Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

An unprecedented octanuclear copper core with C_{3i} symmetry and a paramagnetic ground state

Dmytro S. Nesterov,[a] Julia Jezierska,[b] Oksana V. Nesterova,[a] Armando J. L. Pombeiro*[a] and Andrew Ozarowski*[c]

[a] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisbon, Portugal. Fax: +351 218464455; E-mail: pombeiro@tecnico.ulisboa.pt*

[b] *Faculty of Chemistry, University of Wroclaw, 14 Joliot-Curie Str., 50-383, Wroclaw, Poland*

[c] *National High Magnetic Field Laboratory, Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, Florida 32310, USA. Fax: 850-644-1366; E-mail: ozarowsk@magnet.fsu.edu*

Experimental Section

All chemicals were of reagent grade and used as received. All experiments were carried out in air. Elemental analyses for CHN and for metals (atomic absorption spectroscopy) were performed by the Microanalytical Service of the Instituto Superior Técnico.

Synthesis of $[Cu_8O(tbDea)_6(H_2O)_2](BF_4)_2\cdot 3CH_3OH$ (**1**·$3CH_3OH$)

Copper tetrafluoroborate hydrate (0.59 g; 2.5 mmol, calculated for anhydrous basis) and N-*tert*-butyldiethanolamine (0.81 g, 5 mmol) in CH_3OH (20 mL) were heated to 50–60° and stirred magnetically (2 h). A blue powder of **1** starts to precipitate after 30 min. After 2 h the resulting mixture was filtered. Dark blue crystals of **1** suitable for X-ray analysis grew after a few days. They were filtered off, washed with CH_3OH and finally dried *in vacuo* at room temperature. Yield: 0.26 g, 47% (per copper). $C_{51}H_{118}B_2Cu_8F_8N_6O_{18}$ (M = 1785.52). Calcd.: C, 34.31; H, 6.66; N, 4.71. Found: C, 34.3; H, 6.8; N, 4.7% (data for crystalline sample).

Details of the single-crystal X-ray diffraction analysis and refinement for **1**·$3CH_3OH$

The X-ray diffraction data for **1** were collected using a Bruker AXS KAPPA APEX II diffractometer with graphite-monochromated Mo-Kα radiation. Data were collected using omega scans of 0.5° per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections. Absorption corrections were applied using SADABS.[S1] The structure was solved by direct methods and refined against F^2 using the program SHELXL-97.[S2] Methanol molecule is disordered over two positions, each with 0.5 occupation. The positions of the H(103) and H(203) hydrogen atoms of the coordinated water molecule were calculated on the basis of geometry and force-field considerations using CALC-OH program[S3] within WinGX package[S4] and refined using a riding model. All the other hydrogen atoms were placed at calculated positions and refined the same model with Uiso = nUeq (n = 1.5 for H atoms of methyl group and water H atoms, and n = 1.2 for other H atoms). The OH hydrogen atom from the uncoordinated methanol molecule (O5, C9) was not localized.

Magnetic measurements

Magnetic susceptibility data of a powdered sample of **1**·$3CH_3OH$ were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8−300 K at a magnetic induction of 0.5 T. Corrections for the sample holders were applied. Diamagnetic corrections for the molecules were determined from Pascal's constants.[S5]

High Field EPR Spectroscopy.

High-frequency EPR spectra were recorded with a home-built spectrometer at the EMR facility of NHMFL.[S6] The instrument is a transmission-type device in which waves are propagated in cylindrical light-pipes. The microwaves were generated by a phase-locked oscillator (Virginia Diodes) operating at a frequency of 13±1 GHz and generating its harmonics, of which the 4th, 8th, 12th, 16th, 24th and 32nd were available. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed.

Thermogravimetric measurements

A Perkin-Elmer STA-6000 model thermogravimetric analyzer was used for determination of the thermal stability of complex **1**·$3CH_3OH$. Samples weighing 5–30 mg were heated from 30 to 1000 °C at a heating rate of 1–50 °C min^{-1} at open air.

Electrospray-ionization mass spectrometry

ESI-MS(+) spectra were run on a 500-MS LC Ion Trap instrument (Varian Inc, Alto Palo, CA, USA) equipped with an electrospray (ESI) ion source, using *ca.* 10^{-3} M solutions of **1**·$3CH_3OH$ in water or methanol. The theoretical patterns of the isotopic distributions were calculated using IsoPro 3.1 software (available at http://sites.google.com/site/isoproms/).

Table S1. Selected bond lengths (Å) and angles (°) for **1**·3CH$_3$OH^a

Cu(1)–O(1)	1.907(5)	Cu(2)–O(4)	1.8418(16)
Cu(1)–O(1^a)	1.897(5)	Cu(2)–O(3)	1.869(9)
Cu(1)–N(1)	2.138(6)	Cu(2)–O(2)	2.100(5)
Cu(1)–O(2)	2.380(5)		
Cu(1)–O(2^b)	2.005(5)		
O(1)–Cu(1)–O(1^a)	176.63(15)	N(1)–Cu(1)–O(2)	79.8(2)
O(1^a)–Cu(1)–O(2^b)	94.6(2)	N(1)–Cu(1)–O(2^b)	166.1(2)
O(1)–Cu(1)–O(2^b)	87.3(2)	O(2)–Cu(1)–O(1^a)	77.40(19
N(1)–Cu(1)–O(1^a)	94.7(2)	O(1)–Cu(1)–O(2)	99.30(19)
N(1)–Cu(1)–O(1)	84.0(2)	O(2)–Cu(1)–O(2^b)	112.3(2)
O(4)–Cu(2)–O(2)	80.68(14)	O(2)–Cu(2)–O(2^c)	117.43(7)
O(3)–Cu(2)–O(2)	99.32(14)		

[a] Symmetry transformation used to generate equivalent atoms: ^{a} 1/3+y, 2/3-x+y, 2/3–z; ^{b} 1/3+x–y, –1/3+x, 2/3–z; ^{c} 1–y, x–y, z.

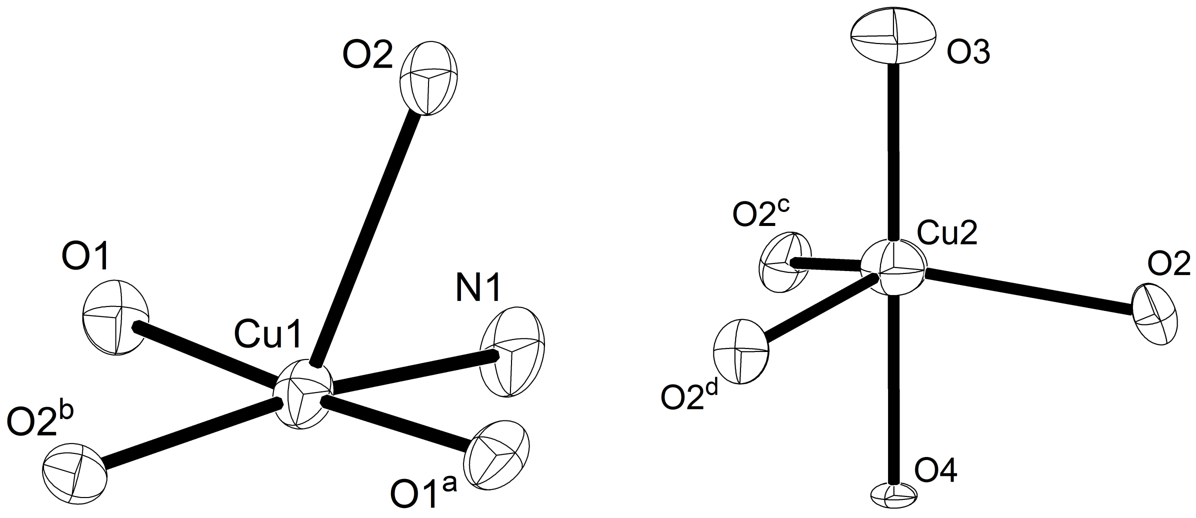

Figure S1. Plots of the coordination environments of independent copper atoms in the crystal structure of the dication of **1**. Thermal ellipsoids are shown at 50% level. Symmetry transformation used to generate equivalent atoms: ^{a} 1/3+y, 2/3-x+y, 2/3–z; ^{b} 1/3+x–y, –1/3+x, 2/3–z; ^{c} 1–y, x–y, z.

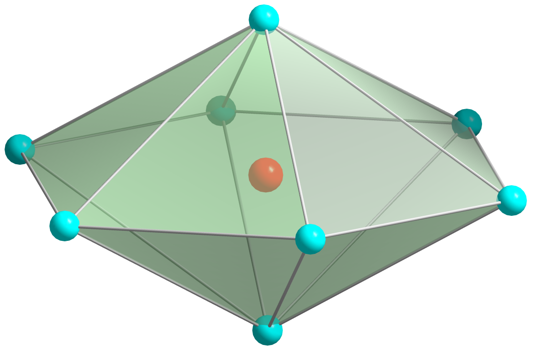

Figure S2. Polyhedron (a compressed hexagonal bipyramid) with the volume of 28.7 Å^3 formed by eight copper atoms in the dication of **1**. Central oxygen atom is shown by red colour.

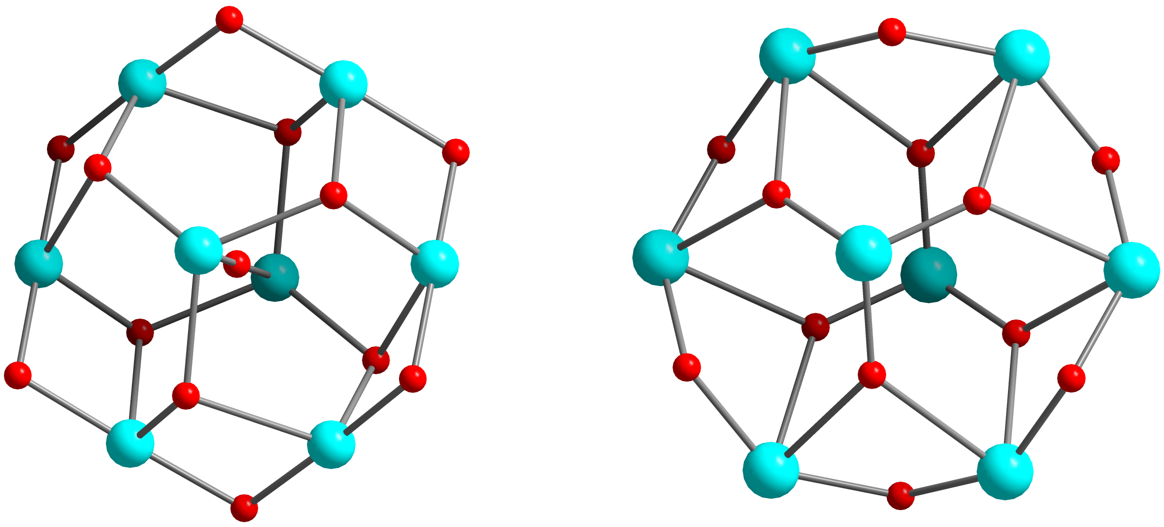

Figure S3. Comparison of the molecular structure types (MSTs) of the dication of **1**, $M_8(\mu_3\text{-}X)_6(\mu\text{-}X)_7$ (left) and typical octanuclear MST $M_8(\mu_3\text{-}X)_6(\mu\text{-}X)_6$ (right). The only difference is the central μ-X bridging atom, observed in **1**.

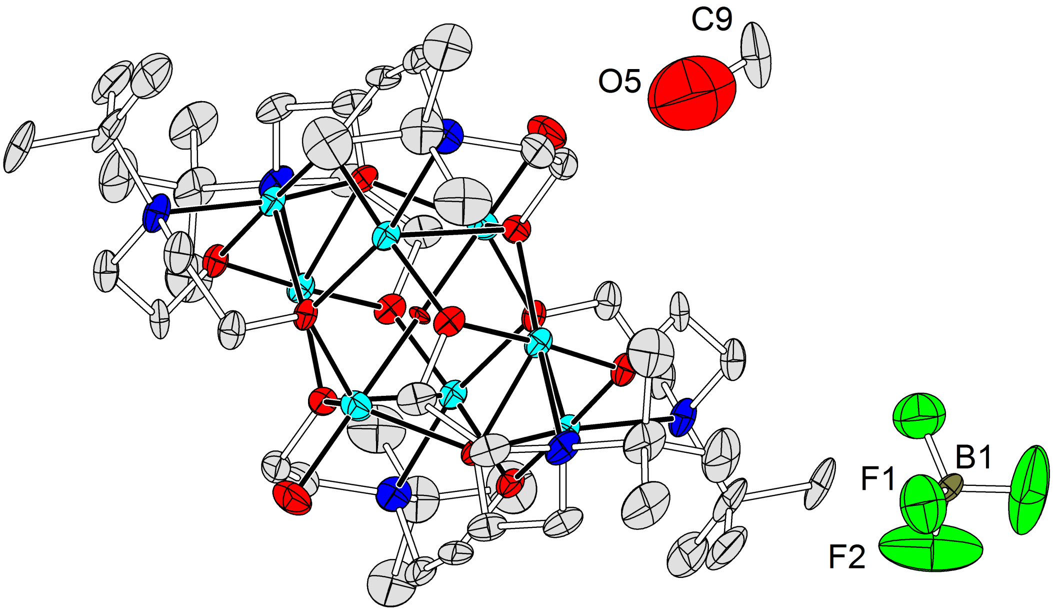

Figure S4. The crystal structure of **1**·$3CH_3OH$ showing the uncoordinated BF_4^- anion and a methanol molecule.

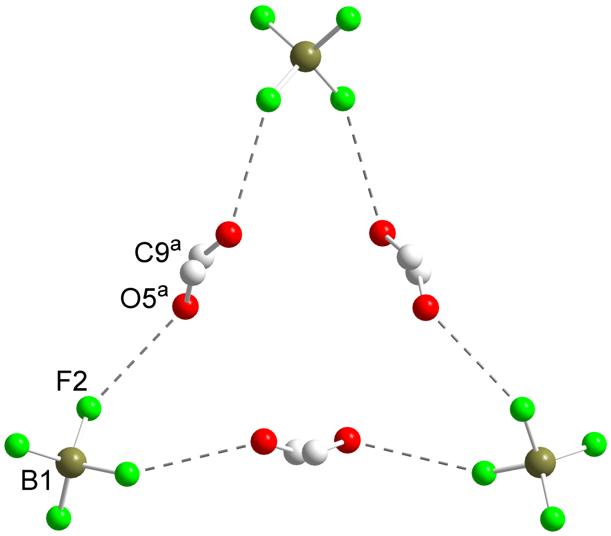

Figure S5. Hydrogen bonding scheme in the crystal structure of **1**·3CH_3OH. d(F2···O5^a) = 2.69 Å (^{a} 4/3–x+y, –1/3+y, 5/3+z). Methanol molecule is disordered over two positions, each with 0.5 occupation.

The differential thermal analysis curve of compound **1**·3CH_3OH reveals few decomposition steps over the 40–700 °C temperature range (Fig. S4). The first one involves the elimination of the solvated methanol (stage 1; 40–180 °C; calculated and observed mass residues are 94.8 and 95.4%, respectively). A sharp variation of the weight at the 185–190 °C range (stage 2) can be associated with the decomposition and elimination of uncoordinated BF_4^- anions (calculated mass residue is 85.0%). A broad weight loss in the 190–600 °C region reveals the decomposition of the organic ligand, resulting in an oxide material, CuO (stage 3; calculated and observed mass residues are 35.7 and 35.3%, respectively). In general, the thermal behaviour of **1**·3CH_3OH exhibits an oxidative character being typical for other copper complexes with resembling ligands.[S7]

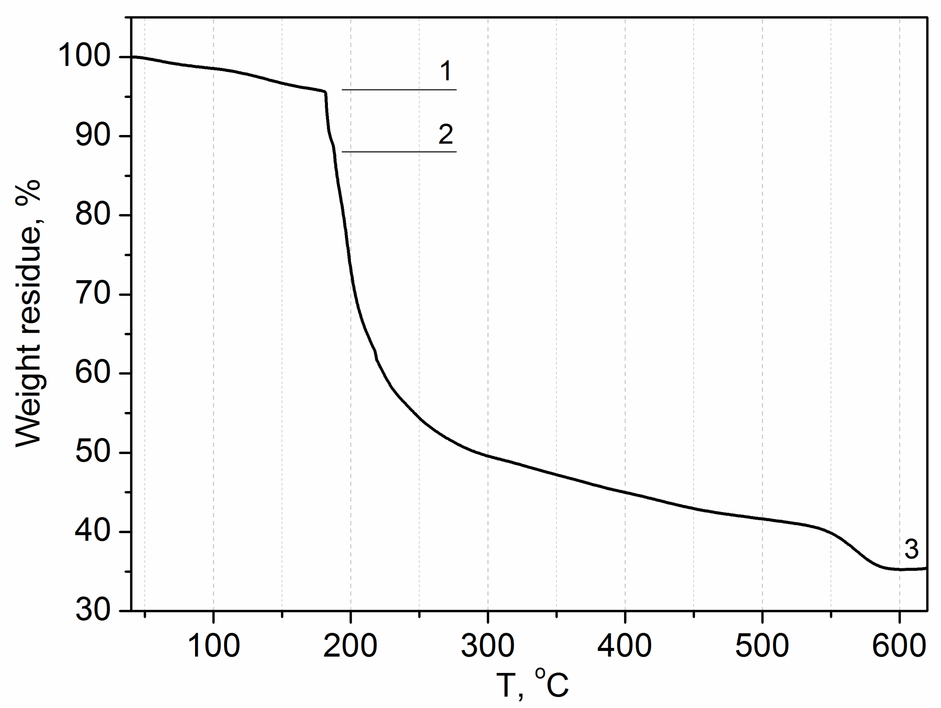

Figure S6. Thermogravimetric plot showing the loss in weight with the increase of temperature for complex **1**·3CH_3OH at 10° / min heating speed (air atmosphere).

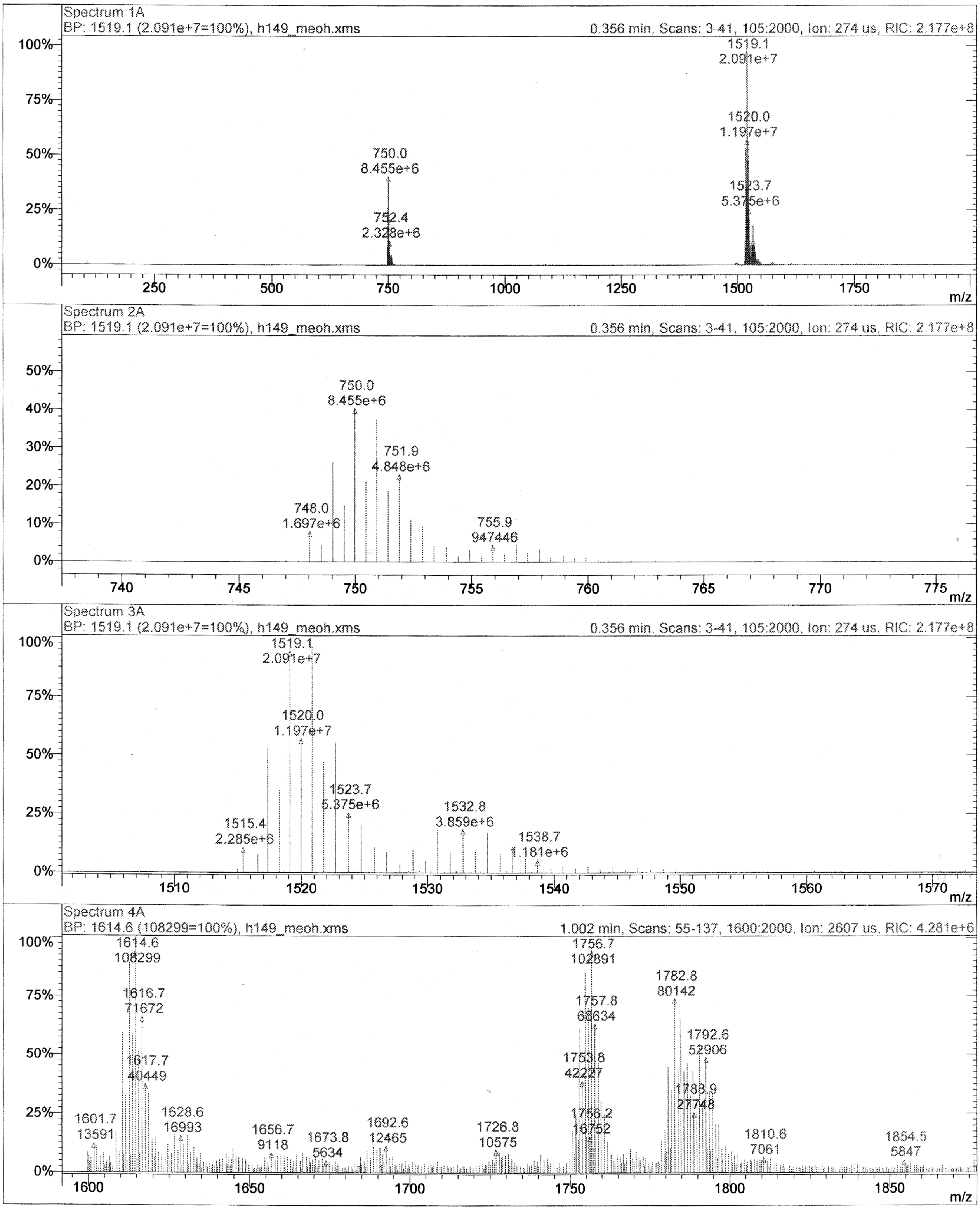

Figure S7. ESI-MS spectra of a methanol solution of **1**·3CH_3OH.

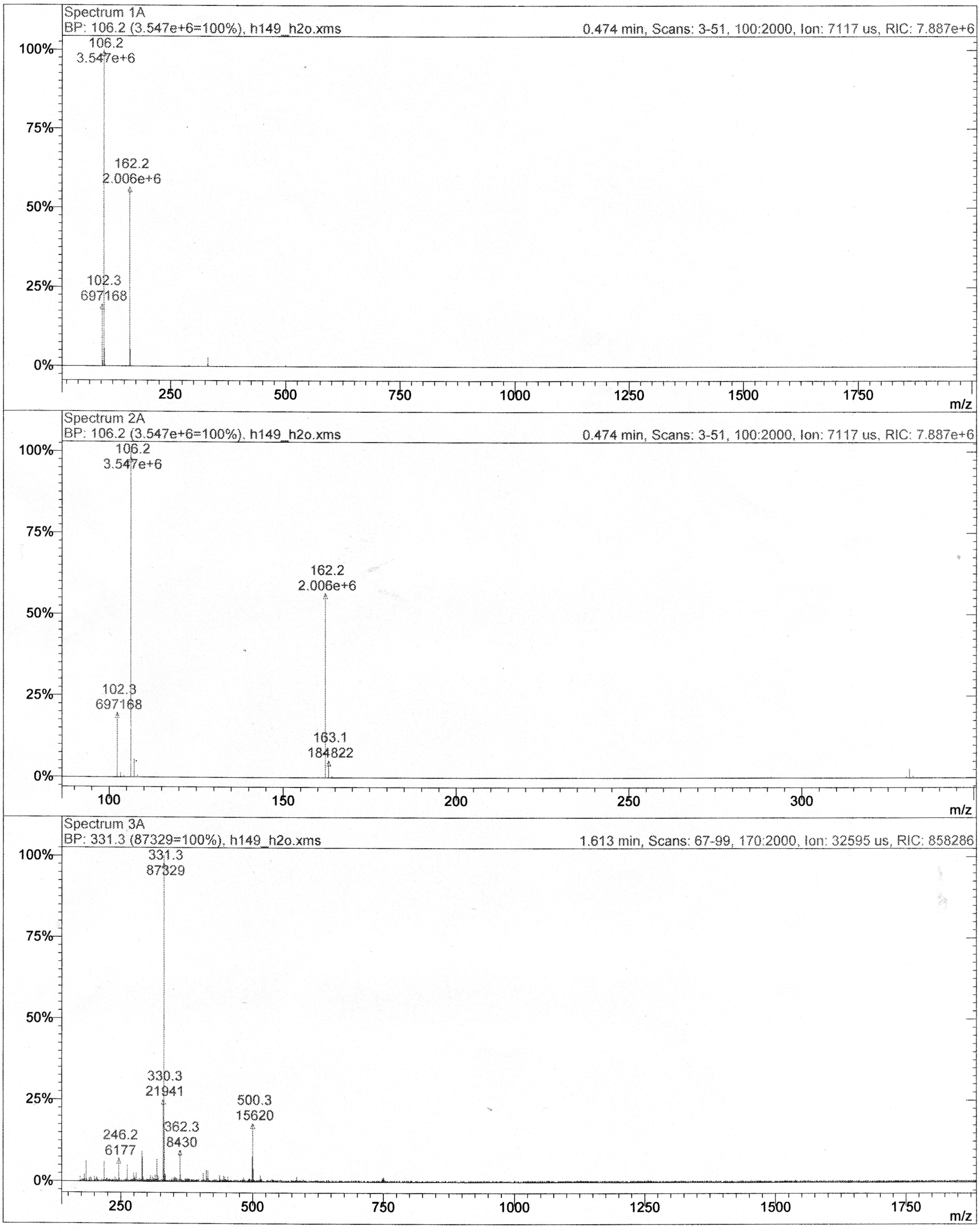

Figure S8. ESI-MS spectra of a water solution of **1**·3CH$_3$OH.

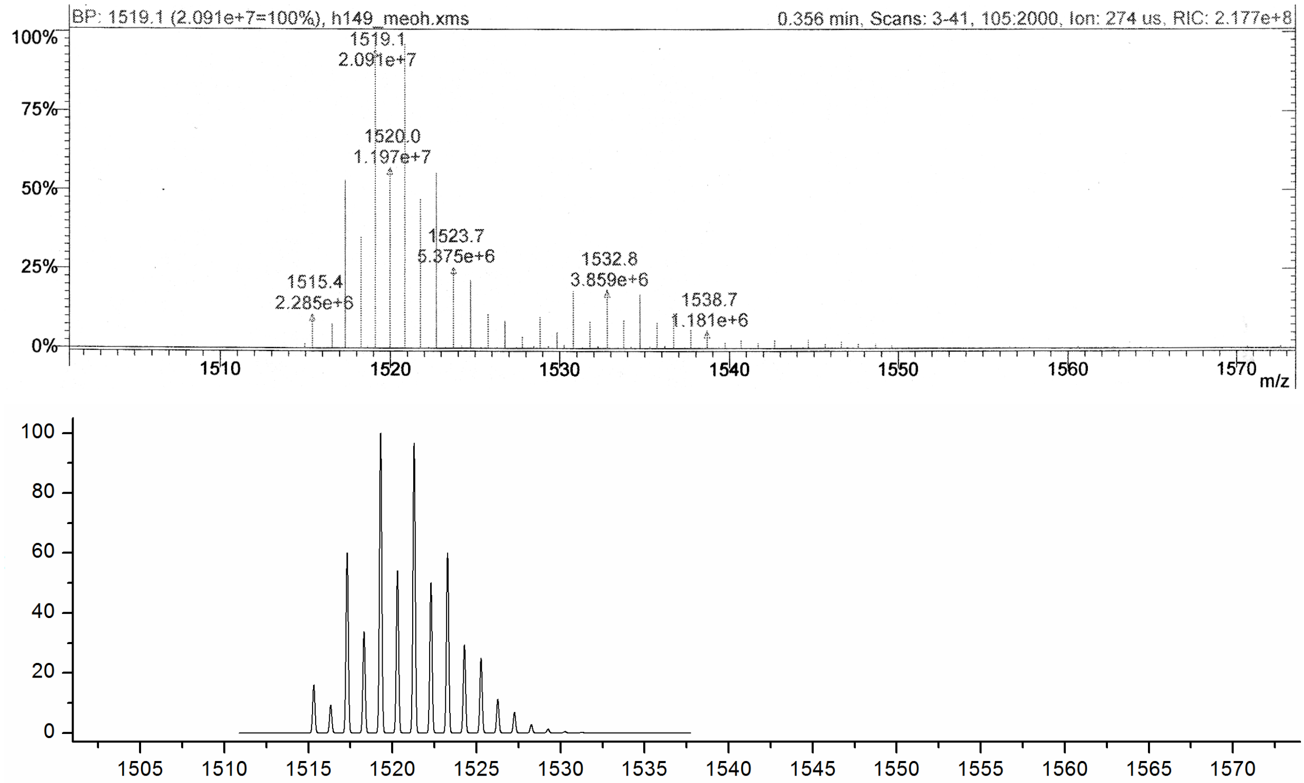

Figure S11. Observed in methanol (top) and calculated (bottom) isotopic distribution patterns for $\{[Cu_8O(tbDea)_6(H_2O)_2] + 5H\}^+$.

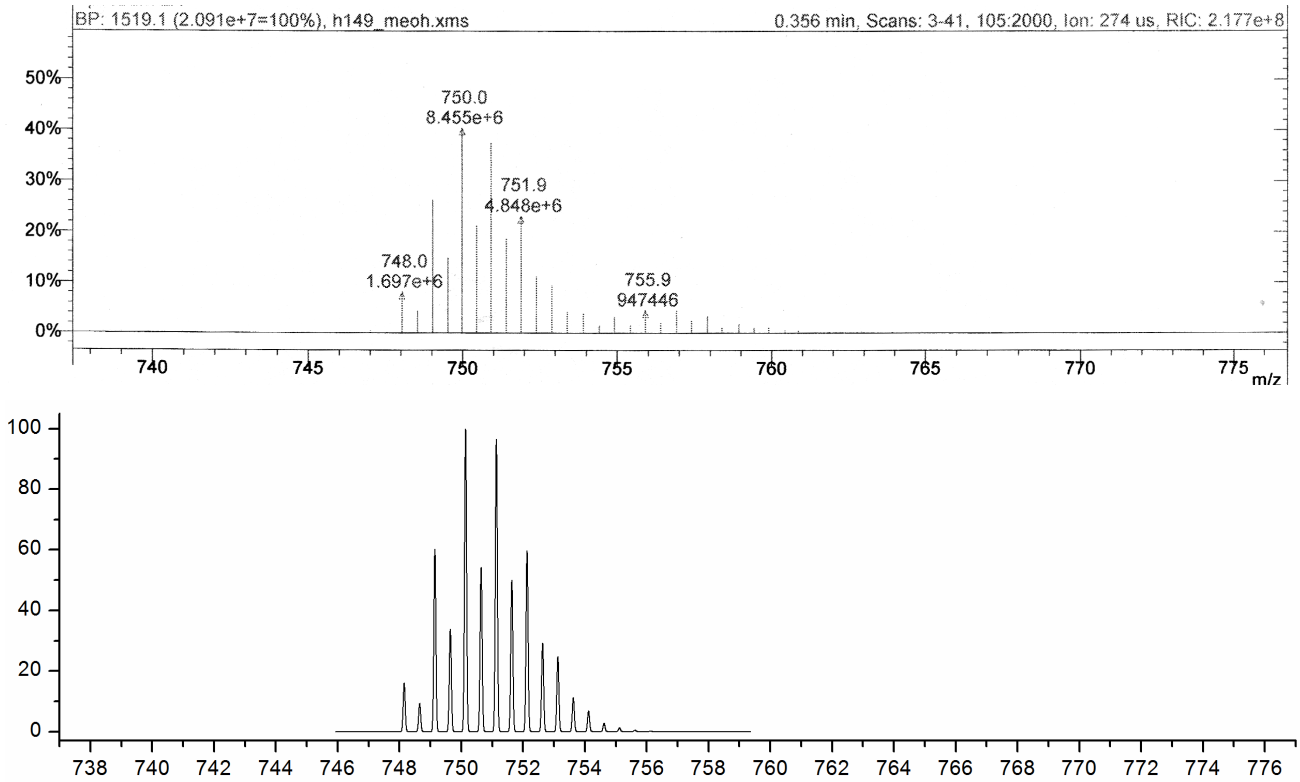

Figure S12. Observed in methanol (top) and calculated (bottom) isotopic distribution patterns for the cation of **1** with eliminated water molecule $\{[Cu_8O(tbDea)_6(H_2O)] + 3H\}^{2+}$.

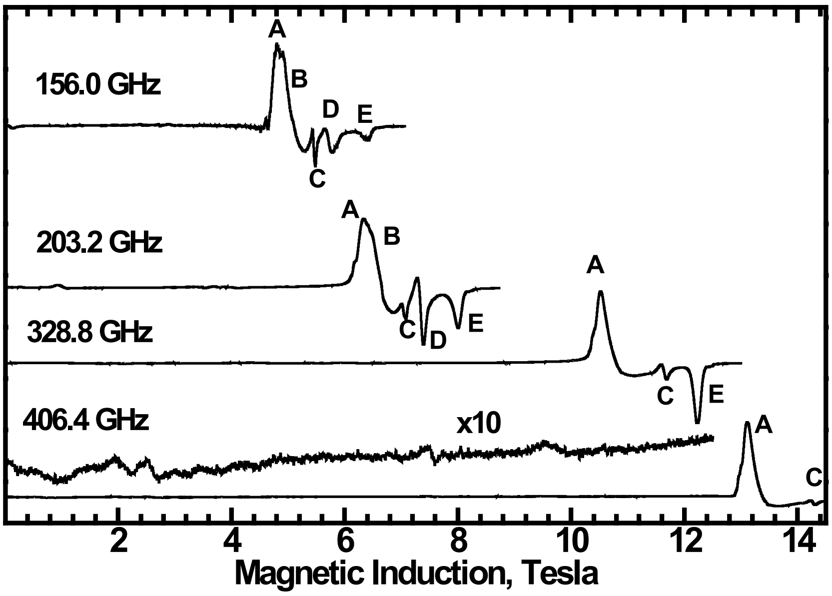

Figure S13. EPR spectra of **1**·$3CH_3OH$ recorded at 3.0 K with microwave frequency as indicated.

The large zero-field splitting observed in Figures 4 and 5.

The spin Hamiltonian (1) from the main text,

$$\begin{aligned}\hat{\mathbf{H}} = {} & J_A(\hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2\,\hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_3\,\hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_4\,\hat{\mathbf{S}}_5 + \hat{\mathbf{S}}_5\,\hat{\mathbf{S}}_6 + \hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_6) + \\ & J_B(\hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_3\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_5\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_2\,\hat{\mathbf{S}}_8 + \hat{\mathbf{S}}_4\,\hat{\mathbf{S}}_8 + \hat{\mathbf{S}}_6\,\hat{\mathbf{S}}_8\,) + \\ & J_C(\hat{\mathbf{S}}_2\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_4\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_6\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_8 + \hat{\mathbf{S}}_3\,\hat{\mathbf{S}}_8 + \hat{\mathbf{S}}_5\,\hat{\mathbf{S}}_8\,) + J_D\,\hat{\mathbf{S}}_7\,\hat{\mathbf{S}}_8\end{aligned}$$

describes the isotropic exchange interactions. Anisotropic interactions of a form

$$\hat{\mathbf{H}}_{\mathrm{ij}} = D_{ij}(\hat{\mathbf{S}}_{\mathrm{zi}}\,\hat{\mathbf{S}}_{\mathrm{zj}} - \hat{\mathbf{S}}_{\mathrm{i}}\,\hat{\mathbf{S}}_{\mathrm{j}}\,/3) + E_{\mathrm{ij}}(\hat{\mathbf{S}}_{\mathrm{xi}}\,\hat{\mathbf{S}}_{\mathrm{xj}} + \hat{\mathbf{S}}_{\mathrm{yi}}\,\hat{\mathbf{S}}_{\mathrm{yj}})$$

exist within each pair of ions (i,j). A reasonable estimate of the D_{ij} magnitude is 1 cm^{-1} (0.66 cm^{-1} in copper acetate, some 2 cm^{-1} in hydroxo and alkoxo bridged copper dimers). If one assumes that each of the interactions in the equatorial plane of the octanuclear molecule carries a D of 1 cm^{-1} and diagonalizes the resulting 256x256 matrix, then it is found that D corresponding to the "giant spin" Hamiltonian (formula 2 in the main text)

$$\hat{\mathbf{H}} = D\{(\hat{\mathbf{S}}_z^{\,2} - \mathrm{S(S{+}1)/3}\} + \mathrm{E}(\hat{\mathbf{S}}_x^{\,2} - \hat{\mathbf{S}}_y^{\,2})$$

will be just 0.2 cm^{-1} in the lowest S=2 state and 0.3 cm^{-1} in the lowest S=3 state. Some resonances observed at near zero magnetic field at very high frequencies in figs 4 and 5 indicate zero field splitting as large as 13.5 cm^{-1} and they must correspond to transitions between different coupled S states.

DFT Calculations (Broken Symmetry) of the Exchange Integrals. "Broken symmetry" Density Functional Theory calculations were performed by using the ORCA software.[S8] In this method, a self-consistent field (SCF) calculation is first performed for the maximum spin state of the dinuclear species. Next, a "broken symmetry" state is set up with all unpaired electrons being spin-up on one metal and spin-down on the other, and another SCF calculation is ran. The energies of the high-spin and broken symmetry states are finally used to estimate the exchange integral value, J (for Hamiltonian $\hat{\mathbf{H}} = J\,\hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_2$) based on the equation $J = 2(\boldsymbol{E}_{\mathrm{HS}} - \boldsymbol{E}_{\mathrm{BS}})/(\langle \boldsymbol{S}^2\rangle_{\mathrm{HS}} - \langle \boldsymbol{S}^2\rangle_{\mathrm{BS}})$, where $\boldsymbol{E}_{\mathrm{HS}}$ and $\boldsymbol{E}_{\mathrm{BS}}$ are the energies of the high-spin (HS) and the broken-symmetry (BS) states and $\langle \boldsymbol{S}\rangle^2$ are the expectation values of the spin-squared operator in the HS and BS states. To calculate the exchange interaction between a pair of copper atoms in our octanuclear system, all other copper atoms were replaced by zinc. Ahlrichs-type basis set TZVPP for copper(II) and SVP for other atoms were used, combined with the B3LYP functional.[S9] Ahlrichs polarisation functions from basis H - Kr R and auxiliary bases from the TurboMole library were also used.[S10] The X-Ray atom coordinates were used in calculations.

The following exchange integrals were obtained: $J_{12} = J_A = –90$ cm^{-1}, $J_{17} = J_B = 30$ cm^{-1}, $J_{18} = J_C = 14$ cm^{-1}, $J_{78} = J_D = 4800$ cm^{-1}. The experimental results were $J_A = –44$ cm^{-1}, $J_B = 134$ cm^{-1}, $J_C = 24$ cm^{-1}, $J_D = 460$ cm^{-1}. The integrals J_A, J_B and J_C cannot be distinguished experimentally because of the form of spin Hamiltonian (1) in the main text. The –44 cm^{-1} value from the fitting was assigned to J_A because only J_A is expected to be ferromagnetic.

Example of a DFT calculation:
Shortened output of the ORCA calculations for the exchange integral between copper atoms in the hexa-membered equatorial ring og the molecule

```
                                      INPUT FILE
============================================================================
====
NAME = EqToEq.txt
|  1> #H149 simplified structure
|  2> #All Cu except two in the equatorial ring replaced by Zn
|  3> #
|  4> ! PAL3 UKS B3LYP/G SVP TightSCF Grid4 NoFinalGrid
|  5> %scf BrokenSym 1,1
|  6> end
|  7> * xyz 2 3
|  8> Cu   15.88382    -0.26123     8.02445 newgto "TZVPP" end
|  9> #equatorial
| 10> O   16.01903     1.43515     8.88591
| 11> N   17.31510    -0.87002     9.48897
| 12> Cu   14.61625     2.45672     8.12149  newgto "TZVPP" end
| 13> #equatorial
| 14> O   13.21475     3.42201     7.26002
| 15> N   15.85912     3.39186     6.65697
| 16> Zn   12.89557     0.00112     9.91465
| 17> #newgto "TZVPP" end
| 18> #axial
| 19> O   10.93406    -0.66676     9.57535
| 20> O   12.89557     0.00112    11.78653
| 21> Zn   12.89686    -0.00112     6.23128
| 22> #newgto "TZVPP" end
| 23> #axial
| 24> O   14.85837     0.66676     6.57059
| 25> O   12.89686    -0.00112     4.35940
| 26> O   15.70050    -1.98687     7.26002
| 27> O   13.29987     2.03266     9.57535
| 28> O   14.45472    -1.36590     9.57535
| 29> O   12.49256    -2.03266     6.57059
| 30> O   11.33771     1.36590     6.57059
| 31> O   12.89686    -0.00112     8.07216
| 32> C   18.70596    -1.19726     8.92709
| 33> H   12.17145     0.26804     4.08573
| 34> C   15.67857     1.16487     5.51222
| 35> H   15.11178     1.49657     4.79776
| 36> H   16.21441     0.44004     5.15378
| 37> N   14.35220    -4.26188     6.65697
| 38> C   16.70963    -2.06393    10.16709
| 39> H   17.25707    -2.30405    10.92999
| 40> H   16.71543    -2.81110     9.55193
| 41> C   17.40409     0.28256    10.42381
| 42> H   18.22816     0.76504    10.25428
| 43> H   17.43310    -0.04691    11.33445
| 44> C   16.22795     1.23411    10.27608
| 45> H   15.43483     0.85439    10.68296
| 46> H   16.42333     2.07957    10.71202
| 47> H   19.35980    -1.23344     9.62895
| 48> H   18.70345    -2.03232     8.45385
```

```
| 49> H   18.92649    -0.51286     8.29110
| 50> Zn   11.62865     2.71795     8.02445
| 51> O   10.09193     1.98687     8.88591
| 52> N   11.44023     4.26188     9.48897
| 53> C   11.02820     5.63002     8.92709
| 54> C   10.49623     1.82716     5.51222
| 55> H   10.49236     1.17045     4.79776
| 56> H   10.85603     2.65362     5.15378
| 57> C   12.77693     4.33448    10.16709
| 58> H   12.71115     4.92864    10.92999
| 59> H   13.42109     4.71309     9.55193
| 60> C   10.39757     3.76265    10.42381
| 61> H    9.56770     4.23508    10.25428
| 62> H   10.66839     3.95251    11.33445
| 63> C   10.16157     2.26831    10.27608
| 64> H   10.88698     1.77132    10.68296
| 65> H    9.33170     2.01479    10.71202
| 66> H   10.73262     6.21435     9.62895
| 67> H   11.75264     6.04537     8.45385
| 68> H   10.32523     5.47879     8.29110
| 69> Zn   11.17618    -2.45672     8.02445
| 70> O   12.57768    -3.42201     8.88591
| 71> N    9.93331    -3.39186     9.48897
| 72> C    8.95449    -4.43276     8.92709
| 73> H   13.49073     0.49365     4.08573
| 74> C   12.51384    -2.99203     5.51222
| 75> H   13.08450    -2.66703     4.79776
| 76> H   11.61820    -3.09366     5.15378
| 77> C    9.20209    -2.27055    10.16709
| 78> H    8.72042    -2.62459    10.92999
| 79> H    8.55212    -1.90199     9.55193
| 80> C   10.88698    -4.04521    10.42381
| 81> H   10.89279    -5.00012    10.25428
| 82> H   10.58715    -3.90561    11.33445
| 83> C   12.29912    -3.50243    10.27608
| 84> H   12.36683    -2.62570    10.68296
| 85> H   12.93361    -4.09435    10.71202
| 86> H    8.59623    -4.98091     9.62895
| 87> H    8.23256    -4.01305     8.45385
| 88> H    9.43693    -4.96594     8.29110
| 89> Zn    9.90861     0.26123     8.12149
| 90> O    9.77340    -1.43515     7.26002
| 91> N    8.47733     0.87002     6.65697
| 92> C    7.08647     1.19726     7.21885
| 93> H   13.62098    -0.26804    12.06020
| 94> C   10.11386    -1.16487    10.63371
| 95> H   10.68065    -1.49657    11.34817
| 96> H    9.57802    -0.44004    10.99215
| 97> C    9.08280     2.06393     5.97884
| 98> H    8.53536     2.30405     5.21594
| 99> H    9.07700     2.81110     6.59400
|100> C    8.38834    -0.28256     5.72212
|101> H    7.56427    -0.76504     5.89165
|102> H    8.35933     0.04691     4.81149
|103> C    9.56448    -1.23411     5.86985
|104> H   10.35760    -0.85439     5.46298
|105> H    9.36910    -2.07957     5.43391
|106> H    6.43263     1.23344     6.51698
|107> H    7.08898     2.03232     7.69208
|108> H    6.86594     0.51286     7.85484
|109> Zn   14.16378    -2.71795     8.12149
```

```
|110> C   14.76423    -5.63002     7.21885
|111> C   15.29620    -1.82716    10.63371
|112> H   15.30007    -1.17045    11.34817
|113> H   14.93640    -2.65362    10.99215
|114> C   13.01551    -4.33448     5.97884
|115> H   13.08128    -4.92864     5.21594
|116> H   12.37134    -4.71309     6.59400
|117> C   15.39486    -3.76265     5.72212
|118> H   16.22473    -4.23508     5.89165
|119> H   15.12404    -3.95251     4.81149
|120> C   15.63086    -2.26831     5.86985
|121> H   14.90545    -1.77132     5.46298
|122> H   16.46073    -2.01479     5.43391
|123> H   15.05981    -6.21435     6.51698
|124> H   14.03979    -6.04537     7.69208
|125> H   15.46720    -5.47879     7.85484
|126> C   16.83794     4.43276     7.21885
|127> H   12.30170    -0.49365    12.06020
|128> C   13.27859     2.99203    10.63371
|129> H   12.70793     2.66703    11.34817
|130> H   14.17423     3.09366    10.99215
|131> C   16.59034     2.27055     5.97884
|132> H   17.07201     2.62459     5.21594
|133> H   17.24031     1.90199     6.59400
|134> C   14.90545     4.04521     5.72212
|135> H   14.89964     5.00011     5.89165
|136> H   15.20528     3.90561     4.81149
|137> C   13.49331     3.50243     5.86985
|138> H   13.42560     2.62570     5.46298
|139> H   12.85882     4.09435     5.43391
|140> H   17.19620     4.98091     6.51698
|141> H   17.55987     4.01305     7.69208
|142> H   16.35550     4.96594     7.85484
|143> **                         ****END OF INPUT****
   =========================================================================


*****************************************************
               *                     SUCCESS                    *
               *           SCF CONVERGED AFTER  38 CYCLES       *
               *****************************************************


----------------
TOTAL SCF ENERGY
----------------

Total Energy       :       -16595.39481037 Eh         -451583.65086 eV

Components:
Nuclear Repulsion  :        24627.19158182 Eh          670139.95220 eV
Electronic Energy  :       -41222.58639219 Eh        -1121723.60306 eV

One Electron Energy:       -72168.43661518 Eh        -1963802.99811 eV
Two Electron Energy:        30945.85022299 Eh          842079.39506 eV

Virial components:
Potential Energy   :       -33156.94262977 Eh         -902246.27827 eV
Kinetic Energy     :        16561.54781939 Eh          450662.62741 eV
Virial Ratio       :            2.00204371
```

```
DFT components:
N(Alpha)           :      324.998909362502 electrons
N(Beta)            :      322.998905765540 electrons
N(Total)           :      647.997815128042 electrons
E(X)               :     -713.518426473385 Eh
E(C)               :      -32.543475441260 Eh
E(XC)              :     -746.061901914645 Eh
```

High-Spin state

```
                 SPIN UP ORBITALS
  NO   OCC          E(Eh)            E(eV)


324   1.0000      -0.294406        -8.0112 HOMO
 325   0.0000      -0.155224        -4.2239 LUMO

                 SPIN DOWN ORBITALS
  NO   OCC          E(Eh)            E(eV)
322   1.0000      -0.291128        -7.9220 HOMO
 323   0.0000      -0.227104        -6.1798 LUMO

MULLIKEN ATOMIC CHARGES AND SPIN POPULATIONS
--------------------------------------------
   0 Cu:    0.591729    0.625935
   3 Cu:    0.594057    0.624458

                ***UHF Natural Orbitals were saved in EqToEq.uno***

QR-MO GENERATION
  Dim     = 1288
  Mult    =    3
  NEl     = 648
  N(DOMO) = 323
  N(SOMO) =    2
  N(VMO)  = 963


                ***Quasi-Restricted Orbitals were saved in EqToEq.qro***

Orbital Energies of Quasi-Restricted MO's
323( 1) :    -0.318221 a.u.    -8.659 eV alpha=  -11.233 beta=   -6.086
 324( 1) :    -0.311537 a.u.    -8.477 eV alpha=  -11.008 beta=   -5.947

LOCALIZED MOLECULAR ORBITAL COMPOSITIONS
----------------------------------------

The Mulliken populations for each LMO on each atom are computed
The LMO`s will be ordered according to atom index and type
  (A) Strongly localized MO`s have populations of >=0.000 on one atom
  (B) Two center bond orbitals have populations of >=0.100 on two atoms
  (C) Other MO`s are considered to be `delocalized`

FOUND   -   2 strongly local MO`s
        -   0 two center bond MO`s
        -   0 significantly delocalized MO`s

Rather strongly localized orbitals:
```

```
MO 324:   3Cu -   0.667686
MO 323:   0Cu -   0.669190
Localized MO's were stored in: EqToEq.unoloc
----------------------------
 BROKEN SYMMETRY INFORMATION
----------------------------

first open orbital = 323
last open orbital  = 324
HOMO(alpha)        = 323
HOMO(beta)         = 323
The new occupation numbers
323:    1.000    1.000
 324:    0.000    0.000

Broken-symmetry state
*****************************************************
               *                     SUCCESS                    *
               *           SCF CONVERGED AFTER  17 CYCLES       *
               *****************************************************


----------------
TOTAL SCF ENERGY
----------------

Total Energy       :       -16595.39460416 Eh         -451583.64525 eV

Components:
Nuclear Repulsion  :        24627.19158182 Eh          670139.95220 eV
Electronic Energy  :       -41222.58618598 Eh        -1121723.59745 eV

One Electron Energy:       -72168.43641553 Eh        -1963802.99268 eV
Two Electron Energy:        30945.85022955 Eh          842079.39524 eV

Virial components:
Potential Energy   :       -33156.94272013 Eh         -902246.28073 eV
Kinetic Energy     :        16561.54811596 Eh          450662.63548 eV
Virial Ratio       :            2.00204368


DFT components:
N(Alpha)           :      323.998905082647 electrons
N(Beta)            :      323.998909737771 electrons
N(Total)           :      647.997814820419 electrons
E(X)               :     -713.517779495250 Eh
E(C)               :      -32.543503112921 Eh
E(XC)              :     -746.061282608171 Eh

----------------
ORBITAL ENERGIES
----------------
                 SPIN UP ORBITALS
  NO   OCC          E(Eh)            E(eV)
323   1.0000       -0.292226        -7.9519
 324   0.0000       -0.225750        -6.1430

SPIN DOWN ORBITALS
  NO   OCC          E(Eh)            E(eV)
323   1.0000       -0.292150        -7.9498
 324   0.0000       -0.224370        -6.1054
```

```
********************************
                    * MULLIKEN POPULATION ANALYSIS *
                    ********************************

--------------------------------------------
MULLIKEN ATOMIC CHARGES AND SPIN POPULATIONS
--------------------------------------------
   0 Cu:    0.592525    0.626783
   3 Cu:    0.594671   -0.624379

--------------------------
UHF CORRESPONDING ORBITALS
--------------------------
Transforming orbitals                          ... done
Choosing virtual orbitals in the orth. comp.   ... done

                ***UHF Corresponding Orbitals were saved in EqToEq.uco***


Now the overlap between the corresponding orbitals will be plotted
Since there are an equal number of alpha and beta orbitals each orbital in
the
alpha set is matched by an orbital in the beta set. If all overlaps are
close to
one you have a normal UHF solution with some spin polarization
If you have a broken symmetry solution there will be overlaps that are
significantly smaller than one. These orbitals are the non-orthogonal
magnetic
orbitals of the broken symmetry UHF solution.

----------------------
 Orbital    Overlap(*)
----------------------
322:      0.99948
 323:      0.04890

------------------------------------------
BROKEN SYMMETRY MAGNETIC COUPLING ANALYSIS
------------------------------------------

S(High-Spin)      =   1.0
<S**2>(High-Spin) =   2.0048
<S**2>(BrokenSym) =   1.0022
E(High-Spin)      = -16595.394810 Eh
E(BrokenSym)      = -16595.394604 Eh
E(High-Spin)-E(BrokenSym)= -0.0056 eV    -45.253 cm**-1 (FERROMAGNETIC
coupling)

          ---------------------------------------------------------
          | Spin-Hamiltonian Analysis based on H(HDvV)= -2J*SA*SB |
    -------                                                   ----------
-
    | J(1) =      45.25 cm**-1    (from -(E[HS]-E[BS])/Smax**2)
|
    | J(2) =      22.63 cm**-1    (from -(E[HS]-E[BS])/(Smax*(Smax+1))
|
    | J(3) =      45.13 cm**-1    (from -(E[HS]-E[BS])/(<S**2>HS-<S**2>BS))
|
    ------------------------------------------------------------------------
-
```

References

S1. Bruker. APEX2 & SAINT; AXS Inc.: Madison, WI, 2004.

S2. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

S3. M. Nardelli, *J. Appl. Crystallogr.*, 1999, **32**, 563.

S4. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

S5. G. A. Bain and J. F. Berry, *J. Chem. Educ.*, **2008**, 85, 532.

S6. A. K. Hassan, L. A. Pardi, J. Krzystek, A. Sienkiewicz, P. Goy, M. Rohrer and L.-C. Brunel, *J. Magn. Reson.*, 2000, **142**, 300.

S7. V. T. Yilmaz, Y. Topcu, F. Yilmaz and C. Thoene, *Polyhedron*, 2001, 20, 3209; A. Karadag, V. T. Yilmaz and C. Thoene, *Polyhedron*, 2001, **20**, 635.

S8. (a) Neese, F. *ORCA - An ab initio*, *Density Functional and Semiempirical Program Package*, Version 2.9.1, **2012**. (b) Neese, F. - The ORCA program system WIREs, *Comput. Mol. Sci.* **2012**, *2*, 73.

S9. (a) Becke, D. A. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33,* 8822. (c) Perdew, J. P. *Phys. Rev. B.* **1986**, *34*, 7406. (d) Kendall, R. A.; Früchtl, H.A. *Theor. Chem. Acc.* **1997**, *97*, 158.

S10. (a) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571. (b) Ahlrichs, R. *et al*., unpublished. The Ahlrichs auxiliary basis sets were obtained from the TurboMole basis set library under ftp.chemie.uni-karlsruhe.de/pub/jbasen.