**Supporting Information for:**

An Investigation into the Unusual Linkage Isomerisation and Nitrite Reduction Activity of a Novel Tris(2-pyridyl) Copper Complex

Isolda Roger, Claire Wilson, Hans M. Senn, Stephen Sproules and Mark D. Symes\*

WestCHEM, School of Chemistry, University of Glasgow, University Avenue, Glasgow, G12 8QQ, UK.

\*E-mail: mark.symes@glasgow.ac.uk

EXPERIMENTAL SECTION

**General Experimental Remarks:** Unless otherwise stated, all syntheses were conducted under nitrogen in air- and moisture-free solvents obtained from a commercial solvent purification system. Sodium hydride (60% dispersion in mineral oil), methyl iodide (99%), [Cu(CH3CN)4]PF6 (97%), benzoic acid (99.5%) and tetrabutylammonium nitrite (97%, TBA-NO2) were supplied by Sigma Aldrich. Tetrabutylammonium hexafluorophosphate (TBA-PF6) (98%) was obtained from Alfa Aesar. 6-methyl-tris(2-pyridyl)methanol was prepared according to the published procedure.[[1]](#endnote-2)

All 1H and 13C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 300 K. Chemical shifts are reported in parts per million from low to high field. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, d = doublet, s = singlet. UV-Vis spectra were recorded on a JASCO V-670 spectrophotometer using 1 cm pathlength cuvettes. CHN analyses were collected by the services facility at the School of Chemistry, University of Glasgow, as were LM-MS mass spectra (ESI, positive mode, Bruker micrOTOF-Q machine). IR spectra were collected in the solid state on a Shimadzu IRAffinity-1S Fourier Transform Infrared Spectrophotometer. X-band EPR spectra were recorded on a Bruker ELEXSYS E500 Spectrometer and simulations were performed using Bruker's Xsophe Program Package.[[2]](#endnote-3) Melting points were gauged using an Electrothermal IA 9000 digital melting point machine. Experiments performed at “room temperature” were carried out at 20 °C. Electrochemical experiments were performed as below.

**Electrochemical Methods:** Electrochemical studies were performed in a single chamber cell in a three-electrode configuration using a CH Instruments CHI700 series potentiostat. The supporting electrolyte was 0.1 M TBA-PF6 in acetonitrile. A large surface area strip of carbon felt (Alfa Aesar) was used as the counter electrode, along with an Ag/AgNO3 pseudo reference electrode. Potentials are reported relative to the ferrocenium/ferrocene couple, the position of which was judged by adding ferrocene to the samples analysed. Working electrodes were washed with acetone and deionised water prior to use. Cyclic voltammograms were collected at room temperature under an atmosphere of Ar at a scan rate of 100 mV/s. A glassy carbon disc electrode (area = 0.071 cm2, CH Instruments) was used as the working electrode for cyclic voltammetry. Measurements were conducted without stirring and with *i*R compensation enabled.

**Computational Methods:** All calculations were performed with the program Gaussian 09[[3]](#endnote-4) at the density-functional theory (DFT) level. The M06-L exchange-correlation functional was used,[[4]](#endnote-5) which is a pure functional of the meta-GGA type, which has been shown to perform well for transition-metal complexes.[[5]](#endnote-6),[[6]](#endnote-7) The def2-TZVP basis set was used,[[7]](#endnote-8) with the “W06” auxiliary basis for density fitting.[[8]](#endnote-9) The effect of exact exchange was gauged by comparing to the M06 functional,[[9]](#endnote-10) which is a hybrid meta-GGA with 27% exact-exchange admixture. No significant differences in structures, energies, or spin density distributions were found. Interestingly, however, vibrational frequencies calculated with M06 were blue-shifted by as much as 80 cm–1 compared to M06-L. Modes involving N–O stretching were particularly strongly affected. The agreement with experiment was significantly better for the M06-L frequencies. All computational results reported in the paper were therefore obtained with M06-L/def2-TZVP. All structures were fully optimised; stationary points were identified as minima by the absence of imaginary frequencies. Gibbs free energies were calculated based on the usual harmonic-oscillator/rigid-rotor/ideal-gas approximation at 298.15 K and 101.325 kPa. Structures were manipulated and visualised with the programs Avogadro,[[10]](#endnote-11),[[11]](#endnote-12) Jmol,[[12]](#endnote-13) and ChemCraft.[[13]](#endnote-14)

**Crystallography:** Crystallographic data were collected at the University of Glasgow on a Bruker APEX-II CCD diffractometer.A green, column-shaped crystal of dimensions 0.46 × 0.1 × 0.06 mm was used for single crystal X-ray diffraction data collection. C18H17CuN5O5 crystallised in the triclinic space group *P*-1(space group No. 2), with unit cell dimensions a = 8.7123 (17), b = 8.7388 (17), *c* = 14.342 (3), α = 72.586 (4)°, β = 73.955 (4)°, γ = 62.928 (4)° and V = 915.0 (3) Å3, T = 100 K. 15440 reflections were measured by ω scans, 3197 independent reflections with *R*int = 0.079, θmax = 25.0°, θmin = 1.5° using Mo *Kα* radiation, λ = 0.71073 Å. The structure was solved using SHELXS and refined using SHELXL (both within OLEX2).[[14]](#endnote-15),[[15]](#endnote-16) OLEX2 was also used for molecular graphics and to prepare material for publication. CCDC 1547352 contains the supplementary crystallographic data for this paper.

**Additional single crystal crystallographic data for [Cu1(NO2)2] (CCDC 1547352).**

**Refinement**

Crystal data, data collection and structure refinement details are summarised in Table S1.

**Computing details**

Cell refinement: *SAINT* v8.34A (Bruker, 2013); data reduction: *SAINT* v8.34A (Bruker, 2013); program(s) used to refine structure: *SHELXL* (Sheldrick, 2008); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

**References**

[[16]](#endnote-17)Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

[[17]](#endnote-18)Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

*Special details*

|  |
| --- |
| *Refinement*. There is disorder present in both coordinated nitro anions. For one nitro group this is two orientations of the same binding mode present (N1a/b with occupancies approx. 0.55/0.45) and for the other there are two linkage isomers present N2a O-bound and N2b N bound with approx. 0.62/0.38 occupancy. All N—O bonds were restrained to be the same and rigid group displacement ellipsoid restraints were also applied to these atoms. |

**(2015gu0007\_0m)**

*Crystal data*

|  |  |
| --- | --- |
| C18H17CuN5O5 | *Z* = 2 |
| *Mr* = 446.90 | *F*(000) = 458 |
| Triclinic, *P*¯1 | *D*x = 1.622 Mg m-3 |
| *a* = 8.7123 (17) Å | Mo *K*a radiation, l = 0.71073 Å |
| *b* = 8.7388 (17) Å | Cell parameters from 8828 reflections |
| *c* = 14.342 (3) Å | q = 2.7–27.6° |
| a = 72.586 (4)° | m = 1.24 mm-1 |
| b = 73.955 (4)° | *T* = 100 K |
| g = 62.928 (4)° | Column, green |
| *V* = 915.0 (3) Å3 | 0.46 × 0.1 × 0.06 mm |

*Data collection*

|  |  |
| --- | --- |
| Bruker APEX-II CCD  diffractometer | 2653 reflections with *I* > 2s(*I*) |
| f and w scans | *R*int = 0.079 |
| Absorption correction: multi-scan  *SADABS2012*/1 (Bruker,2012) was used for absorption correction. wR2(int) was 0.1439 before and 0.1107 after correction. The Ratio of minimum to maximum transmission is 0.8308. The l/2 correction factor is 0.0015. | qmax = 25.0°, qmin = 1.5° |
| *T*min = 0.585, *T*max = 0.704 | *h* = -10®10 |
| 15440 measured reflections | *k* = -10®10 |
| 3197 independent reflections | *l* = -13®17 |

*Refinement*

|  |  |
| --- | --- |
| Refinement on *F*2 | 340 restraints |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| *R*[*F*2 > 2s(*F*2)] = 0.055 | H-atom parameters constrained |
| *wR*(*F*2) = 0.141 | *w* = 1/[s2(*F*o2) + (0.0557*P*)2 + 1.9438*P*]  where *P* = (*F*o2 + 2*F*c2)/3 |
| *S* = 1.13 | (D/s)max < 0.001 |
| 3197 reflections | Dρmax = 0.74 e Å-3 |
| 311 parameters | Dρmin = -0.44 e Å-3 |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2)*

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | *x* | *y* | *z* | *U*iso\*/*U*eq | Occ. (<1) |
| Cu1 | 0.74845 (7) | 0.73593 (7) | 0.71794 (4) | 0.0252 (2) |  |
| O1 | 1.1176 (4) | 0.8747 (4) | 0.8032 (2) | 0.0233 (7) |  |
| O1A | 0.7409 (15) | 0.6796 (19) | 0.5536 (12) | 0.063 (3) | 0.55 (3) |
| O2A | 0.5356 (19) | 0.823 (2) | 0.6562 (8) | 0.049 (3) | 0.55 (3) |
| O3A | 0.6738 (7) | 0.5462 (7) | 0.7674 (4) | 0.0362 (17) | 0.680 (10) |
| O4A | 0.8201 (5) | 0.4175 (5) | 0.8773 (3) | 0.0422 (9) |  |
| O1B | 0.7318 (15) | 0.718 (2) | 0.5849 (12) | 0.045 (3) | 0.45 (3) |
| O2B | 0.469 (2) | 0.8749 (18) | 0.6297 (11) | 0.053 (4) | 0.45 (3) |
| O3B | 0.6725 (13) | 0.4177 (14) | 0.7742 (8) | 0.036 (3) | 0.320 (10) |
| N1 | 0.7231 (4) | 0.8014 (4) | 0.8541 (2) | 0.0204 (7) |  |
| N2 | 0.7983 (4) | 0.9508 (5) | 0.6562 (2) | 0.0195 (7) |  |
| N3 | 1.0295 (5) | 0.5931 (4) | 0.7083 (2) | 0.0210 (7) |  |
| N1A | 0.580 (2) | 0.764 (6) | 0.578 (2) | 0.058 (8) | 0.55 (3) |
| N2A | 0.7204 (9) | 0.4200 (9) | 0.8357 (6) | 0.0392 (19) | 0.680 (10) |
| N1B | 0.579 (2) | 0.793 (7) | 0.565 (3) | 0.051 (6) | 0.45 (3) |
| N2B | 0.7457 (18) | 0.488 (2) | 0.8009 (9) | 0.024 (3) | 0.320 (10) |
| C1 | 1.0038 (5) | 0.8267 (5) | 0.7755 (3) | 0.0186 (8) |  |
| C2 | 1.0333 (6) | 1.0305 (6) | 0.8447 (3) | 0.0307 (11) |  |
| H2A | 1.0982 | 1.1049 | 0.8150 | 0.046\* |  |
| H2B | 1.0309 | 0.9971 | 0.9165 | 0.046\* |  |
| H2C | 0.9134 | 1.0953 | 0.8308 | 0.046\* |  |
| C11 | 0.8734 (5) | 0.7919 (5) | 0.8678 (3) | 0.0188 (8) |  |
| C12 | 0.9187 (6) | 0.7419 (5) | 0.9606 (3) | 0.0211 (9) |  |
| H12 | 1.0300 | 0.7267 | 0.9681 | 0.025\* |  |
| C13 | 0.7982 (6) | 0.7143 (6) | 1.0426 (3) | 0.0251 (9) |  |
| H13 | 0.8265 | 0.6795 | 1.1073 | 0.030\* |  |
| C14 | 0.6380 (6) | 0.7373 (6) | 1.0300 (3) | 0.0272 (10) |  |
| H14 | 0.5521 | 0.7250 | 1.0858 | 0.033\* |  |
| C15 | 0.6032 (6) | 0.7788 (6) | 0.9343 (3) | 0.0253 (9) |  |
| C16 | 0.4337 (6) | 0.7980 (8) | 0.9174 (4) | 0.0420 (13) |  |
| H16A | 0.4242 | 0.8455 | 0.8471 | 0.063\* |  |
| H16B | 0.3373 | 0.8781 | 0.9572 | 0.063\* |  |
| H16C | 0.4279 | 0.6830 | 0.9368 | 0.063\* |  |
| C21 | 0.9220 (5) | 0.9656 (5) | 0.6873 (3) | 0.0192 (8) |  |
| C22 | 0.9857 (6) | 1.0911 (6) | 0.6363 (3) | 0.0269 (10) |  |
| H22 | 1.0803 | 1.0932 | 0.6558 | 0.032\* |  |
| C23 | 0.9122 (6) | 1.2142 (6) | 0.5567 (3) | 0.0333 (11) |  |
| H23 | 0.9530 | 1.3034 | 0.5221 | 0.040\* |  |
| C24 | 0.7778 (6) | 1.2042 (6) | 0.5285 (3) | 0.0306 (10) |  |
| H24 | 0.7206 | 1.2898 | 0.4761 | 0.037\* |  |
| C25 | 0.7286 (6) | 1.0681 (6) | 0.5776 (3) | 0.0272 (10) |  |
| H25 | 0.6422 | 1.0564 | 0.5553 | 0.033\* |  |
| C31 | 1.1177 (5) | 0.6558 (5) | 0.7387 (3) | 0.0184 (8) |  |
| C32 | 1.2967 (6) | 0.5722 (6) | 0.7360 (3) | 0.0248 (9) |  |
| H32 | 1.3563 | 0.6189 | 0.7584 | 0.030\* |  |
| C33 | 1.3871 (6) | 0.4185 (6) | 0.6997 (3) | 0.0327 (11) |  |
| H33 | 1.5101 | 0.3577 | 0.6970 | 0.039\* |  |
| C34 | 1.2952 (7) | 0.3549 (6) | 0.6676 (3) | 0.0344 (11) |  |
| H34 | 1.3543 | 0.2503 | 0.6420 | 0.041\* |  |
| C35 | 1.1186 (6) | 0.4450 (6) | 0.6731 (3) | 0.0295 (10) |  |
| H35 | 1.0563 | 0.4008 | 0.6511 | 0.035\* |  |

*Atomic displacement parameters (Å2)*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | *U*11 | *U*22 | *U*33 | *U*12 | *U*13 | *U*23 |
| Cu1 | 0.0252 (3) | 0.0384 (4) | 0.0193 (3) | -0.0182 (3) | -0.0024 (2) | -0.0083 (2) |
| O1 | 0.0237 (15) | 0.0315 (17) | 0.0211 (15) | -0.0158 (13) | -0.0036 (12) | -0.0068 (13) |
| O1A | 0.078 (6) | 0.102 (7) | 0.043 (7) | -0.066 (5) | 0.000 (4) | -0.024 (5) |
| O2A | 0.044 (5) | 0.088 (7) | 0.027 (4) | -0.040 (5) | -0.014 (3) | -0.003 (4) |
| O3A | 0.035 (3) | 0.039 (3) | 0.040 (3) | -0.020 (3) | -0.009 (2) | -0.005 (2) |
| O4A | 0.050 (2) | 0.039 (2) | 0.040 (2) | -0.0204 (18) | -0.0141 (16) | -0.0016 (16) |
| O1B | 0.051 (5) | 0.075 (7) | 0.030 (5) | -0.045 (5) | -0.008 (4) | -0.007 (4) |
| O2B | 0.046 (7) | 0.076 (7) | 0.034 (6) | -0.036 (6) | -0.020 (5) | 0.022 (5) |
| O3B | 0.035 (6) | 0.037 (7) | 0.047 (7) | -0.019 (5) | -0.020 (5) | -0.005 (5) |
| N1 | 0.0192 (17) | 0.0249 (19) | 0.0157 (16) | -0.0102 (15) | -0.0021 (13) | -0.0006 (14) |
| N2 | 0.0139 (16) | 0.0279 (19) | 0.0139 (16) | -0.0056 (14) | 0.0000 (13) | -0.0070 (14) |
| N3 | 0.0278 (18) | 0.0220 (18) | 0.0130 (16) | -0.0104 (15) | -0.0014 (14) | -0.0045 (14) |
| N1A | 0.077 (7) | 0.108 (17) | 0.023 (7) | -0.069 (6) | -0.008 (4) | -0.008 (11) |
| N2A | 0.028 (4) | 0.039 (4) | 0.053 (4) | -0.010 (3) | -0.006 (3) | -0.018 (3) |
| N1B | 0.053 (7) | 0.087 (12) | 0.036 (9) | -0.054 (6) | -0.019 (4) | 0.010 (9) |
| N2B | 0.016 (6) | 0.029 (6) | 0.028 (5) | -0.010 (5) | -0.003 (4) | -0.007 (4) |
| C1 | 0.0177 (19) | 0.025 (2) | 0.0145 (18) | -0.0096 (17) | -0.0048 (15) | -0.0033 (15) |
| C2 | 0.038 (3) | 0.035 (3) | 0.029 (2) | -0.023 (2) | -0.002 (2) | -0.011 (2) |
| C11 | 0.022 (2) | 0.019 (2) | 0.0154 (18) | -0.0070 (17) | -0.0016 (15) | -0.0063 (15) |
| C12 | 0.024 (2) | 0.022 (2) | 0.0186 (19) | -0.0103 (18) | -0.0051 (16) | -0.0036 (16) |
| C13 | 0.032 (2) | 0.026 (2) | 0.015 (2) | -0.0108 (19) | -0.0036 (17) | -0.0039 (17) |
| C14 | 0.028 (2) | 0.031 (3) | 0.020 (2) | -0.013 (2) | 0.0031 (17) | -0.0060 (18) |
| C15 | 0.022 (2) | 0.030 (2) | 0.021 (2) | -0.0090 (19) | 0.0007 (16) | -0.0064 (17) |
| C16 | 0.028 (3) | 0.062 (4) | 0.035 (3) | -0.019 (2) | 0.001 (2) | -0.012 (3) |
| C21 | 0.018 (2) | 0.023 (2) | 0.0117 (18) | -0.0051 (17) | 0.0019 (15) | -0.0068 (15) |
| C22 | 0.031 (2) | 0.031 (2) | 0.020 (2) | -0.016 (2) | 0.0007 (18) | -0.0064 (17) |
| C23 | 0.043 (3) | 0.034 (3) | 0.018 (2) | -0.017 (2) | -0.0003 (19) | -0.0005 (19) |
| C24 | 0.029 (2) | 0.034 (3) | 0.015 (2) | -0.005 (2) | -0.0003 (18) | -0.0033 (18) |
| C25 | 0.019 (2) | 0.037 (3) | 0.016 (2) | -0.0033 (19) | -0.0033 (16) | -0.0056 (17) |
| C31 | 0.0217 (19) | 0.022 (2) | 0.0084 (18) | -0.0094 (16) | -0.0003 (15) | 0.0008 (15) |
| C32 | 0.024 (2) | 0.030 (2) | 0.016 (2) | -0.0109 (18) | -0.0001 (16) | -0.0017 (17) |
| C33 | 0.027 (2) | 0.036 (3) | 0.020 (2) | -0.005 (2) | 0.0021 (18) | -0.0030 (19) |
| C34 | 0.042 (3) | 0.029 (3) | 0.022 (2) | -0.006 (2) | 0.0012 (19) | -0.0087 (19) |
| C35 | 0.043 (3) | 0.028 (2) | 0.018 (2) | -0.015 (2) | -0.0048 (18) | -0.0055 (18) |

*Geometric parameters (Å, º) for (2015gu0007\_0m)*

|  |  |  |  |
| --- | --- | --- | --- |
| Cu1—O2A | 2.005 (16) | C2—H2C | 0.9800 |
| Cu1—O3A | 1.922 (5) | C11—C12 | 1.379 (6) |
| Cu1—O1B | 2.010 (18) | C12—H12 | 0.9500 |
| Cu1—N1 | 2.122 (3) | C12—C13 | 1.386 (6) |
| Cu1—N2 | 2.009 (3) | C13—H13 | 0.9500 |
| Cu1—N3 | 2.169 (4) | C13—C14 | 1.372 (6) |
| Cu1—N2B | 2.147 (14) | C14—H14 | 0.9500 |
| O1—C1 | 1.419 (5) | C14—C15 | 1.393 (6) |
| O1—C2 | 1.443 (5) | C15—C16 | 1.489 (6) |
| O1A—N1A | 1.255 (12) | C16—H16A | 0.9800 |
| O2A—N1A | 1.264 (11) | C16—H16B | 0.9800 |
| O3A—N2A | 1.227 (8) | C16—H16C | 0.9800 |
| O4A—N2A | 1.171 (7) | C21—C22 | 1.377 (6) |
| O4A—N2B | 1.276 (12) | C22—H22 | 0.9500 |
| O1B—N1B | 1.258 (13) | C22—C23 | 1.383 (6) |
| O2B—N1B | 1.251 (13) | C23—H23 | 0.9500 |
| O3B—N2B | 1.249 (12) | C23—C24 | 1.385 (7) |
| N1—C11 | 1.339 (5) | C24—H24 | 0.9500 |
| N1—C15 | 1.357 (5) | C24—C25 | 1.375 (7) |
| N2—C21 | 1.344 (5) | C25—H25 | 0.9500 |
| N2—C25 | 1.345 (5) | C31—C32 | 1.383 (6) |
| N3—C31 | 1.339 (5) | C32—H32 | 0.9500 |
| N3—C35 | 1.338 (6) | C32—C33 | 1.387 (7) |
| C1—C11 | 1.542 (5) | C33—H33 | 0.9500 |
| C1—C21 | 1.540 (5) | C33—C34 | 1.388 (7) |
| C1—C31 | 1.525 (6) | C34—H34 | 0.9500 |
| C2—H2A | 0.9800 | C34—C35 | 1.364 (7) |
| C2—H2B | 0.9800 | C35—H35 | 0.9500 |
|  |  |  |  |
| O2A—Cu1—N1 | 119.5 (3) | C12—C11—C1 | 119.6 (4) |
| O2A—Cu1—N2 | 95.3 (4) | C11—C12—H12 | 120.7 |
| O2A—Cu1—N3 | 148.2 (3) | C11—C12—C13 | 118.6 (4) |
| O3A—Cu1—O2A | 76.8 (4) | C13—C12—H12 | 120.7 |
| O3A—Cu1—N1 | 99.38 (19) | C12—C13—H13 | 120.1 |
| O3A—Cu1—N2 | 172.10 (19) | C14—C13—C12 | 119.7 (4) |
| O3A—Cu1—N3 | 100.9 (2) | C14—C13—H13 | 120.1 |
| O1B—Cu1—N1 | 168.9 (4) | C13—C14—H14 | 120.5 |
| O1B—Cu1—N3 | 97.3 (4) | C13—C14—C15 | 119.1 (4) |
| O1B—Cu1—N2B | 98.4 (5) | C15—C14—H14 | 120.5 |
| N1—Cu1—N3 | 92.30 (13) | N1—C15—C14 | 121.0 (4) |
| N1—Cu1—N2B | 88.1 (3) | N1—C15—C16 | 118.3 (4) |
| N2—Cu1—O1B | 90.7 (4) | C14—C15—C16 | 120.7 (4) |
| N2—Cu1—N1 | 84.50 (13) | C15—C16—H16A | 109.5 |
| N2—Cu1—N3 | 85.73 (13) | C15—C16—H16B | 109.5 |
| N2—Cu1—N2B | 166.6 (3) | C15—C16—H16C | 109.5 |
| N2B—Cu1—N3 | 83.4 (4) | H16A—C16—H16B | 109.5 |
| C1—O1—C2 | 115.2 (3) | H16A—C16—H16C | 109.5 |
| N1A—O2A—Cu1 | 108.6 (10) | H16B—C16—H16C | 109.5 |
| N2A—O3A—Cu1 | 128.3 (5) | N2—C21—C1 | 118.1 (3) |
| N1B—O1B—Cu1 | 114.1 (14) | N2—C21—C22 | 120.9 (4) |
| C11—N1—Cu1 | 112.3 (3) | C22—C21—C1 | 120.7 (4) |
| C11—N1—C15 | 119.1 (3) | C21—C22—H22 | 119.9 |
| C15—N1—Cu1 | 122.8 (3) | C21—C22—C23 | 120.2 (4) |
| C21—N2—Cu1 | 118.0 (3) | C23—C22—H22 | 119.9 |
| C21—N2—C25 | 119.0 (4) | C22—C23—H23 | 120.8 |
| C25—N2—Cu1 | 122.5 (3) | C22—C23—C24 | 118.4 (4) |
| C31—N3—Cu1 | 118.6 (3) | C24—C23—H23 | 120.8 |
| C35—N3—Cu1 | 122.8 (3) | C23—C24—H24 | 120.6 |
| C35—N3—C31 | 118.5 (4) | C25—C24—C23 | 118.8 (4) |
| O1A—N1A—O2A | 115.8 (15) | C25—C24—H24 | 120.6 |
| O4A—N2A—O3A | 115.6 (7) | N2—C25—C24 | 122.4 (4) |
| O2B—N1B—O1B | 113.1 (16) | N2—C25—H25 | 118.8 |
| O4A—N2B—Cu1 | 117.4 (7) | C24—C25—H25 | 118.8 |
| O3B—N2B—Cu1 | 120.2 (10) | N3—C31—C1 | 114.1 (3) |
| O3B—N2B—O4A | 122.4 (13) | N3—C31—C32 | 122.4 (4) |
| O1—C1—C11 | 109.1 (3) | C32—C31—C1 | 123.5 (4) |
| O1—C1—C21 | 109.4 (3) | C31—C32—H32 | 120.8 |
| O1—C1—C31 | 106.5 (3) | C31—C32—C33 | 118.4 (4) |
| C21—C1—C11 | 115.7 (3) | C33—C32—H32 | 120.8 |
| C31—C1—C11 | 108.7 (3) | C32—C33—H33 | 120.5 |
| C31—C1—C21 | 107.1 (3) | C32—C33—C34 | 119.0 (4) |
| O1—C2—H2A | 109.5 | C34—C33—H33 | 120.5 |
| O1—C2—H2B | 109.5 | C33—C34—H34 | 120.5 |
| O1—C2—H2C | 109.5 | C35—C34—C33 | 118.9 (4) |
| H2A—C2—H2B | 109.5 | C35—C34—H34 | 120.5 |
| H2A—C2—H2C | 109.5 | N3—C35—C34 | 122.8 (4) |
| H2B—C2—H2C | 109.5 | N3—C35—H35 | 118.6 |
| N1—C11—C1 | 118.1 (3) | C34—C35—H35 | 118.6 |
| N1—C11—C12 | 122.2 (4) |  |  |
|  |  |  |  |
| Cu1—O2A—N1A—O1A | -5 (5) | C11—C1—C21—N2 | -50.5 (5) |
| Cu1—O3A—N2A—O4A | 1.9 (10) | C11—C1—C21—C22 | 135.5 (4) |
| Cu1—O1B—N1B—O2B | 5 (6) | C11—C1—C31—N3 | 63.4 (4) |
| Cu1—N1—C11—C1 | 29.0 (4) | C11—C1—C31—C32 | -117.0 (4) |
| Cu1—N1—C11—C12 | -146.9 (3) | C11—C12—C13—C14 | -0.1 (6) |
| Cu1—N1—C15—C14 | 147.6 (4) | C12—C13—C14—C15 | 3.5 (7) |
| Cu1—N1—C15—C16 | -31.8 (5) | C13—C14—C15—N1 | -1.8 (7) |
| Cu1—N2—C21—C1 | -6.2 (5) | C13—C14—C15—C16 | 177.6 (4) |
| Cu1—N2—C21—C22 | 167.8 (3) | C15—N1—C11—C1 | -177.1 (4) |
| Cu1—N2—C25—C24 | -172.5 (3) | C15—N1—C11—C12 | 6.9 (6) |
| Cu1—N3—C31—C1 | -1.0 (4) | C21—N2—C25—C24 | -0.8 (6) |
| Cu1—N3—C31—C32 | 179.4 (3) | C21—C1—C11—N1 | 34.7 (5) |
| Cu1—N3—C35—C34 | -179.7 (3) | C21—C1—C11—C12 | -149.2 (4) |
| O1—C1—C11—N1 | 158.5 (3) | C21—C1—C31—N3 | -62.3 (4) |
| O1—C1—C11—C12 | -25.4 (5) | C21—C1—C31—C32 | 117.3 (4) |
| O1—C1—C21—N2 | -174.2 (3) | C21—C22—C23—C24 | -1.8 (7) |
| O1—C1—C21—C22 | 11.8 (5) | C22—C23—C24—C25 | -3.0 (7) |
| O1—C1—C31—N3 | -179.3 (3) | C23—C24—C25—N2 | 4.4 (7) |
| O1—C1—C31—C32 | 0.4 (5) | C25—N2—C21—C1 | -178.2 (3) |
| N1—C11—C12—C13 | -5.2 (6) | C25—N2—C21—C22 | -4.3 (6) |
| N2—C21—C22—C23 | 5.6 (6) | C31—N3—C35—C34 | 0.4 (6) |
| N3—C31—C32—C33 | 0.4 (6) | C31—C1—C11—N1 | -85.8 (4) |
| C1—C11—C12—C13 | 178.9 (4) | C31—C1—C11—C12 | 90.3 (4) |
| C1—C21—C22—C23 | 179.4 (4) | C31—C1—C21—N2 | 70.8 (4) |
| C1—C31—C32—C33 | -179.2 (4) | C31—C1—C21—C22 | -103.2 (4) |
| C2—O1—C1—C11 | -60.2 (4) | C31—C32—C33—C34 | 0.1 (6) |
| C2—O1—C1—C21 | 67.3 (4) | C32—C33—C34—C35 | -0.4 (6) |
| C2—O1—C1—C31 | -177.3 (3) | C33—C34—C35—N3 | 0.1 (7) |
| C11—N1—C15—C14 | -3.3 (6) | C35—N3—C31—C1 | 178.9 (3) |
| C11—N1—C15—C16 | 177.3 (4) | C35—N3—C31—C32 | -0.7 (6) |

Document origin: *publCIF*.[[18]](#endnote-19)

1. Hannon MJ, Mayers PC, Taylor PC. 1998 Preparation of substituted tris(2-pyridyl)methanol derivatives as mimics of the metal binding site of carbonic anhydrase. *Tetrahedron Lett.* **39**, 8509-8512. (http://doi.org/10.1016/S0040-4039(98)01850-4) [↑](#endnote-ref-2)
2. Hanson GR, Gates KE, Noble CJ, Griffin M, Mitchell A, Benson S. 2004 XSophe-Sophe-XeprView®. A computer simulation software suite (v. 1.1.3) for the analysis of continuous wave EPR spectra. *J. Inorg. Biochem.* **98**, 903-916. (https://doi.org/10.1016/j.jinorgbio.2004.02.003.) [↑](#endnote-ref-3)
3. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, *et al.* 2013 *Gaussian 09*. Revision D.01. Wallingford, CT, Gaussian, Inc. [↑](#endnote-ref-4)
4. Zhao Y, Truhlar DG. 2006 A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **125**, 194101. (http://doi.org/10.1063/1.2370993) [↑](#endnote-ref-5)
5. Zhao Y, Truhlar DG. 2008 Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **41**, 157–167. (http://doi.org/10.1021/ar700111a) [↑](#endnote-ref-6)
6. Zhang W, Truhlar DG, Tang M. 2013 Tests of Exchange-Correlation Functional Approximations Against Reliable Experimental Data for Average Bond Energies of 3d Transition Metal Compounds. *J. Chem. Theory Comput.* **9**, 3965-3977. (http://doi.org/10.1021/ct400418u) [↑](#endnote-ref-7)
7. Weigend F, Ahlrichs R. 2005 Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **7**, 3297–3305. (http://doi.org/10.1039/B508541A) [↑](#endnote-ref-8)
8. Weigend F. 2006 Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **8**, 1057–1065. (http://doi.org/10.1039/b515623h) [↑](#endnote-ref-9)
9. Zhao Y, Truhlar DG. 2008 The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215–241. (http://doi.org/10.1007/s00214-007-0310-x) [↑](#endnote-ref-10)
10. 2016 *Avogadro*, an open–source molecular builder and visualization tool. v. 1.2.0. [↑](#endnote-ref-11)
11. Hanwell MD, Curtis DE, Lonie DC, Vandermeersch T, Zurek E, Hutchison GR. 2012 Avogadro: an advanced semantic chemical editor, visualization, and analysis platform. *J. Cheminf.* **4**, 17. (http://doi.org/10.1186/1758-2946-4-17) [↑](#endnote-ref-12)
12. 2017 *JMol*, an open–source Java viewer for chemical structures in 3D. v. 14.13.1. [↑](#endnote-ref-13)
13. Andrienko G.A. 2016 *ChemCraft*. V. 1.8 (Build 506) [↑](#endnote-ref-14)
14. Sheldrick GM. 2008 A short history of SHELX. *Acta Cryst. A,* **64***,* 112-122. (https://doi.org/10.1107/S0108767307043930) [↑](#endnote-ref-15)
15. Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H. 2009 OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **42**, 339-341. (http://dx.doi.org/10.1107/S0021889808042726) [↑](#endnote-ref-16)
16. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339. [↑](#endnote-ref-17)
17. G. M. Sheldrick, *Acta Cryst.* 2008, A**64**, 112–122 [↑](#endnote-ref-18)
18. S. P. Westrip, *J. Apply. Cryst.*, 2010, **43**, 920. [↑](#endnote-ref-19)