(2) | -2(2) | -1(2) | 8(2) |
Table S4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 × 10^3).

|       | x     | y     | z     | U(eq) |
|-------|-------|-------|-------|-------|
| HW11  | 9280  | 3320  | 7150  | 28    |
| HW12  | 10500 | 3870  | 8090  | 27    |
| HW21  | 6180  | 5030  | 8640  | 28    |
| HW22  | 7600  | 5700  | 9210  | 29    |
| H(1)  | 12756 | 6776  | 10729 | 26    |
| H(3)  | 9253  | 9039  | 6681  | 26    |
| H(4)  | 7895  | 8407  | 5122  | 27    |
| H(1A) | 10762 | 9846  | 8206  | 24    |
| H(3A) | 12333 | 10917 | 9836  | 26    |
| H(5)  | 14138 | 12173 | 11533 | 29    |
| H(7)  | 15737 | 9876  | 13533 | 34    |
| H(8)  | 14451 | 7836  | 12391 | 31    |
| H(11A)| 16028 | 13410 | 13048 | 50    |
| H(11B)| 17187 | 12655 | 13620 | 50    |
| H(11C)| 15294 | 12490 | 14032 | 50    |
| H(13A)| 7651  | 6005  | 3966  | 45    |
| H(13B)| 6835  | 7121  | 3591  | 45    |
| H(13C)| 5757  | 5912  | 4334  | 45    |
Table S5. Bond lengths [Å] and angles [°] for 2.

| Bond                  | Length/Angle |
|-----------------------|--------------|
| Cu(1)-OW1             | 1.928(3)     |
| Cu(1)-O(1)            | 1.948(3)     |
| Cu(1)-N(2)            | 1.977(3)     |
| Cu(1)-OW2             | 2.226(4)     |
| Cu(1)-S(1)            | 2.2663(15)   |
| S(1)-C(12)            | 1.708(4)     |
| OW1-HW11              | 0.92(6)      |
| OW1-HW12              | 0.77(6)      |
| OW2-HW21              | 1.06(5)      |
| OW2-HW22              | 0.70(6)      |
| O(1)-C(10)            | 1.245(5)     |
| O(51)-N(5)            | 1.248(5)     |
| O(52)-N(5)            | 1.242(5)     |
| O(53)-N(5)            | 1.260(5)     |
| O(61)-N(6)            | 1.235(5)     |
| O(62)-N(6)            | 1.262(5)     |
| O(63)-N(6)            | 1.250(5)     |
| N(1)-C(10)            | 1.349(5)     |
| N(1)-C(9)             | 1.380(6)     |
| N(1)-H(1)             | 0.88         |
| N(2)-C(1)             | 1.289(6)     |
| N(2)-N(3)             | 1.366(5)     |
| N(3)-C(12)            | 1.346(5)     |
| N(3)-H(3)             | 0.88         |
| N(4)-C(12)            | 1.319(5)     |
| N(4)-C(13)            | 1.457(5)     |
| N(4)-H(4)             | 0.88         |
| C(1)-C(2)             | 1.448(5)     |
| C(1)-H(1A)            | 0.95         |
| C(2)-C(3)             | 1.372(6)     |
| C(2)-C(10)            | 1.450(6)     |
| C(3)-C(4)             | 1.415(6)     |
| C(3)-H(3A)            | 0.95         |
| C(4)-C(9)             | 1.405(6)     |
| C(4)-C(5)             | 1.418(6)     |
| C(5)-C(6)             | 1.380(6)     |
| C(5)-H(5)             | 0.95         |
| C(6)-C(7)             | 1.408(7)     |
| C(6)-C(11)            | 1.513(6)     |
| C(7)-C(8)             | 1.372(7)     |
| C(7)-H(7)             | 0.95         |
| C(8)-C(9)             | 1.408(6)     |
| C(8)-H(8)             | 0.95         |
| C(11)-H(11A)          | 0.98         |
| C(11)-H(11B)          | 0.98         |
| C(11)-H(11C)          | 0.98         |
| C(13)-H(13A)          | 0.98         |
| C(13)-H(13B)          | 0.98         |
| C(13)-H(13C)          | 0.98         |
| OW1-Cu(1)-O(1)        | 87.95(14)    |
| OW1-Cu(1)-N(2)        | 172.41(15)   |
| O(1)-Cu(1)-N(2)       | 91.19(13)    |
| OW1-Cu(1)-OW2         | 90.86(16)    |
| O(1)-Cu(1)-OW2        | 85.35(14)    |
| N(2)-Cu(1)-OW2        | 96.58(14)    |
| OW1-Cu(1)-S(1)        | 92.53(11)    |
| Bond                        | Angle (°)  |
|-----------------------------|------------|
| O(1)-Cu(1)-S(1)            | 171.79(10) |
| N(2)-Cu(1)-S(1)            | 87.25(11)  |
| OW2-Cu(1)-S(1)             | 102.83(11) |
| C(12)-S(1)-Cu(1)           | 95.24(15)  |
| Cu(1)-OW1-HW11             | 122(3)     |
| Cu(1)-OW1-HW12             | 120(4)     |
| HW11-OW1-HW12              | 119(5)     |
| Cu(1)-OW2-HW21             | 135(3)     |
| Cu(1)-OW2-HW22             | 119(5)     |
| HW21-OW2-HW22              | 89(5)      |
| C(10)-O(1)-Cu(1)           | 128.7(3)   |
| C(10)-N(1)-C(9)            | 125.6(4)   |
| C(10)-N(1)-H(1)            | 117.2      |
| C(9)-N(1)-H(1)             | 117.2      |
| C(1)-N(2)-N(3)             | 116.9(3)   |
| C(1)-N(2)-Cu(1)            | 127.1(3)   |
| N(3)-N(2)-Cu(1)            | 115.9(3)   |
| C(12)-N(3)-N(2)            | 119.6(3)   |
| C(12)-N(3)-H(3)            | 120.2      |
| N(2)-N(3)-H(3)             | 120.2      |
| C(12)-N(4)-C(13)           | 124.3(4)   |
| C(12)-N(4)-H(4)            | 117.8      |
| C(13)-N(4)-H(4)            | 117.8      |
| O(52)-N(5)-O(51)           | 120.8(4)   |
| O(52)-N(5)-O(53)           | 120.3(4)   |
| O(51)-N(5)-O(53)           | 118.9(4)   |
| O(61)-N(6)-O(63)           | 119.8(3)   |
| O(61)-N(6)-O(62)           | 119.9(3)   |
| O(63)-N(6)-O(62)           | 120.3(3)   |
| N(2)-C(1)-C(2)             | 124.9(4)   |
| N(2)-C(1)-H(1A)            | 117.5      |
| C(2)-C(1)-H(1A)            | 117.5      |
| C(3)-C(2)-C(1)             | 118.7(4)   |
| C(3)-C(2)-C(10)            | 119.7(4)   |
| C(1)-C(2)-C(10)            | 121.6(4)   |
| C(2)-C(3)-C(4)             | 122.0(4)   |
| C(2)-C(3)-H(3A)            | 119        |
| C(4)-C(3)-H(3A)            | 119        |
| C(9)-C(4)-C(3)             | 117.8(4)   |
| C(9)-C(4)-C(5)             | 118.8(4)   |
| C(3)-C(4)-C(5)             | 123.4(4)   |
| C(6)-C(5)-C(4)             | 121.3(4)   |
| C(6)-C(5)-H(5)             | 119.3      |
| C(4)-C(5)-H(5)             | 119.3      |
| C(5)-C(6)-C(7)             | 118.0(4)   |
| C(5)-C(6)-C(11)            | 121.1(4)   |
| C(7)-C(6)-C(11)            | 120.9(4)   |
| C(8)-C(7)-C(6)             | 122.7(4)   |
| C(8)-C(7)-H(7)             | 118.6      |
| C(6)-C(7)-H(7)             | 118.6      |
| C(7)-C(8)-C(9)             | 118.9(4)   |
| C(7)-C(8)-H(8)             | 120.6      |
| C(9)-C(8)-H(8)             | 120.6      |
| N(1)-C(9)-C(4)             | 118.6(4)   |
| N(1)-C(9)-C(8)             | 121.1(4)   |
| C(4)-C(9)-C(8)             | 120.3(4)   |
| O(1)-C(10)-N(1)            | 117.9(4)   |
| O(1)-C(10)-C(2)            | 125.9(4)   |
| Bond                              | Angle     |
|-----------------------------------|-----------|
| N(1)-C(10)-C(2)                  | 116.1(4)  |
| C(6)-C(11)-H(11A)                | 109.5     |
| C(6)-C(11)-H(11B)                | 109.5     |
| H(11A)-C(11)-H(11B)              | 109.5     |
| C(6)-C(11)-H(11C)                | 109.5     |
| H(11A)-C(11)-H(11C)              | 109.5     |
| H(11B)-C(11)-H(11C)              | 109.5     |
| N(4)-C(12)-N(3)                  | 115.5(4)  |
| N(4)-C(12)-S(1)                  | 122.7(3)  |
| N(3)-C(12)-S(1)                  | 121.9(3)  |
| N(4)-C(13)-H(13A)                | 109.5     |
| N(4)-C(13)-H(13B)                | 109.5     |
| H(13A)-C(13)-H(13B)              | 109.5     |
| N(4)-C(13)-H(13C)                | 109.5     |
| H(13A)-C(13)-H(13C)              | 109.5     |
| H(13B)-C(13)-H(13C)              | 109.5     |
| Bond | Torsion Angle [°] |
|------|------------------|
| C(1)-N(2)-N(3)-C(12) | 177.8(4) |
| Cu(1)-N(2)-N(3)-C(12) | −3.5(5) |
| N(3)-N(2)-C(1)-C(2) | −179.1(4) |
| Cu(1)-N(2)-C(1)-C(2) | 2.3(6) |
| N(2)-C(1)-C(2)-C(3) | −178.9(4) |
| N(2)-C(1)-C(2)-C(10) | 2.1(7) |
| C(1)-C(2)-C(3)-C(4) | −179.6(4) |
| C(10)-C(2)-C(3)-C(4) | −0.6(6) |
| C(2)-C(3)-C(4)-C(9) | −1.5(6) |
| C(2)-C(3)-C(4)-C(5) | 177.7(4) |
| C(9)-C(4)-C(5)-C(6) | −0.5(6) |
| C(3)-C(4)-C(5)-C(6) | −179.7(4) |
| C(4)-C(5)-C(6)-C(7) | −0.7(6) |
| C(4)-C(5)-C(6)-C(11) | 179.8(4) |
| C(5)-C(6)-C(7)-C(8) | 1.3(7) |
| C(11)-C(6)-C(7)-C(8) | −179.2(4) |
| C(6)-C(7)-C(8)-C(9) | −0.7(7) |
| C(10)-N(1)-C(9)-C(4) | 2.6(6) |
| C(10)-N(1)-C(9)-C(8) | −177.1(4) |
| C(3)-C(4)-C(9)-N(1) | 0.7(6) |
| C(5)-C(4)-C(9)-N(1) | −178.6(4) |
| C(3)-C(4)-C(9)-C(8) | −179.6(4) |
| C(5)-C(4)-C(9)-C(8) | 1.1(6) |
| C(7)-C(8)-C(9)-N(1) | 179.2(4) |
| C(7)-C(8)-C(9)-C(4) | −0.5(7) |
| Cu(1)-O(1)-C(10)-N(1) | 170.4(3) |
| Cu(1)-O(1)-C(10)-C(2) | −7.8(6) |
| C(9)-N(1)-C(10)-O(1) | 177.0(4) |
| C(9)-N(1)-C(10)-C(2) | −4.6(6) |
| C(3)-C(2)-C(10)-O(1) | −178.2(4) |
| C(1)-C(2)-C(10)-O(1) | 0.7(7) |
| C(3)-C(2)-C(10)-N(1) | 3.5(6) |
| C(1)-C(2)-C(10)-N(1) | −177.5(4) |
| C(13)-N(4)-C(12)-N(3) | 179.2(4) |
| C(13)-N(4)-C(12)-S(1) | −0.1(6) |
| N(2)-N(3)-C(12)-N(4) | −178.0(3) |
| N(2)-N(3)-C(12)-S(1) | 1.3(6) |
| Cu(1)-S(1)-C(12)-N(4) | −179.7(3) |
| Cu(1)-S(1)-C(12)-N(3) | 1.1(4) |
**Table S7. Squares Planes for 2.**

Least-squares planes ($x,y,z$ in crystal coordinates) and deviations from them

(* indicates atom used to define plane)

$$7.0664 (0.0066) \times - 0.7771 (0.0106) \times - 5.9994 (0.0131) \times = 1.8713 (0.0126)$$

| Atom | Coefficients |
|------|--------------|
| S1   | 0.0156 (0.0015) |
| C12  | -0.0076 (0.0024) |
| N3   | -0.0143 (0.0026) |
| N2   | 0.0248 (0.0020) |
| Cu1  | -0.0185 (0.0012) |
| N4   | -0.0048 (0.0051) |
| C13  | 0.0198 (0.0066) |
| OW2  | -2.1881 (0.0043) |
| OW1  | 0.1943 (0.0046) |

Rms deviation of fitted atoms = 0.0171

$$6.7710 (0.0076) \times - 0.5716 (0.0122) \times - 6.7952 (0.0136) \times = 1.1226 (0.0142)$$

| Atom | Coefficients |
|------|--------------|
| O1   | 0.0553 (0.0023) |
| C10  | -0.0133 (0.0028) |
| C2   | -0.0340 (0.0028) |
| C1   | 0.0107 (0.0029) |
| N2   | 0.0322 (0.0024) |
| Cu1  | -0.0509 (0.0016) |
| N1   | -0.1112 (0.0053) |
| C3   | -0.0752 (0.0056) |
| OW2  | -2.2509 (0.0042) |
| OW1  | 0.1228 (0.0051) |

Rms deviation of fitted atoms = 0.0368

$$6.9081 (0.0069) \times - 0.6846 (0.0128) \times - 6.4568 (0.0103) \times = 1.4673 (0.0129)$$

| Atom | Coefficients |
|------|--------------|
| O1   | 0.0553 (0.0023) |
| C10  | -0.0133 (0.0028) |
| C2   | -0.0340 (0.0028) |
| C1   | 0.0107 (0.0029) |
| N2   | 0.0322 (0.0024) |
| Cu1  | -0.0509 (0.0016) |
| N1   | -0.1112 (0.0053) |
| C3   | -0.0752 (0.0056) |
| OW2  | -2.2509 (0.0042) |
| OW1  | 0.1228 (0.0051) |

Rms deviation of fitted atoms = 0.0368
* 0.0440 (0.0032) C10
* −0.0027 (0.0033) C2
* −0.0239 (0.0034) C3
* −0.0143 (0.0036) C4
* 0.0115 (0.0034) C5
* 0.0254 (0.0035) C6
* −0.0009 (0.0036) C7
* −0.0136 (0.0035) C8
* −0.0150 (0.0037) C9
* −0.0106 (0.0031) N1
0.0986 (0.0044) O1
−0.0046 (0.0053) C1

Rms deviation of fitted atoms = 0.0201

6.8630 (0.0063) x − 0.5639 (0.0106) y − 6.5133 (0.0098) z = 1.4810 (0.0089)

Angle to previous plane (with approximate esd) = 0.718 (0.140)

* 0.0402 (0.0013) S1
* −0.0974 (0.0012) Cu1
* 0.0602 (0.0014) O1
* −0.0062 (0.0024) C1
* −0.0126 (0.0031) N2
* 0.0159 (0.0024) N3
0.0563 (0.0045) C12
0.1241 (0.0047) N4
−0.0149 (0.0049) C2
0.0137 (0.0049) C10

Rms deviation of fitted atoms = 0.0503
Figure S7. Ortep view of compound 1 showing the two independent molecules in the unit cell (1a (Cu2) and 1b (Cu1)) with the numbering scheme. (Ellipsoids drawn at 50% probability).
Figure S8. Molecular Packing of 1.
Figure S9. Molecular Packing of 1 down the $b$ axis.
Figure S10. Selected short H-bonding interactions in 1.
Figure S11. A view of the short H-bonding interactions involving the NH$_2$ groups (N4 and N8 respectively).
A suitable green crystal, with approximate dimensions 0.06 x 0.04 x 0.03 mm³, was mounted on a nylon loop and placed in a cold nitrogen stream at 110(2) K, on a BRUKER GADDS X-ray diffractometer that was used for the unit cell determination and the data collection. The goniometer was controlled using the FRAMBO software, v.4.1.05.[1] The crystal to detector distance was set at 5.0 cm. The X-ray radiation employed was from a Cu X-ray tube (Kα = 1.5418 Å at 40 kV and 40 mA) and monochromated with a graphite monochromator (175 mm collimator with 0.5 mm pinholes).

For the final cell constants determination 180 data frames were collected with Δω = 0.5 °. These reflections were used to determine the unit cell using the program Cell Now.[2]

Integrated intensities were obtained by using the APEX2 program.[3] Data were corrected for Lorentz and polarization factors, as well as for crystal decay. The SADABS [4] program was used for the absorption correction. Statistical tests indicated a non-centrosymmetric space group (P1); this choice was later confirmed by the successful refinement.

The structure was solved by direct methods [5] and refined by full matrix least-squares [5] (the function minimized being \[ \sum \{w(F_o^2 - (1/k) F_c^2)^2\} \]).

While the hydrogen atoms bound to carbons were placed in idealized positions, those bound to the nitrogen and oxygen atoms were located from difference Fourier maps, and refined using a riding model. H4P and H18P could not be located from the difference Fourier maps and were modeled based on the hydrogen bonding acceptors positions. All non-hydrogen atoms were refined using Anisotropic Displacements Parameters. Program “X-seed” was employed for the final data presentation and structure plots.[6]

Three clathrated water molecules were also located from the Fourier difference maps.

References

1. FRAMBO v. 4.1.05 “Program for Data Collection on Area Detectors” BRUKER-Nonius Inc., 5465 East Cheryl Parkway, Madison, WI 53711–5373 USA
2. Sheldrick, G. M. “Cell_Now (version 2008/1): Program for Obtaining Unit Cell Constants from Single Crystal Data”: University of Göttingen, Germany
3. APEX2 “Program for Data Collection and Integration on Area Detectors” BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711–5373 USA
4. Sheldrick, G.M. “SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames”, University of Göttingen, 2008
5. Sheldrick, G.M. (2008). ActaCryst. A64, 112–122; as implemented in SHELXTL, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711–5373 USA
6. Barbour, L.J.,(2001) “X-Seed (version 2.0): A Software Tool for Supramolecular Crystallography” J. Supramol. Chem. 2001, 1, 189–191.
Table S8. Crystal data and structure refinement for 1.

| Property                                      | Value                      |
|-----------------------------------------------|----------------------------|
| Empirical formula                             | C$_{24}$H$_{36}$Cu$_2$N$_{12}$O$_{20}$S$_2$ |
| Formula weight                                | 1003.85                    |
| Temperature                                   | 110(2) K                   |
| Wavelength                                    | 1.54178 Å                  |
| Crystal system                                | Triclinic                  |
| Space group                                   | P1                         |
| Unit cell dimensions                          | a = 8.5216(3) Å, α = 110.055(2)° |
|                                             | b = 10.0064(4) Å, β = 96.958(3)° |
|                                             | c = 12.0178(5) Å, γ = 90.040(2)° |
| Volume                                        | 954.56(6) Å³               |
| Z                                             | 1                          |
| Density (calculated)                          | 1.746 Mg/m³                |
| Absorption coefficient                        | 3.270 mm⁻¹                 |
| F(000)                                        | 514                        |
| Crystal size                                  | 0.06 × 0.04 × 0.03 mm³     |
| Theta range for data collection               | 3.95 to 60.00 °            |
| Index ranges                                  | -9 <= h <= 9, -10 <= k <= 10, -13 <= l <= 13 |
| Reflections collected                         | 21621                      |
| Independent reflections                       | 5333 [R(int) = 0.0472]     |
| Completeness to theta = 60.00 °               | 97.90%                     |
| Absorption correction                         | Semi-empirical from equivalents |
| Max. and min. transmission                    | 0.9083 and 0.8279          |
| Refinement method                             | Full-matrix least-squares on F2 |
| Data / restraints / parameters                | 5333 / 3 / 544             |
| Goodness-of-fit on F2                         | 1.024                      |
| Final R indices [I > 2σ(I)]                   | R1 = 0.0268, wR2 = 0.0601  |
|                                             | R1 = 0.0293, wR2 = 0.0611  |
| Absolute structure parameter                  | 0.023(16)                  |
| Extinction coefficient                        | 0.0043(2)                  |
Table S9. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for 
1. U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

| Atom | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| Cu(1)| 9216(1) | 1531(1) | 2326(1) | 14(1) |
| Cu(2)| 8637(1) | 5238(1) | −737(1) | 15(1) |
| S(1) | 11516(1) | 1160(1) | 1499(1) | 17(1) |
| S(2) | 6345(1) | 5538(1) | 119(1)  | 18(1) |
| C(1) | 8407(4) | 4481(4) | 2660(3) | 14(1) |
| C(2) | 6975(4) | 4363(4) | 3137(3) | 15(1) |
| C(3) | 6488(4) | 3037(4) | 3282(3) | 14(1) |
| C(4) | 4134(5) | 4169(4) | 4067(3) | 13(1) |
| C(5) | 4585(4) | 5459(4) | 3910(3) | 14(1) |
| C(6) | 6019(4) | 5502(4) | 3443(3) | 17(1) |
| C(7) | 2755(4) | 4067(4) | 4543(3) | 17(1) |
| C(8) | 1815(4) | 5220(4) | 4843(3) | 18(1) |
| C(9) | 2199(4) | 6508(4) | 4680(3) | 16(1) |
| C(10)| 3587(4) | 6607(4) | 4225(3) | 16(1) |
| C(11)| 1094(5) | 7735(4) | 4994(4) | 22(1) |
| C(12)| 11075(4) | 2827(4) | 1432(3) | 15(1) |
| C(13)| 9522(4) | 8009(4) | −894(3) | 15(1) |
| C(14)| 10984(4) | 7515(4) | −1349(3) | 15(1) |
| C(15)| 11496(4) | 6102(4) | −1485(3) | 12(1) |
| C(16)| 13782(5) | 6633(4) | −2309(3) | 14(1) |
| C(17)| 13337(4) | 8039(4) | −2092(3) | 16(1) |
| C(18)| 11918(4) | 8448(4) | −1613(3) | 13(1) |
| C(19)| 15143(4) | 6147(4) | −2833(3) | 18(1) |
| C(20)| 16083(4) | 7095(4) | −3103(3) | 19(1) |
| C(21)| 15710(4) | 8513(4) | −2858(3) | 20(1) |
| C(22)| 14358(4) | 8975(4) | −2377(3) | 16(1) |
| C(23)| 16790(5) | 9510(5) | −3168(4) | 29(1) |
| C(24)| 6183(4) | 7266(4) | 2321(3) | 16(1) |
| N(1) | 9399(4) | 3501(3) | 2345(3) | 12(1) |
| N(2) | 10715(3) | 3844(3) | 1904(3) | 17(1) |
| N(3) | 5115(3) | 3042(3) | 3738(2) | 14(1) |
| N(4) | 12858(3) | 3191(3) | 929(3)  | 18(1) |
| N(5) | 8497(4) | 7245(3) | −637(3) | 14(1) |
| N(6) | 7166(3) | 7925(3) | −219(3) | 16(1) |
| N(7) | 12846(3) | 5741(3) | −1974(2) | 14(1) |
| N(8) | 5021(4) | 8038(3) | 741(3)  | 18(1) |
| N(9) | 3906(4) | 2130(3) | 6658(3) | 22(1) |
| N(10)| 9939(4) | 1752(4) | 5242(3) | 24(1) |
| N(11)| 1680(4) | 7079(3) | 1696(3) | 16(1) |
| N(12)| 6239(4) | 1402(3) | 179(2)  | 16(1) |
| O(1) | 7247(3) | 1920(3) | 3024(2) | 18(1) |
| O(2) | 8813(3) | 473(3)  | 2060(2) | 15(1) |
| O(3) | 10800(3) | 5200(3) | −1173(2) | 16(1) |
| O(4) | 9025(3) | 3417(3) | −500(2) | 17(1) |
| O(5) | 7905(3) | 4110(3) | −2708(2) | 24(1) |
| O(6) | 3544(3) | 2824(3) | 7691(2) | 24(1) |
| O(7) | 3173(3) | 980(3)  | 6044(2) | 25(1) |
| O(8) | 4997(3) | 2581(3) | 6247(2) | 27(1) |
| O(9) | 9168(3) | 966(3)  | 5633(2) | 26(1) |
| O(10)| 10424(3) | 1248(3) | 4253(2) | 25(1) |
| O(11)| 10235(4) | 3026(3) | 5872(2) | 36(1) |
| O(12)| 3523(3) | 6502(3) | 1676(2) | 20(1) |
| O(13)| 2862(3) | 6339(3) | 1475(2) | 19(1) |
| O(14)| 1794(3) | 8393(3) | 1927(2) | 24(1) |
|   |   |   |   |   |
|---|---|---|---|---|
| O(15) | 5065(3) | 854(3) | 434(2) | 22(1) |
| O(16) | 7539(3) | 815(3) | 138(2) | 21(1) |
| O(17) | 6108(3) | 2529(3) | −29(3) | 35(1) |
| O(18) | 7249(3) | 9002(3) | 3670(2) | 22(1) |
| O(19) | 4228(3) | 276(3) | 3795(2) | 22(1) |
| O(20) | 670(3) | 1569(3) | 8017(2) | 22(1) |
Table S10. Bond lengths [Å] and angles [°] for 1.

| Bond Length/Bond Angle                         | Value     |
|-----------------------------------------------|-----------|
| Cu(1)-O(2)                                    | 1.943(3)  |
| Cu(1)-O(1)                                    | 1.946(3)  |
| Cu(1)-N(1)                                    | 1.969(3)  |
| Cu(1)-S(1)                                    | 2.2776(10)|
| Cu(2)-O(4)                                    | 1.961(2)  |
| Cu(2)-O(3)                                    | 1.973(3)  |
| Cu(2)-N(5)                                    | 1.975(3)  |
| Cu(2)-O(5)                                    | 2.234(2)  |
| Cu(2)-S(2)                                    | 2.2888(10)|
| Cu(2)-H(4P)                                   | 2.0848    |
| S(1)-C(12)                                    | 1.706(4)  |
| S(2)-C(24)                                    | 1.694(4)  |
| C(1)-N(1)                                     | 1.282(5)  |
| C(1)-C(2)                                     | 1.430(5)  |
| C(1)-H(1A)                                    | 0.95      |
| C(2)-C(6)                                     | 1.373(5)  |
| C(2)-C(3)                                     | 1.463(5)  |
| C(3)-O(1)                                     | 1.255(4)  |
| C(3)-N(3)                                     | 1.350(5)  |
| C(4)-N(3)                                     | 1.380(5)  |
| C(4)-C(7)                                     | 1.387(6)  |
| C(4)-C(5)                                     | 1.425(5)  |
| C(5)-C(10)                                    | 1.403(5)  |
| C(5)-C(6)                                     | 1.412(5)  |
| C(6)-H(6A)                                    | 0.95      |
| C(7)-C(8)                                     | 1.374(5)  |
| C(7)-H(7A)                                    | 0.95      |
| C(8)-C(9)                                     | 1.411(5)  |
| C(8)-H(8A)                                    | 0.95      |
| C(9)-C(10)                                    | 1.379(5)  |
| C(9)-C(11)                                    | 1.519(5)  |
| C(10)-H(10A)                                  | 0.95      |
| C(11)-H(11A)                                  | 0.98      |
| C(11)-H(11B)                                  | 0.98      |
| C(11)-H(11C)                                  | 0.98      |
| C(12)-N(4)                                    | 1.326(5)  |
| C(12)-N(2)                                    | 1.339(4)  |
| C(13)-N(5)                                    | 1.291(5)  |
| C(13)-C(14)                                   | 1.441(5)  |
| C(13)-H(13A)                                  | 0.95      |
| C(14)-C(18)                                   | 1.367(5)  |
| C(14)-C(15)                                   | 1.441(5)  |
| C(15)-O(3)                                    | 1.262(4)  |
| C(15)-N(7)                                    | 1.348(4)  |
| C(16)-N(7)                                    | 1.386(5)  |
| C(16)-C(19)                                   | 1.395(5)  |
| C(16)-C(17)                                   | 1.401(5)  |
| C(17)-C(18)                                   | 1.403(5)  |
| C(17)-C(22)                                   | 1.429(5)  |
| C(18)-H(18A)                                  | 0.95      |
| C(19)-C(20)                                   | 1.386(5)  |
| C(19)-H(19A)                                  | 0.95      |
| C(20)-C(21)                                   | 1.392(6)  |
| C(20)-H(20A)                                  | 0.95      |
| C(21)-C(22)                                   | 1.362(5)  |
| C(21)-C(23)                                   | 1.523(6)  |
| Bond                        | Distance  |
|-----------------------------|-----------|
| C(22)-H(22A)                | 0.95      |
| C(23)-H(23A)                | 0.98      |
| C(23)-H(23B)                | 0.98      |
| C(23)-H(23C)                | 0.98      |
| C(24)-N(8)                  | 1.333(5)  |
| C(24)-N(6)                  | 1.336(5)  |
| N(1)-N(2)                   | 1.387(4)  |
| N(2)-H(2N)                  | 0.9       |
| N(3)-H(3N)                  | 0.9       |
| N(4)-H(4M)                  | 0.9       |
| N(4)-H(4N)                  | 0.9       |
| N(5)-N(6)                   | 1.381(4)  |
| N(6)-H(6N)                  | 0.9       |
| N(7)-H(7N)                  | 0.8999    |
| N(8)-H(8M)                  | 0.9       |
| N(9)-O(7)                   | 1.251(4)  |
| N(9)-O(8)                   | 1.256(4)  |
| N(9)-O(6)                   | 1.274(4)  |
| N(10)-O(10)                 | 1.243(4)  |
| N(10)-O(11)                 | 1.246(4)  |
| N(10)-O(9)                  | 1.265(4)  |
| N(11)-O(14)                 | 1.248(4)  |
| N(11)-O(13)                 | 1.251(4)  |
| N(11)-O(12)                 | 1.265(4)  |
| N(12)-O(17)                 | 1.239(4)  |
| N(12)-O(16)                 | 1.252(4)  |
| N(12)-O(15)                 | 1.259(4)  |
| O(2)-H(2O)                  | 0.85      |
| O(2)-H(2P)                  | 0.85      |
| O(4)-H(4O)                  | 0.85      |
| O(4)-H(4P)                  | 0.85      |
| O(5)-H(5O)                  | 0.85      |
| O(5)-H(5P)                  | 0.85      |
| O(18)-H(18O)                | 0.85      |
| O(18)-H(18P)                | 0.85      |
| O(19)-H(19O)                | 0.85      |
| O(19)-H(19P)                | 0.8501    |
| O(20)-H(20O)                | 0.85      |
| O(20)-H(20P)                | 0.85      |
| O(2)-Cu(1)-O(1)             | 88.29(11) |
| O(2)-Cu(1)-N(1)             | 170.60(12)|
| O(1)-Cu(1)-N(1)             | 90.80(12) |
| O(2)-Cu(1)-S(1)             | 93.83(8)  |
| O(1)-Cu(1)-S(1)             | 177.77(8) |
| N(1)-Cu(1)-S(1)             | 86.99(10) |
| O(4)-Cu(2)-O(3)             | 87.56(11) |
| O(4)-Cu(2)-N(5)             | 167.95(11)|
| O(3)-Cu(2)-N(5)             | 90.48(12) |
| O(4)-Cu(2)-O(5)             | 91.00(10) |
| O(3)-Cu(2)-O(5)             | 84.96(10) |
| N(3)-Cu(2)-O(5)             | 100.67(11)|
| O(4)-Cu(2)-S(2)             | 93.35(8)  |
| O(3)-Cu(2)-S(2)             | 169.23(8) |
| N(5)-Cu(2)-S(2)             | 86.40(9)  |
| O(5)-Cu(2)-S(2)             | 105.74(7) |
| O(4)-Cu(2)-H(4P)            | 24        |
| O(3)-Cu(2)-H(4P)            | 86.3      |
C(18)-C(17)-C(22) 123.7(3)
C(14)-C(18)-C(17) 121.6(3)
C(14)-C(18)-H(18A) 119.2
C(17)-C(18)-H(18A) 119.2
C(20)-C(19)-C(16) 118.7(4)
C(20)-C(19)-H(19A) 120.7
C(16)-C(19)-H(19A) 120.7
C(19)-C(20)-C(21) 121.8(4)
C(19)-C(20)-H(20A) 119.1
C(21)-C(20)-H(20A) 119.1
C(22)-C(21)-C(20) 119.3(4)
C(22)-C(21)-C(23) 121.0(4)
C(20)-C(21)-C(23) 119.6(3)
C(21)-C(22)-C(17) 121.2(4)
C(21)-C(22)-H(22A) 119.4
C(20)-C(22)-H(22A) 119.4
C(21)-C(23)-H(23A) 109.5
C(21)-C(23)-H(23B) 109.5
H(23A)-C(23)-H(23B) 109.5
C(21)-C(23)-H(23C) 109.5
H(23A)-C(23)-H(23C) 109.5
H(23B)-C(23)-H(23C) 109.5
N(8)-C(24)-N(6) 115.8(3)
N(8)-C(24)-S(2) 121.6(3)
N(6)-C(24)-S(2) 122.6(3)
C(1)-N(1)-N(2) 116.2(3)
C(1)-N(1)-Cu(1) 127.6(3)
N(2)-N(1)-Cu(1) 116.0(2)
C(12)-N(2)-N(1) 119.5(3)
C(12)-N(2)-H(2N) 119.8
N(1)-N(2)-H(2N) 116.2
C(3)-N(3)-C(4) 126.2(3)
C(3)-N(3)-H(3N) 111.7
C(4)-N(3)-H(3N) 122
C(12)-N(4)-H(4M) 114.4
C(12)-N(4)-H(4N) 123.1
H(4M)-N(4)-H(4N) 121
C(13)-N(5)-N(6) 116.0(3)
C(13)-N(5)-Cu(2) 127.6(3)
N(6)-N(5)-Cu(2) 116.4(2)
C(24)-N(6)-N(5) 118.7(3)
C(24)-N(6)-H(6N) 126.6
N(5)-N(6)-H(6N) 109.8
C(15)-N(7)-H(7N) 125.1(3)
C(15)-N(7)-H(7N) 112.1
C(16)-N(7)-H(7N) 122.3
C(24)-N(8)-H(8M) 119
C(24)-N(8)-H(8N) 120.1
H(8M)-N(8)-H(8N) 119.8
O(7)-N(9)-O(8) 119.4(3)
O(7)-N(9)-O(6) 119.8(3)
O(8)-N(9)-O(6) 120.9(3)
O(10)-N(10)-O(11) 120.7(3)
O(10)-N(10)-O(9) 120.2(3)
O(11)-N(10)-O(9) 119.1(3)
O(14)-N(11)-O(13) 120.5(3)
O(14)-N(11)-O(12) 119.2(3)
O(13)-N(11)-O(12) 120.3(3)
| Bond                        | Angle (°) |
|-----------------------------|-----------|
| O(17)-N(12)-O(16)          | 119.8(3)  |
| O(17)-N(12)-O(15)          | 119.8(3)  |
| O(16)-N(12)-O(15)          | 120.4(3)  |
| C(3)-O(1)-Cu(1)            | 129.4(2)  |
| Cu(1)-O(2)-H(2O)           | 113.9     |
| Cu(1)-O(2)-H(2P)           | 119.8     |
| H(2O)-O(2)-H(2P)           | 92.2      |
| C(15)-O(3)-Cu(2)           | 128.0(2)  |
| Cu(2)-O(4)-H(4O)           | 117.7     |
| Cu(2)-O(4)-H(4P)           | 86.2      |
| H(4O)-O(4)-H(4P)           | 100.2     |
| Cu(2)-O(5)-H(5O)           | 94.9      |
| Cu(2)-O(5)-H(5P)           | 91.2      |
| H(5O)-O(5)-H(5P)           | 117       |
| H(18O)-O(18)-H(18P)        | 113.9     |
| H(19O)-O(19)-H(19P)        | 106.2     |
| H(20O)-O(20)-H(20P)        | 99.1      |
Table S11. Anisotropic displacement parameters ($\AA^2 \times 10^3$) for 1. The anisotropic displacement factor exponent takes the form: 

\[-2\pi^2 [h^2 a^4 U_{11} + \ldots + 2hk a b U_{12}^2] \]

|       | U11 | U22 | U33 | U23 | U13 | U12 |
|-------|-----|-----|-----|-----|-----|-----|
| Cu(1) | 14(1)| 10(1)| 20(1)| 6(1)| 5(1)| 1(1) |
| Cu(2) | 15(1)| 10(1)| 20(1)| 6(1)| 5(1)| 0(1)|
|   | O(15) | O(16) | O(17) | O(18) | O(19) | O(20) |
|---|-------|-------|-------|-------|-------|-------|
| O(15) | 21(2) | 15(2) | 36(2) | 12(1) | 13(1) | 1(1) |
| O(16) | 17(2) | 15(2) | 32(2) | 8(1)  | 7(1)  | 7(1) |
| O(17) | 24(2) | 24(2) | 74(2) | 34(2) | 13(2) | 5(1) |
| O(18) | 18(2) | 21(2) | 27(2) | 9(1)  | 2(1)  | −2(1) |
| O(19) | 19(2) | 24(2) | 23(2) | 8(1)  | 4(1)  | −3(1) |
| O(20) | 26(2) | 19(2) | 22(1) | 9(1)  | 5(1)  | 2(1) |
Table S12. Hydrogen coordinates (× 10⁴) and isotropic displacement parameters (Å² × 10³) for 1.

| Hydrogen | x    | y    | z    | U(eq) |
|----------|------|------|------|-------|
| H(1A)    | 8643 | 5362 | 2568 | 17    |
| H(6A)    | 6336 | 6356 | 3336 | 20    |
| H(7A)    | 2464 | 3213 | 4661 | 20    |
| H(8A)    | 873  | 5149 | 5172 | 21    |
| H(10A)   | 3873 | 7471 | 4122 | 20    |
| H(11A)   | 1589 | 8571 | 4905 | 32    |
| H(11B)   | 885  | 7963 | 5821 | 32    |
| H(11C)   | 96   | 7463 | 4457 | 32    |
| H(13A)   | 9294 | 8974 | -772 | 18    |
| H(18A)   | 11599| 9396 | -1469| 15    |
| H(19A)   | 15420| 5184 | -3000| 21    |
| H(20A)   | 17007| 6768 | -3465| 22    |
| H(22A)   | 14089| 9936 | -2228| 19    |
| H(23A)   | 16800| 10470| -2574| 43    |
| H(23B)   | 16398| 9538 | -3961| 43    |
| H(23C)   | 17866| 9165 | -3171| 43    |
| H(2N)    | 10653| 4616 | 1681 | 26    |
| H(3N)    | 4869 | 2187 | 3780 | 21    |
| H(4M)    | 13518| 2491 | 635  | 27    |
| H(4N)    | 13113| 4100 | 1024 | 27    |
| H(6N)    | 7320 | 8872 | -25  | 24    |
| H(7N)    | 13010| 4805 | -2160| 21    |
| H(8M)    | 5014 | 8968 | 830  | 28    |
| H(8N)    | 4372 | 7683 | 1119 | 28    |
| H(2O)    | 9641 | -953 | 2007 | 23    |
| H(2P)    | 8561 | -725 | 2625 | 23    |
| H(4O)    | 8256 | 2995 | -349 | 26    |
| H(4P)    | 9429 | 3911 | 205  | 26    |
| H(5O)    | 7202 | 3567 | -2616| 36    |
| H(5P)    | 8821 | 3784 | -2795| 36    |
| H(18O)   | 7962 | 9471 | 4226 | 33    |
| H(18P)   | 6355 | 9378 | 3705 | 33    |
| H(19O)   | 3438 | -205 | 3327 | 32    |
| H(19P)   | 4012 | 434  | 4500 | 32    |
| H(20O)   | 76   | 1405 | 7359 | 33    |
| H(20P)   | 1456 | 1977 | 7871 | 33    |
Figure S12. 3a, 3b, nitrate counter ions and clathrated, water molecule with the numbering.
Figure S13. ORTEP view of the unit cell of 3.
Figure S14. Molecular Packing of 3.
Figure S15. Molecular Packing of 3.
A suitable crystal (a green block with dimensions 0.08 × 0.06 × 0.04 mm^3) was mounted on a nylon loop and placed in a cold nitrogen stream at 110(2) K on a BRUKER GADDS diffractometer (controlled using the FRAMBO software, v.4.1.05) for the crystal screening, unit cell determination, and data collection. Experimental set up and data collection parameters were as described previously.

Data reduction, structure solution and refinement were carried out as for the previous structure. Statistical tests indicated a centrosymmetric space group (P-1). This choice was later confirmed by the successful refinement.

At the end of the refinement, we noted that the thermal parameters of the O8 and O9 atoms were significantly elongated indicating a possible disorder. However, no model for disorder was found, that could improve the description or the agreement factors significantly.

A clathrated water molecule was found from the Fourier difference maps.

Figure S16. Selected short H-bonding interactions in 3.
| Table S13. Crystal data and structure refinement for 3. |
|--------------------------------------------------------|
| **Empirical formula**                                  | C$_{29}$H$_{40}$Cu$_2$N$_{12}$O$_{17}$S$_2$ |
| **Formula weight**                                     | 1019.93                                      |
| **Temperature**                                        | 110 (2) K                                    |
| **Wavelength**                                         | 1.54178 Å                                    |
| **Crystal system**                                     | Triclinic                                    |
| **Space group**                                        | P$\overline{1}$                              |
| **Unit cell dimensions**                               |                                            |
| $a = 10.3073(5)$ Å                                     | $\alpha = 109.017(4)^{\circ}$               |
| $b = 13.3389(7)$ Å                                     | $\beta = 94.252(4)^{\circ}$                 |
| $c = 15.2916(8)$ Å                                     | $\gamma = 94.665(4)^{\circ}$                |
| **Volume**                                             | 1969.75(17) Å                                |
| **Z**                                                  | 2                                            |
| **Density (calculated)**                               | 1.720 Mg/m3                                  |
| **Absorption coefficient**                             | 3.123 mm$^{-1}$                              |
| **F(000)**                                             | 1048                                         |
| **Crystal size**                                       | 0.08 x 0.06 x 0.04 mm$^3$                    |
| **Theta range for data collection**                    | 3.53 to 59.99$^{\circ}$                     |
| **Index ranges**                                       | $-11 \leq h \leq 11, -14 \leq k \leq 14, -17 \leq l \leq 17$ |
| **Reflections collected**                              | 30628                                        |
| **Independent reflections**                            | 5585 [R(int) = 0.0677]                       |
| **Completeness to theta = 59.99$^{\circ}$**            | 95.50%                                       |
| **Absorption correction**                              | Semi-empirical from equivalents              |
| **Max. and min. transmission**                         | 0.8853 and 0.7882                            |
| **Refinement method**                                  | Full-matrix least-squares on F2              |
| **Data / restraints / parameters**                     | 5585 / 0 / 564                               |
| **Goodness-of-fit on F2**                              | 1.047                                        |
| **Final R indices [I > 2sigma(I)]**                    | R1 = 0.0484, wR2 = 0.1250                    |
| **R indices (all data)**                               | R1 = 0.0630, wR2 = 0.1303                    |
Table S14. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for 3. U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.

|     | x       | y       | z       | U(eq) |
|-----|---------|---------|---------|-------|
| Cu(1)| 1734(1) | 9977(1) | 1706(1) | 15(1) |
| Cu(2)| 6881(1) | 5162(1) | 1839(1) | 16(1) |
| S(1) | 2174(1) | 10912(1)| 3242(1) | 17(1) |
| S(2) | 7330(1) | 5988(1) | 3389(1) | 17(1) |
| C(1) | 4250(4) | 9348(3) | 996(3)  | 14(1) |
| C(2) | 3619(4) | 8804(3) | 65(3)   | 13(1) |
| C(3) | 2231(4) | 8748(3) | −160(3) | 13(1) |
| C(4) | 2483(4) | 7732(3) | −1757(3)| 14(1) |
| C(5) | 3827(4) | 7755(3) | −1550(3)| 17(1) |
| C(6) | 4383(4) | 8304(3) | −619(3) | 17(1) |
| C(7) | 1875(4) | 7212(3) | −2661(3)| 18(1) |
| C(8) | 2639(4) | 6740(3) | −3348(3)| 19(1) |
| C(9) | 4002(4) | 6732(3) | −3171(3)| 19(1) |
| C(10)| 4583(4)| 7240(3) | −2275(3)| 19(1) |
| C(11)| 4780(4)| 6174(3) | −3943(3)| 22(1) |
| C(12)| 3816(4)| 10834(3)| 3293(3) | 16(1) |
| C(13)| 4172(4)| 11834(3)| 4977(3) | 20(1) |
| C(14)| 3686(5)| 11089(4)| 5471(3) | 28(1) |
| C(15)|−1151(4)| 9137(4) | 1011(3) | 32(1) |
| C(16)| 9323(4)| 4463(3) | 1084(3) | 13(1) |
| C(17)| 8648(4)| 3944(3) | 164(3)  | 12(1) |
| C(18)| 7242(4)| 3825(3) | −10(3)  | 16(1) |
| C(19)| 7417(4)| 2814(3) | −1627(3)| 16(1) |
| C(20)| 8778(4)| 2934(3) | −1480(3)| 14(1) |
| C(21)| 9381(4)| 3498(3) | −558(3) | 15(1) |
| C(22)| 6751(4)| 2254(3) | −2516(3)| 20(1) |
| C(23)| 7487(4)| 1803(3) | −3235(3)| 19(1) |
| C(24)| 8865(4)| 1898(3) | −3109(3)| 19(1) |
| C(25)| 9498(4)| 2464(3) | −2241(3)| 18(1) |
| C(26)| 9620(4)| 1335(3) | −3901(3)| 20(1) |
| C(27)| 8961(4)| 5869(3) | 3421(3) | 17(1) |
| C(28)| 9367(4)| 6897(3) | 5095(3) | 18(1) |
| C(29)| 8830(4)| 6197(3) | 5627(3) | 24(1) |
| N(1) | 3638(3)| 9846(2) | 1691(2) | 14(1) |
| N(2) | 4397(3)| 10311(3)| 2532(2) | 16(1) |
| N(3) | 1752(3)| 8237(2) | −1053(2)| 14(1) |
| N(4) | 4609(3)| 11265(3)| 4071(2) | 17(1) |
| N(5) | 1588(3)| 12069(3)| 1268(2) | 23(1) |
| N(6) | 8745(3)| 4914(2) | 1812(2) | 15(1) |
| N(7) | 9518(3)| 5332(2) | 2651(2) | 15(1) |
| N(8) | 6719(3)| 3261(3) | −881(2) | 15(1) |
| N(9) | 9772(3)| 6274(3) | 4195(2) | 16(1) |
| N(10)| 6745(4)| 7347(3) | 1540(3) | 23(1) |
| N(11)| 2961(3)| 5860(3) | 3509(2) | 17(1) |
| N(12)| 2178(3)| 9206(3) | 6622(2) | 17(1) |
| O(1) | 1420(3)| 9132(2) | 403(2)  | 19(1) |
| O(2) | 811(3)| 11396(2)| 1448(2) | 28(1) |
| O(3) | 1222(3)| 12911(3)| 1266(3) | 44(1) |
| O(4) | 2674(3)| 11791(3)| 1048(2) | 39(1) |
| O(5) |−136(3)| 9570(2) | 1802(2) | 23(1) |
| O(6) | 6461(3)| 4191(2) | 582(2)  | 18(1) |
| O(7) | 7453(3)| 6618(2) | 1304(2) | 29(1) |
| O(8) | 6885(6)| 7976(3) | 2334(3) | 91(2) |
| O(9) | 5937(3)| 7473(3) | 967(3)  | 60(1) |
| O(10) | 5068(3) | 5429(2) | 1834(2) | 26(1) |
|-------|--------|--------|--------|------|
| O(11) | 2474(3) | 6262(2) | 4251(2) | 26(1) |
| O(12) | 2250(3) | 5349(2) | 2774(2) | 26(1) |
| O(13) | 4169(3) | 5982(2) | 3502(2) | 21(1) |
| O(14) | 2654(3) | 8794(2) | 5875(2) | 24(1) |
| O(15) | 2920(3) | 9598(2) | 7377(2) | 24(1) |
| O(16) | 972(3)  | 9205(2) | 6623(2) | 24(1) |
| O(17) | 3084(3) | 4271(2) | 710(2)  | 32(1) |
**Table S15. Bond lengths [Å] and angles [°] for 3.**

| Bond                  | Length/Angle [Å/°] |
|-----------------------|--------------------|
| Cu(1)-O(1)            | 1.930(3)           |
| Cu(1)-N(1)            | 1.986(3)           |
| Cu(1)-O(5)            | 1.989(3)           |
| Cu(1)-S(1)            | 2.2632(11)         |
| Cu(1)-O(2)            | 2.318(3)           |
| Cu(2)-O(6)            | 1.929(3)           |
| Cu(2)-O(10)           | 1.931(3)           |
| Cu(2)-N(6)            | 1.977(3)           |
| Cu(2)-S(2)            | 2.2582(11)         |
| Cu(2)-O(7)            | 2.388(3)           |
| S(1)-C(12)            | 1.701(4)           |
| S(2)-C(27)            | 1.700(4)           |
| C(1)-N(1)             | 1.295(5)           |
| C(1)-C(2)             | 1.445(5)           |
| C(1)-H(1A)            | 0.93               |
| C(2)-C(6)             | 1.383(5)           |
| C(2)-C(3)             | 1.437(5)           |
| C(3)-O(1)             | 1.261(4)           |
| C(3)-N(3)             | 1.346(5)           |
| C(4)-N(3)             | 1.382(5)           |
| C(4)-C(5)             | 1.394(6)           |
| C(4)-C(7)             | 1.401(5)           |
| C(5)-C(6)             | 1.422(5)           |
| C(5)-C(10)            | 1.424(6)           |
| C(6)-H(6A)            | 0.93               |
| C(7)-C(8)             | 1.375(6)           |
| C(7)-H(7A)            | 0.93               |
| C(8)-C(9)             | 1.413(6)           |
| C(8)-H(8A)            | 0.93               |
| C(9)-C(10)            | 1.380(6)           |
| C(9)-C(11)            | 1.501(5)           |
| C(10)-H(10A)          | 0.93               |
| C(11)-H(11A)          | 0.96               |
| C(11)-H(11B)          | 0.96               |
| C(11)-H(11C)          | 0.96               |
| C(12)-N(4)            | 1.321(5)           |
| C(12)-N(2)            | 1.358(5)           |
| C(13)-N(4)            | 1.470(5)           |
| C(13)-C(14)           | 1.509(6)           |
| C(13)-H(13A)          | 0.97               |
| C(13)-H(13B)          | 0.97               |
| C(14)-H(14A)          | 0.96               |
| C(14)-H(14B)          | 0.96               |
| C(14)-H(14C)          | 0.96               |
| C(15)-O(5)            | 1.466(5)           |
| C(15)-H(15A)          | 0.96               |
| C(15)-H(15B)          | 0.96               |
| C(15)-H(15C)          | 0.96               |
| C(16)-N(6)            | 1.295(5)           |
| C(16)-C(17)           | 1.444(5)           |
| C(16)-H(16A)          | 0.93               |
| C(17)-C(21)           | 1.382(5)           |
| C(17)-C(18)           | 1.441(5)           |
| C(18)-O(6)            | 1.261(5)           |
| C(18)-N(8)            | 1.344(5)           |
| C(19)-N(8)            | 1.387(5)           |
| Bond                  | Distance (Å) |
|----------------------|--------------|
| C(19)-C(20)          | 1.392(6)     |
| C(19)-C(22)          | 1.411(6)     |
| C(20)-C(25)          | 1.423(5)     |
| C(20)-C(21)          | 1.430(5)     |
| C(21)-H(21A)         | 0.93         |
| C(22)-C(23)          | 1.383(6)     |
| C(22)-H(22A)         | 0.93         |
| C(23)-C(24)          | 1.409(6)     |
| C(23)-H(23A)         | 0.93         |
| C(24)-C(25)          | 1.377(6)     |
| C(24)-C(26)          | 1.510(5)     |
| C(25)-H(25A)         | 0.93         |
| C(26)-H(26A)         | 0.96         |
| C(26)-H(26B)         | 0.96         |
| C(26)-H(26C)         | 0.96         |
| C(27)-N(9)           | 1.325(5)     |
| C(27)-N(7)           | 1.359(5)     |
| C(28)-N(9)           | 1.468(5)     |
| C(28)-C(29)          | 1.522(5)     |
| C(28)-H(28A)         | 0.97         |
| C(28)-H(28B)         | 0.97         |
| C(29)-H(29A)         | 0.96         |
| C(29)-H(29B)         | 0.96         |
| C(29)-H(29C)         | 0.96         |
| N(1)-N(2)            | 1.379(4)     |
| N(2)-H(2N)           | 0.8999       |
| N(3)-H(3N)           | 0.9001       |
| N(4)-H(4N)           | 0.9          |
| N(5)-O(3)            | 1.214(5)     |
| N(5)-O(4)            | 1.244(4)     |
| N(5)-O(2)            | 1.264(4)     |
| N(6)-N(7)            | 1.380(4)     |
| N(7)-H(7N)           | 0.9          |
| N(8)-H(8N)           | 0.9          |
| N(9)-H(9N)           | 0.9          |
| N(10)-O(8)           | 1.219(5)     |
| N(10)-O(9)           | 1.225(5)     |
| N(10)-O(7)           | 1.238(5)     |
| N(11)-O(13)          | 1.243(4)     |
| N(11)-O(11)          | 1.248(4)     |
| N(11)-O(12)          | 1.251(4)     |
| N(12)-O(16)          | 1.243(4)     |
| N(12)-O(14)          | 1.251(4)     |
| N(12)-O(15)          | 1.265(4)     |
| O(5)-H(5O)           | 0.85         |
| O(10)-H(10O)         | 0.85         |
| O(10)-H(10P)         | 0.8501       |
| O(17)-H(17O)         | 0.8499       |
| O(17)-H(17P)         | 0.85         |
| O(1)-Cu(1)-N(1)      | 90.78(12)    |
| O(1)-Cu(1)-O(5)      | 87.45(11)    |
| N(1)-Cu(1)-O(5)      | 157.64(13)   |
| O(1)-Cu(1)-S(1)      | 177.16(9)    |
| N(1)-Cu(1)-S(1)      | 87.04(9)     |
| O(5)-Cu(1)-S(1)      | 93.88(8)     |
| O(1)-Cu(1)-O(2)      | 91.84(11)    |
| N(1)-Cu(1)-O(2)      | 122.28(12)   |
| O(5)-Cu(1)-O(2)      | 80.07(11)    |
| Bond/Structure | Value |
|---------------|-------|
| S(1)-Cu(1)-O(2) | 90.86(8) |
| O(6)-Cu(2)-O(10) | 88.00(12) |
| O(6)-Cu(2)-N(6) | 91.27(12) |
| O(10)-Cu(2)-N(6) | 178.02(12) |
| O(6)-Cu(2)-S(2) | 168.12(9) |
| O(10)-Cu(2)-S(2) | 93.69(9) |
| N(6)-Cu(2)-S(2) | 91.27(12) |
| O(10)-Cu(2)-O(7) | 86.45(12) |
| S(2)-Cu(2)-O(7) | 99.93(8) |
| C(12)-S(1)-Cu(1) | 96.06(14) |
| C(27)-S(2)-Cu(2) | 95.74(14) |
| N(1)-C(1)-C(2) | 123.9(4) |
| N(1)-C(1)-H(1A) | 118.1 |
| C(2)-C(1)-H(1A) | 118.1 |
| C(6)-C(2)-C(3) | 119.6(4) |
| C(6)-C(2)-C(1) | 118.3(4) |
| C(3)-C(2)-C(1) | 122.1(4) |
| O(1)-C(3)-N(3) | 117.1(4) |
| O(1)-C(3)-C(2) | 117.0(4) |
| N(3)-C(3)-C(2) | 118.8(3) |
| N(3)-C(4)-C(5) | 120.2(4) |
| N(3)-C(4)-C(7) | 121.0(4) |
| C(5)-C(4)-C(6) | 118.1(4) |
| C(5)-C(4)-C(10) | 118.9(4) |
| C(6)-C(5)-C(10) | 122.9(4) |
| C(2)-C(6)-H(6A) | 119.4 |
| C(5)-C(6)-H(6A) | 119.4 |
| C(8)-C(7)-C(4) | 118.5(4) |
| C(8)-C(7)-H(7A) | 120.7 |
| C(4)-C(7)-H(7A) | 120.7 |
| C(7)-C(8)-C(9) | 122.6(4) |
| C(7)-C(8)-H(8A) | 118.7 |
| C(9)-C(8)-H(8A) | 118.7 |
| C(10)-C(9)-C(8) | 118.1(4) |
| C(10)-C(9)-C(11) | 121.6(4) |
| C(8)-C(9)-C(11) | 120.3(4) |
| C(9)-C(10)-C(5) | 120.8(4) |
| C(9)-C(10)-H(10A) | 119.6 |
| C(5)-C(10)-H(10A) | 119.6 |
| C(9)-C(11)-H(11A) | 109.5 |
| C(9)-C(11)-H(11B) | 109.5 |
| H(11A)-C(11)-H(11B) | 109.5 |
| C(9)-C(11)-H(11C) | 109.5 |
| H(11A)-C(11)-H(11C) | 109.5 |
| H(11B)-C(11)-H(11C) | 109.5 |
| N(4)-C(12)-N(2) | 115.4(4) |
| N(4)-C(12)-S(1) | 122.8(3) |
| N(2)-C(12)-S(1) | 121.8(3) |
| N(4)-C(13)-C(14) | 112.6(3) |
| N(4)-C(13)-H(13A) | 109.1 |
| C(14)-C(13)-H(13A) | 109.1 |
| N(4)-C(13)-H(13B) | 109.1 |
| C(14)-C(13)-H(13B) | 109.1 |
| H(13A)-C(13)-H(13B) | 107.8 |
C(13)-C(14)-H(14A) 109.5
C(13)-C(14)-H(14B) 109.5
H(14A)-C(14)-H(14B) 109.5
C(13)-C(14)-H(14C) 109.5
H(14A)-C(14)-H(14C) 109.5
H(14B)-C(14)-H(14C) 109.5
O(5)-C(15)-H(15A) 109.5
O(5)-C(15)-H(15B) 109.5
H(15A)-C(15)-H(15B) 109.5
O(5)-C(15)-H(15C) 109.5
H(15A)-C(15)-H(15C) 109.5
H(15B)-C(15)-H(15C) 109.5
N(6)-C(16)-C(17) 124.0(4)
N(6)-C(16)-H(16A) 118
C(17)-C(16)-H(16A) 118
C(21)-C(17)-C(18) 119.5(4)
C(21)-C(17)-C(16) 118.4(4)
C(18)-C(17)-C(16) 122.0(4)
O(6)-C(18)-N(8) 117.3(4)
O(6)-C(18)-C(17) 126.0(4)
N(8)-C(18)-C(17) 116.7(4)
N(8)-C(19)-C(20) 118.7(3)
N(8)-C(19)-C(22) 120.2(4)
C(20)-C(19)-C(22) 121.1(4)
C(19)-C(20)-C(25) 118.9(4)
C(19)-C(20)-C(21) 117.8(4)
C(25)-C(20)-C(21) 123.3(4)
C(17)-C(21)-C(20) 121.6(4)
C(17)-C(21)-H(21A) 119.2
C(20)-C(21)-H(21A) 119.2
C(23)-C(22)-C(19) 118.2(4)
C(23)-C(22)-H(22A) 120.9
C(19)-C(22)-H(22A) 120.9
C(22)-C(23)-C(24) 122.2(4)
C(22)-C(23)-H(23A) 118.9
C(24)-C(23)-H(23A) 118.9
C(25)-C(24)-C(23) 118.8(4)
C(25)-C(24)-C(26) 121.0(4)
C(23)-C(24)-C(26) 120.2(4)
C(24)-C(25)-C(20) 120.8(4)
C(24)-C(25)-H(25A) 119.6
C(20)-C(25)-H(25A) 119.6
C(24)-C(26)-H(26A) 109.5
C(24)-C(26)-H(26B) 109.5
H(26A)-C(26)-H(26B) 109.5
C(24)-C(26)-H(26C) 109.5
H(26A)-C(26)-H(26C) 109.5
H(26B)-C(26)-H(26C) 109.5
N(9)-C(27)-N(7) 115.3(4)
N(9)-C(27)-S(2) 122.7(3)
N(7)-C(27)-S(2) 121.9(3)
N(9)-C(28)-C(29) 112.7(3)
N(9)-C(28)-H(28A) 109.1
C(29)-C(28)-H(28A) 109.1
N(9)-C(28)-H(28B) 109.1
C(29)-C(28)-H(28B) 109.1
H(28A)-C(28)-H(28B) 107.8
C(28)-C(29)-H(29A) 109.5
| Bond                  | Angle (°) |
|----------------------|-----------|
| C(28)-C(29)-H(29B)  | 109.5     |
| H(29A)-C(29)-H(29B) | 109.5     |
| C(28)-C(29)-H(29C)  | 109.5     |
| H(29A)-C(29)-H(29C) | 109.5     |
| H(29B)-C(29)-H(29C) | 109.5     |
| C(1)-N(1)-N(2)      | 115.9(3)  |
| C(1)-N(1)-Cu(1)     | 128.0(3)  |
| N(2)-N(1)-Cu(1)     | 116.1(2)  |
| C(12)-N(2)-N(1)     | 119.0(3)  |
| C(12)-N(2)-H(2N)    | 116       |
| N(1)-N(2)-H(2N)     | 124.9     |
| C(3)-N(3)-C(4)      | 125.2(3)  |
| C(3)-N(3)-H(3N)     | 112.8     |
| C(4)-N(3)-H(3N)     | 121.8     |
| C(12)-N(4)-C(13)    | 124.0(4)  |
| C(12)-N(4)-H(4N)    | 116.4     |
| C(13)-N(4)-H(4N)    | 119.6     |
| O(3)-N(5)-O(4)      | 123.7(4)  |
| O(3)-N(5)-O(2)      | 119.5(4)  |
| O(4)-N(5)-O(2)      | 116.7(4)  |
| C(16)-N(6)-N(7)     | 117.1(3)  |
| C(16)-N(6)-Cu(2)    | 126.8(3)  |
| N(7)-N(6)-Cu(2)     | 115.9(2)  |
| C(27)-N(7)-N(6)     | 118.8(3)  |
| C(27)-N(7)-H(7N)    | 127.4     |
| N(6)-N(7)-H(7N)     | 113.6     |
| C(18)-N(8)-C(19)    | 125.6(3)  |
| C(18)-N(8)-H(8N)    | 118.1     |
| C(19)-N(8)-H(8N)    | 116.3     |
| C(27)-N(9)-C(28)    | 123.7(3)  |
| C(27)-N(9)-H(9N)    | 109.7     |
| C(28)-N(9)-H(9N)    | 126.2     |
| O(8)-N(10)-O(9)     | 119.3(5)  |
| O(8)-N(10)-O(7)     | 120.5(4)  |
| O(9)-N(10)-O(7)     | 120.2(4)  |
| O(13)-N(11)-O(11)   | 119.4(3)  |
| O(13)-N(11)-O(12)   | 119.8(3)  |
| O(11)-N(11)-O(12)   | 120.8(3)  |
| O(16)-N(12)-O(14)   | 119.8(3)  |
| O(16)-N(12)-O(15)   | 120.2(3)  |
| O(14)-N(12)-O(15)   | 120.0(3)  |
| C(3)-O(1)-Cu(1)     | 129.2(3)  |
| N(5)-O(2)-Cu(1)     | 115.9(3)  |
| C(15)-O(5)-Cu(1)    | 124.9(2)  |
| C(15)-O(5)-H(5O)    | 113.5     |
| Cu(1)-O(5)-H(5O)    | 114.1     |
| C(18)-O(6)-Cu(2)    | 127.8(3)  |
| N(10)-O(7)-Cu(2)    | 114.0(2)  |
| Cu(2)-O(10)-H(10O)  | 127.2     |
| Cu(2)-O(10)-H(10P)  | 118.9     |
| H(10O)-O(10)-H(10P) | 109.4     |
| H(17O)-O(17)-H(17P) | 99.9      |
Table S16. Anisotropic displacement parameters (Å$^2 \times 10^3$) for 3. The anisotropic displacement factor exponent takes the form: $-2\pi^2 \left[ h^2 a^* U_{11} + \ldots + 2 h k a \cdot b \cdot U_{12} \right]$.

|       | U11  | U22  | U33  | U23  | U13  | U12  |
|-------|------|------|------|------|------|------|
| Cu(1) | 10(1)| 21(1)| 14(1)| 5(1) | 1(1) | 4(1) |
| Cu(2) | 10(1)| 21(1)| 17(1)| 7(1) | 2(1) | 4(1) |
| S(1)  | 10(1)| 22(1)| 18(1)| 4(1) | 2(1) | 6(1) |
| S(2)  | 12(1)| 21(1)| 18(1)| 5(1) | 2(1) | 5(1) |
| C(1)  | 12(2)| 14(2)| 15(2)| 6(2) | −3(2)| 1(2) |
| C(2)  | 12(2)| 15(2)| 15(2)| 8(2) | −1(2)| 2(2) |
| C(3)  | 13(2)| 11(2)| 17(2)| 7(2) | 2(2) | 1(2) |
| C(4)  | 17(2)| 11(2)| 14(2)| 5(2) | 2(2) | 2(2) |
| C(5)  | 17(2)| 19(2)| 18(2)| 10(2)| 4(2) | 0(2) |
| C(6)  | 16(2)| 18(2)| 19(2)| 8(2) | 2(2) | 2(2) |
| C(7)  | 14(2)| 21(2)| 22(2)| 10(2)| −1(2)| 1(2) |
| C(8)  | 24(3)| 19(2)| 13(2)| 6(2) | −4(2)| 2(2) |
| C(9)  | 22(3)| 18(2)| 17(2)| 6(2) | 2(2) | 1(2) |
| C(10)| 14(2)| 23(2)| 19(2)| 6(2) | 5(2) | 1(2) |
| C(11)| 25(3)| 20(2)| 16(2)| 0(2) | 3(2) | 0(2) |
| C(12)| 15(2)| 18(2)| 17(2)| 8(2) | 2(2) | 3(2) |
| C(13)| 16(2)| 24(2)| 12(2)| −2(2)| −1(2)| 2(2) |
| C(14)| 33(3)| 33(3)| 20(3)| 8(2) | 10(2)| 7(2) |
| C(15)| 31(3)| 33(3)| 29(3)| 7(2) | 4(2) | 0(2) |
| C(16)| 10(2)| 8(2) | 20(2)| 4(2) | 1(2) | 0(2) |
| C(17)| 13(2)| 12(2)| 17(2)| 11(2)| 1(2) | 3(2) |
| C(18)| 15(2)| 15(2)| 23(2)| 12(2)| 1(2) | 3(2) |
| C(19)| 18(2)| 15(2)| 19(2)| 8(2) | 0(2) | 4(2) |
| C(20)| 14(2)| 13(2)| 19(2)| 10(2)| −1(2)| −2(2)|
| C(21)| 14(2)| 13(2)| 23(2)| 11(2)| −1(2)| 1(2) |
| C(22)| 16(2)| 22(2)| 22(2)| 10(2)| 1(2) | 0(2) |
| C(23)| 22(3)| 13(2)| 21(2)| 7(2) | −4(2)| 5(2) |
| C(24)| 25(3)| 18(2)| 15(2)| 10(2)| 3(2) | 0(2) |
| C(25)| 17(2)| 21(2)| 20(2)| 11(2)| 4(2) | 1(2) |
| C(26)| 24(3)| 21(2)| 18(2)| 7(2) | 4(2) | 2(2) |
| C(27)| 16(2)| 15(2)| 23(2)| 10(2)| 6(2) | 0(2) |
| C(28)| 17(2)| 26(2)| 9(2) | 2(2) | 0(2) | 2(2) |
| C(29)| 24(3)| 26(3)| 23(2)| 9(2) | 4(2) | 4(2) |
| N(1) | 14(2)| 16(2)| 11(2)| 5(2) | −1(2)| −2(2) |
| N(2) | 10(2)| 22(2)| 11(2)| −1(2)| −1(1)| 1(2) |
| N(3) | 7(2) | 20(2)| 15(2)| 4(2) | 1(2) | 0(2) |
| N(4) | 15(2)| 21(2)| 15(2)| 4(2) | 1(2) | 5(2) |
| N(5) | 7(2) | 35(3)| 32(2)| 19(2)| 1(2) | 0(2) |
| N(6) | 15(2)| 13(2)| 15(2)| 5(2) | −1(2)| −2(2)|
| N(7) | 10(2)| 19(2)| 12(2)| 1(2) | 0(1) | 1(2) |
| N(8) | 6(2) | 19(2)| 19(2)| 6(2) | −2(2)| 0(2) |
| N(9) | 9(2) | 23(2)| 13(2)| 3(2) | 2(2) | 2(2) |
| N(10)| 17(2)| 30(2)| 28(2)| 16(2)| 8(2) | 1(2) |
| N(11)| 16(2)| 17(2)| 18(2)| 6(2) | 0(2) | 1(2) |
| N(12)| 19(2)| 15(2)| 19(2)| 7(2) | 0(2) | 3(2) |
| O(1) | 12(2)| 26(2)| 18(2)| 4(1) | 5(1) | 5(1) |
| O(2) | 23(2)| 29(2)| 33(2)| 13(2)| −2(1)| 2(2) |
| O(3) | 34(2)| 27(2)| 79(3)| 27(2)| 0(2) | 6(2) |
| O(4) | 19(2)| 53(2)| 43(2)| 16(2)| 0(2) | 4(2) |
| O(5) | 13(2)| 34(2)| 17(2)| 3(1) | 2(1) | 1(1) |
| O(6) | 9(2) | 23(2)| 22(2)| 6(1) | 3(1) | 2(1) |
| O(7) | 21(2)| 32(2)| 40(2)| 18(2)| 7(2) | 9(2) |
| O(8) | 197(6)| 44(3)| 36(3)| 112(2)| 46(3)| 22(3) |
| O(9) | 17(2)| 83(3)| 110(3)| 77(3)| −11(2)| 2(2) |
| O(10) | 14(2) | 38(2) | 21(2) | 4(1) | 2(1) | 5(2) |
|-------|-------|-------|-------|------|------|------|
| O(11) | 15(2) | 44(2) | 17(2) | 8(1) | 3(1) | 2(2) |
| O(12) | 18(2) | 32(2) | 20(2) | -1(1) | 0(1) | 0(2) |
| O(13) | 11(2) | 30(2) | 18(2) | 3(1) | 0(1) | 1(1) |
| O(14) | 16(2) | 40(2) | 16(2) | 8(1) | 3(1) | 5(2) |
| O(15) | 17(2) | 28(2) | 20(2) | 0(1) | 0(1) | -1(1) |
| O(16) | 7(2)  | 34(2) | 26(2) | 2(1) | 0(1) | 4(1) |
| O(17) | 33(2) | 32(2) | 25(2) | 7(1) | 1(2) | -11(2)|
**Table S17.** Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 3.

|       | x    | y    | z    | U(eq) |
|-------|------|------|------|-------|
| H(1A) | 5149 | 9340 | 1102 | 17    |
| H(6A) | 5278 | 8326 | −467 | 21    |
| H(7A) | 975  | 7186 | −2795| 22    |
| H(8A) | 2242 | 6413 | −3953| 23    |
| H(10A)| 5479 | 7245 | −2142| 23    |
| H(11A)| 5695 | 6404 | −3756| 32    |
| H(11B)| 4519 | 6345 | −4489| 32    |
| H(11C)| 4623 | 5417 | −4078| 32    |
| H(13A)| 3475 | 12248| 4884 | 24    |
| H(13B)| 4894 | 12327| 5366 | 24    |
| H(14A)| 3416 | 11497| 6058 | 43    |
| H(14B)| 4376 | 10686| 5575 | 43    |
| H(14C)| 2956 | 10610| 5096 | 43    |
| H(15A)| −1999| 9190 | 1232 | 48    |
| H(15B)| −1054| 8403 | 689  | 48    |
| H(15C)| −1063| 9537 | 594  | 48    |
| H(16A)| 10229| 4475 | 1158 | 15    |
| H(21A)| 10288| 3567 | −440 | 18    |
| H(22A)| 5843 | 2191 | −2615| 24    |
| H(23A)| 7057 | 1423 | −3821| 22    |
| H(25A)| 10408| 2540 | −2151| 22    |
| H(26A)| 10521| 1633 | −3765| 31    |
| H(26B)| 9257 | 1424 | −4464| 31    |
| H(26C)| 9562 | 588  | −3977| 31    |
| H(28A)| 8700 | 7331 | 4991 | 22    |
| H(28B)| 10112| 7374 | 5470 | 22    |
| H(29A)| 8542 | 6638 | 6195 | 36    |
| H(29B)| 9505 | 5801 | 5769 | 36    |
| H(29C)| 8106 | 5711 | 5254 | 36    |
| H(2N) | 5260 | 10253| 2525 | 23    |
| H(3N) | 874  | 8196 | −1143| 22    |
| H(4N) | 5465 | 11192| 4027 | 26    |
| H(7N) | 10371| 5251 | 2606 | 22    |
| H(8N) | 5841 | 3161 | −1000| 23    |
| H(9N) | 10600| 6176 | 4065 | 23    |
| H(10O)| −421 | 9949 | 2297 | 34    |
| H(10P)| 4443 | 5105 | 1417 | 39    |
| H(17O)| 2646 | 3860 | 931  | 48    |
| H(17P)| 3097 | 3853 | 137  | 48    |
Table S18. Cytotoxicity in A375 cancer cells.

| Compounds   | 12 h  | 24 h  | 48 h  | 72 h  |
|-------------|-------|-------|-------|-------|
| cisplatin   | 21.2 ± 4.3 | 8.3 ± 2.1 | 3.3 ± 0.7 | 1.3 ± 0.6 |
| 1           | 19.3 ± 3.6 | 5.5 ± 2.1 | 1.1 ± 0.4 | 0.6 ± 0.2 |
| 2           | 5.3 ± 1.1   | 2.5 ± 0.6   | 0.6 ± 0.1   | 0.027 ± 0.005 |
| 3           | 7.1 ± 1.9   | 3.0 ± 0.8   | 0.7 ± 0.1   | 0.031 ± 0.001 |
| cisplatin   | 21.2 ± 4.3 | 8.3 ± 2.1 | 3.3 ± 0.7 | 1.3 ± 0.6 |

IC₅₀ values were calculated by four parameter logistic model (p < 0.05). Cells (5 × 10^3·mL⁻¹) were treated for 12, 24, 48 and 72 h with increasing concentrations of tested compounds dissolved in DMSO. Cytotoxicity was assessed by MTT test. S.D. = standard deviation. Cells (5·10³·mL⁻¹) were treated for 12, 24, 48 and 72 h with increasing concentrations of tested compounds dissolved in DMSO. Cytotoxicity was assessed by MTT test.

Figure S17. Dose-response curves for cell viability assessed in A375 cells.