original
RECEIVED JAN 1 1 2000
JA992680F

Supporting Information

Experimental details including figures (S1 – S2), tables (S1 – S12) listing crystallographic experimental details, final atomic coordinates, thermal parameters, and full bond distances and angles for **1a-BPh$_4$**, **1b**, and **1c**, and figures (S3 – S5) displaying fully labeled ORTEP drawings for **1a-BPh$_4$**, **1b**, and **1c** (38 pages print/PDF). See any current masthead page for ordering information and Web access instructions.

Preparation of Complexes. **[Cu(Me$_2$-tpa)]PF$_6$(1a).** Me$_2$-tpa (0.64 g, 2.0 mmol) in ethanol (20 cm^3) was added to solid [Cu(CH$_3$CN)$_4$]ClO$_4$ (0.65 g, 2.0 mmol) under N$_2$ atmosphere to give an yellow solution. Addition of NH$_4$PF$_6$ (0.65 g, 4.0 mmol) in water (3 cm^3) gave yellow crystals (0.75 g, 72 %). Anal. Calcd for C$_{22}$H$_{28}$N$_4$CuPF$_6$: C, 45.59; H, 4.21; N, 10.63%. Found: C, 45.77; H, 4.13; N, 10.58%. UV-Vis (λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) in CH$_2$Cl$_2$): 334 (ca.11000).

[Cu(Me$_2$-tpa)]BPh$_4$ (1a-BPh$_4$). Me$_2$-tpa (0.32 g, 1.0 mmol) in methanol (20 cm^3) was added to solid [Cu(CH$_3$CN)$_4$]ClO$_4$ (0.33 g, 1.0 mmol) under N$_2$ atmosphere to give an yellow solution, to which NaBPh$_4$ (0.68 g, 2.0 mmol) in methanol (5 cm^3) was added to produce pale yellow crystals. Recrystallization from methanol/acetonitrile (5 : 1) mixture afforded yellow crystals suitable for X-ray crystallography (0.28 g, 40 %). Anal. Calcd for C$_{44}$H$_{42}$N$_4$CuB: C, 75.37; H, 6.04; N, 7.99%. Found: C, 75.16; H, 6.10; N, 7.88%.

[Cu$_2$(O)$_2$(Me$_2$-tpa)$_2$](PF$_6$)$_2$·2(CH$_3$)$_2$CO (1b). [Cu(Me$_2$-tpa)]PF$_6$ (ca. 50 mg) was dissolved in acetone/methanol (10:1) mixture (ca. 2 cm^3) at –78 °C under N$_2$ atmosphere and then O$_2$ gas was introduced into the solution to produce a brown solution, which was allowed to stand for a few hours to give brown crystals suitable for X-ray analysis.

[Cu$_2$(OH)$_2$(Me$_2$-tpa)$_2$](ClO$_4$)$_2$ (1c). To a solution of Cu(ClO$_4$)$_2$·6H$_2$O (1.85 g, 5.0 mmol) and Me$_2$-tpa (1.62 g, 5.1 mmol) in 35 cm^3 of methanol was added a methanol solution (10 cm^3) containing triethylamine (30 mmol) with stirring under N$_2$ atmosphere to

produce a light blue powder. Recrystallization from methanol afforded blue crystals suitable for X-ray crystallography (2.18 g, 43%). Anal. Calcd for $C_{40}H_{48}N_8Cu_2Cl_2O_{11}$: C, 47.34; H, 4.77; N, 11.04%. Found: C, 47.43; H, 4.63; N, 11.12%.

Low Temperature UV-Vis Spectroscopy. Electronic spectra were measured at -80 °C in CH_2Cl_2 on a Hitachi U-3400 spectrophotometer specially equipped by an Otsuka Denshi optical glass fiber attachment with the corrected light path length of 0.315 cm and on a Shimadzu MultiSpec-1500 diode array spectrophotometer using 1 mm quartz cell with a Unisoku thermostated cell holder designed for low-temperature experiments. Typical experiment was as follows. A three-necked flask (30 cm^3) equipped with an optical glass fiber in one neck to monitor the spectrum was immersed in a Tokyo Rikakikai EYELA LOW TEMP. PAIRSTIRRER PSL-1800 at –80 °C with magnetic stirring. The other necks were sealed by septums to inject O_2 or N_2 gas by a syringe needle. A dichloromethane solution of **1a** (ca 25 cm^3, 0.11 mM/Cu_2) was transferred from a volumetric flask to the above system under N_2. After the electronic spectrum of **1a** was measured, O_2 gas was introduced into the system by direct bubbling of O_2 for >5 minutes through a syringe needle. The electronic spectrum of a brown solution was recorded. The brown bis(μ-oxo) species **1b** was reconverted into **1a** by gentle bubbling of N_2 gas into the system for >30 minutes. This cycle can be repeated for several times.

The reversible conversion between **1a** and **1b** was also monitored using 1 mm cell system described above. In this case, reconversion from **1b** to **1a** by bubbling of N_2 gas was much faster and effected for ca. 5 minutes. This faster reconversion is probably due to a partial warming of the system by bubbling of N_2 gas.

Dioxygen Evolution Analysis. An apparatus used for the experiment is shown in Figure S1. GC measurement was performed on a Shimadzu GC-8A gas chromatograph equipped with a TCD detector with a 3 m column (2.6 mm i. d.) of molecular sieve 5A (30 – 60 mesh). A typical experiment was as follows. Complex **1a** (72.0 mg, 0.137 mmol) was dissolved in 20 cm^3 of acetone in a Schlenk tube (ca. 30 cm^3) at –78 °C under Ar atmosphere and O_2 gas was introduced into the system with stirring for 10 min. The dead space of this set-up was ~37 cm^3. After O_2 gas was purged by freeze-vacuum technique three times, the

system was filled with Ar gas and equilibrated to ambient pressure. After 10 minutes, a 1.0 cm^3 portion of the inner gas was taken up by a pressure-lock syringe and subjected to GC measurement (no measurable dioxygen was detected at this stage within experimental error). Then PPh_3 (72.2 mg, 0.275 mmol) was added to the resulting brown solution, which was stirred for 150 minutes to give a pale green solution. The amount of dioxygen evolved was monitored by GC measurement (1.37 cm^3 of O_2 gas was obtained from the following calibration line). The amount of dioxygen was calibrated by injecting the appropriate amounts of O_2 gas (0.2, 0.5, 1.0, 1.3 and 1.5 cm^3) in the same conditions without **1a** and PPh_3, where the pressure changes by injecting O_2 gas were ignored. A fairly good calibration line was obtained as seen in Figure S2. Yield: ca. 88 ± 2% based on a dimer for two experiments. No measurable $O{=}PPh_3$ was detected, which were confirmed by GCMS and ^1H NMR measurements. The same experiment carried out without PPh_3 indicated that about 20% of dioxygen evolution was detected after 150 minutes and no more dioxygen evolution was detected after complete decomposition.

Monooxygenase Activity. Ligand Recovery Experiments. A typical experiment was as follows. Complex **1a** (73 mg, 0.139 mmol) was dissolved in 20 cm^3 of acetone in a Schlenk tube at –78 °C under N_2 atmosphere and then O_2 was introduced into the solution with stirring to produce a brown solution. After removal of dioxygen by freeze-vacuum technique three times, the system was filled with N_2 gas and the brown solution was allowed to stand at –78 °C to decompose. After decomposition, solvent was removed under reduced pressure. Demetallation was carried out by the reaction with concentrated aqueous NH_4OH (20 cm^3) containing Na_4edta (ca. 10 equiv), and then ligand and its reaction products were extracted into chloroform (3 × 20 cm^3). The reaction products were identified by ^1H NMR and MS. The amounts of ligand and its reaction product were determined by ^1H NMR by addition of 2,6-dimethyl-*p*-benzoquinone as an internal standard. Total amounts of Me_2-tpa and (6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine recovered were more than 92% for 3 experiments. Yield of (6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine was 50 ± 6% based on a dimer for three experiments. 6-Methylpyridine-2-carbaldehyde was recovered from a decomposed solution by a vacuum

distillation. The MS spectrum revealed that isotope scrambling of ^{16}O and ^{18}O occurs at about 40% during the recovery experiments as found for $[Cu_2(O)_2(Bn_3\text{-tacn})_2]^{2+}$.[3b]

X-ray Crystallography. General Procedures. X-ray diffraction study of $[Cu(Me_2\text{-tpa})]BPh_4$ (**1a-BPh4**) was performed with a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation (λ= 0.71070 Å). Cell constants and orientation matrices were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $25° < 2\theta < 30°$. The data were collected at room temperature using the ω-2θ scan technique to a maximum 2θ value of 55.0° at a speed of 4.0°/min (in ω) for **1a-BPh4**. The intensities of three reflections were measured after every 150 reflections. No appreciable decay was observed. The weak reflections ($I < 10.0\ \sigma(I)$) were rescanned (maximum of 5 scans) and the counts were accumulated to ensure good counting statistics. The data were corrected for Lorentz and polarization effects. Absorption corrections based on ψ scans were applied for **1a-BPh4**.

X-ray diffraction studies of $[Cu_2(O)_2(Me_2\text{-tpa})_2](PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**) and $[Cu_2(OH)_2(Me_2\text{-tpa})](ClO_4)_2$ (**1c**) were performed on a Rigaku RAXIS–IV imaging plate area detector using graphite monochromated Mo–Kα radiation (λ= 0.71070 Å). Crystal–to–detector distance was 120 mm. Three oscillation photographs were taken with ϕ angles of 0°, 45°, and 90° to determine cell constants and orientation matrix. Intensity data were collected by taking oscillation photographs with continuous ϕ angles. The cell constants were refined by using these oscillation photographs. The data were corrected for Lorentz and polarization effects, but not for absorption effect.

Initial atomic coordinates were obtained by a direct method (SHELXS–86).[1] The structures were expanded using a Fourier technique[2] and refined by a full–matrix least–squares method by using the teXsan[3] crystallographic software package of Molecular Structure Corporation. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions (0.95 Å). They were included, but not refined, in the final least-squares cycles.

$[Cu(Me_2\text{-tpa})]BPh_4$ (1a-BPh4). A prismatic crystal having approximate dimensions of $0.35 \times 0.20 \times 0.10$ mm was mounted in a glass capillary with mother liquor.

Data were collected at 22 °C.

The structure was solved in the monoclinic space group $P2_1/c$. There are one complex cation and one tetraphenylborate anion in the asymmetric unit. The final cycle of full-matrix least-squares refinement was based on 3275 reflections ($I > 3.00\ \sigma(I)$) and 452 variable parameters and converged with R=0.053, Rw=0.077. The maximum shift was 0.00 in the final least-squares cycles. The maximum and minimum peaks on the final difference Fourier map were 0.58 and -0.31 $e^-/Å^3$, respectively.

$[Cu_2(O)_2(Me_2\text{-tpa})_2](PF_6)_2 \cdot 2(CH_3)_2CO$ (1b). Since the complex is only stable at low temperature, a single crystal (0.12 × 0.10 × 0.06 mm) was picked up on a hand–made cold copper plate mounted inside a liquid N_2 dewar vessel and mounted on a glass rod at ca. –80 °C. Data were collected at –120 °C. Three oscillation photographs were taken with oscillation angle 2° and exposure time of 12 min for each frame. Intensity data were collected by taking oscillation photographs to a maximum 2θ value of 51.3° (total oscillation range 105°; 70 frames; oscillation angle 1.5°; exposure time 12 min).

The structure was solved and refined in the monoclinic space group $P2_1/c$. The asymmetric unit consists of half of bis(μ–oxo)dicopper(III) cation, one hexafluorophosphate anion and one acetone molecule. The final cycle of full-matrix least-squares refinement based on 1780 reflections ($I > 3.00\sigma(I)$) and 335 variable parameters was well converged with R = 0.078 and Rw = 0.107. The maximum shift was 0.00 in the final least-squares cycles. The maximum and minimum peaks in the final difference Fourier map were 1.23 and -0.52 $e^-/Å^3$, respectively. Two peaks (1.23 and 1.21 $e^-/Å^3$) were remained in the vicinity of the metal ion on the final difference Fourier map.

$[Cu_2(OH)_2(Me_2\text{-tpa})_2](ClO_4)_2$ (1c). Single crystals suitable for X-ray crystallography were obtained by recrystallization from an methanol solution. A single crystal with dimensions of 0.25 × 0.25 × 0.30 mm was mounted on a glass rod at room temperature. Three oscillation photographs were taken with oscillation angle 2° and exposure time of 7 min for each frame at the crystal–to–detector distance 120 mm. Intensity data were collected by taking oscillation photographs to a maximum 2θ value of 51.6°(total oscillation range 120°; 30 frames; oscillation angle 4°; exposure time 30 min) at 23 °C.

The structure was solved and refined in the monoclinic space group $P2_1/n$. The asymmetric unit consists of half of bis(μ–hydroxo)dicopper(II) cation and one perchlorate anion. The full-matrix least-squares refinement was converged by using 3535 reflections ($I > 3.00\sigma(I)$) and 280 variable parameters with $R = 0.059$ and $Rw = 0.097$. The maximum shift was 0.00 in the final least-squares cycles. The maximum and minimum peaks on the final difference Fourier map were 0.92 and -0.67 $e^-/Å^3$, respectively.

(1) G. M. Sheldrick, SHELXS–86. A Program for Crystal Structure Determination. University of Göttingen, FRG, 1986.

(2) P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits, (1994). The DIRDIF–94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

Table S1. Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for [Cu(Me$_2$-tpa)]BPh$_4$ (**1a-BPh$_4$**).

<u>Crystal Data</u>	
Empirical Formula	$C_{44}H_{42}N_4BCu$
Crystal Color, Habit	pale yellow, block
Crystal Size (mm)	0.35 × 0.20 × 0.10
Crystal System	Monoclinic
Space Group	$P2_1/c$ (No. 14)
a =	13.193(1)Å
b =	13.597(3) Å
c =	20.855(2) Å
β =	95.082(9)°
Volume	3726.5(7) Å^3
Z	4
Formula Weight	701.20
Density (calcd.)	1.250 g/cm^3
Absorption Coefficient	6.22 cm^{-1}
F_{000}	1472.00
<u>Data Collection</u>	
Diffractometer Used	Rigaku AFC7R
Radiation	MoKα (λ = 0.71069 Å)
Temperature	22.0 °C
Scan Type	ω-2θ
Scan Rate	4.0° /min (in ω) (up to 5 scans)
$2\theta_{max}$	55.0°
Index Ranges	$0 \le h \le 17$, $-17 \le k \le 0$, $-26 \le l \le 26$
Total Reflections	9321
Total Independent Reflections	8945 (R_{int} = 0.040)
Reflections ($I > 3.00\sigma(I)$)	3275
<u>Structure Solution and Refinement</u>	
System Used	teXsan, version 1.8
Solution	Direct Methods (SHELXS86)
Refinement	Full-Matrix Least-Squares
Weighting Scheme	$w = 1 / [\sigma^2(F_o)]$
	$= [\sigma_c^2(F_o) + p^2F_o^2/4]^{-1}$

Table S1 (continued). Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for [Cu(Me$_2$-tpa)]BPh$_4$ (**1a-BPh$_4$**).

	$\sigma_c(F_o)$ = e.s.d. based on counting statistics; p-factor = 0.082.
Final R Indices (I>3.00σ(I))	R = 0.053, where $R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$ R_w = 0.077, where $R_w = [(\Sigma\, w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma\, wF_o^2)]^{1/2}$
Goodness-of-Fit	1.38, where GOF = $[\Sigma\, w(\lvert F_o\rvert-\lvert F_c\rvert)^2 / (N_o-N_v)]^{1/2}$, and N_o and N_v denote the number of observations and parameters.
Data / Parameters	3275 / 452 = 7.2
Maximum and Minimum Difference Peaks	0.58, -0.31 e$^-$/Å^3
Max Shift / Error in Final Cycle	0.00

Table S2. Fractional Atomic Coordinates Including Hydrogen Atoms and Isotropic Thermal Parameters of [Cu(Me_2-tpa)]BPh_4 (**1a-BPh_4**).[a,b]

Atom	x	y	z	B_{eq}[c]
Cu(1)	0.29053(5)	0.24505(6)	0.18147(4)	4.62(2)
N(1)	0.1639(3)	0.3333(3)	0.1387(2)	3.9(1)
N(2)	0.2972(4)	0.3490(4)	0.2498(2)	5.1(1)
N(3)	0.3502(3)	0.2768(3)	0.0984(2)	4.3(1)
N(4)	0.1848(3)	0.1384(3)	0.1797(2)	4.0(1)
C(1)	0.1784(5)	0.4305(5)	0.1693(3)	5.3(2)
C(2)	0.2328(5)	0.4230(5)	0.2367(3)	5.3(2)
C(3)	0.2172(6)	0.4963(6)	0.2820(4)	7.2(2)
C(4)	0.2768(9)	0.4902(8)	0.3410(4)	8.9(3)
C(5)	0.3444(8)	0.4143(9)	0.3525(5)	9.3(3)
C(6)	0.3561(6)	0.3431(7)	0.3076(4)	7.8(2)
C(7)	0.1762(4)	0.3341(5)	0.0703(3)	5.1(2)
C(8)	0.2852(5)	0.3226(4)	0.0546(3)	4.4(1)
C(9)	0.3128(5)	0.3528(5)	-0.0040(3)	5.5(2)
C(10)	0.4103(7)	0.3354(7)	-0.0196(4)	7.9(2)
C(11)	0.4757(6)	0.2890(7)	0.0241(5)	7.7(2)
C(12)	0.4451(5)	0.2602(5)	0.0828(3)	5.6(2)
C(13)	0.5135(7)	0.2097(8)	0.1291(5)	9.5(3)
C(14)	0.0743(4)	0.2812(5)	0.1557(3)	4.9(2)
C(15)	0.0905(4)	0.1711(4)	0.1575(3)	4.2(1)
C(16)	0.0123(5)	0.1054(6)	0.1420(3)	5.7(2)
C(17)	0.0292(7)	0.0071(6)	0.1505(4)	6.9(2)
C(18)	0.1237(7)	-0.0259(5)	0.1751(4)	6.4(2)
C(19)	0.2007(5)	0.0410(5)	0.1896(3)	4.9(2)
C(20)	0.3041(7)	0.0095(5)	0.2143(4)	7.6(2)
B(1)	1.1991(5)	0.7318(4)	0.0517(3)	3.6(1)
C(21)	1.2915(4)	0.6734(5)	0.0929(3)	4.6(1)
C(22)	1.3382(4)	0.5900(5)	0.0716(3)	5.0(2)
C(23)	1.4132(5)	0.5386(6)	0.1091(5)	7.6(2)
C(24)	1.4449(7)	0.5716(9)	0.1697(6)	10.0(3)
C(25)	1.4026(8)	0.6541(10)	0.1921(4)	9.9(3)
C(26)	1.3285(7)	0.7044(7)	0.1543(4)	8.2(2)
C(27)	1.2315(5)	0.8477(4)	0.0412(3)	4.1(1)
C(28)	1.3317(5)	0.8796(5)	0.0504(4)	6.2(2)
C(29)	1.3606(6)	0.9759(7)	0.0387(4)	7.6(2)

Table S2 (continued). Fractional Atomic Coordinates Including Hydrogen Atoms and Isotropic Thermal Parameters of [Cu(Me$_2$-tpa)]BPh$_4$ (**1a-BPh$_4$**).[a,b]

Atom	x	y	z	B_{eq}[c]
C(30)	1.2893(8)	1.0444(6)	0.0179(3)	6.9(2)
C(31)	1.1884(6)	1.0156(5)	0.0077(3)	6.3(2)
C(32)	1.1639(5)	0.9209(5)	0.0193(3)	5.6(2)
C(33)	1.1748(4)	0.6781(4)	-0.0179(2)	3.5(1)
C(34)	1.2177(4)	0.7065(4)	-0.0740(3)	4.5(1)
C(35)	1.2042(5)	0.6529(6)	-0.1312(3)	5.9(2)
C(36)	1.1495(5)	0.5677(6)	-0.1334(3)	5.8(2)
C(37)	1.1049(5)	0.5346(4)	-0.0801(3)	4.9(2)
C(38)	1.1187(4)	0.5908(4)	-0.0243(3)	4.1(1)
C(39)	1.0933(4)	0.7273(4)	0.0909(3)	3.8(1)
C(40)	0.9991(5)	0.7581(4)	0.0624(3)	4.8(1)
C(41)	0.9106(5)	0.7595(5)	0.0936(3)	5.3(2)
C(42)	0.9120(6)	0.7235(5)	0.1547(4)	5.6(2)
C(43)	1.0000(7)	0.6879(5)	0.1833(3)	6.4(2)
C(44)	1.0896(5)	0.6918(5)	0.1526(3)	5.2(2)
H(1)	0.2178	0.4704	0.1435	6.3940
H(2)	0.1137	0.4601	0.1720	6.3940
H(3)	0.1688	0.5475	0.2732	8.6110
H(4)	0.2703	0.5388	0.3731	10.6280
H(5)	0.3840	0.4111	0.3928	11.1422
H(6)	0.4035	0.2910	0.3159	9.3176
H(7)	0.1374	0.2816	0.0507	6.0833
H(8)	0.1510	0.3949	0.0530	6.0833
H(9)	0.2652	0.3854	-0.0336	6.6450
H(10)	0.4313	0.3555	-0.0600	9.5150
H(11)	0.5434	0.2762	0.0142	9.2389
H(12)	0.4873	0.1462	0.1370	11.4504
H(13)	0.5782	0.2035	0.1128	11.4504
H(14)	0.5204	0.2461	0.1681	11.4504
H(15)	0.0583	0.3027	0.1970	5.8482
H(16)	0.0192	0.2959	0.1247	5.8482
H(17)	-0.0529	0.1286	0.1255	6.8447
H(18)	-0.0240	-0.0386	0.1394	8.2225
H(19)	0.1355	-0.0942	0.1821	7.7244
H(20)	0.3055	-0.0600	0.2192	9.0742

Table S2 (continued). Fractional Atomic Coordinates Including Hydrogen Atoms and Isotropic Thermal Parameters of [Cu(Me$_2$-tpa)]BPh$_4$ (**1a-BPh$_4$**).[a,b]

Atom	x	y	z	B_{eq}[c]
H(21)	0.3514	0.0285	0.1848	9.0742
H(22)	0.3219	0.0396	0.2549	9.0742
H(23)	1.3183	0.5666	0.0295	6.0332
H(24)	1.4422	0.4809	0.0927	9.1128
H(25)	1.4960	0.5370	0.1956	11.9552
H(26)	1.4240	0.6774	0.2340	11.9048
H(27)	1.3014	0.7629	0.1710	9.8544
H(28)	1.3827	0.8337	0.0653	7.4590
H(29)	1.4302	0.9941	0.0452	9.0889
H(30)	1.3085	1.1105	0.0106	8.2991
H(31)	1.1373	1.0614	-0.0072	7.6164
H(32)	1.0942	0.9031	0.0118	6.6697
H(33)	1.2578	0.7646	-0.0731	5.3917
H(34)	1.2330	0.6759	-0.1687	7.0729
H(35)	1.1421	0.5305	-0.1721	6.9798
H(36)	1.0662	0.4756	-0.0814	5.9004
H(37)	1.0875	0.5682	0.0124	4.9169
H(38)	0.9953	0.7795	0.0189	5.7774
H(39)	0.8495	0.7853	0.0725	6.3714
H(40)	0.8520	0.7235	0.1767	6.7049
H(41)	1.0010	0.6597	0.2250	7.6309
H(42)	1.1507	0.6689	0.1752	6.2322

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit.

[b] The hydrogen atoms were placed at the calculated positions and not refined.

[c] $B_{eq} = 8\pi^2/3\ (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$

Table S3. Anisotropic Thermal Parameters for Non-hydrogen Atoms in [Cu(Me$_2$-tpa)]BPh$_4$ (**1a-BPh$_4$**).[a,b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.0489(4)	0.0640(5)	0.0619(4)	0.0011(4)	0.0015(3)	0.0144(4)
N(1)	0.048(3)	0.051(3)	0.049(3)	-0.005(2)	0.008(2)	0.006(2)
N(2)	0.059(3)	0.071(4)	0.063(3)	-0.011(3)	0.007(3)	0.001(3)
N(3)	0.042(2)	0.056(3)	0.067(3)	0.001(2)	0.013(2)	0.007(2)
N(4)	0.055(3)	0.052(3)	0.046(3)	-0.005(2)	0.007(2)	0.008(2)
C(1)	0.067(4)	0.063(4)	0.074(4)	0.002(3)	0.011(4)	0.009(3)
C(2)	0.079(5)	0.065(4)	0.062(4)	-0.019(4)	0.028(4)	-0.008(3)
C(3)	0.101(6)	0.086(5)	0.092(6)	-0.011(5)	0.044(5)	-0.011(5)
C(4)	0.136(9)	0.142(9)	0.063(5)	-0.052(7)	0.036(6)	-0.035(6)
C(5)	0.108(8)	0.16(1)	0.084(6)	-0.027(7)	-0.002(6)	-0.002(7)
C(6)	0.092(6)	0.147(8)	0.057(4)	-0.046(5)	0.008(4)	-0.020(5)
C(7)	0.052(3)	0.089(5)	0.053(4)	0.004(3)	0.011(3)	0.017(3)
C(8)	0.062(4)	0.054(4)	0.053(4)	-0.007(3)	0.014(3)	0.006(3)
C(9)	0.073(4)	0.076(5)	0.063(4)	-0.008(4)	0.013(3)	0.010(3)
C(10)	0.098(6)	0.138(8)	0.071(5)	-0.013(6)	0.041(5)	0.014(5)
C(11)	0.080(5)	0.116(7)	0.104(6)	0.007(5)	0.049(5)	0.015(5)
C(12)	0.053(3)	0.075(5)	0.085(5)	0.001(4)	0.011(3)	0.011(4)
C(13)	0.083(6)	0.142(8)	0.140(9)	0.017(6)	0.023(6)	0.027(7)
C(14)	0.048(3)	0.063(4)	0.076(4)	0.006(3)	0.017(3)	0.010(3)
C(15)	0.053(4)	0.061(4)	0.046(3)	-0.010(3)	0.014(3)	0.002(3)
C(16)	0.062(4)	0.091(6)	0.064(4)	-0.021(4)	0.006(3)	-0.016(4)
C(17)	0.097(6)	0.084(6)	0.083(5)	-0.035(5)	0.025(5)	-0.035(4)
C(18)	0.110(6)	0.060(5)	0.079(5)	-0.019(5)	0.036(5)	-0.014(4)
C(19)	0.074(4)	0.061(4)	0.054(4)	0.000(4)	0.020(3)	0.002(3)
C(20)	0.113(7)	0.062(5)	0.113(6)	0.019(4)	0.017(5)	0.019(4)
B(1)	0.055(4)	0.043(4)	0.040(3)	-0.005(3)	0.004(3)	-0.003(3)
C(21)	0.056(4)	0.061(4)	0.057(4)	-0.015(3)	-0.001(3)	0.002(3)
C(22)	0.044(3)	0.055(4)	0.090(5)	-0.012(3)	-0.003(3)	0.016(4)
C(23)	0.052(4)	0.074(5)	0.157(8)	-0.006(4)	-0.018(5)	0.043(5)
C(24)	0.069(6)	0.151(10)	0.15(1)	-0.007(6)	-0.041(6)	0.064(8)
C(25)	0.116(8)	0.17(1)	0.081(6)	-0.030(8)	-0.046(6)	0.015(7)
C(26)	0.109(6)	0.118(7)	0.078(5)	-0.009(6)	-0.029(5)	-0.006(5)
C(27)	0.066(4)	0.043(3)	0.048(3)	-0.007(3)	0.012(3)	-0.008(3)
C(28)	0.068(5)	0.064(5)	0.105(6)	-0.006(4)	0.011(4)	0.001(4)
C(29)	0.084(6)	0.085(6)	0.119(7)	-0.029(5)	0.016(5)	-0.005(5)

Table S3 (continued). Anisotropic Thermal Parameters for Non-hydrogen Atoms in [Cu(Me$_2$-tpa)]BPh$_4$ (**1a-BPh$_4$**).[a,b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(30)	0.137(8)	0.058(5)	0.071(5)	-0.039(5)	0.026(5)	-0.004(4)
C(31)	0.096(6)	0.059(5)	0.089(5)	-0.004(4)	0.023(4)	0.018(4)
C(32)	0.076(5)	0.059(4)	0.076(4)	-0.012(4)	0.006(4)	0.019(4)
C(33)	0.044(3)	0.043(3)	0.045(3)	0.008(3)	-0.001(2)	-0.001(2)
C(34)	0.052(3)	0.062(4)	0.057(4)	0.000(3)	0.009(3)	-0.008(3)
C(35)	0.072(5)	0.104(6)	0.049(4)	0.005(4)	0.016(3)	-0.014(4)
C(36)	0.065(4)	0.093(6)	0.063(4)	0.002(4)	0.005(3)	-0.026(4)
C(37)	0.063(4)	0.054(4)	0.068(4)	0.010(3)	0.000(3)	-0.018(3)
C(38)	0.058(4)	0.051(4)	0.046(3)	0.000(3)	0.005(3)	-0.004(3)
C(39)	0.063(3)	0.038(3)	0.045(3)	0.001(3)	0.006(3)	-0.009(2)
C(40)	0.066(4)	0.058(4)	0.060(3)	-0.016(3)	0.013(3)	0.007(3)
C(41)	0.069(4)	0.054(4)	0.081(4)	-0.009(3)	0.020(3)	0.001(4)
C(42)	0.081(5)	0.055(4)	0.081(5)	0.002(3)	0.036(4)	-0.006(3)
C(43)	0.114(6)	0.079(5)	0.054(4)	0.023(5)	0.039(4)	0.014(3)
C(44)	0.095(5)	0.059(4)	0.046(4)	0.017(4)	0.020(3)	0.004(3)

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit.

[b] The anisotropic thermal parameter is of the form:

$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table S4. Selected Bond Distances and Angles of [Cu(Me$_2$-tpa)]BPh$_4$ (**1a-BPh$_4$**).

Bond Distances(Å)

cation molecule

Cu1	-	N1	2.182(4)	Cu1	-	N2	2.004(5)
Cu1	-	N3	2.011(5)	Cu1	-	N4	2.010(4)
N1	-	C1	1.472(8)	N1	-	C7	1.450(7)
N1	-	C14	1.448(7)	N2	-	C2	1.329(8)
N2	-	C6	1.377(8)	N3	-	C8	1.349(7)
N3	-	C12	1.340(7)	N4	-	C15	1.364(7)
N4	-	C19	1.353(7)	C1	-	C2	1.525(9)
C2	-	C3	1.401(9)	C3	-	C4	1.40(1)
C4	-	C5	1.37(1)	C5	-	C6	1.37(1)
C7	-	C8	1.511(8)	C8	-	C9	1.369(8)
C9	-	C10	1.375(10)	C10	-	C11	1.35(1)
C11	-	C12	1.380(10)	C12	-	C13	1.44(1)
C14	-	C15	1.512(9)	C15	-	C16	1.382(8)
C16	-	C17	1.36(1)	C17	-	C18	1.38(1)
C18	-	C19	1.378(9)	C19	-	C20	1.479(10)

anion molecule

C21	-	B1	1.633(8)	C27	-	B1	1.653(8)
C33	-	B1	1.633(8)	C39	-	B1	1.680(8)
C21	-	C22	1.383(9)	C21	-	C26	1.396(9)
C22	-	C23	1.392(9)	C23	-	C24	1.37(1)
C24	-	C25	1.35(1)	C25	-	C26	1.38(1)
C27	-	C28	1.388(8)	C27	-	C32	1.386(8)
C28	-	C29	1.39(1)	C29	-	C30	1.37(1)
C30	-	C31	1.39(1)	C31	-	C32	1.354(9)
C33	-	C34	1.398(8)	C33	-	C38	1.398(8)
C34	-	C35	1.397(8)	C35	-	C36	1.364(10)
C36	-	C37	1.379(9)	C37	-	C38	1.390(8)
C39	-	C40	1.394(8)	C39	-	C44	1.379(8)
C40	-	C41	1.386(9)	C41	-	C42	1.364(9)
C42	-	C43	1.347(10)	C43	-	C44	1.394(9)

Table S4 (continued). Selected Bond Distances and Angles of [Cu(Me_2-tpa)]BPh_4 (**1a-BPh_4**).

Bond Angles(deg)

cation molecule

N1	-	Cu1	-	N2	83.5(2)	N1	-	Cu1	-	N3	82.8(2)
N1	-	Cu1	-	N4	83.4(2)	N2	-	Cu1	-	N3	117.7(2)
N2	-	Cu1	-	N4	120.6(2)	N3	-	Cu1	-	N4	117.6(2)
Cu1	-	N1	-	C1	104.6(3)	Cu1	-	N1	-	C7	105.0(3)
Cu1	-	N1	-	C14	104.1(3)	C1	-	N1	-	C7	113.4(5)
C1	-	N1	-	C14	114.2(5)	C7	-	N1	-	C14	114.1(5)
Cu1	-	N2	-	C2	113.6(4)	Cu1	-	N2	-	C6	124.5(6)
C2	-	N2	-	C6	121.7(6)	Cu1	-	N3	-	C8	114.1(4)
Cu1	-	N3	-	C12	128.2(4)	C8	-	N3	-	C12	117.7(5)
Cu1	-	N4	-	C15	112.4(4)	Cu1	-	N4	-	C19	127.2(4)
C15	-	N4	-	C19	119.7(5)	N1	-	C1	-	C2	111.7(5)
N2	-	C2	-	C1	118.8(6)	N2	-	C2	-	C3	122.0(7)
C1	-	C2	-	C3	119.2(7)	C2	-	C3	-	C4	116.4(8)
C3	-	C4	-	C5	120.3(8)	C4	-	C5	-	C6	121.6(9)
N2	-	C6	-	C5	118.0(9)	N1	-	C7	-	C8	113.8(5)
N3	-	C8	-	C7	117.4(5)	N3	-	C8	-	C9	122.7(6)
C7	-	C8	-	C9	119.8(6)	C8	-	C9	-	C10	119.2(7)
C9	-	C10	-	C11	118.3(7)	C10	-	C11	-	C12	120.7(7)
N3	-	C12	-	C11	121.4(6)	N3	-	C12	-	C13	117.6(6)
C11	-	C12	-	C13	121.0(7)	N1	-	C14	-	C15	112.0(5)
N4	-	C15	-	C14	117.0(5)	N4	-	C15	-	C16	120.6(6)
C14	-	C15	-	C16	122.3(6)	C15	-	C16	-	C17	119.5(7)
C16	-	C17	-	C18	119.9(7)	C17	-	C18	-	C19	119.4(7)
N4	-	C19	-	C18	120.8(7)	N4	-	C19	-	C20	117.6(6)
C18	-	C19	-	C20	121.6(7)						

anion molecule

C21	-	B1	-	C27	110.1(5)	C21	-	B1	-	C33	109.2(5)
C21	-	B1	-	C39	109.9(4)	C27	-	B1	-	C33	109.9(4)
C27	-	B1	-	C39	109.6(4)	C33	-	B1	-	C39	108.1(4)
C22	-	C21	-	B1	124.3(5)	C26	-	C21	-	B1	121.3(6)
C28	-	C27	-	B1	122.2(6)	C32	-	C27	-	B1	124.2(5)
C34	-	C33	-	B1	123.9(5)	C38	-	C33	-	B1	121.6(5)
C40	-	C39	-	B1	122.0(5)	C44	-	C39	-	B1	124.5(5)
C22	-	C21	-	C26	114.3(6)	C21	-	C22	-	C23	123.2(7)

Table S4 (continued). Selected Bond Distances and Angles of [Cu(Me_2-tpa)]BPh_4 (**1a-BPh_4**).

C22	-	C23	-	C24	119.8(8)	C23	-	C24	-	C25	119.1(8)
C24	-	C25	-	C26	120.4(9)	C21	-	C26	-	C25	123.1(9)
C28	-	C27	-	C32	113.4(6)	C27	-	C28	-	C29	122.8(7)
C28	-	C29	-	C30	120.4(7)	C29	-	C30	-	C31	118.7(7)
C30	-	C31	-	C32	118.9(7)	C27	-	C32	-	C31	125.8(7)
C34	-	C33	-	C38	114.0(5)	C33	-	C34	-	C35	122.7(6)
C34	-	C35	-	C36	119.9(6)	C35	-	C36	-	C37	120.9(6)
C36	-	C37	-	C38	117.5(6)	C33	-	C38	-	C37	125.0(5)
C40	-	C39	-	C44	113.5(6)	C39	-	C40	-	C41	124.1(6)
C40	-	C41	-	C42	119.4(7)	C41	-	C42	-	C43	118.8(6)
C42		C43	-	C44	121.1(6)	C39	-	C44	-	C43	122.9(6)

Table S5. Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for $[Cu_2(O)_2(Me_2\text{-tpa})_2](PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**).

<u>Crystal Data</u>	
Empirical Formula	$C_{46}H_{56}N_8O_4F_{12}P_2Cu_2$
Crystal Color, Habit	brown, block
Crystal Size (mm)	0.12 × 0.10 × 0.06
Crystal System	Monoclinic
Space Group	$P2_1/c$ (No. 14)
a =	11.426(5)Å
b =	15.616(8) Å
c =	15.768(4) Å
β =	107.05(2)°
Volume	2689(1) Å^3
Z	2
Formula Weight	1202.02
Density (calcd.)	1.484 g/cm^3
Absorption Coefficient	9.40 cm^{-1}
F_{000}	1232.00
<u>Data Collection</u>	
Diffractometer Used	Rigaku RAXIS-IV
Radiation	MoKα (λ = 0.71070 Å)
Temperature	-120 °C
$2\theta_{max}$	51.3°
Detector Aperture	300 mm x 300 mm
Data Images	70 exposures @ 12.0 minutes
Oscillation Range	105.0°
Detector Position	120.00 mm
Detector Swing Angle	1.50°
Pixel Size	0.10 mm
Index Ranges	$0 \le h \le 13$, $0 \le k \le 18$, $-18 \le l \le 16$
Total Independent Reflections	3556
Reflections ($I > 3.00\sigma(I)$)	1780
<u>Structure Solution and Refinement</u>	
System Used	teXsan, version 1.8
Solution	Direct Methods (SHELXS86)

Table S5 (continued). Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for $[Cu_2(O)_2(Me_2\text{-tpa})_2](PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**).

Refinement	Full-Matrix Least-Squares
Weighting Scheme	$w = 1 / [\sigma^2(F_o)]$
	$= [\sigma_c^2(F_o) + p^2F_o^2/4]^{-1}$
	$\sigma_c(F_o)$ = e.s.d. based on counting statistics;
	p-factor = 0.086
Final R Indices ($I>3.00\sigma(I)$)	R = 0.078, where
	$R = \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma \|F_o\|$
	R_w = 0.107, where
	$R_w = [(\Sigma\, w(\|F_o\| - \|F_c\|)^2 / \Sigma\, wF_o^2)]^{1/2}$
Goodness-of-Fit	1.48, where GOF =
	$[\Sigma\, w(\|F_o\|-\|F_c\|)^2 / (N_o-N_v)]^{1/2}$,
	and N_o and N_v denote the number of
	observations and parameters.
Data / Parameters	1780 / 335 = 5.3
Maximum and Minimum Difference Peaks	1.23, -0.52 $e^-/Å^3$ (near a metal ion)
Max Shift / Error in final cycle	0.00

Table S6. Fractional Atomic Coordinates Including Hydrogen Atoms and Isotropic Thermal Parameters of $[Cu_2(O)_2(Me_2\text{-tpa})_2](PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**).[a,b]

Atom	x	y	z	B_{eq}[c]
Cu(1)	0.9733(2)	0.0433(1)	0.0683(1)	2.38(4)
O(1)	1.0776(8)	-0.0371(6)	0.0509(6)	2.7(2)
N(1)	0.8516(10)	0.1295(7)	0.0780(7)	2.7(3)
N(2)	1.029(1)	0.0430(8)	0.1948(7)	3.0(3)
N(3)	1.079(1)	0.1832(8)	0.0789(8)	3.2(3)
N(4)	0.798(1)	-0.0434(9)	0.0938(8)	3.4(3)
C(1)	0.867(1)	0.148(1)	0.173(1)	3.9(4)
C(2)	0.965(1)	0.0929(10)	0.2355(9)	2.9(4)
C(3)	0.990(2)	0.096(1)	0.325(1)	4.4(5)
C(4)	1.087(2)	0.046(1)	0.376(1)	5.8(5)
C(5)	1.154(2)	-0.002(1)	0.335(1)	4.9(5)
C(6)	1.121(1)	-0.0054(10)	0.244(1)	3.3(4)
C(7)	0.864(1)	0.2078(9)	0.0295(10)	3.0(3)
C(8)	0.993(1)	0.2429(9)	0.0587(9)	2.9(4)
C(9)	1.013(2)	0.332(1)	0.067(1)	4.6(5)
C(10)	1.135(2)	0.356(1)	0.092(1)	5.6(5)
C(11)	1.227(1)	0.298(1)	0.114(1)	5.0(5)
C(12)	1.193(2)	0.211(1)	0.108(1)	4.6(5)
C(13)	1.292(2)	0.144(1)	0.124(1)	6.7(6)
C(14)	0.724(1)	0.093(1)	0.0384(10)	3.5(4)
C(15)	0.707(2)	0.011(1)	0.0796(9)	4.1(4)
C(16)	0.596(1)	-0.004(1)	0.098(1)	4.4(4)
C(17)	0.584(2)	-0.085(2)	0.135(1)	5.9(6)
C(18)	0.682(2)	-0.143(1)	0.150(1)	5.2(5)
C(19)	0.784(2)	-0.122(1)	0.129(1)	4.2(4)
C(20)	0.895(2)	-0.180(1)	0.146(1)	5.5(5)
P(1)	0.6346(4)	0.2928(3)	0.2370(3)	3.29(10)
F(1)	0.7330(10)	0.3205(6)	0.1906(7)	5.9(3)
F(2)	0.6683(9)	0.3695(6)	0.3047(7)	5.9(3)
F(3)	0.535(1)	0.3495(7)	0.1708(8)	8.4(4)
F(4)	0.5983(8)	0.2144(6)	0.1693(6)	5.1(3)
F(5)	0.7315(9)	0.2351(7)	0.3022(6)	6.1(3)
F(6)	0.5291(9)	0.2624(7)	0.2787(7)	6.2(3)
O(2)	0.748(1)	0.0670(9)	0.4590(10)	7.3(4)
C(21)	0.637(3)	0.074(1)	0.416(1)	7.2(7)

Table S6 (continued). Fractional Atomic Coordinates Including Hydrogen Atoms and Isotropic Thermal Parameters of $[Cu_2(O)_2(Me_2\text{-tpa})_2](PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**).[a,b]

Atom	x	y	z	B_{eq}[c]
C(22)	0.551(2)	0.119(2)	0.447(2)	11(1)
C(23)	0.601(2)	0.040(1)	0.323(1)	6.9(6)
H(1)	0.7913	0.1374	0.1848	4.6374
H(2)	0.8891	0.2061	0.1844	4.6374
H(3)	0.9432	0.1316	0.3523	5.2777
H(4)	1.1062	0.0463	0.4389	6.8334
H(5)	1.2231	-0.0334	0.3688	5.8619
H(6)	1.1633	-0.0428	0.2160	3.9805
H(7)	0.8421	0.1952	-0.0322	3.5561
H(8)	0.8096	0.2501	0.0397	3.5561
H(9)	0.9480	0.3721	0.0573	5.4886
H(10)	1.1549	0.4150	0.0932	6.6689
H(11)	1.3104	0.3153	0.1322	5.9327
H(12)	1.3700	0.1714	0.1440	8.0476
H(13)	1.2856	0.1140	0.0711	8.0476
H(14)	1.2833	0.1059	0.1687	8.0476
H(15)	0.7105	0.0834	-0.0233	4.2136
H(16)	0.6654	0.1326	0.0466	4.2136
H(17)	0.5319	0.0373	0.0858	5.2805
H(18)	0.5115	-0.0993	0.1495	7.1449
H(19)	0.6751	-0.1979	0.1745	6.2539
H(20)	0.9625	-0.1528	0.1875	6.5994
H(21)	0.9140	-0.1895	0.0922	6.5994
H(22)	0.8782	-0.2327	0.1696	6.5994
H(23)	0.5485	0.0939	0.5005	13.4461
H(24)	0.4730	0.1134	0.4034	13.4461
H(25)	0.5741	0.1766	0.4543	13.4461
H(26)	0.5145	0.0478	0.2968	8.3513
H(27)	0.6430	0.0708	0.2889	8.3513
H(28)	0.6198	-0.0187	0.3237	8.3513

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit.

[b] The hydrogen atoms were placed at the calculated positions and not refined.

[c] $B_{eq} = 8\pi^2/3\ (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$

Table S7. Anisotropic Thermal Parameters for Non-hydrogen Atoms in $[Cu_2(O)_2(Me_2\text{-}tpa)_2](PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**).[a,b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.0284(9)	0.034(1)	0.0295(10)	0.0059(10)	0.0108(7)	0.0001(9)
O(1)	0.032(5)	0.038(6)	0.032(5)	0.017(5)	0.009(4)	0.002(5)
N(1)	0.027(6)	0.036(7)	0.042(8)	0.005(6)	0.013(6)	0.011(6)
N(2)	0.043(7)	0.037(7)	0.035(7)	0.006(7)	0.011(6)	0.001(6)
N(3)	0.026(7)	0.044(8)	0.045(8)	-0.012(7)	0.001(6)	-0.009(7)
N(4)	0.045(8)	0.041(8)	0.043(8)	-0.009(8)	0.012(6)	0.008(7)
C(1)	0.05(1)	0.05(1)	0.038(10)	0.008(9)	0.006(8)	-0.003(8)
C(2)	0.028(8)	0.044(10)	0.034(10)	-0.010(8)	0.005(7)	-0.006(8)
C(3)	0.09(1)	0.04(1)	0.04(1)	0.01(1)	0.033(9)	0.003(9)
C(4)	0.12(2)	0.05(1)	0.04(1)	0.05(1)	0.02(1)	0.00(1)
C(5)	0.07(1)	0.06(1)	0.04(1)	0.03(1)	0.001(9)	0.008(9)
C(6)	0.046(10)	0.031(9)	0.05(1)	0.005(8)	0.019(8)	0.002(8)
C(7)	0.031(8)	0.034(9)	0.047(9)	0.003(8)	0.009(7)	-0.006(7)
C(8)	0.05(1)	0.034(8)	0.031(9)	-0.009(9)	0.019(7)	0.004(7)
C(9)	0.06(1)	0.04(1)	0.08(1)	-0.007(10)	0.03(1)	0.010(9)
C(10)	0.08(1)	0.06(1)	0.06(1)	-0.04(1)	0.01(1)	0.01(1)
C(11)	0.038(10)	0.09(2)	0.04(1)	-0.01(1)	-0.007(8)	0.01(1)
C(12)	0.06(1)	0.05(1)	0.05(1)	0.02(1)	0.011(9)	-0.001(9)
C(13)	0.04(1)	0.09(2)	0.11(2)	-0.01(1)	0.01(1)	-0.02(1)
C(14)	0.036(9)	0.06(1)	0.032(9)	-0.021(9)	0.006(7)	-0.002(8)
C(15)	0.07(1)	0.06(1)	0.019(8)	0.03(1)	0.006(8)	-0.005(8)
C(16)	0.026(8)	0.10(2)	0.05(1)	-0.018(10)	0.026(8)	-0.02(1)
C(17)	0.06(1)	0.12(2)	0.05(1)	-0.02(1)	0.014(10)	0.03(1)
C(18)	0.09(2)	0.06(1)	0.06(1)	-0.03(1)	0.03(1)	0.013(10)
C(19)	0.06(1)	0.05(1)	0.04(1)	-0.02(1)	0.012(9)	-0.002(8)
C(20)	0.08(1)	0.04(1)	0.09(2)	0.02(1)	0.03(1)	0.02(1)
P(1)	0.038(2)	0.035(2)	0.059(3)	0.001(2)	0.024(2)	-0.007(2)
F(1)	0.087(8)	0.054(6)	0.107(9)	-0.018(6)	0.064(7)	-0.009(6)
F(2)	0.056(6)	0.077(7)	0.096(8)	-0.023(6)	0.032(6)	-0.044(6)
F(3)	0.103(10)	0.083(9)	0.12(1)	0.044(8)	0.020(8)	-0.002(8)
F(4)	0.045(5)	0.067(7)	0.081(7)	-0.002(5)	0.014(5)	-0.035(6)
F(5)	0.083(8)	0.083(8)	0.058(7)	0.028(6)	0.011(6)	0.008(6)
F(6)	0.069(7)	0.075(7)	0.114(9)	-0.019(6)	0.063(7)	-0.031(7)
O(2)	0.10(1)	0.08(1)	0.075(10)	0.010(9)	-0.011(9)	0.008(8)
C(21)	0.11(2)	0.06(1)	0.08(2)	0.00(1)	-0.02(2)	0.03(1)

Table S7 (continued). Anisotropic Thermal Parameters for Non-hydrogen Atoms in $[Cu_2(O)_2(Me_2\text{-tpa})_2](PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**).[a,b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(22)	0.09(2)	0.20(3)	0.14(3)	0.03(2)	0.03(2)	0.06(2)
C(23)	0.10(2)	0.08(2)	0.07(1)	-0.01(1)	0.00(1)	0.01(1)

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit.

[b] The anisotropic thermal parameter is of the form:

$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table S8. Selected Bond Distances and Angles of $[Cu_2(O)_2(Me_2\text{-tpa})_2]$-$(PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**).

Bond Distances(Å)

cation molecule

Cu1	-	O1	1.806(9)	Cu1	-	O1*	1.799(8)
Cu1	-	N1	1.97(1)	Cu1	-	N2	1.91(1)
Cu1	-	N3	2.48(1)	Cu1	-	N4	2.55(1)
N1	-	C1	1.49(2)	N1	-	C7	1.47(2)
N1	-	C14	1.52(2)	N2	-	C2	1.35(2)
N2	-	C6	1.34(2)	N3	-	C8	1.32(2)
N3	-	C12	1.32(2)	N4	-	C15	1.31(2)
N4	-	C19	1.38(2)	C1	-	C2	1.51(2)
C2	-	C3	1.36(2)	C3	-	C4	1.40(2)
C4	-	C5	1.37(2)	C5	-	C6	1.36(2)
C7	-	C8	1.52(2)	C8	-	C9	1.41(2)
C9	-	C10	1.38(2)	C10	-	C11	1.35(3)
C11	-	C12	1.40(2)	C12	-	C13	1.51(2)
C14	-	C15	1.47(2)	C15	-	C16	1.40(2)
C16	-	C17	1.41(3)	C17	-	C18	1.41(3)
C18	-	C19	1.35(2)	C19	-	C20	1.51(2)
Cu1	···	Cu1	2.758(4)	O1	···	O1*	2.32(1)

anion molecule

P1	-	F1	1.57(1)	P1	-	F2	1.575(10)
P1	-	F3	1.57(1)	P1	-	F4	1.598(9)
P1	-	F5	1.558(10)	P1	-	F6	1.60(1)

solvent molecule

O2	-	C21	1.26(3)	C21	-	C22	1.40(4)
C21	-	C23	1.50(3)				

Bond Angles(deg)

cation molecule

O1	-	Cu1	-	O1*	80.2(4)	O1	-	Cu1	-	N1	175.7(4)
O1	-	Cu1	-	N2	97.2(5)	O1	-	Cu1	-	N3	107.0(4)
O1	-	Cu1	-	N4	103.9(5)	O1	-	Cu1	-	N1	95.6(4)
O1	-	Cu1	-	N2	176.7(5)	O1	-	Cu1	-	N3	96.9(4)
O1	-	Cu1	-	N4	96.2(4)	N1	-	Cu1	-	N2	86.9(5)

Table S8 (continued). Selected Bond Distances and Angles of $[Cu_2(O)_2(Me_2\text{-tpa})_2]\text{-}(PF_6)_2\cdot 2(CH_3)_2CO$ (**1b**).

N1	-	Cu1	-	N3	74.6(4)	N1	-	Cu1	-	N4	75.2(5)
N2	-	Cu1	-	N3	85.7(5)	N2	-	Cu1	-	N4	82.5(4)
N3	-	Cu1	-	N4	148.1(4)	Cu1	-	O1	-	Cu1*	99.8(4)
Cu1	-	N1	-	C1	109.3(8)	Cu1	-	N1	-	C7	110.5(9)
Cu1	-	N1	-	C14	108.8(10)	C1	-	N1	-	C7	111(1)
C1	-	N1	-	C14	107(1)	C7	-	N1	-	C14	109(1)
Cu1	-	N2	-	C2	115.8(9)	Cu1	-	N2	-	C6	124(1)
C2	-	N2	-	C6	119(1)	Cu1	-	N3	-	C8	106.9(8)
Cu1	-	N3	-	C12	136(1)	C8	-	N3	-	C12	115(1)
Cu1	-	N4	-	C15	104(1)	Cu1	-	N4	-	C19	136(1)
C15	-	N4	-	C19	118(1)	N1	-	C1	-	C2	113(1)
N2	-	C2	-	C1	114(1)	N2	-	C2	-	C3	122(1)
C1	-	C2	-	C3	122(1)	C2	-	C3	-	C4	117(1)
C3	-	C4	-	C5	119(1)	C4	-	C5	-	C6	119(1)
N2	-	C6	-	C5	121(1)	N1	-	C7	-	C8	112(1)
N3	-	C8	-	C7	114(1)	N3	-	C8	-	C9	125(1)
C7	-	C8	-	C9	120(1)	C8	-	C9	-	C10	114(1)
C9	-	C10	-	C11	122(1)	C10	-	C11	-	C12	116(1)
N3	-	C12	-	C11	124(1)	N3	-	C12	-	C13	116(1)
C11	-	C12	-	C13	118(1)	N1	-	C14	-	C15	112(1)
N4	-	C15	-	C14	115(1)	N4	-	C15	-	C16	125(1)
C14	-	C15	-	C16	118(1)	C15	-	C16	-	C17	115(1)
C16	-	C17	-	C18	118(1)	C17	-	C18	-	C19	120(1)
N4	-	C19	-	C18	121(1)	N4	-	C19	-	C20	114(1)
C18	-	C19	-	C20	123(1)						

anion molecule

F1	-	P1	-	F2	92.3(6)	F1	-	P1	-	F3	90.8(7)
F1	-	P1	-	F4	88.9(6)	F1	-	P1	-	F5	90.0(6)
F1	-	P1	-	F6	176.5(6)	F2	-	P1	-	F3	90.5(6)
F2	-	P1	-	F4	178.8(6)	F2	-	P1	-	F5	90.5(6)
F2	-	P1	-	F6	90.7(5)	F3	-	P1	-	F4	89.5(6)
F3	-	P1	-	F5	178.8(7)	F3	-	P1	-	F6	87.4(7)
F4	-	P1	-	F5	89.6(5)	F4	-	P1	-	F6	88.1(5)
F5	-	P1	-	F6	91.9(6)						

Table S8 (continued). Selected Bond Distances and Angles of $[Cu_2(O)_2(Me_2\text{-tpa})_2]$-$(PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**).

solvent molecule											
O2	-	C21	-	C22	123(2)		O2	-	C21	-	C23	116(2)
C22	-	C21	-	C23	119(2)							

Table S9. Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for $[Cu_2(OH)_2(Me_2\text{-tpa})](ClO_4)_2$ (**1c**).

Crystal Data	
Empirical Formula	$C_{40}H_{46}N_8O_{10}Cl_2Cu_2$
Crystal Color, Habit	blue, block
Crystal Size (mm)	0.30 × 0.25 × 0.25
Crystal System	Monoclinic
Space Group	$P2_1/n$ (No14)
a =	11.388(2)Å
b =	13.588(3) Å
c =	15.464(3) Å
β =	106.51(1)°
Volume	2294.2(7) Å^3
Z	2
Formula Weight	996.85
Density (calcd.)	1.443 g/cm^3
Absorption Coefficient	11.01 cm^{-1}
F_{000}	1028.00
Data Collection	
Diffractometer Used	Rigaku RAXIS-IV
Radiation	MoKα (λ = 0.71070 Å)
Temperature	23 °C
$2\theta_{max}$	51.6°
Detector Aperture	300 mm x 300 mm
Data Images	30 exposures @ 30.0 minutes
Oscillation Range	120.0°
Detector Position	120.00 mm
Detector Swing Angle	4.00°
Pixel Size	0.10 mm
Index Ranges	$0 \le h \le 13$, $0 \le k \le 18$, $-18 \le l \le 18$
Total Independent Reflections	4193
Reflections ($I>3.00\sigma(I)$)	3535
Structure Solution and Refinement	
System Used	teXsan, version 1.8
Solution	Direct Methods (SHELXS86)

Table S9 (continued). Summary of Crystal Data, Data Collection Parameters, and Structure Refinement for $[Cu_2(OH)_2(Me_2\text{-tpa})](ClO_4)_2$ (**1c**).

Refinement	Full-Matrix Least-Squares
Weighting Scheme	$w = 1 / [\sigma^2(F_o)]$
	$= [\sigma_c^2(F_o) + p^2F_o^2/4]^{-1}$
	$\sigma_c(F_o)$ = e.s.d. based on counting statistics;
	p-factor = 0.095.
Final R Indices ($I>3.00\sigma(I)$)	R = 0.059, where
	$R = \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma \|F_o\|$
	R_w = 0.097, where
	$R_w = [(\Sigma\, w(\|F_o\| - \|F_c\|)^2 / \Sigma\, wF_o^2)]^{1/2}$
Goodness-of-Fit	1.62, where GOF =
	$[\Sigma\, w(\|F_o\|-\|F_c\|)^2 / (N_o-N_v)]^{1/2}$,
	and N_o and N_v denote the number of
	observations and parameters.
Data / Parameters	3535 / 280 = 12.6
Maximum and Minimum Difference Peaks	0.92, -0.67 $e^-/Å^3$ (near a metal ion)
Max Shift / Error in Final Cycle	0.00

Table S10. Fractional Atomic Coordinates Including Hydrogen Atoms and Isotropic Thermal Parameters of $[Cu_2(OH)_2(Me_2\text{-tpa})](ClO_4)_2$ (**1c**).[a,b]

Atom	x	y	z	B_{eq}[c]
Cu(1)	0.04047(4)	0.94552(3)	0.93160(3)	3.13(1)
O(1)	-0.0269(3)	0.9190(2)	1.0307(2)	3.80(6)
N(1)	0.1252(3)	0.9797(3)	0.8328(2)	3.45(7)
N(2)	0.0724(3)	0.8060(3)	0.9024(2)	3.62(7)
N(3)	-0.1203(3)	0.9661(3)	0.7938(3)	4.26(8)
N(4)	0.2918(4)	0.9180(3)	1.0077(3)	4.76(9)
C(1)	0.1251(5)	0.8868(3)	0.7797(3)	4.5(1)
C(2)	0.1229(4)	0.7961(3)	0.8348(3)	3.83(9)
C(3)	0.1652(6)	0.7066(4)	0.8137(4)	6.3(2)
C(4)	0.1553(8)	0.6255(4)	0.8638(6)	8.0(2)
C(5)	0.1011(7)	0.6367(4)	0.9337(5)	6.4(2)
C(6)	0.0614(5)	0.7270(4)	0.9516(4)	4.7(1)
C(7)	0.0524(5)	1.0553(3)	0.7742(4)	4.5(1)
C(8)	-0.0807(5)	1.0288(4)	0.7416(3)	4.37(10)
C(9)	-0.1567(7)	1.0673(5)	0.6629(5)	6.7(2)
C(10)	-0.2772(8)	1.0412(7)	0.6392(5)	8.6(2)
C(11)	-0.3187(6)	0.9767(6)	0.6898(5)	7.4(2)
C(12)	-0.2391(5)	0.9394(4)	0.7682(4)	5.3(1)
C(13)	-0.2793(6)	0.8706(6)	0.8274(5)	6.9(2)
C(14)	0.2528(4)	1.0154(3)	0.8732(4)	4.4(1)
C(15)	0.3290(4)	0.9412(4)	0.9359(4)	4.6(1)
C(16)	0.4305(5)	0.8998(5)	0.9188(5)	6.1(2)
C(17)	0.4958(6)	0.8301(6)	0.9830(6)	7.7(2)
C(18)	0.4568(5)	0.8048(6)	1.0527(5)	6.7(2)
C(19)	0.3545(5)	0.8501(5)	1.0656(4)	5.8(1)
C(20)	0.3054(7)	0.8204(6)	1.1426(5)	7.9(2)
Cl(1)	0.1827(1)	0.32799(9)	0.89983(10)	5.23(3)
O(2)	0.2922(5)	0.3836(5)	0.9188(5)	10.7(2)
O(3)	0.155(1)	0.2916(7)	0.8193(5)	16.9(3)
O(4)	0.0994(6)	0.3884(4)	0.9216(5)	9.8(2)
O(5)	0.2009(5)	0.2486(4)	0.9624(4)	9.5(2)
H(1)	0.0552	0.8874	0.7281	5.4587
H(2)	0.1969	0.8861	0.7597	5.4587
H(3)	0.2012	0.7017	0.7638	7.6115
H(4)	0.1845	0.5623	0.8513	9.2849

Table S10 (continued). Fractional Atomic Coordinates Including Hydrogen Atoms and Isotropic Thermal Parameters of $[Cu_2(OH)_2(Me_2\text{-tpa})](ClO_4)_2$ (**1c**).[a,b]

Atom	x	y	z	B_{eq}[c]
H(5)	0.0952	0.5800	0.9701	7.7741
H(6)	0.0255	0.7335	1.0003	5.8328
H(7)	0.0620	1.1163	0.8060	5.6687
H(8)	0.0829	1.0642	0.7226	5.6687
H(9)	-0.1281	1.1127	0.6261	8.3546
H(10)	-0.3327	1.0697	0.5875	10.3121
H(11)	-0.4008	0.9543	0.6701	8.6502
H(12)	-0.3632	0.8570	0.8045	8.2270
H(13)	-0.2344	0.8094	0.8306	8.2270
H(14)	-0.2617	0.8964	0.8868	8.2270
H(15)	0.2892	1.0309	0.8262	5.3890
H(16)	0.2507	1.0756	0.9060	5.3890
H(17)	0.4566	0.9182	0.8671	7.5725
H(18)	0.5682	0.8006	0.9751	9.0821
H(19)	0.5005	0.7541	1.0934	8.0750
H(20)	0.2987	0.8786	1.1775	9.6677
H(21)	0.2222	0.7959	1.1183	9.6677
H(22)	0.3532	0.7738	1.1790	9.6677

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit.

[b] The hydrogen atoms were placed at the calculated positions and not refined.

[c] $B_{eq} = 8\pi^2/3\ (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$

Table S11. Anisotropic Thermal Parameters for Non-hydrogen Atoms in $[Cu_2(OH)_2(Me_2\text{-}tpa)](ClO_4)_2$ (**1c**).[a,b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.0494(3)	0.0345(3)	0.0423(4)	0.0017(2)	0.0245(2)	-0.0006(2)
O(1)	0.065(2)	0.037(1)	0.053(2)	-0.001(1)	0.032(1)	-0.003(1)
N(1)	0.051(2)	0.038(2)	0.049(2)	0.000(1)	0.025(2)	0.001(2)
N(2)	0.055(2)	0.040(2)	0.049(2)	0.002(2)	0.026(2)	0.001(2)
N(3)	0.052(2)	0.058(2)	0.049(2)	0.004(2)	0.011(2)	0.000(2)
N(4)	0.058(2)	0.057(2)	0.069(3)	0.002(2)	0.024(2)	-0.005(2)
C(1)	0.077(3)	0.050(2)	0.055(3)	0.005(2)	0.039(2)	-0.002(2)
C(2)	0.059(2)	0.038(2)	0.057(2)	0.002(2)	0.030(2)	-0.005(2)
C(3)	0.112(5)	0.056(3)	0.092(4)	0.013(3)	0.065(4)	-0.007(3)
C(4)	0.156(7)	0.034(3)	0.151(7)	0.015(3)	0.104(6)	0.001(3)
C(5)	0.115(5)	0.047(3)	0.096(4)	0.007(3)	0.055(4)	0.007(3)
C(6)	0.074(3)	0.040(2)	0.077(3)	0.000(2)	0.041(3)	0.004(2)
C(7)	0.070(3)	0.051(3)	0.055(3)	-0.003(2)	0.028(2)	0.006(2)
C(8)	0.071(3)	0.051(2)	0.043(2)	0.007(2)	0.014(2)	0.005(2)
C(9)	0.093(5)	0.091(5)	0.061(4)	0.007(4)	0.005(3)	0.019(3)
C(10)	0.109(6)	0.133(7)	0.061(4)	0.004(5)	-0.013(4)	0.021(4)
C(11)	0.064(3)	0.110(5)	0.085(5)	-0.010(4)	-0.013(3)	-0.002(4)
C(12)	0.057(3)	0.067(3)	0.072(4)	-0.005(2)	0.010(3)	-0.006(3)
C(13)	0.066(3)	0.099(5)	0.100(5)	-0.012(3)	0.026(3)	0.009(4)
C(14)	0.054(2)	0.049(2)	0.073(3)	-0.009(2)	0.035(2)	0.000(2)
C(15)	0.046(2)	0.061(3)	0.072(3)	-0.004(2)	0.023(2)	-0.005(2)
C(16)	0.058(3)	0.093(4)	0.091(4)	0.006(3)	0.036(3)	0.000(3)
C(17)	0.056(3)	0.107(6)	0.128(6)	0.030(3)	0.024(4)	0.004(5)
C(18)	0.069(4)	0.094(5)	0.085(4)	0.021(3)	0.010(3)	0.007(4)
C(19)	0.073(3)	0.075(4)	0.065(3)	0.009(3)	0.009(3)	0.002(3)
C(20)	0.117(5)	0.102(5)	0.077(4)	0.013(5)	0.023(4)	0.004(4)
Cl(1)	0.0837(8)	0.0505(6)	0.0777(9)	0.0002(6)	0.0440(7)	0.0018(6)
O(2)	0.116(4)	0.139(5)	0.163(6)	-0.042(4)	0.055(4)	0.021(5)
O(3)	0.35(1)	0.212(8)	0.121(5)	-0.147(9)	0.127(7)	-0.083(6)
O(4)	0.120(4)	0.103(4)	0.159(6)	0.041(3)	0.054(4)	0.010(4)
O(5)	0.117(4)	0.087(3)	0.168(6)	0.014(3)	0.058(4)	0.051(4)

[a] Numbers in parentheses are the estimated standard deviation in the last significant digit.

[b] The anisotropic thermal parameter is of the form:

$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table S12. Selected Bond Distances and Bond Angles of $[Cu_2(OH)_2(Me_2\text{-tpa})](ClO_4)_2$ (**1c**).

Bond Distances(Å)

cation molecule

Cu1	-	O1	1.933(3)	Cu1	-	O1*	1.950(3)
Cu1	-	N1	2.079(3)	Cu1	-	N2	2.007(4)
Cu1	-	N3	2.398(4)	Cu1	-	N4	2.793(4)
N1	-	C1	1.506(6)	N1	-	C7	1.462(6)
N1	-	C14	1.491(6)	N2	-	C2	1.334(6)
N2	-	C6	1.341(6)	N3	-	C8	1.336(6)
N3	-	C12	1.348(7)	N4	-	C15	1.334(7)
N4	-	C19	1.342(7)	C1	-	C2	1.502(6)
C2	-	C3	1.381(6)	C3	-	C4	1.370(9)
C4	-	C5	1.396(9)	C5	-	C6	1.364(7)
C7	-	C8	1.499(7)	C8	-	C9	1.382(8)
C9	-	C10	1.36(1)	C10	-	C11	1.35(1)
C11	-	C12	1.387(9)	C12	-	C13	1.470(9)
C14	-	C15	1.493(7)	C15	-	C16	1.376(7)
C16	-	C17	1.420(10)	C17	-	C18	1.32(1)
C18	-	C19	1.382(9)	C19	-	C20	1.51(1)
Cu1	···	Cu1	2.9368(9)				

anion molecule

Cl1	-	O2	1.416(5)	Cl1	-	O3	1.293(7)
Cl1	-	O4	1.367(6)	Cl1	-	O5	1.424(5)

Bond Angles(deg)

cation molecule

O1	-	Cu1	-	O1*	81.7(1)	O1	-	Cu1	-	N1	175.2(1)
O1	-	Cu1	-	N2	98.1(1)	O1	-	Cu1	-	N3	110.6(1)
O1	-	Cu1	-	N4	103.4(1)	O1	-	Cu1	-	N1	95.8(1)
O1	-	Cu1	-	N2	173.8(1)	O1	-	Cu1	-	N3	92.9(1)
O1	-	Cu1	-	N4	99.2(1)	N1	-	Cu1	-	N2	83.9(1)
N1	-	Cu1	-	N3	73.6(1)	N1	-	Cu1	-	N4	72.9(1)
N2	-	Cu1	-	N3	92.9(1)	N2	-	Cu1	-	N4	74.9(1)
N3	-	Cu1	-	N4	145.3(1)	Cu1	-	O1	-	Cu1	98.3(1)
Cu1	-	N1	-	C1	106.5(3)	Cu1	-	N1	-	C7	108.2(3)
Cu1	-	N1	-	C14	111.4(3)	C1	-	N1	-	C7	109.8(4)

Table S12 (continued). Selected Bond Distances and Bond Angles of $[Cu_2(OH)_2(Me_2\text{-}tpa)](ClO_4)_2$ (**1c**).

C1	-	N1	-	C14	110.6(3)	C7	-	N1	-	C14	110.2(3)
Cu1	-	N2	-	C2	114.6(3)	Cu1	-	N2	-	C6	125.1(3)
C2	-	N2	-	C6	119.6(4)	Cu1	-	N3	-	C8	107.9(3)
Cu1	-	N3	-	C12	132.8(4)	C8	-	N3	-	C12	118.5(4)
Cu1	-	N4	-	C15	98.5(3)	Cu1	-	N4	-	C19	131.3(4)
C15		N4	-	C19	119.0(5)	N1	-	C1	-	C2	112.1(4)
N2	-	C2	-	C1	116.3(4)	N2	-	C2	-	C3	122.0(4)
C1	-	C2	-	C3	121.7(4)	C2	-	C3	-	C4	119.0(5)
C3	-	C4	-	C5	118.4(5)	C4	-	C5	-	C6	120.0(6)
N2	-	C6	-	C5	121.0(5)	N1	-	C7	-	C8	112.3(4)
N3	-	C8	-	C7	115.7(4)	N3	-	C8	-	C9	122.7(5)
C7	-	C8	-	C9	121.7(5)	C8	-	C9	-	C10	118.0(6)
C9	-	C10	-	C11	120.4(6)	C10	-	C11	-	C12	119.7(6)
N3	-	C12	-	C11	120.7(6)	N3	-	C12	-	C13	116.9(5)
C11	-	C12	-	C13	122.4(6)	N1	-	C14	-	C15	111.7(4)
N4	-	C15	-	C14	115.8(4)	N4	-	C15	-	C16	123.1(5)
C14	-	C15	-	C16	121.1(5)	C15	-	C16	-	C17	116.2(6)
C16	-	C17	-	C18	120.8(6)	C17	-	C18	-	C19	119.7(6)
N4	-	C19	-	C18	121.3(6)	N4	-	C19	-	C20	117.8(6)
C18	-	C19		C20	120.8(6)						
anion molecule											
O2	-	Cl1	-	O3	111.4(5)	O2	-	Cl1	-	O4	105.1(4)
O2	-	Cl1	-	O5	108.3(4)	O3	-	Cl1	-	O4	118.0(7)
O3	-	Cl1	-	O5	108.3(5)	O4	-	Cl1	-	O5	105.4(4)

Figure Captions

Figure S1. An apparatus used for the dioxygen evolution experiment.

Figure S2. Calibration line for the determination of the amount of dioxygen evolution. Detailed conditions are given in Supporting Information.

Figure S3. Fully labeled ORTEP view (50% probability) of a complex cation of **1a-BPh$_4$**. Hydrogen atoms are omitted for clarity.

Figure S4. Fully labeled ORTEP view (50% probability) of a complex cation of **1b**. Hydrogen atoms are omitted for clarity.

Figure S5. Fully labeled ORTEP views (50% probability) of **1c**. Hydrogen atoms are omitted for clarity.

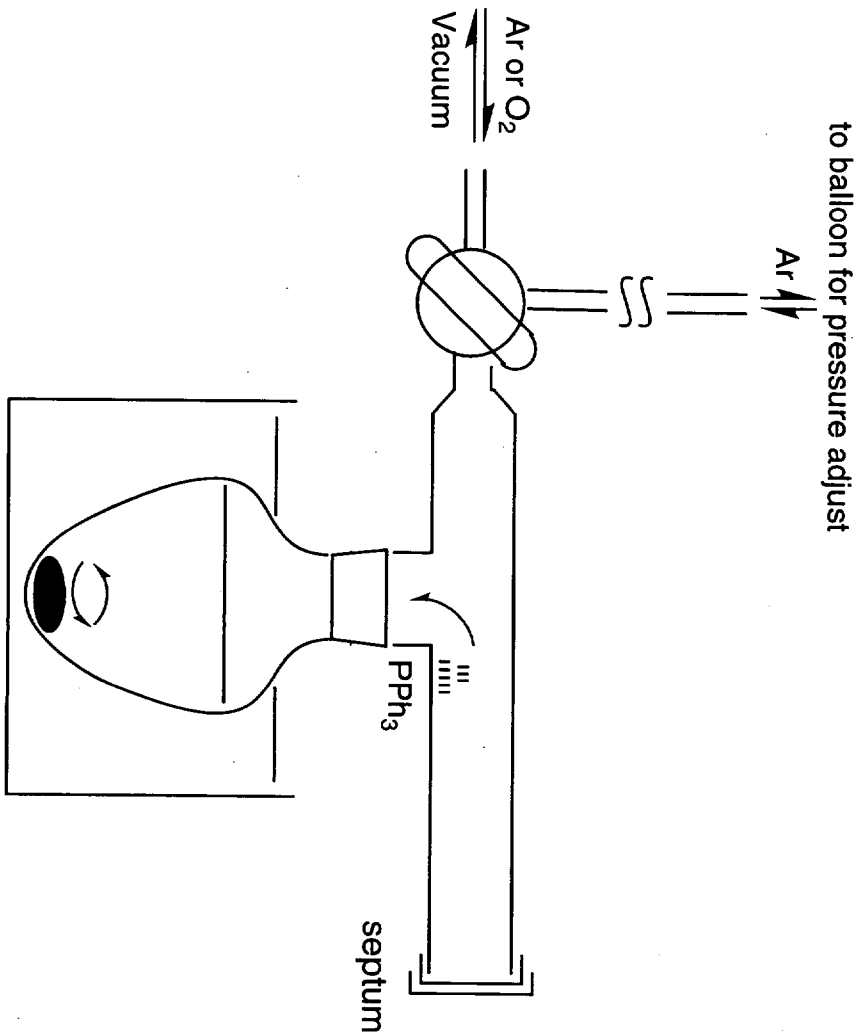

Figure S1. M. Suzuki et al.
An apparatus used for the dioxygen evolution experiment.

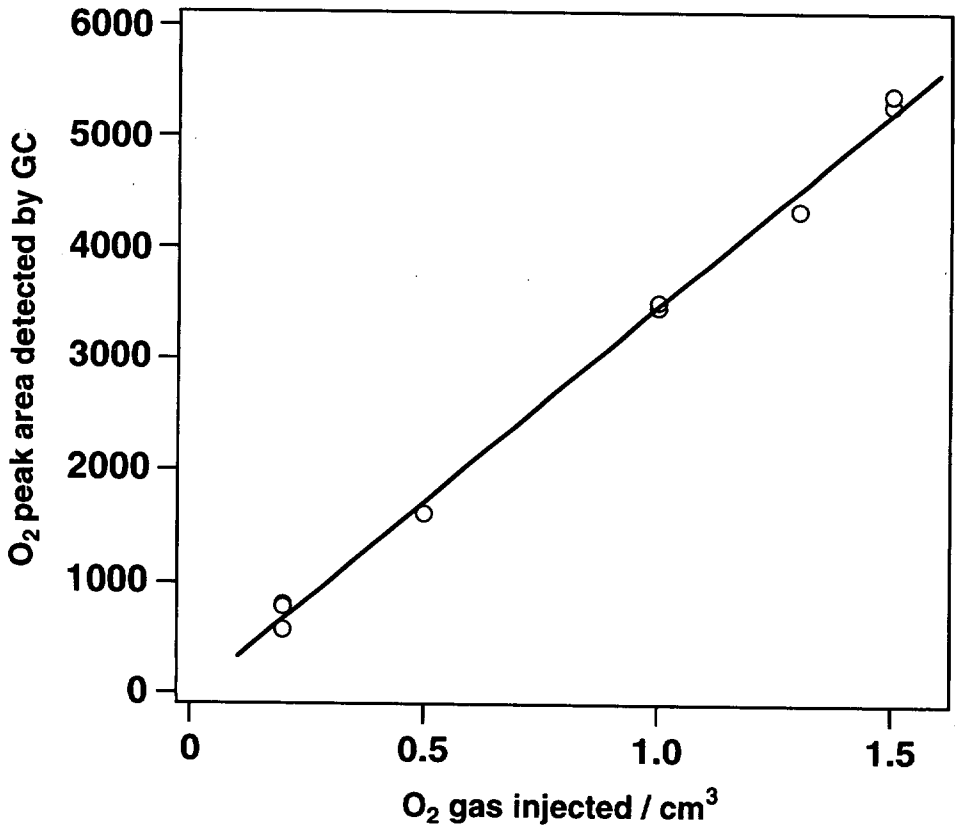

Figure S2. M. Suzuki et al.
Calibration line for the determination of the amount of dioxygen evolution.
Detailed conditions are given in Supporting Information.

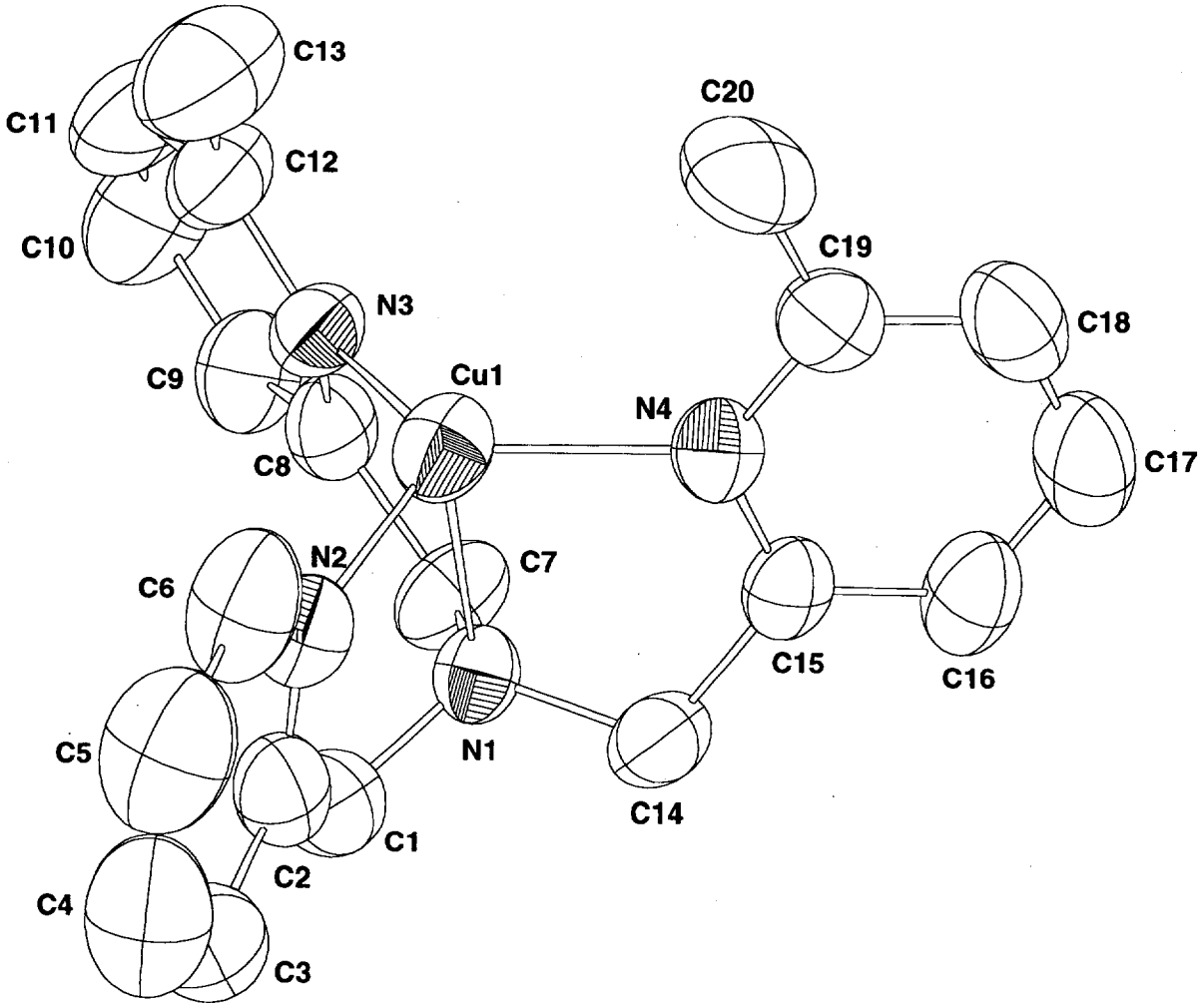

Figure S3. M. Suzuki et al.
Fully labeled ORTEP view (50% probability) of a complex cation of **1a-BPh4**.
Hydrogen atoms are omitted for clarity.

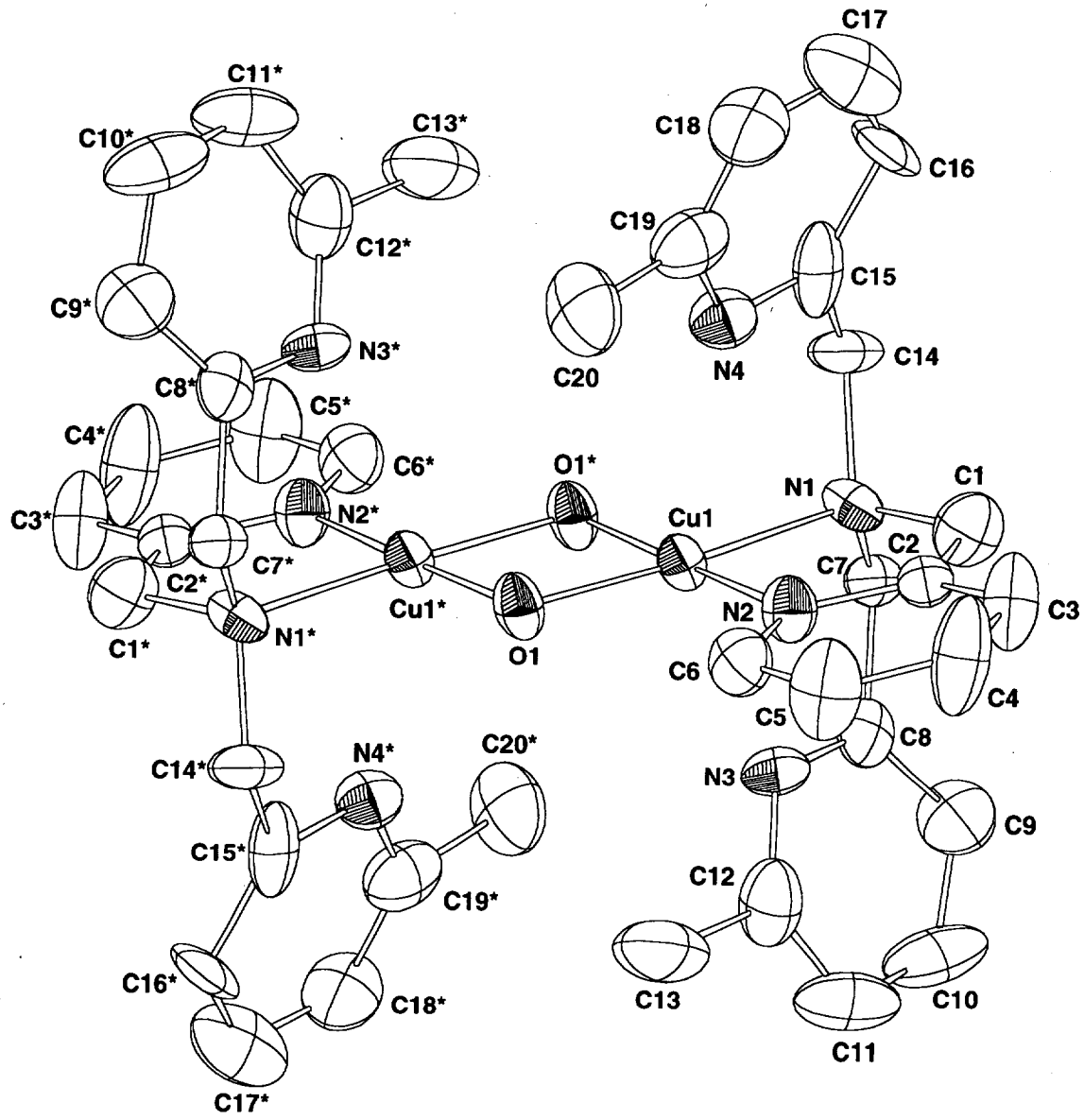

Figure S4. M. Suzuki et al.
Fully labeled ORTEP view (50% probability) of a complex cation of **1b**. Hydrogen atoms are omitted for clarity.

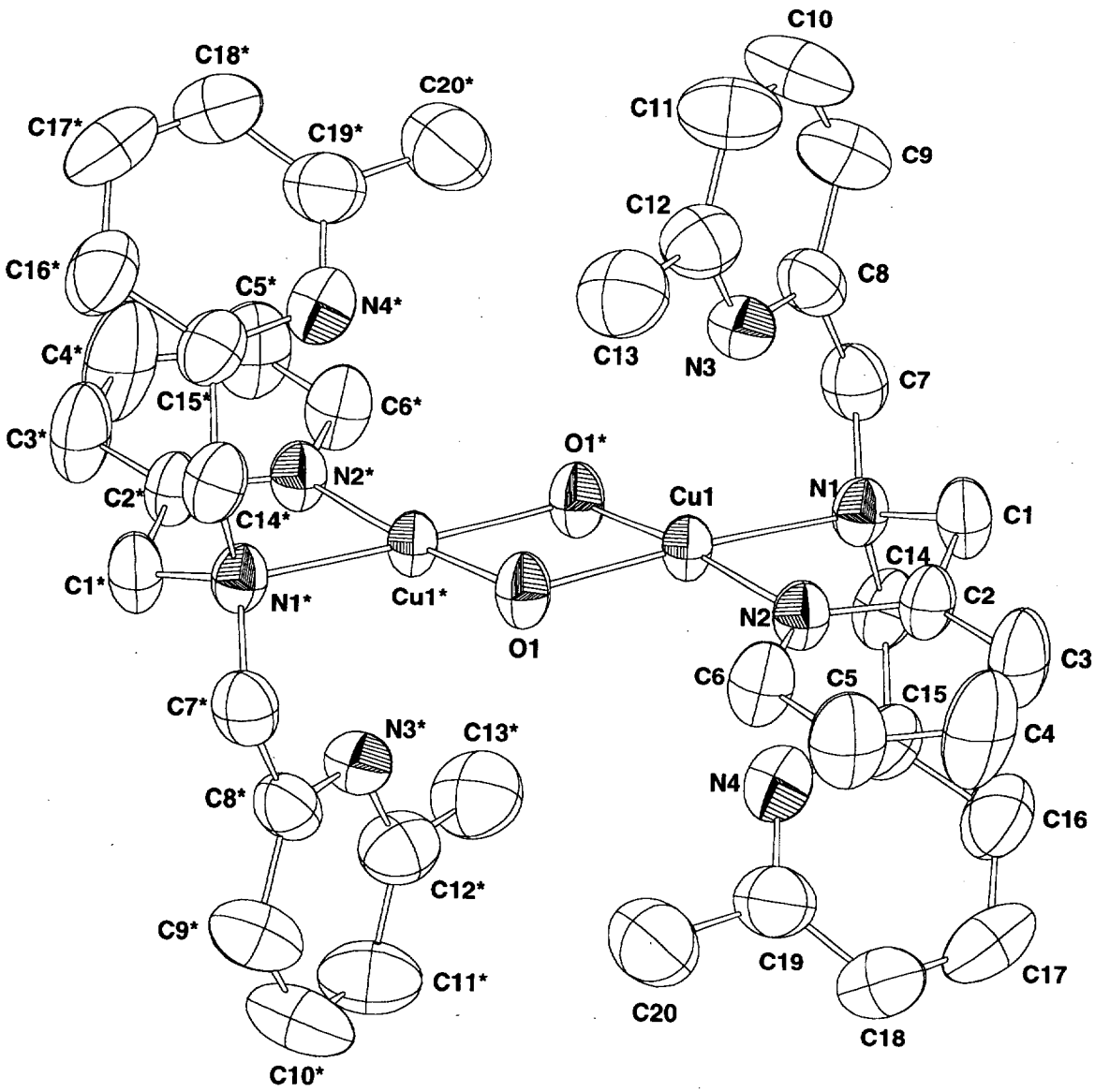

Figure S5. M. Suzuki et al.
Fully labeled ORTEP views (50% probability) of a complex cation of **1c**. Hydrogen atoms are omitted for clarity.