Supporting Information

Regioselective Oxidative Liberation of Aryl-Substituted Tripyrrinone Metal Complexes from N-Confused Porphyrin

Hiroyuki Furuta, Hiromitsu Maeda, and Atsuhiro Osuka

Synthetic procedures and spectral data of tripyrrinones (**3**, **5**) and the metal complexes.
UV/vis absorption spectra of **3** and the metal complexes. (Supporting Figure 1)
DFT calculations on tripyrrinone (**3**) isomers. (Supporting Figure 2)
X-ray information for **3-Cu**.

Synthetic procedures and spectral data of 3 and the metal complexes.

Cu(II) complex of 14-benzoyl-5,10-diphenyltripyrrine-1-one, 3-Cu: To a solution of N-confused tetraphenylporphyrin (NCTPP) (20.0 mg, 0.033 mmol) in 50 ml of toluene, $Cu(OAc)_2$ (5.92 mg, 0.033 mmol) was added and the solution was stirred at reflux temperature for 1 day. After evaporation, the residues were purified by silica gel column (Wakogel C-200). Recrystallization from hexane/CH_2Cl_2 gave **3-Cu** as a green solid in 34% yield. R_f = 0.62 (5% MeOH/CH_2Cl_2). UV/vis ($CHCl_3$): λ_{max}[nm] (ε x 10^{-4}) 262.5 (2.3), 320.0 (2.5), 352.0 (2.8), 410.0 (2.8), 621.0 (1.5), 673.0 (1.8). FABMS: *m/z* (% intensity) = 554.3 (60, M^+), 555.3 (100, M^++1). Calcd for $C_{33}H_{21}CuN_3O_2$, 554.10.

14-Benzoyl-5,10-diphenyltripyrrine-1-one, 3: To a solution of **3-Cu** (7.4 mg, 0.013 mmol) in 2 ml of TFA, 0.4 ml of conc. H_2SO_4 was added and the mixture solution was stirred for 30 min. After adding $CHCl_3$, the solution was washed with water and Et_3N. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated. Recrystallization from hexane/CH_2Cl_2 gave **3** as a purple solid in 74% yield. R_f = 0.74 (5% MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 12.05 (br, 1H, NH), 10.09 (br, 1H, NH), 7.99 (d, *J* = 7.0 Hz, 1H, Ar), 7.57 – 7.29 (m, 13H, Ar), 6.99 (d, *J* = 6.0 Hz, 1H, βH), 6.92 (d, *J* = 4.5 Hz, 1H, βH), 6.83 (d, *J* = 4.5 Hz, 1H, βH), 6.54 (d, *J* = 3.5 Hz, 1H, βH), 6.37 (d, *J* = 4.5 Hz, 1H, βH), 6.99 (d, *J* = 4.5 Hz, 1H, βH). UV/vis ($CHCl_3$): λ_{max}[nm] (ε x 10^{-4}) 355.0 (2.3), 537.0 (1.4), 678.0 (0.18), 768.0 (0.13). FABMS: *m/z* (% intensity) = 493.3 (50, M^+), 494.3 (100,

M^++1). Calcd for $C_{33}H_{23}N_3O_2$, 493.18.

Zn(II) complex of 14-benzoyl-5,10-diphenyltripyrrine-1-one, 3-Zn: To a solution of **3** (10 mg, 0.02 mmol) in 2 ml of CH_2Cl_2, excess $Zn(OAc)_2 \cdot 2H_2O$ was added and the solution was stirred for 3 days at refluxing temperature. After adding CH_2Cl_2, the organic phase was washed with water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated. Recrystallization from CH_2Cl_2/hexane gave **3-Zn** as blue solid quantitatively. R_f = 0.56 (5% MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 7.87 (br, 2H, Ar), 7.52 – 7.12 (m, 13H, Ar), 6.82 (br, 1H, βH), 6.69 (br, 1H, βH), 6.55 (br, 1H, βH), 6.40 (br, 1H, βH), 6.18 (br, 2H, βH). UV/vis ($CHCl_3$): λ_{max}[nm] 347.5, 608.0, 651.5, 764.5. FABMS: *m/z* (% intensity) = 555.1 (100, M^+). Calcd for $C_{33}H_{23}N_3O_3Zn$, 573.10.

Ni(II) complex of 14-benzoyl-5,10-diphenyltripyrrine-1-one, 3-Ni: To a solution of **3** (10 mg, 0.02 mmol) in 10 ml of toluene, excess hydrous $Ni(acac)_2$ was added and the solution stirred at reflux temperature for 40 min. After evaporation, greenish-blue Ni(II) complex (**3-Ni**) was isolated by silica gel column and recrystallized from CH_2Cl_2/hexane in ca. 60% yield. R_f = 0.71 (5% MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 8.34 (d, *J* = 7.5 Hz, 2H, Ar), 7.62 – 7.49 (m, 8H, Ar), 7.43 – 7.42 (m, 3H, Ar), 7.35 – 7.32 (m, 2H, Ar), 7.33 (d, *J* = 4.5 Hz, 1H, βH), 7.08 (d, *J* = 5.0 Hz, 1H, βH), 6.97 (d, *J* = 5.5 Hz, 1H, βH), 6.67 (d, *J* = 5.0 Hz, 1H, βH), 6.56 (d, *J* = 5.0 Hz, 1H, βH), 6.28 (d, *J* = 5.5 Hz, 1H, βH). UV/vis ($CHCl_3$): λ_{max}[nm] 316.0, 372.5, 399.5, 642.5, 698.0. FABMS: *m/z* (% intensity) = 549.1 (50, M^+), 550.1 (100, M^++1), 551.1 (60, M^++2). Calcd for $C_{33}H_{21}N_3NiO_3$, 549.10.

Pd(II) complex of 14-benzoyl-5,10-diphenyltripyrrine-1-one, 3-Pd: To a solution of **3** (10 mg, 0.02 mmol) in 20 ml of toluene, 4.5 mg (0.02 mmol)of $Pd(OAc)_2$ was added and the solution was stirred at reflux temperature for 80 min. After evaporation, greenish-blue Pd(II) complex (**3-Pd**) was isolated by silica gel column and recrystallized from CH_2Cl_2/hexane in ca. 50% yield. R_f = 0.70 (5% MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 8.33 (d, *J* = 7.0 Hz, 2H, Ar), 7.56 – 7.34 (m, 13H, Ar), 7.31 (d, *J* = 4.5 Hz, 1H, βH), 6.96 (d, *J* = 5.0 Hz, 1H, βH), 6.88 (d, *J* = 5.5 Hz, 1H, βH), 6.57 (d, *J* = 4.5 Hz, 1H, βH), 6.48 (d, *J* = 5.0 Hz, 1H, βH), 6.26 (d, *J* = 5.5 Hz, 1H, βH). UV/vis ($CHCl_3$): λ_{max}[nm] 350.0, 396.5, 582.5, 626.5, 685.0. FABMS: *m/z* (% intensity) = 597.1 (100, M^+), 598.1 (80, M^++1). Calcd for $C_{33}H_{21}N_3PdO_3$, 597.07.

Pt(II) complex of 14-benzoyl-5,10-diphenyltripyrrine-1-one, 3-Pt: To a solution of **3** (10 mg, 0.02 mmol) in 20 ml of toluene, 5.3 mg (0.02 mmol) of $PtCl_2$ was added and the solution was stirred at reflux temperature for 17 h. After evaporation, greenish-blue Pt(II) complex (**3-Pt**) was isolated by silica gel column and recrystallized from CH_2Cl_2/hexane in ca. 20% yield. R_f = 0.71 (5% MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 8.40 (d, *J* = 8.0 Hz, 2H, Ar), 7.61 – 7.28 (m, 14H, Ar + βH), 7.12 (d, *J* = 5.0 Hz, 1H, βH), 6.95 (d, *J* = 5.5 Hz, 1H, βH), 6.81 (d, *J* = 5.0 Hz, 1H, βH), 6.69 (d, *J* = 5.0 Hz, 1H, βH), 6.40 (d, *J* = 5.5 Hz, 1H, βH). UV/vis ($CHCl_3$): λ_{max}[nm] 343.0, 405.5, 551.5, 636.5, 691.0. FABMS: *m/z* (% intensity) = 686.2 (85, M^+), 687.2 (100, M^++1).

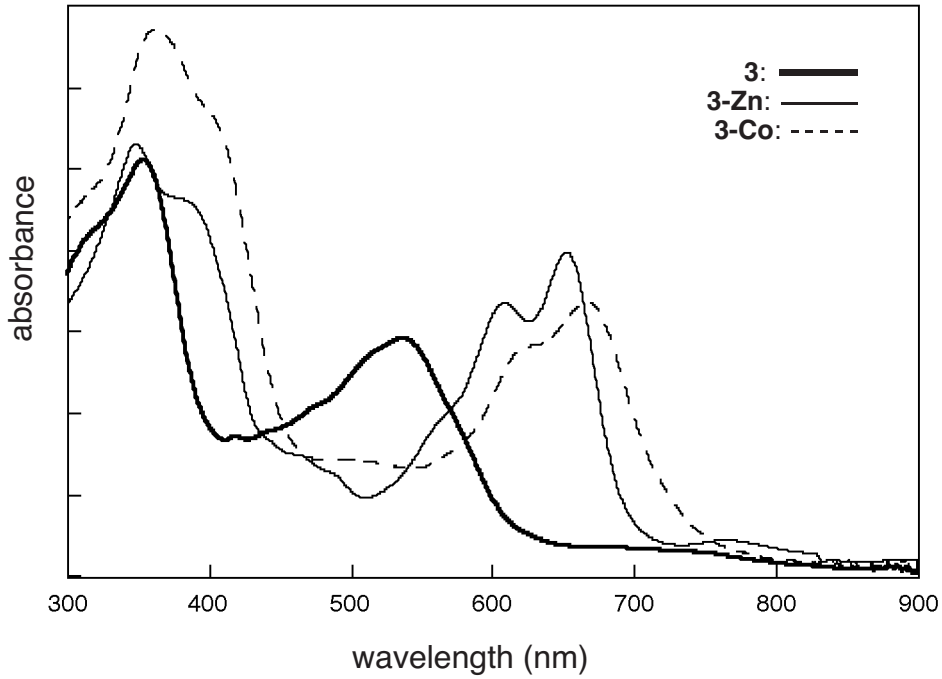
Calcd for $C_{33}H_{21}N_3PtO_3$, 686.13.

Co complex of 14-benzoyl-5,10-diphenyltripyrrine-1-one, 3-Co: To a solution of **3** (9.2 mg, 0.018 mmol) in 20 ml of toluene, 10.8 mg (0.043 mmol) of $Co(OAc)_2 \cdot 4H_2O$ was added and the solution was stirred at reflux temperature for 70 min. After evaporation, greenish-blue Ni(II) complex (**3-Co**) was isolated by silica gel column and recrystallized from CH_2Cl_2/hexane in ca. 20% yield. R_f = 0.53 (5% MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 17.35, 14.57, 11.49, 11.12, 10.96, 10.05, 9.13, 6.50, 7.94. UV/vis ($CHCl_3$): λ_{max}[nm] 360.0, 665.5. FABMS: *m/z* (% intensity) = 550.4 (35, M^+), 551.4 (100, M^++1). Calcd for $C_{33}H_{21}N_3CoO_3$, 550.10.

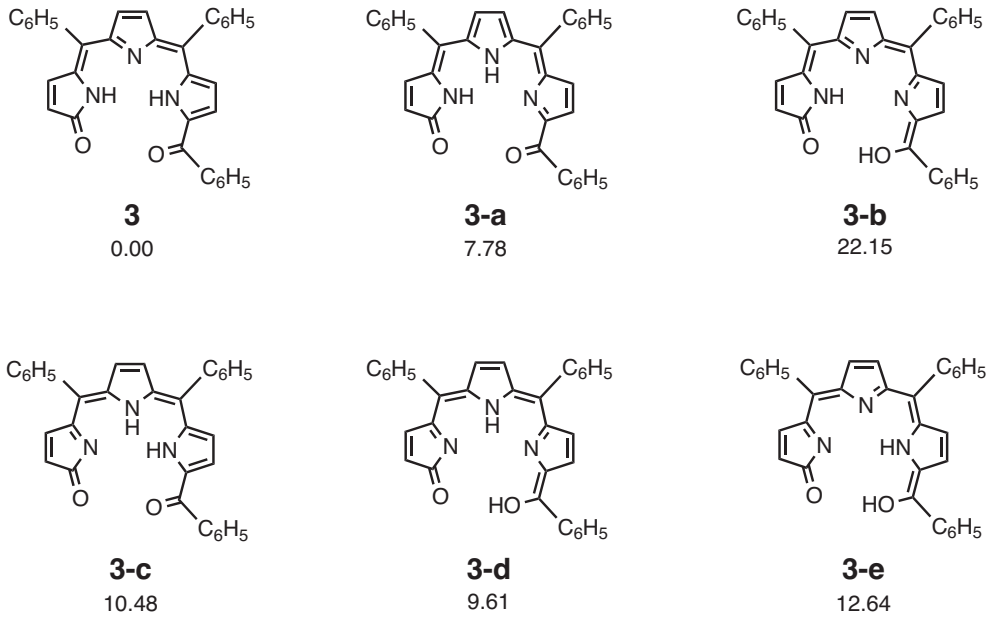
Cu(II) complex of 14-2'-pyridylcarbonyl-5,10-diphenyltripyrrine-1-one, 5-Cu: To a solution of 5,10,15-triphenyl-20-(2'-pyridyl)-2-aza-21-carbaporphyrin, (**4**) (17.0 mg, 0.028 mmol) in 30 ml of toluene, $Cu(OAc)_2$ (5.01 mg, 0.028 mmol) was added and the solution was stirred at reflux temperature for 6 h. After the solvent was removed by evaporation, the residues were purified by silica gel column (Wakogel C-200). Recrystallization from hexane/CH_2Cl_2 gave **5-Cu** as a green solid. R_f = 0.50 (5% MeOH/CH_2Cl_2). UV/vis ($CHCl_3$): λ_{max}[nm] 350.5, 408.0, 614.5, 666.0. FABMS: *m/z* (% intensity) = 555.0 (40, M^+), 556.0 (100, M^++1). Calcd for $C_{33}H_{21}CuN_3O_2$, 555.10.

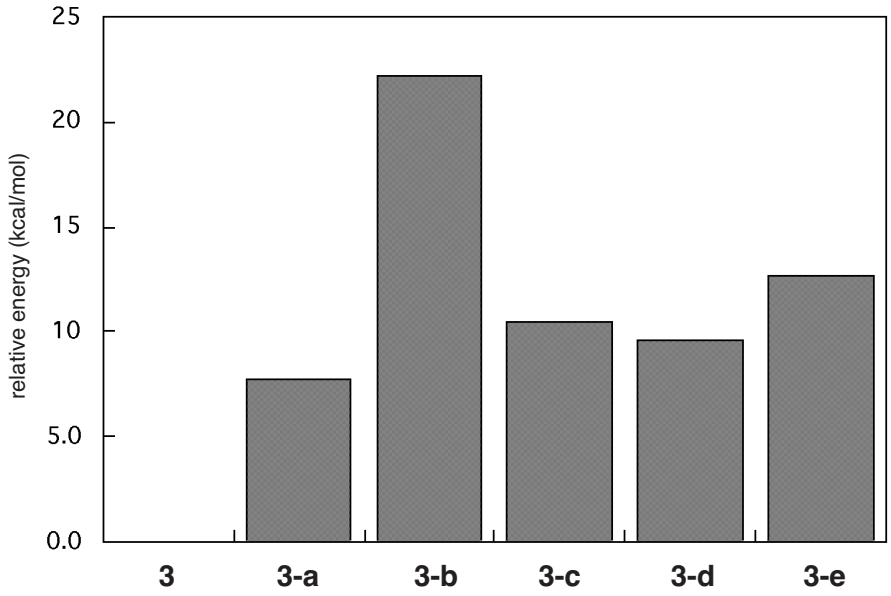
Ni(II) complex of 14-2'-pyridylcarbonyl-5,10-diphenyltripyrrine-1-one, 5-Ni: To a solution of **5-Cu** in 2 ml of TFA, 0.4 ml of conc. H_2SO_4 was added and the solution was stirred for 1 day. After adding $CHCl_3$, the solution was washed with water and Et_3N. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated. The tautomeric or conformational mixture of crude compounds (**5**) was yielded quantitatively after silica gel column chromatography. To a solution of crude **5** in 10 ml of toluene, excess hydrous $Ni(acac)_2$ was added and the solution was stirred at room temperature for 10 min. After evaporation, greenish-blue Ni(II) complex (**5-Ni**) was isolated quantitatively by silica gel column and was recrystallized from CH_2Cl_2/hexane. R_f = 0.45 (5% MeOH/CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 8.75 (d, *J* = 5.0 Hz, 1H, m-Py), 8.34 (d, *J* = 7.0 Hz, 2H, Ph), 7.61 – 7.32 (m, 10H, Ar), 7.32 (d, *J* = 4.0 Hz, 1H, βH), 7.11 (d, *J* = 5.0 Hz, 1H, βH), 7.04 (d, *J* = 5.0 Hz, 1H, βH), 6.66 (d, *J* = 4.0 Hz, 1H, βH), 6.62 (d, *J* = 5.0 Hz, 1H, βH), 6.32 (d, *J* = 5.5 Hz, 1H, βH). UV/vis ($CHCl_3$): λ_{max}[nm] 370.0, 396.5, 585.0, 639.5, 691.5. MALDI-TOFMS: *m/z* (% intensity) = 550. (100, M^+). Calcd for $C_{32}H_{20}N_4NiO_3$, 550.09.

Supporting Figure 1. UV/vis absorption spectra of **3** and metal (Zn(II), Co) complexes in $CHCl_3$.



Supporting Figure 2. Relative total energies of tautomers of **3** at B3LYP/6-31G** level





X-ray information for 3-Cu.

X-ray Experimental.

Crystallographic Data for **3-Cu**.

Supporting Table 1. Atomic Coordinates and Biso/Beq for **3-Cu**.

Supporting Table 2. Anisotropic displacement parameters for **3-Cu**.

Supporting Table 3. Bond lengths (Å) for **3-Cu**.

Supporting Table 4. Bond angles (°) for **3-Cu**.

Supporting Table 5. Torsion angles (°) for **3-Cu**.

Supporting Table 6. Least Squares Planes.

Supporting Figure 3. (a) Top view of **3-Cu**·$CHCl_3$, showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale. (b) Side view of **3-Cu**. Solvents are omitted for clarity. (c), (d) π-stacked dimer of **3-Cu**.

Experimental

Data Collection

A violet prism crystal of $C_{34}H_{22}N_3CuO_2Cl_3$ having approximate dimensions of 0.40 x 0.10 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation.

Indexing was performed from 2 stills which were exposed for 1 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 8.1991(3) Å

b = 23.4409(8) Å $\beta = 100.742(2)^o$

c = 15.6336(6) Å

V = 2952.0(2) $Å^3$

For Z = 4 and F.W. = 674.47, the calculated density is 1.52 g/cm^3. The systematic absences of:

h0l: h+l ± 2n

0k0: k ± 2n

uniquely determine the space group to be:

$P2_1/n$ (#14)

The data were collected at a temperature of 23 ± 1°C to a maximum 2θ value of 55.0°. A total of 44 oscillation images were collected. A sweep of data was done using w scans from 130.0 to 190.0° in 5.0° step, at χ=45.0° and φ = 0.0°. The exposure rate was 3.3 [sec./°]. The detector at the zero swing position. A second sweep was performed using w scans from 0.0 to 160.0° in 5.0° step, at χ=45.0° and φ = 180.0°. The exposure rate was 3.3 [sec./°]. The detector at the zero swing position. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 6449 reflections which were collected, 6306 were unique (R_{int} = 0.057); equivalent reflections were merged. The linear absorption coefficient, μ, for Mo-Kα radiation is 10.5 cm^{-1}. A symmetry-related absorption correction using the program ABSCOR was applied which resulted in transmission factors ranging from 0.92 to 1.10. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement[3] on F was based on 2602 observed reflections ($I > 3.00\sigma(I)$) and 410 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.041$$

$$R_w = [\, \Sigma \, \omega \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, \omega \, Fo^2]^{1/2} = 0.047$$

The standard deviation of an observation of unit weight[4] was 0.05. Unit weights were used. Plots of $\Sigma \, \omega \, (|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin q/l and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.31 and -0.32 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for Df' and Df'' were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the CrystalStructure[9,10] crystallographic software package.

References

(1) SIR92: Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G., and Camalli, M. (1994) J. Appl. Cryst., 27, 435.

(2) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least Squares function minimized:

$\Sigma\omega(|F_o|-|F_c|)^2$ where w = Least Squares weights.

(4) Standard deviation of an observation of unit weight:

$[\Sigma\omega(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations

N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) CrystalStructure 2.00: Crystal Structure Analysis Package, Rigaku and MSC (2001).

(10) CRYSTALS Issue 10: Watkin, D.J., Prout, C.K. Carruthers, J.R. & Betteridge, P.W. Chemical Crystallography Laboratory, Oxford, UK.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{34}H_{22}N_3CuO_2Cl_3$
Formula Weight	674.47
Crystal Color, Habit	violet, prism
Crystal Dimensions	0.40 X 0.10 X 0.10 mm
Crystal System	monoclinic
Lattice Type	Primitive
Indexing Images	2 stills @ 0.8 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 8.1991(3) Å
	b = 23.4409(8) Å
	c = 15.6336(6) Å
	β = 100.742(2) ^{o}
	V = 2952.0(2) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.517 g/cm^3
F_{000}	1372.00
μ(MoKα)	10.49 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα (l = 0.71069 Å)
	graphite monochromated
Detector Aperture	270 mm x 256 mm
Data Images	44 exposures
ω oscillation Range (c=45.0, f=0.0)	130.0 - 190.0^o
Exposure Rate	3.3 sec./^{o}
Detector Swing Angle	0.00^o

ω oscillation Range (c=45.0, f=180.0)	0.0 - 160.0^{o}
Exposure Rate	3.3 sec./^{o}
Detector Swing Angle	0.00^{o}
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2q_{max}$	55.0^{o}
No. of Reflections Measured	Total: 6449
	Unique: 6306 (R_{int} = 0.057)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.9231 - 1.1019)
	Decay (0.00% increase)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma\ \omega\ (\|Fo\| - \|Fc\|)^2$
Least Squares Weights	1
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	2602
No. Variables	410
Reflection/Parameter Ratio	6.35
Residuals: R; Rw	0.041 ; 0.047
Goodness of Fit Indicator	0.05
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.31 e^{-}/Å^3
Minimum peak in Final Diff. Map	-0.32 e^{-}/Å^3

Supporting Table 1. Atomic coordinates and B_{iso}/B_{eq} for **3-Cu**.

atom	x	y	z	B_{eq}
Cu(1)	0.8115(1)	0.46020(3)	0.38550(5)	2.98(2)
Cl(1)	0.2139(4)	0.6799(1)	0.2024(2)	8.93(9)
Cl(2)	0.1189(3)	0.5733(1)	0.1191(1)	6.51(6)
Cl(3)	0.3742(3)	0.6417(1)	0.0653(2)	7.91(8)
O(1)	0.5299(7)	0.5283(3)	0.2393(3)	6.1(2)
O(2)	0.6855(5)	0.5301(2)	0.4170(3)	3.5(1)
N(1)	0.7594(7)	0.4685(2)	0.2616(3)	3.3(1)
N(2)	0.9584(6)	0.3947(2)	0.3806(3)	2.7(1)
N(3)	0.8461(6)	0.4528(2)	0.5081(3)	3.0(1)
C(1)	0.6439(9)	0.5041(3)	0.2128(4)	4.1(2)
C(2)	0.675(1)	0.5051(3)	0.1222(5)	4.7(2)
C(3)	0.7978(9)	0.4700(3)	0.1191(4)	4.1(2)
C(4)	0.8536(8)	0.4447(3)	0.2056(4)	3.4(2)
C(5)	0.9729(8)	0.4033(3)	0.2247(4)	3.2(1)
C(6)	1.0115(7)	0.3768(3)	0.3089(4)	2.9(1)
C(7)	1.1122(8)	0.3268(3)	0.3300(4)	3.2(1)
C(8)	1.1189(8)	0.3151(3)	0.4146(4)	3.2(1)
C(9)	1.0241(7)	0.3584(3)	0.4490(4)	2.9(1)
C(10)	1.0112(7)	0.3666(3)	0.5361(4)	2.9(1)
C(11)	0.9277(8)	0.4138(3)	0.5640(4)	2.9(1)
C(12)	0.9039(9)	0.4284(3)	0.6491(4)	4.0(2)
C(13)	0.8057(9)	0.4764(3)	0.6423(4)	4.2(2)
C(14)	0.7719(8)	0.4914(3)	0.5534(4)	3.0(1)
C(15)	0.6807(7)	0.5338(3)	0.4974(4)	3.0(1)
C(16)	1.0633(8)	0.3836(3)	0.1549(4)	3.3(2)
C(17)	1.009(1)	0.3383(3)	0.1030(5)	4.9(2)
C(18)	1.092(1)	0.3227(3)	0.0361(5)	5.6(2)
C(19)	1.230(1)	0.3510(4)	0.0243(6)	5.7(2)
C(20)	1.287(1)	0.3959(4)	0.0762(5)	6.0(2)
C(21)	1.2043(9)	0.4126(3)	0.1426(5)	4.6(2)

Supporting Table 1. (continued)

atom	x	y	z	B_{eq}
C(22)	1.0848(8)	0.3236(3)	0.6021(4)	3.2(1)
C(23)	1.0318(9)	0.2678(3)	0.5956(5)	4.5(2)
C(24)	1.096(1)	0.2285(4)	0.6584(5)	5.2(2)
C(25)	1.215(1)	0.2445(4)	0.7278(5)	5.2(2)
C(26)	1.2687(9)	0.2994(4)	0.7356(5)	5.2(2)
C(27)	1.2029(8)	0.3397(3)	0.6731(4)	4.1(2)
C(28)	0.5821(8)	0.5806(3)	0.5256(4)	3.1(2)
C(29)	0.5590(8)	0.5877(3)	0.6110(4)	3.9(2)
C(30)	0.4707(9)	0.6337(3)	0.6329(5)	4.2(2)
C(31)	0.4041(9)	0.6729(3)	0.5711(5)	4.5(2)
C(32)	0.4231(9)	0.6656(3)	0.4860(5)	4.5(2)
C(33)	0.5108(8)	0.6198(3)	0.4631(5)	3.8(2)
C(34)	0.283(1)	0.6200(3)	0.1532(5)	5.4(2)
H(1)	0.617(1)	0.5272(3)	0.0753(5)	5.7(2)
H(2)	0.8438(9)	0.4616(3)	0.0691(4)	5.0(2)
H(3)	1.1642(8)	0.3056(3)	0.2908(4)	3.9(2)
H(4)	1.1758(8)	0.2843(3)	0.4467(4)	3.8(2)
H(5)	0.9493(9)	0.4087(3)	0.7011(4)	4.8(2)
H(6)	0.7678(9)	0.4959(3)	0.6881(4)	5.1(2)
H(7)	0.918(1)	0.3167(3)	0.1141(5)	6.0(2)
H(8)	1.050(1)	0.2927(3)	-0.0027(5)	6.9(3)
H(9)	1.287(1)	0.3392(4)	-0.0201(6)	7.1(3)
H(10)	1.383(1)	0.4160(4)	0.0676(5)	7.5(3)
H(11)	1.2419(9)	0.4441(3)	0.1792(5)	5.6(2)
H(12)	0.9488(9)	0.2566(3)	0.5477(5)	5.3(2)
H(13)	1.060(1)	0.1900(4)	0.6531(5)	6.3(2)
H(14)	1.258(1)	0.2174(4)	0.7712(5)	6.3(2)
H(15)	1.3535(9)	0.3103(4)	0.7828(5)	6.1(2)
H(16)	1.2367(8)	0.3785(3)	0.6790(4)	4.9(2)
H(17)	0.6052(8)	0.5608(3)	0.6542(4)	4.7(2)

Supporting Table 1. (continued)

atom	x	y	z	B_{eq}
H(18)	0.4537(9)	0.6378(3)	0.6911(5)	5.2(2)
H(19)	0.3462(9)	0.7050(3)	0.5873(5)	5.6(2)
H(20)	0.3761(9)	0.6925(3)	0.4430(5)	5.5(2)
H(21)	0.5224(8)	0.6146(3)	0.4043(5)	4.7(2)
H(22)	0.364(1)	0.6010(3)	0.1944(5)	6.5(2)

$B_{eq} = 8/3\ p^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos g + 2U_{13}(aa^*cc^*)\cos b + 2U_{23}(bb^*cc^*)\cos a)$

Supporting Table 2. Anisotropic Displacement Parameters for **3-Cu**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.0471(4)	0.0373(4)	0.0314(4)	0.0040(4)	0.0138(3)	0.0008(4)
Cl(1)	0.162(3)	0.067(2)	0.126(2)	-0.012(2)	0.068(2)	-0.015(2)
Cl(2)	0.101(2)	0.079(2)	0.067(1)	-0.021(1)	0.014(1)	0.003(1)
Cl(3)	0.087(2)	0.129(2)	0.093(2)	-0.008(2)	0.039(2)	0.011(2)
O(1)	0.081(4)	0.105(5)	0.048(3)	0.046(4)	0.021(3)	0.011(3)
O(2)	0.059(3)	0.043(3)	0.034(2)	0.009(2)	0.022(2)	0.004(2)
N(1)	0.049(3)	0.046(3)	0.034(3)	0.011(3)	0.010(3)	0.001(3)
N(2)	0.037(3)	0.036(3)	0.030(3)	0.002(2)	0.009(2)	-0.001(2)
N(3)	0.043(3)	0.041(3)	0.030(3)	0.000(3)	0.010(2)	-0.004(2)
C(1)	0.059(5)	0.061(5)	0.038(4)	0.013(4)	0.014(4)	0.006(3)
C(2)	0.074(5)	0.066(5)	0.040(4)	0.021(4)	0.012(4)	0.016(4)
C(3)	0.072(5)	0.059(5)	0.029(3)	0.008(4)	0.016(4)	0.003(3)
C(4)	0.056(4)	0.040(4)	0.035(4)	-0.004(3)	0.014(3)	-0.002(3)
C(5)	0.046(4)	0.043(4)	0.034(3)	-0.003(3)	0.013(3)	-0.006(3)
C(6)	0.042(4)	0.037(4)	0.033(3)	-0.005(3)	0.015(3)	-0.002(3)
C(7)	0.048(4)	0.045(4)	0.031(3)	0.000(3)	0.016(3)	-0.006(3)
C(8)	0.044(4)	0.031(3)	0.046(4)	0.006(3)	0.011(3)	0.000(3)
C(9)	0.037(4)	0.032(3)	0.040(4)	-0.000(3)	0.006(3)	0.002(3)
C(10)	0.034(3)	0.037(4)	0.039(4)	-0.002(3)	0.011(3)	-0.004(3)
C(11)	0.033(3)	0.046(4)	0.032(3)	-0.002(3)	0.004(3)	0.003(3)
C(12)	0.064(5)	0.059(5)	0.028(3)	0.003(4)	0.009(4)	0.003(3)
C(13)	0.063(5)	0.064(5)	0.035(4)	0.004(4)	0.013(4)	-0.006(3)
C(14)	0.042(4)	0.036(4)	0.038(4)	-0.005(3)	0.015(3)	-0.002(3)
C(15)	0.034(3)	0.033(3)	0.049(4)	-0.006(3)	0.013(3)	-0.001(3)
C(16)	0.054(4)	0.040(4)	0.034(3)	0.005(3)	0.011(3)	0.006(3)
C(17)	0.084(6)	0.050(5)	0.057(5)	-0.003(4)	0.029(5)	-0.009(4)
C(18)	0.103(7)	0.061(5)	0.055(5)	0.019(5)	0.028(5)	-0.017(4)
C(19)	0.082(6)	0.078(6)	0.067(6)	0.034(5)	0.038(5)	0.005(5)
C(20)	0.069(6)	0.104(7)	0.065(6)	0.001(5)	0.039(5)	0.013(5)
C(21)	0.054(5)	0.077(5)	0.046(4)	-0.008(4)	0.014(4)	-0.007(4)

Supporting Table 2. (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(22)	0.037(4)	0.047(4)	0.038(4)	0.003(3)	0.009(3)	0.009(3)
C(23)	0.062(5)	0.051(5)	0.054(5)	0.005(4)	0.004(4)	0.014(4)
C(24)	0.081(6)	0.060(5)	0.060(5)	-0.002(5)	0.017(5)	0.019(4)
C(25)	0.067(6)	0.074(6)	0.059(5)	0.016(5)	0.015(5)	0.033(4)
C(26)	0.045(5)	0.101(7)	0.047(5)	0.000(5)	-0.001(4)	0.017(5)
C(27)	0.047(4)	0.069(5)	0.039(4)	-0.002(4)	0.009(4)	0.004(4)
C(28)	0.044(4)	0.030(3)	0.048(4)	-0.006(3)	0.014(4)	-0.005(3)
C(29)	0.056(5)	0.055(4)	0.039(4)	-0.003(4)	0.012(4)	-0.009(3)
C(30)	0.059(5)	0.063(5)	0.043(4)	0.001(4)	0.026(4)	-0.012(4)
C(31)	0.056(5)	0.050(5)	0.070(5)	0.003(4)	0.021(4)	-0.010(4)
C(32)	0.062(5)	0.054(5)	0.058(5)	0.008(4)	0.020(4)	0.002(4)
C(33)	0.050(4)	0.044(4)	0.054(4)	-0.001(3)	0.022(4)	-0.002(3)
C(34)	0.071(6)	0.066(5)	0.067(5)	-0.001(4)	0.008(5)	0.009(4)

The general temperature factor expression:$\exp(-2p^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Supporting Table 3. Bond lengths (Å) for **3-Cu**.

atom	atom	distance	atom	atom	distance
Cu(1)	O(2)	2.045(4)	Cu(1)	N(1)	1.914(5)
Cu(1)	N(2)	1.961(5)	Cu(1)	N(3)	1.893(5)
Cl(1)	C(34)	1.745(8)	Cl(2)	C(34)	1.737(8)
Cl(3)	C(34)	1.758(8)	O(1)	C(1)	1.229(8)
O(2)	C(15)	1.267(7)	N(1)	C(1)	1.382(8)
N(1)	C(4)	1.387(8)	N(2)	C(6)	1.345(7)
N(2)	C(9)	1.394(7)	N(3)	C(11)	1.353(7)
N(3)	C(14)	1.360(7)	C(1)	C(2)	1.485(9)
C(2)	C(3)	1.309(9)	C(3)	C(4)	1.468(8)
C(4)	C(5)	1.372(8)	C(5)	C(6)	1.436(8)
C(5)	C(16)	1.501(8)	C(6)	C(7)	1.435(8)
C(7)	C(8)	1.343(8)	C(8)	C(9)	1.442(8)
C(9)	C(10)	1.399(8)	C(10)	C(11)	1.412(8)
C(10)	C(22)	1.487(8)	C(11)	C(12)	1.422(8)
C(12)	C(13)	1.376(9)	C(13)	C(14)	1.409(8)
C(14)	C(15)	1.440(8)	C(15)	C(28)	1.477(8)
C(16)	C(17)	1.360(9)	C(16)	C(21)	1.385(9)
C(17)	C(18)	1.40(1)	C(18)	C(19)	1.35(1)
C(19)	C(20)	1.36(1)	C(20)	C(21)	1.39(1)
C(22)	C(23)	1.375(9)	C(22)	C(27)	1.382(9)
C(23)	C(24)	1.378(9)	C(24)	C(25)	1.37(1)
C(25)	C(26)	1.36(1)	C(26)	C(27)	1.39(1)
C(28)	C(29)	1.394(8)	C(28)	C(33)	1.389(9)
C(29)	C(30)	1.376(9)	C(30)	C(31)	1.37(1)
C(31)	C(32)	1.38(1)	C(32)	C(33)	1.375(9)
C(2)	H(1)	0.950(9)	C(3)	H(2)	0.950(8)
C(7)	H(3)	0.950(8)	C(8)	H(4)	0.950(8)
C(12)	H(5)	0.950(9)	C(13)	H(6)	0.950(8)
C(17)	H(7)	0.95(1)	C(18)	H(8)	0.95(1)
C(19)	H(9)	0.95(1)	C(20)	H(10)	0.95(1)

Supporting Table 3. (continued)

atom	atom	distance	atom	atom	distance
C(21)	H(11)	0.95(1)	C(23)	H(12)	0.950(9)
C(24)	H(13)	0.95(1)	C(25)	H(14)	0.95(1)
C(26)	H(15)	0.95(1)	C(27)	H(16)	0.95(1)
C(29)	H(17)	0.950(9)	C(30)	H(18)	0.95(1)
C(31)	H(19)	0.95(1)	C(32)	H(20)	0.950(9)
C(33)	H(21)	0.950(9)	C(34)	H(22)	0.950(9)

Supporting Table 4. Bond angles(^{o}) for **3-Cu**.

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Cu(1)	N(1)	97.8(2)	O(2)	Cu(1)	N(2)	167.8(2)
N(1)	Cu(1)	N(2)	93.6(2)	O(2)	Cu(1)	N(3)	79.4(2)
N(1)	Cu(1)	N(3)	175.8(2)	N(2)	Cu(1)	N(3)	89.5(2)
Cu(1)	O(2)	C(15)	113.9(4)	Cu(1)	N(1)	C(1)	128.4(4)
Cu(1)	N(1)	C(4)	123.6(4)	C(1)	N(1)	C(4)	107.4(5)
Cu(1)	N(2)	C(6)	125.1(4)	Cu(1)	N(2)	C(9)	126.9(4)
C(6)	N(2)	C(9)	108.0(5)	Cu(1)	N(3)	C(11)	132.7(4)
Cu(1)	N(3)	C(14)	118.0(4)	C(11)	N(3)	C(14)	109.2(5)
O(1)	C(1)	N(1)	125.4(6)	O(1)	C(1)	C(2)	126.2(7)
N(1)	C(1)	C(2)	108.3(6)	C(1)	C(2)	C(3)	107.2(6)
C(2)	C(3)	C(4)	109.2(6)	N(1)	C(4)	C(3)	107.8(6)
N(1)	C(4)	C(5)	127.2(6)	C(3)	C(4)	C(5)	125.0(6)
C(4)	C(5)	C(6)	122.2(6)	C(4)	C(5)	C(16)	119.2(6)
C(6)	C(5)	C(16)	118.6(6)	N(2)	C(6)	C(5)	125.3(6)
N(2)	C(6)	C(7)	109.0(5)	C(5)	C(6)	C(7)	125.7(5)
C(6)	C(7)	C(8)	108.0(5)	C(7)	C(8)	C(9)	107.3(6)
N(2)	C(9)	C(8)	107.6(5)	N(2)	C(9)	C(10)	125.0(5)
C(8)	C(9)	C(10)	127.1(6)	C(9)	C(10)	C(11)	122.5(6)
C(9)	C(10)	C(22)	119.2(5)	C(11)	C(10)	C(22)	118.3(6)
N(3)	C(11)	C(10)	122.7(6)	N(3)	C(11)	C(12)	107.6(6)
C(10)	C(11)	C(12)	129.6(6)	C(11)	C(12)	C(13)	107.8(6)
C(12)	C(13)	C(14)	106.5(6)	N(3)	C(14)	C(13)	108.8(6)
N(3)	C(14)	C(15)	112.0(5)	C(13)	C(14)	C(15)	139.2(6)
O(2)	C(15)	C(14)	116.6(6)	O(2)	C(15)	C(28)	117.9(6)
C(14)	C(15)	C(28)	125.6(6)	C(5)	C(16)	C(17)	121.6(6)
C(5)	C(16)	C(21)	119.3(6)	C(17)	C(16)	C(21)	119.1(7)
C(16)	C(17)	C(18)	120.2(8)	C(17)	C(18)	C(19)	120.6(8)
C(18)	C(19)	C(20)	120.1(8)	C(19)	C(20)	C(21)	120.1(8)
C(16)	C(21)	C(20)	119.9(7)	C(10)	C(22)	C(23)	120.7(6)
C(10)	C(22)	C(27)	120.3(6)	C(23)	C(22)	C(27)	118.9(6)

Supporting Table 4. (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(22)	C(23)	C(24)	120.6(7)	C(23)	C(24)	C(25)	120.3(8)
C(24)	C(25)	C(26)	120.1(7)	C(25)	C(26)	C(27)	120.1(8)
C(22)	C(27)	C(26)	120.0(7)	C(15)	C(28)	C(29)	123.7(6)
C(15)	C(28)	C(33)	117.6(6)	C(29)	C(28)	C(33)	118.7(6)
C(28)	C(29)	C(30)	120.3(7)	C(29)	C(30)	C(31)	120.5(7)
C(30)	C(31)	C(32)	119.7(7)	C(31)	C(32)	C(33)	120.4(7)
C(28)	C(33)	C(32)	120.4(7)	Cl(1)	C(34)	Cl(2)	110.3(5)
Cl(1)	C(34)	Cl(3)	109.4(4)	Cl(2)	C(34)	Cl(3)	111.1(5)
C(1)	C(2)	H(1)	126.4(4)	C(3)	C(2)	H(1)	126.5(4)
C(2)	C(3)	H(2)	126.0(4)	C(4)	C(3)	H(2)	124.8(4)
C(6)	C(7)	H(3)	126.0(3)	C(8)	C(7)	H(3)	126.0(4)
C(7)	C(8)	H(4)	127.0(4)	C(9)	C(8)	H(4)	125.7(4)
C(11)	C(12)	H(5)	125.7(4)	C(13)	C(12)	H(5)	126.5(4)
C(12)	C(13)	H(6)	127.1(4)	C(14)	C(13)	H(6)	126.3(4)
C(16)	C(17)	H(7)	119.2(4)	C(18)	C(17)	H(7)	120.6(5)
C(17)	C(18)	H(8)	120.3(5)	C(19)	C(18)	H(8)	119.1(5)
C(18)	C(19)	H(9)	120.0(5)	C(20)	C(19)	H(9)	120.0(5)
C(19)	C(20)	H(10)	120.1(5)	C(21)	C(20)	H(10)	119.7(5)
C(16)	C(21)	H(11)	118.8(4)	C(20)	C(21)	H(11)	121.2(5)
C(22)	C(23)	H(12)	119.4(4)	C(24)	C(23)	H(12)	120.0(5)
C(23)	C(24)	H(13)	120.1(5)	C(25)	C(24)	H(13)	119.6(5)
C(24)	C(25)	H(14)	120.1(5)	C(26)	C(25)	H(14)	119.8(5)
C(25)	C(26)	H(15)	120.2(5)	C(27)	C(26)	H(15)	119.7(5)
C(22)	C(27)	H(16)	119.2(4)	C(26)	C(27)	H(16)	120.8(5)
C(28)	C(29)	H(17)	119.6(4)	C(30)	C(29)	H(17)	120.1(4)
C(29)	C(30)	H(18)	119.7(4)	C(31)	C(30)	H(18)	119.8(4)
C(30)	C(31)	H(19)	119.7(4)	C(32)	C(31)	H(19)	120.6(4)
C(31)	C(32)	H(20)	119.7(4)	C(33)	C(32)	H(20)	119.8(5)
C(28)	C(33)	H(21)	119.3(4)	C(32)	C(33)	H(21)	120.3(5)
Cl(1)	C(34)	H(22)	108.8(3)	Cl(2)	C(34)	H(22)	108.6(3)

Supporting Table 4. (continued)

atom	atom	atom	angle	atom	atom	atom	angle
Cl(3)	C(34)	H(22)	108.5(3)				

Supporting Table 5. Torsion Angles(°) for **3-Cu**.

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
N(1)	Cu(1)	O(2)	C(15)	173.0(7)	N(2)	Cu(1)	O(2)	C(15)	-27.9(3)
N(3)	Cu(1)	O(2)	C(15)	-3.8(8)	O(2)	Cu(1)	N(1)	C(1)	-11.7(1)
O(2)	Cu(1)	N(1)	C(4)	157.7(8)	N(2)	Cu(1)	N(1)	C(1)	172.6(9)
N(2)	Cu(1)	N(1)	C(4)	-17.9(1)	N(3)	Cu(1)	N(1)	C(1)	36.6(9)
N(3)	Cu(1)	N(1)	C(4)	-154.0(8)	O(2)	Cu(1)	N(2)	C(6)	-148.6(2)
O(2)	Cu(1)	N(2)	C(9)	32.4(3)	N(1)	Cu(1)	N(2)	C(6)	10.7(1)
N(1)	Cu(1)	N(2)	C(9)	-168.4(8)	N(3)	Cu(1)	N(2)	C(6)	-172.3(8)
N(3)	Cu(1)	N(2)	C(9)	8.7(1)	O(2)	Cu(1)	N(3)	C(11)	179.5(1)
O(2)	Cu(1)	N(3)	C(14)	3.0(8)	N(1)	Cu(1)	N(3)	C(11)	130.7(8)
N(1)	Cu(1)	N(3)	C(14)	-45.8(9)	N(2)	Cu(1)	N(3)	C(11)	-5.5(1)
N(2)	Cu(1)	N(3)	C(14)	178.1(8)	Cu(1)	O(2)	C(15)	C(14)	3.9(8)
Cu(1)	O(2)	C(15)	C(28)	-175.6(5)	Cu(1)	N(1)	C(1)	O(1)	-16.1(1)
Cu(1)	N(1)	C(1)	C(2)	167.3(5)	C(4)	N(1)	C(1)	O(1)	173.1(9)
C(4)	N(1)	C(1)	C(2)	-3.5(1)	Cu(1)	N(1)	C(4)	C(3)	-168.0(5)
Cu(1)	N(1)	C(4)	C(5)	14.7(1)	C(1)	N(1)	C(4)	C(3)	3.4(1)
C(1)	N(1)	C(4)	C(5)	-174.0(9)	Cu(1)	N(2)	C(6)	C(5)	1.6(1)
Cu(1)	N(2)	C(6)	C(7)	-178.2(4)	C(9)	N(2)	C(6)	C(5)	-179.2(8)
C(9)	N(2)	C(6)	C(7)	1.0(1)	Cu(1)	N(2)	C(9)	C(8)	177.5(4)
Cu(1)	N(2)	C(9)	C(10)	-7.8(1)	C(6)	N(2)	C(9)	C(8)	-1.7(1)
C(6)	N(2)	C(9)	C(10)	173.1(8)	Cu(1)	N(3)	C(11)	C(10)	0.5(1)
Cu(1)	N(3)	C(11)	C(12)	-176.7(4)	C(14)	N(3)	C(11)	C(10)	177.1(8)
C(14)	N(3)	C(11)	C(12)	-0.0(1)	Cu(1)	N(3)	C(14)	C(13)	176.7(5)
Cu(1)	N(3)	C(14)	C(15)	-1.9(8)	C(11)	N(3)	C(14)	C(13)	-0.5(1)
C(11)	N(3)	C(14)	C(15)	-179.2(7)	O(1)	C(1)	C(2)	C(3)	-174.2(9)
N(1)	C(1)	C(2)	C(3)	2.4(1)	C(1)	C(2)	C(3)	C(4)	-0.3(1)
C(2)	C(3)	C(4)	N(1)	-1.9(1)	C(2)	C(3)	C(4)	C(5)	175.5(9)
N(1)	C(4)	C(5)	C(6)	2.5(1)	N(1)	C(4)	C(5)	C(16)	-179.2(7)
C(3)	C(4)	C(5)	C(6)	-174.4(8)	C(3)	C(4)	C(5)	C(16)	3.9(1)
C(4)	C(5)	C(6)	N(2)	-11.3(1)	C(4)	C(5)	C(6)	C(7)	168.5(8)
C(16)	C(5)	C(6)	N(2)	170.4(8)	C(16)	C(5)	C(6)	C(7)	-9.8(1)

Supporting Figure 5. (continued)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(4)	C(5)	C(16)	C(17)	-92.2(1)	C(4)	C(5)	C(16)	C(21)	87.3(1)
C(6)	C(5)	C(16)	C(17)	86.1(1)	C(6)	C(5)	C(16)	C(21)	-94.4(1)
N(2)	C(6)	C(7)	C(8)	0.0(9)	C(5)	C(6)	C(7)	C(8)	-179.8(8)
C(6)	C(7)	C(8)	C(9)	-1.0(9)	C(7)	C(8)	C(9)	N(2)	1.7(1)
C(7)	C(8)	C(9)	C(10)	-172.9(8)	N(2)	C(9)	C(10)	C(11)	0.1(1)
N(2)	C(9)	C(10)	C(22)	178.8(7)	C(8)	C(9)	C(10)	C(11)	173.8(8)
C(8)	C(9)	C(10)	C(22)	-7.5(1)	C(9)	C(10)	C(11)	N(3)	3.8(1)
C(9)	C(10)	C(11)	C(12)	-179.7(8)	C(22)	C(10)	C(11)	N(3)	-174.9(8)
C(22)	C(10)	C(11)	C(12)	1.5(1)	C(9)	C(10)	C(22)	C(23)	-60.4(1)
C(9)	C(10)	C(22)	C(27)	122.4(1)	C(11)	C(10)	C(22)	C(23)	118.4(1)
C(11)	C(10)	C(22)	C(27)	-58.8(1)	N(3)	C(11)	C(12)	C(13)	0.5(1)
C(10)	C(11)	C(12)	C(13)	-176.4(8)	C(11)	C(12)	C(13)	C(14)	-0.8(1)
C(12)	C(13)	C(14)	N(3)	0.8(1)	C(12)	C(13)	C(14)	C(15)	178.9(1)
N(3)	C(14)	C(15)	O(2)	-1.5(1)	N(3)	C(14)	C(15)	C(28)	178.0(7)
C(13)	C(14)	C(15)	O(2)	-179.6(1)	C(13)	C(14)	C(15)	C(28)	-0.1(2)
O(2)	C(15)	C(28)	C(29)	176.3(7)	O(2)	C(15)	C(28)	C(33)	-4.6(1)
C(14)	C(15)	C(28)	C(29)	-3.1(1)	C(14)	C(15)	C(28)	C(33)	176.0(8)
C(5)	C(16)	C(17)	C(18)	177.0(9)	C(21)	C(16)	C(17)	C(18)	-2.5(2)
C(5)	C(16)	C(21)	C(20)	-178.0(9)	C(17)	C(16)	C(21)	C(20)	1.5(2)
C(16)	C(17)	C(18)	C(19)	2.7(2)	C(17)	C(18)	C(19)	C(20)	-1.8(2)
C(18)	C(19)	C(20)	C(21)	0.8(2)	C(19)	C(20)	C(21)	C(16)	-0.6(2)
C(10)	C(22)	C(23)	C(24)	-177.8(8)	C(27)	C(22)	C(23)	C(24)	-0.6(2)
C(10)	C(22)	C(27)	C(26)	178.6(8)	C(23)	C(22)	C(27)	C(26)	1.4(2)
C(22)	C(23)	C(24)	C(25)	-0.4(2)	C(23)	C(24)	C(25)	C(26)	0.5(2)
C(24)	C(25)	C(26)	C(27)	0.3(2)	C(25)	C(26)	C(27)	C(22)	-1.3(2)
C(15)	C(28)	C(29)	C(30)	177.4(8)	C(33)	C(28)	C(29)	C(30)	-1.6(1)
C(15)	C(28)	C(33)	C(32)	-177.4(8)	C(29)	C(28)	C(33)	C(32)	1.7(1)
C(28)	C(29)	C(30)	C(31)	0.1(1)	C(29)	C(30)	C(31)	C(32)	1.3(2)
C(30)	C(31)	C(32)	C(33)	-1.2(2)	C(31)	C(32)	C(33)	C(28)	-0.4(2)

Supporting Table 6. Least Squares Planes for **3-Cu**.

Plane number 1

Co-ordinates of the defining atoms projected onto the best plane

Type	Serial	XP	YP	ZP
N	1	-1.908	-1.185	-0.147
N	2	0.041	0.855	-0.004
N	3	1.890	-1.129	0.070
C	1	-2.707	-2.295	-0.342
C	2	-4.117	-1.905	-0.091
C	3	-4.122	-0.624	0.181
C	4	-2.746	-0.115	0.131
C	5	-2.389	1.201	0.279
C	6	-1.037	1.652	0.103
C	7	-0.617	3.021	0.008
C	8	0.715	3.037	-0.157
C	9	1.165	1.667	-0.144
C	10	2.489	1.213	-0.146
C	11	2.823	-0.151	-0.003
C	12	4.101	-0.773	0.022
C	13	3.905	-2.133	0.099
C	14	2.512	-2.336	0.140

Co-ordinates of other atoms projected onto the best plane

Type	Serial	XP	YP	ZP
CU	1	-0.002	-1.106	0.011

Plane number 2

Co-ordinates of the defining atoms projected onto the best plane

Type	Serial	XP	YP	ZP
N	1	-1.216	-0.034	-0.020

C	1	-0.367	-1.124	0.017
C	2	1.032	-0.628	-0.007
C	3	0.978	0.680	-0.004
C	4	-0.427	1.106	0.015

Plane number 3

Co-ordinates of the defining atoms projected onto the best plane

Type	Serial	XP	YP	ZP
N	2	-1.184	0.137	0.008
C	6	-0.533	-1.039	-0.003
C	7	0.881	-0.792	-0.003
C	8	1.070	0.537	0.008
C	9	-0.233	1.156	-0.009

Plane number 4

Co-ordinates of the defining atoms projected onto the best plane

Type	Serial	XP	YP	ZP
N	3	1.135	-0.282	0.001
C	11	0.650	0.981	0.002
C	12	-0.769	0.897	-0.004
C	13	-1.112	-0.436	0.005
C	14	0.096	-1.160	-0.004

Plane number 5

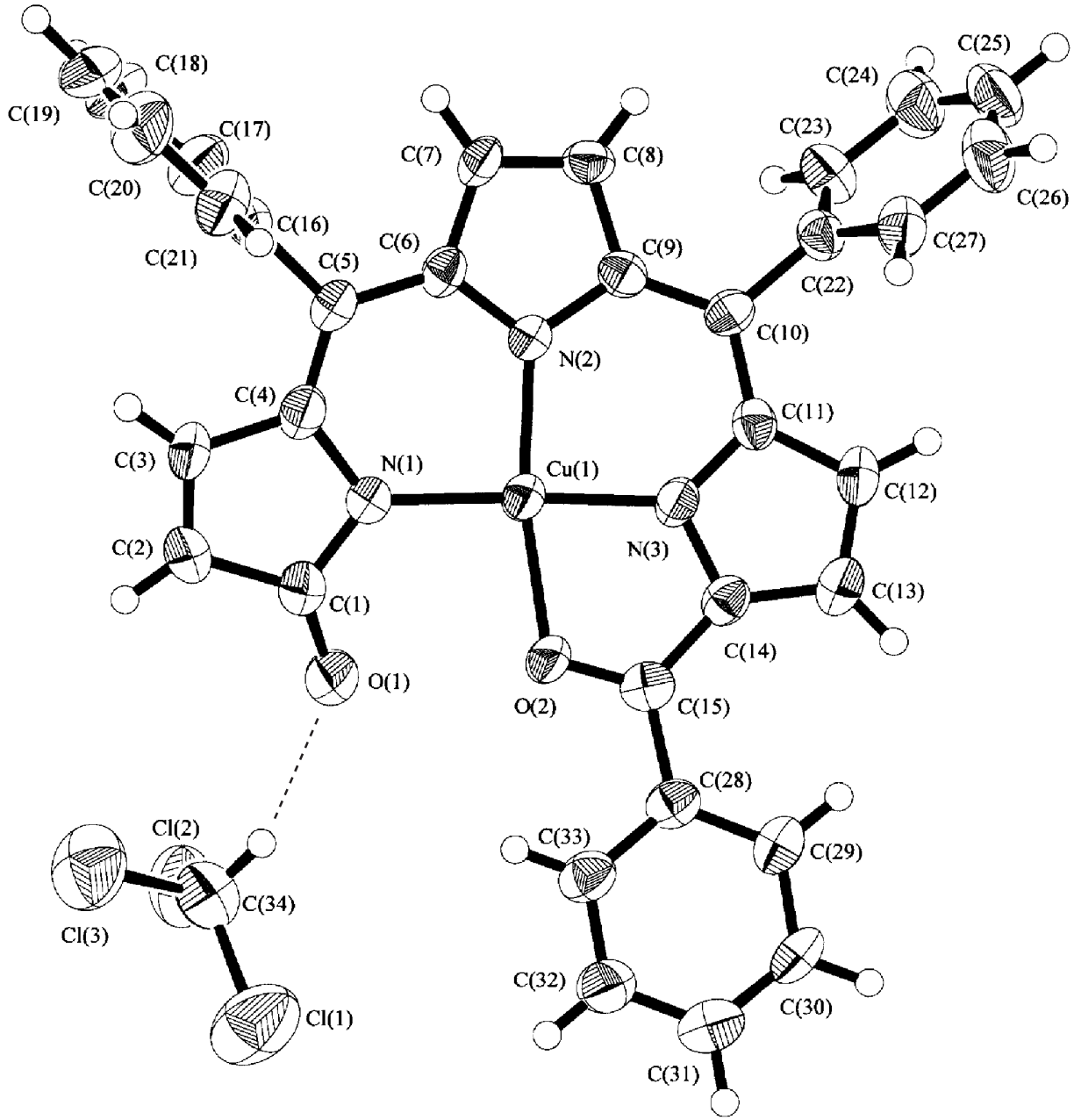
Co-ordinates of the defining atoms projected onto the best plane

Type	Serial	XP	YP	ZP
C	28	-1.370	0.261	0.011
C	29	-0.446	1.305	-0.005
C	30	0.904	1.037	-0.005
C	31	1.357	-0.258	0.009

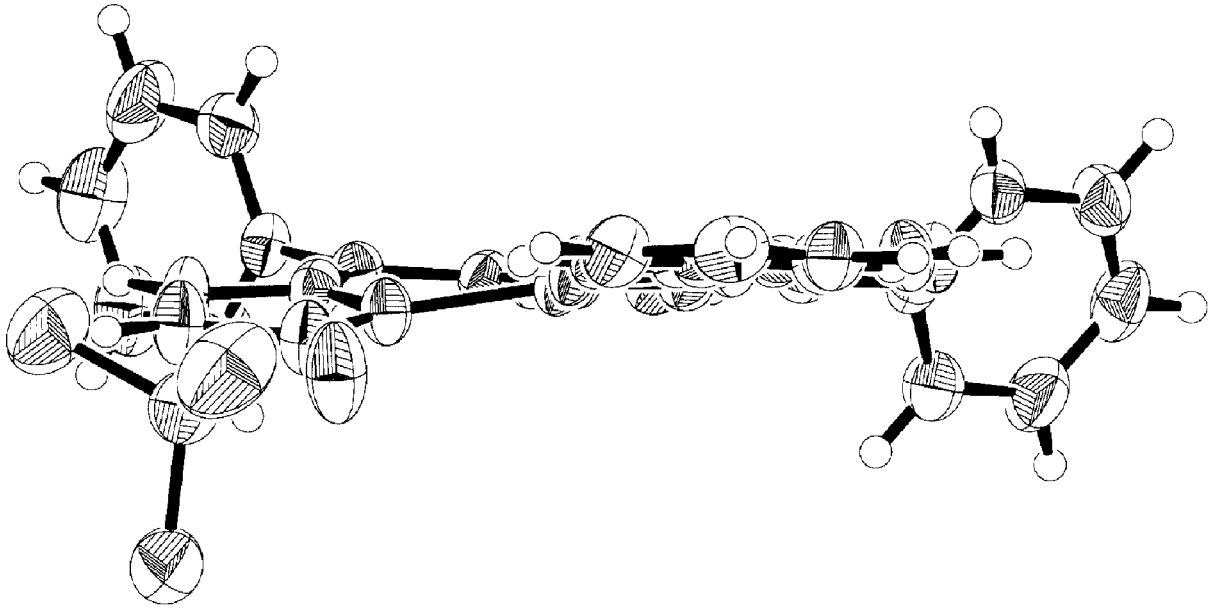
C	32	0.453	-1.298	-0.004
C	33	-0.899	-1.046	-0.007

Angle between plane	1 and plane	2 is	166.66	Degrees
Angle between plane	1 and plane	3 is	173.15	Degrees
Angle between plane	1 and plane	4 is	176.42	Degrees
Angle between plane	1 and plane	5 is	6.72	Degrees
Angle between plane	2 and plane	3 is	14.02	Degrees
Angle between plane	2 and plane	4 is	16.29	Degrees
Angle between plane	2 and plane	5 is	163.01	Degrees
Angle between plane	3 and plane	4 is	5.92	Degrees
Angle between plane	3 and plane	5 is	176.46	Degrees
Angle between plane	4 and plane	5 is	175.98	Degrees

Supporting Figure 3. (a) Top view of **3-Cu**·$CHCl_3$, showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

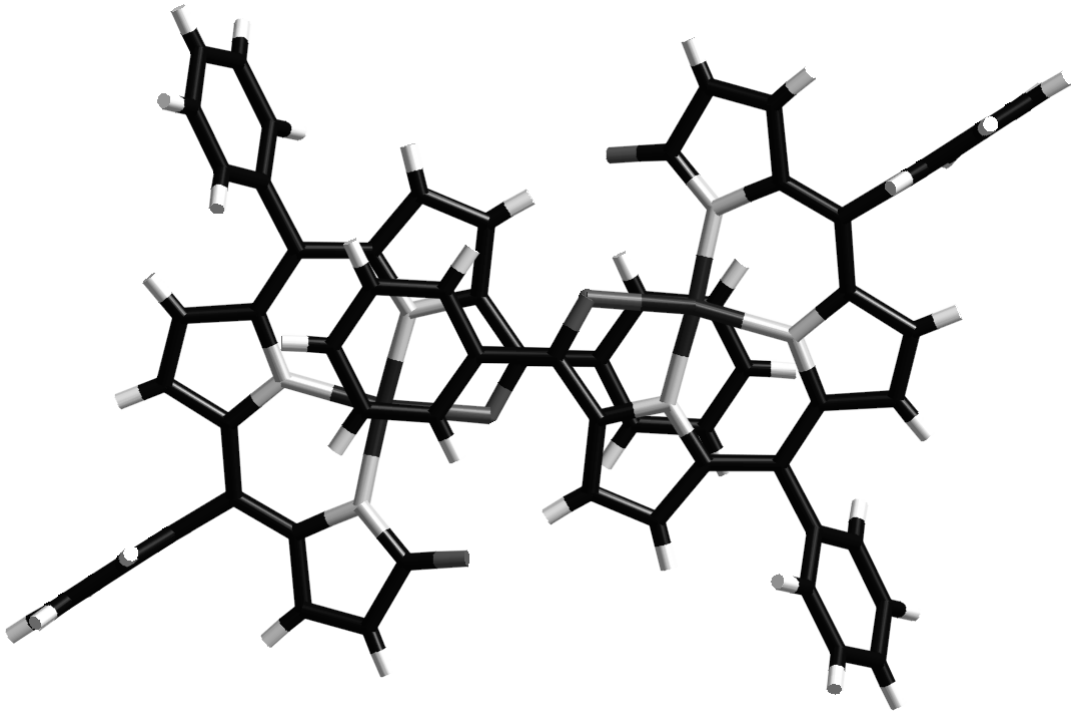


Supporting Figure 3 (b) Side view of **3-Cu**.



Supporting Figure 3 (c), (d) π-stacked dimer of **3-Cu**.

a) top view



b) side view