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Supporting Information

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Fig. 7. ESI mass spectrum of the oxygenated $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{7-Et})]^{1+}(\text{BF}_4^-)$, together with their simulated mass spectra. These spectra are assigned to the species $[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{BF}_4^-)_2$ and $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{BF}_4^-) + 2(\text{CH}_2\text{OHCN})\}^+$, respectively.

[SI Figure 8](#)

Fig. 8. ESI mass spectrum of the oxygenated $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{7-Me})]^{1+}(\text{ClO}_4^-)$.

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Fig. 9. Nanospray-ESI mass spectrum of the benzoic adduct $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{ClO}_4^-) + \text{PhCOOH}\}^+$.

[SI Figure 10](#)

Fig. 10. Nanospray-ESI mass spectrum of the benzoic adduct $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{BF}_4^-) + \text{PhCOOH}\}^+$.

[SI Figure 11](#)

Fig. 11. Nanospray-ESI mass spectrum $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{ClO}_4^-)_2 + \text{H}\}^+$ and the acetic acid adduct $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{ClO}_4^-) + \text{CH}_3\text{COOH}\}^+$.

[SI Figure 12](#)

Fig. 12. Comparisons of the nanospray-ESI mass spectra obtained by reoxidation of $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{7-Et})]^{1+}(\text{ClO}_4^-)$ complexes with $^{16}\text{O}_2$ (a) and $^{18}\text{O}_2$ (b). The $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{7-Et})]^{1+}(\text{ClO}_4^-)$

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complexes had been produced initially by reduction of $[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(^{16}\text{O})]^{2+}(\text{ClO}_4^-)_2$ by benzoin/triethylamine before reaction with dioxygen.

SI Figure 13

Fig. 13. Nanospray-ESI mass spectrum of benzoic acid adduct $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{BF}_4^-) + \text{PhCOOH}\}^+$ together with the acetic acid adduct $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{BF}_4^-) + \text{CH}_3\text{COOH}\}^+$.

SI Figure 14

Fig. 14. Representation of the x-ray crystal structure of $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})](\text{BF}_4^-)_2\}_2(\text{PF}_6^-)$. The PF_6^- anion is shared between two parallel units of $[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{BF}_4^-)_2$. The distance between the centroid of each of the $[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}$ units and the phosphorus atom is 3.395 Å, and the distance between the two $[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}$ units is 6.790 Å.

Table 1. Crystal data and structure refinement for ic12150

Identification code	ic12150	
Empirical formula	C27 H58 B2 Cu3 F11 N6 O3 P0.50	
Formula weight	951.52	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	$a = 15.0144(5)$ Å	$\alpha = 90^\circ$
	$b = 22.3041(5)$ Å	$\beta = 117.8040(10)^\circ$
	$c = 14.0665(5)$ Å	$\gamma = 90^\circ$
Volume	4,166.8(2) Å ³	
Z	4	
Density (calculated)	1.517 Mg/m ³	
Absorption coefficient	1.621 mm ⁻¹	
F(000)	1,958	
Crystal size	0.20 × 0.20 × 0.15 mm ³	
Theta range for data collection	1.78 to 25.00°.	
Index ranges	-17 < = h < = 17, -26 < = k < = 26, -16 < = l < = 16	
Reflections collected	21,089	
Independent reflections	7,318 ($R_{\text{int}} = 0.0454$)	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semiempirical from equivalents	
Max. and min. transmission	0.785 and 0.731	

Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	7,318/0/471	
Goodness-of-fit on F^2	1.154	
Final R indices [$<I>2\sigma(I)$]	$R1 = 0.0796$, $wR2 = 0.2490$	
R indices (all data)	$R1 = 0.1003$, $wR2 = 0.2652$	
Extinction coefficient	0.0192(18)	
Largest diff. peak and hole	1.127 and -0.520 $e\cdot\text{\AA}^{-3}$	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ic12150

	x	y	z	$U(\text{eq})$
Cu(1)	2555(1)	735(1)	6677(1)	52(1)
Cu(2)	2047(1)	313(1)	4076(1)	57(1)
Cu(3)	2464(1)	-843(1)	5942(1)	55(1)
O(1)	2883(4)	-108(2)	6748(3)	45(1)
O(2)	2364(4)	870(2)	5237(4)	53(1)
O(3)	2413(4)	-480(2)	4675(4)	57(1)
N(1)	2775(6)	751(3)	8233(5)	65(2)
N(2)	2455(5)	1631(3)	6712(5)	58(2)
N(3)	1352(5)	991(3)	3078(5)	59(2)
N(4)	1865(6)	-24(3)	2682(5)	66(2)
N(5)	2079(6)	-1631(3)	5083(6)	63(2)
N(6)	3075(7)	-1391(4)	7275(7)	84(2)
C(1)	2764(9)	1394(4)	8537(8)	79(3)
C(2)	2134(7)	1757(4)	7547(7)	66(2)
C(3)	1662(6)	1750(4)	5589(6)	58(2)
C(4)	1987(6)	1446(4)	4834(6)	60(2)
C(5)	1072(7)	1396(4)	3719(6)	64(2)
C(6)	489(8)	703(4)	2153(7)	75(2)
C(7)	830(8)	76(4)	1941(7)	77(3)
C(8)	2031(8)	1287(4)	2708(8)	74(2)
C(9)	2234(10)	911(5)	1963(9)	94(3)
C(10)	2573(10)	259(5)	2330(9)	93(3)
C(11)	2139(8)	-678(4)	2907(7)	72(2)
C(12)	1911(7)	-879(4)	3784(7)	60(2)
C(13)	2250(8)	-1502(4)	4153(7)	69(2)
C(14)	2784(9)	-2078(5)	5827(8)	87(3)

C(15)	2884(12)	-2009(5)	6906(10)	114(4)
C(16)	1927(8)	414(5)	8262(7)	74(2)
C(17)	2010(11)	298(6)	9369(8)	106(4)
C(18)	3733(8)	467(5)	8980(7)	80(3)
C(19)	4628(8)	671(5)	8822(9)	94(3)
C(20)	3424(7)	1932(4)	6945(7)	69(2)
C(21)	3363(9)	2606(4)	6766(10)	86(3)
C(22)	994(7)	-1792(4)	4753(8)	69(2)
C(23)	645(9)	-2377(4)	4132(9)	87(3)
C(24)	4151(14)	-1177(8)	8005(13)	145(6)
C(25)	4722(12)	-1075(9)	7573(16)	153(7)
C(26)	2286(19)	-1255(6)	7873(14)	170(10)
C(27)	2680(30)	-1526(19)	8530(30)	340(20)
P(1)	0	0	5000	50(1)
F(1)	862(3)	-552(2)	5612(4)	60(1)
F(2)	430(3)	97(2)	4101(3)	58(1)
F(3)	823(3)	511(2)	5822(3)	57(1)
B(1)	4836(11)	2232(7)	4953(12)	91(4)
F(4)	5352(11)	2165(6)	6001(8)	229(7)
F(5)	4923(10)	1740(6)	4403(12)	206(5)
F(6)	3866(7)	2316(5)	4587(9)	166(4)
F(7)	5247(8)	2655(6)	4576(10)	190(5)
B(2)	124(12)	3285(6)	3979(11)	93(4)
F(8)	999(11)	3137(5)	4765(13)	273(9)
F(9)	-506(9)	2835(5)	3622(8)	179(5)
F(10)	122(7)	3601(3)	3167(6)	127(3)
F(11)	-173(11)	3685(7)	4503(9)	215(6)

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Bond lengths (Å) and angles (°) for ic12150

Bond lengths, Å	Angles, °
Cu(1)-O(1)	1.934(4)
Cu(1)-O(2)	1.934(5)
Cu(1)-N(2)	2.007(7)
Cu(1)-N(1)	2.056(7)

Cu(1)-F(3)	2.354(4)
Cu(2)-O(3)	1.926(5)
Cu(2)-O(2)	1.927(5)
Cu(2)-N(3)	1.995(7)
Cu(2)-N(4)	1.997(7)
Cu(3)-O(1)	1.925(5)
Cu(3)-O(3)	1.926(5)
Cu(3)-N(5)	2.057(7)
Cu(3)-N(6)	2.061(8)
Cu(3)-F(1)	2.319(4)
O(2)-C(4)	1.411(9)
O(3)-C(12)	1.432(10)
N(1)-C(18)	1.471(12)
N(1)-C(1)	1.497(11)
N(1)-C(16)	1.496(12)
N(2)-C(2)	1.489(10)
N(2)-C(20)	1.492(11)
N(2)-C(3)	1.493(10)
N(3)-C(5)	1.469(11)
N(3)-C(6)	1.487(11)
N(3)-C(8)	1.497(11)
N(4)-C(7)	1.429(13)
N(4)-C(11)	1.508(12)
N(4)-C(10)	1.506(12)
N(5)-C(13)	1.474(11)
N(5)-C(14)	1.475(11)
N(5)-C(22)	1.514(12)
N(6)-C(15)	1.454(14)
N(6)-C(24)	1.53(2)
N(6)-C(26)	1.77(2)
C(1)-C(2)	1.504(13)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.520(11)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700

C(4)-C(5)	1.533(11)
C(4)-H(4A)	0.9800
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-C(7)	1.565(14)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.480(14)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.548(16)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.495(12)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.488(12)
C(12)-H(12A)	0.9800
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-C(15)	1.463(15)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(17)	1.525(12)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-C(19)	1.530(16)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700

C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-C(21)	1.520(13)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-C(23)	1.521(12)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-C(25)	1.28(2)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-C(27)	1.03(4)
C(26)-H(26A)	0.9700
C(26)-H(26B)	0.9700
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
P(1)-F(2)#1	1.681(4)
P(1)-F(2)	1.681(4)
P(1)-F(3)#1	1.681(4)
P(1)-F(3)	1.681(4)
P(1)-F(1)	1.701(4)
P(1)-F(1)#1	1.701(4)
B(1)-F(6)	1.312(16)
B(1)-F(4)	1.316(18)
B(1)-F(7)	1.363(18)
B(1)-F(5)	1.384(17)
B(2)-F(8)	1.305(18)

B(2)-F(9)	1.308(17)
B(2)-F(10)	1.342(14)
B(2)-F(11)	1.359(19)
O(1)-Cu(1)-O(2)	96.64(19)
O(1)-Cu(1)-N(2)	170.8(2)
O(2)-Cu(1)-N(2)	83.9(2)
O(1)-Cu(1)-N(1)	93.0(2)
O(2)-Cu(1)-N(1)	170.0(2)
N(2)-Cu(1)-N(1)	86.2(3)
O(1)-Cu(1)-F(3)	90.81(19)
O(2)-Cu(1)-F(3)	84.80(19)
N(2)-Cu(1)-F(3)	98.4(2)
N(1)-Cu(1)-F(3)	98.0(2)
O(3)-Cu(2)-O(2)	108.3(2)
O(3)-Cu(2)-N(3)	162.4(2)
O(2)-Cu(2)-N(3)	87.1(2)
O(3)-Cu(2)-N(4)	87.9(3)
O(2)-Cu(2)-N(4)	160.4(3)
N(3)-Cu(2)-N(4)	78.9(3)
O(1)-Cu(3)-O(3)	92.7(2)
O(1)-Cu(3)-N(5)	177.4(3)
O(3)-Cu(3)-N(5)	86.4(2)
O(1)-Cu(3)-N(6)	94.8(3)
O(3)-Cu(3)-N(6)	154.1(3)
N(5)-Cu(3)-N(6)	84.9(3)
O(1)-Cu(3)-F(1)	84.44(18)
O(3)-Cu(3)-F(1)	96.2(2)
N(5)-Cu(3)-F(1)	98.1(2)
N(6)-Cu(3)-F(1)	109.1(3)
Cu(3)-O(1)-Cu(1)	142.4(2)
C(4)-O(2)-Cu(2)	110.6(4)
C(4)-O(2)-Cu(1)	113.5(4)
Cu(2)-O(2)-Cu(1)	130.1(3)
C(12)-O(3)-Cu(2)	105.2(4)
C(12)-O(3)-Cu(3)	109.0(5)
Cu(2)-O(3)-Cu(3)	132.2(3)
C(18)-N(1)-C(1)	110.2(7)
C(18)-N(1)-C(16)	109.0(7)

C(1)-N(1)-C(16)	110.5(8)
C(18)-N(1)-Cu(1)	111.7(6)
C(1)-N(1)-Cu(1)	107.7(5)
C(16)-N(1)-Cu(1)	107.7(5)
C(2)-N(2)-C(20)	112.5(7)
C(2)-N(2)-C(3)	114.2(6)
C(20)-N(2)-C(3)	111.6(6)
C(2)-N(2)-Cu(1)	105.2(5)
C(20)-N(2)-Cu(1)	112.1(5)
C(3)-N(2)-Cu(1)	100.6(5)
C(5)-N(3)-C(6)	114.8(7)
C(5)-N(3)-C(8)	112.3(7)
C(6)-N(3)-C(8)	110.1(7)
C(5)-N(3)-Cu(2)	103.8(5)
C(6)-N(3)-Cu(2)	104.1(5)
C(8)-N(3)-Cu(2)	111.2(6)
C(7)-N(4)-C(11)	113.8(8)
C(7)-N(4)-C(10)	112.9(8)
C(11)-N(4)-C(10)	108.1(8)
C(7)-N(4)-Cu(2)	105.1(6)
C(11)-N(4)-Cu(2)	105.0(5)
C(10)-N(4)-Cu(2)	111.7(6)
C(13)-N(5)-C(14)	113.4(7)
C(13)-N(5)-C(22)	112.5(7)
C(14)-N(5)-C(22)	111.8(8)
C(13)-N(5)-Cu(3)	103.7(5)
C(14)-N(5)-Cu(3)	104.4(6)
C(22)-N(5)-Cu(3)	110.5(5)
C(15)-N(6)-C(24)	120.4(12)
C(15)-N(6)-C(26)	105.5(10)
C(24)-N(6)-C(26)	111.0(12)
C(15)-N(6)-Cu(3)	107.9(7)
C(24)-N(6)-Cu(3)	108.0(8)
C(26)-N(6)-Cu(3)	102.6(7)
N(1)-C(1)-C(2)	109.7(7)
N(1)-C(1)-H(1A)	109.7
C(2)-C(1)-H(1A)	109.7
N(1)-C(1)-H(1B)	109.7

C(2)-C(1)-H(1B)	109.7
H(1A)-C(1)-H(1B)	108.2
N(2)-C(2)-C(1)	109.5(7)
N(2)-C(2)-H(2A)	109.8
C(1)-C(2)-H(2A)	109.8
N(2)-C(2)-H(2B)	109.7
C(1)-C(2)-H(2B)	109.8
H(2A)-C(2)-H(2B)	108.2
N(2)-C(3)-C(4)	107.6(6)
N(2)-C(3)-H(3A)	110.2
C(4)-C(3)-H(3A)	110.2
N(2)-C(3)-H(3B)	110.2
C(4)-C(3)-H(3B)	110.2
H(3A)-C(3)-H(3B)	108.5
O(2)-C(4)-C(3)	109.0(6)
O(2)-C(4)-C(5)	110.2(6)
C(3)-C(4)-C(5)	108.7(7)
O(2)-C(4)-H(4A)	109.7
C(3)-C(4)-H(4A)	109.6
C(5)-C(4)-H(4A)	109.6
N(3)-C(5)-C(4)	107.3(7)
N(3)-C(5)-H(5A)	110.3
C(4)-C(5)-H(5A)	110.2
N(3)-C(5)-H(5B)	110.3
C(4)-C(5)-H(5B)	110.3
H(5A)-C(5)-H(5B)	108.5
N(3)-C(6)-C(7)	108.8(8)
N(3)-C(6)-H(6A)	109.9
C(7)-C(6)-H(6A)	109.9
N(3)-C(6)-H(6B)	109.9
C(7)-C(6)-H(6B)	109.9
H(6A)-C(6)-H(6B)	108.3
N(4)-C(7)-C(6)	110.1(7)
N(4)-C(7)-H(7A)	109.6
C(6)-C(7)-H(7A)	109.6
N(4)-C(7)-H(7B)	109.6
C(6)-C(7)-H(7B)	109.6
H(7A)-C(7)-H(7B)	108.2

C(9)-C(8)-N(3)	113.3(8)
C(9)-C(8)-H(8A)	108.9
N(3)-C(8)-H(8A)	108.9
C(9)-C(8)-H(8B)	108.9
N(3)-C(8)-H(8B)	108.9
H(8A)-C(8)-H(8B)	107.7
C(8)-C(9)-C(10)	116.1(8)
C(8)-C(9)-H(9A)	108.3
C(10)-C(9)-H(9A)	108.3
C(8)-C(9)-H(9B)	108.2
C(10)-C(9)-H(9B)	108.3
H(9A)-C(9)-H(9B)	107.4
N(4)-C(10)-C(9)	109.4(9)
N(4)-C(10)-H(10A)	109.8
C(9)-C(10)-H(10A)	109.8
N(4)-C(10)-H(10B)	109.8
C(9)-C(10)-H(10B)	109.8
H(10A)-C(10)-H(10B)	108.2
C(12)-C(11)-N(4)	108.5(7)
C(12)-C(11)-H(11A)	110.0
N(4)-C(11)-H(11A)	110.0
C(12)-C(11)-H(11B)	110.0
N(4)-C(11)-H(11B)	110.0
H(11A)-C(11)-H(11B)	108.4
O(3)-C(12)-C(13)	108.7(7)
O(3)-C(12)-C(11)	107.9(7)
C(13)-C(12)-C(11)	113.3(7)
O(3)-C(12)-H(12A)	109.0
C(13)-C(12)-H(12A)	108.9
C(11)-C(12)-H(12A)	109.0
N(5)-C(13)-C(12)	108.6(6)
N(5)-C(13)-H(13A)	110.0
C(12)-C(13)-H(13A)	110.0
N(5)-C(13)-H(13B)	110.0
C(12)-C(13)-H(13B)	110.0
H(13A)-C(13)-H(13B)	108.4
C(15)-C(14)-N(5)	111.0(8)
C(15)-C(14)-H(14A)	109.4

N(5)-C(14)-H(14A)	109.4
C(15)-C(14)-H(14B)	109.5
N(5)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	108.0
C(14)-C(15)-N(6)	112.1(10)
C(14)-C(15)-H(15A)	109.1
N(6)-C(15)-H(15A)	109.1
C(14)-C(15)-H(15B)	109.3
N(6)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
N(1)-C(16)-C(17)	116.6(9)
N(1)-C(16)-H(16A)	108.1
C(17)-C(16)-H(16A)	108.1
N(1)-C(16)-H(16B)	108.1
C(17)-C(16)-H(16B)	108.1
H(16A)-C(16)-H(16B)	107.3
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.4
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(1)-C(18)-C(19)	113.6(8)
N(1)-C(18)-H(18A)	108.8
C(19)-C(18)-H(18A)	108.8
N(1)-C(18)-H(18B)	108.9
C(19)-C(18)-H(18B)	108.9
H(18A)-C(18)-H(18B)	107.7
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.4
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(2)-C(20)-C(21)	115.5(8)
N(2)-C(20)-H(20A)	108.4
C(21)-C(20)-H(20A)	108.4
N(2)-C(20)-H(20B)	108.4

C(21)-C(20)-H(20B)	108.4
H(20A)-C(20)-H(20B)	107.5
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
N(5)-C(22)-C(23)	114.4(8)
N(5)-C(22)-H(22A)	108.7
C(23)-C(22)-H(22A)	108.7
N(5)-C(22)-H(22B)	108.7
C(23)-C(22)-H(22B)	108.7
H(22A)-C(22)-H(22B)	107.6
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-N(6)	117.8(17)
C(25)-C(24)-H(24A)	107.9
N(6)-C(24)-H(24A)	107.9
C(25)-C(24)-H(24B)	107.8
N(6)-C(24)-H(24B)	107.8
H(24A)-C(24)-H(24B)	107.1
C(24)-C(25)-H(25A)	109.4
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.6
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(27)-C(26)-N(6)	95(3)
C(27)-C(26)-H(26A)	112.9
N(6)-C(26)-H(26A)	112.5
C(27)-C(26)-H(26B)	112.9
N(6)-C(26)-H(26B)	112.5
H(26A)-C(26)-H(26B)	110.0

C(26)-C(27)-H(27A)	108.5
C(26)-C(27)-H(27B)	109.9
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	110.0
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
F(2)#1-P(1)-F(2)	180.00(10)
F(2)#1-P(1)-F(3)#1	90.7(2)
F(2)-P(1)-F(3)#1	89.3(2)
F(2)#1-P(1)-F(3)	89.3(2)
F(2)-P(1)-F(3)	90.7(2)
F(3)#1-P(1)-F(3)	179.995(1)
F(2)#1-P(1)-F(1)	89.7(2)
F(2)-P(1)-F(1)	90.3(2)
F(3)#1-P(1)-F(1)	89.9(2)
F(3)-P(1)-F(1)	90.1(2)
F(2)#1-P(1)-F(1)#1	90.3(2)
F(2)-P(1)-F(1)#1	89.7(2)
F(3)#1-P(1)-F(1)#1	90.1(2)
F(3)-P(1)-F(1)#1	89.9(2)
F(1)-P(1)-F(1)#1	179.998(1)
P(1)-F(1)-Cu(3)	141.0(2)
P(1)-F(3)-Cu(1)	141.0(2)
F(6)-B(1)-F(4)	114.9(15)
F(6)-B(1)-F(7)	111.7(13)
F(4)-B(1)-F(7)	112.2(13)
F(6)-B(1)-F(5)	105.7(12)
F(4)-B(1)-F(5)	112.1(15)
F(7)-B(1)-F(5)	98.9(13)
F(8)-B(2)-F(9)	113.1(12)
F(8)-B(2)-F(10)	117.1(15)
F(9)-B(2)-F(10)	111.3(12)
F(8)-B(2)-F(11)	99.3(15)
F(9)-B(2)-F(11)	110.6(15)
F(10)-B(2)-F(11)	104.2(12)

Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z + 1.

SI Text

Materials and Methods

Preparation of Ligands. The ligands **7-Me** and **7-Et** are variants of a polyamine alcohol described previously (1). They were prepared according to Scheme 5 in the main text.

The synthesis of 3,3'-(1,4-diazepane-1,4-diyl)bis(1-chloropropan-2-ol) (**1**) was adapted from the work of Burness and Bayer on the synthesis of glycidyl amines (2). Piperazine was reacted with epichlorohydrin to prepare **1**, which upon condensation with *N,N,N'*-triethylenediamine yielded **7-Me** and **7-Et** in high yields. The condensation step in Scheme 5 was carried out following the procedures of Hayashi *et al.* (3) and Andreyanova *et al.* (4), as these approaches were more straightforward than the method of Bernhardt and Sharpe (1) and led to significantly higher yields of the desired ligands.

A solution of epichlorohydrin (3.16 g, 34.2 mmol) in methanol (15.0 ml) was added drop-wise at 20°C to a solution of piperazine (1.71 g, 17.1 mmol) in methanol (30.0 ml) under mechanical stirring. After stirring for 3 h at 20°C, *N,N,N'*-trimethylenediamine (3.49 g, 34.2 mmol) or *N,N,N'*-triethylenediamine (4.92 g, 34.2 mmol) was added into the solution and heated to 70°C for 48 h. NaOH (1.37 g, 34.2 mmol) in methanol (5.0 ml) was then added drop-wise to the dark yellow solution and refluxed at 70°C for an additional hour. Upon evaporation of the solution to dryness, the ligands were obtained in 89% yield. 3,3'-(1,4-diazepane-1,4-diyl)bis(1-((2-(dimethylamino)ethyl)(methyl)aminopropan-2-ol) (**7-Me**): ¹H NMR (D₂O, 500 MHz) δ 1.83 (m, 2H, CH₂), 2.24 (s, 12H, CH₃), 2.31 (s, 6H, CH₃), ~2.47-2.63 (m, 16H, CH₂), ~2.83-2.88 (m, 8H, CH₂), 4.02 (m, 2H, CH). ESI-MS (positive ion): *m/z*: 416.4. 3,3'-(1,4-diazepane-1,4-diyl)bis(1-((2-(diethylamino)ethyl)(ethyl)amino)propan-2-ol) (**7-Et**): ¹H NMR (500 MHz, D₂O) δ 0.90-0.94 (m, 9H, CH₃), 1.69 (m, 2H, CH₂), ~2.38-2.56 (m, 28H, CH₂), ~2.71-2.73 (m, 8H, CH₂), 3.86 (m, 2H, CH). ESI-MS (positive ion): *m/z* 501.5.

Preparation of [Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)](BF₄)₂(0.5 PF₆⁻). A solution of the oxygenated [Cu^ICu^ICu^I(7-Et)]¹⁺(BF₄⁻) complex in acetonitrile with 5 equivalents of NaPF₆ was prepared to promote crystallization of the complex for structural determination by x-ray diffraction.

Spectroscopic Characterization of Ligand and Copper Complexes.

UV-visible spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. EPR spectra of the Cu(II) complexes were recorded at X-band at 9.6 GHz, modulation frequency 100 kHz, and modulation amplitude 5 G on a Bruker E580 spectrometer equipped with a Bruker dual-mode ER 4116DM cavity. The sample temperature was maintained at 4 K by using an Oxford Instruments continuous liquid-helium cryostat equipped with a turbo pump to lower the vapor pressure of the liquid helium. ESI and nano-electrospray mass spectra were collected on a Finnigan LCQ mass spectrometer (Thermo Finnigan, San Jose, CA). GC-MS analysis was carried out on a Hewlett-Packard GC (HP 6890)-MS (HP 5973) analyzer equipped with a dimethylpolysiloxane DB1-MS 60-m × 0.253-mm column with a 0.25-μm-thick gold film (J&W Scientific supplied by Agilent Technologies). Splitless injection at an injector temperature of 250°C was used. The column temperature was held initially at 40°C for 20 min then raised to 250°C at the rate of 10°C min⁻¹ and maintained at the final temperature for 39 min to equilibrate.

Identification of Products. The products benzil, benzoic acid, 2,3-butanedione, and acetic acid, were identified by GC-MS. Glycolonitrile was identified by IR spectroscopy. The ν_{CN} stretching frequency was recorded on a Perkin-Elmer SPECTRUM ONE Model B spectrophotometer by using KBr pellets for the oxidized CH₃CN or sealed solution cells (0.1 mm, KBr windows) for the glycolonitrile standard. The latter was derived from reagent grade glycolonitrile (55 wt.% in H₂O; Aldrich) stored over 3-Å molecular sieves to remove as much H₂O as possible.

X-Ray Crystal Structure. Diffraction data were collected on a NONIUS Kappa CCD diffractometer with Mo radiation (λ = 0.71073 Å) at 295(2) K over the θ range of 1°-25°. No significant decay of the crystals was observed during the data collection (~8 h). Reflections (5,586) were observed with I ≥ 2σ(I) among the 7,318 unique reflections, and 21,089 reflections were used in the refinement. Data were processed on a PC using the SHELXTL software package. The structure of IC12150 was solved and refined by full-matrix least-squares on the F² value. All nonhydrogen atoms were refined anisotropically. The positions of hydrogen atoms were identified by calculation, and their contributions to structure factors were included. The final indices were R1 = 0.0796, wR2 = 0.2490, with goodness-of-fit on F² = 1.154. Other data are described in SI Tables 1, 2, and 3.

Results

Reaction of Dioxygen with [Cu^ICu^ICu^I(L)]¹⁺(X) (L = 7-Et and X = BF₄⁻). The oxygenated [Cu^ICu^ICu^I(7-Et)]¹⁺(BF₄⁻) revealed two primary positive ion clusters with multiple peaks as well. One occurred in the range of *m/z* ~876-884 amu with a maximum peak at *m/z* 880 amu, and the other appeared in the range of *m/z* ~904-910 amu with a maximum peak at *m/z* 906 amu (Fig. 7). Again, these two multiple peaks are in accord with a complex with three copper ions based on the statistical distribution of Cu isotopes, but the isotopic patterns attributed to the chlorine atom in the case of oxygenated [Cu^ICu^ICu^I(7-Et)]¹⁺(ClO₄⁻) are now replaced by the isotopic contributions from the boron atom [¹⁰B (76%) and ¹¹B (24%) in natural abundance]. The signal at *m/z* 880 was assigned to {[Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(BF₄⁻)₂ + H}⁺, and the *m/z* 906 cluster was assigned to {[Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(BF₄⁻) + 2(CH₂OHCN)}⁺. Comparison of the mass spectra between {[Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(ClO₄⁻)₂ + H}⁺ and {[Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(BF₄⁻)₂ + H}⁺ yielded a mass difference of 24 amu, which is equal to the mass difference between the two different counteranions (2 × (mass_(ClO₄⁻) - mass_(BF₄⁻)) = 24 amu). This result provides strong support for the formation of the [Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(X)₂ (X = ClO₄⁻ and BF₄⁻) in the two experiments. On the other hand, the clusters centered at *m/z* 918 amu that we tentatively have assigned to the putative {[Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(ClO₄⁻) + 2(CH₂OHCN)}⁺ and at *m/z* 906 amu to {[Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(BF₄⁻) + 2(CH₂OHCN)}⁺ revealed only a mass difference of 12 amu, as expected for the association of only one counteranion with these species. The remaining mass associated with these species strongly suggests additional fragments, and the mass difference of 114 amu is consistent with the involvement of two CH₂OHCN ligands in the case of both oxygenated [Cu^ICu^ICu^I(7-Et)]¹⁺(ClO₄⁻) and oxygenated [Cu^ICu^ICu^I(7-Et)]¹⁺(BF₄⁻).

Reaction of Dioxygen with [Cu^ICu^ICu^I(L)]¹⁺(X) (L = 7-Me and X = ClO₄⁻). The same characteristic mass spectra were obtained for oxygenated [Cu^ICu^ICu^I(7-Me)]¹⁺(ClO₄⁻) (Fig. 8). One of the positive ion clusters occurred at *m/z* ~818-824 amu with a maximum peak at *m/z* 820 amu and the other appeared in the range of *m/z* ~832-838 with a maximum peak at *m/z* 834 amu. Accordingly, the signal at *m/z* 820 amu was assigned to {[Cu^{II}Cu^{II}Cu^{II}(7-Me)(O)]²⁺(ClO₄⁻)₂ + H}⁺. The mass difference observed between the proposed species {[Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(ClO₄⁻)₂ + H}⁺ and {[Cu^{II}Cu^{II}Cu^{II}(7-Me)(O)]²⁺(ClO₄⁻)₂ + H}⁺ was 84 amu, in accordance to the mass difference between the **7-Et** and **7-Me** ligands. As expected, the same mass difference existed between the proposed {[Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(ClO₄⁻) + 2(CH₂OHCN)}⁺ and {[Cu^{II}Cu^{II}Cu^{II}(7-Me)(O)]²⁺(ClO₄⁻) + 2(CH₂OHCN)}⁺ species.

X-Ray Crystal Structure. The crystal structure of [Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)](BF₄⁻)₂(0.5 PF₆⁻) was obtained by slow vaporization of a solution of the oxygenated

[Cu^ICu^ICu^I(7-Et)]¹⁺(BF₄⁻) complex in acetonitrile with 5 equivalents of NaPF₆

to promote crystallization under air and by mounting the crystals onto a capillary tube sealed at one end with epoxy resin. According to the diffraction data, the unit cell consisted of four molecules of the [Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(BF₄⁻)₂ together with two shared PF₆⁻ anions in the unit cell. The two molecules of [Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(BF₄⁻)₂ associated with the closest shared PF₆⁻

anion are shown in SI Fig. 14. These results provide direct evidence for the trapping of an oxygen atom in the oxidized trinuclear copper complex from exogenous dioxygen. The existence of half of a PF₆⁻ anion in addition to one tricopper cluster and two BF₄⁻

anions per unit cell implies charge inequality of the two tricopper cluster units, which we have accordingly assigned to [Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺ and [Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]³⁺, respectively. Because there is no evidence for Cu(III) in the x-ray absorption spectrum of these complexes, presumably, the bridging oxo between Cu(1) and Cu(3) in the [Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]³⁺

cluster is protonated in the crystal structure (see SI Fig. 14). That the bridging oxo between Cu(1) and Cu(3) might, in fact, be a bridging hydroxyl 50% of the time seems plausible, given that the extra PF₆⁻ anion in the crystal structure was required to improve the packing forces and optimize the conditions for crystallization (5).

In the ORTEP drawing of the [Cu^{II}Cu^{II}Cu^{II}(7-Et)(O)]²⁺(BF₄⁻)₂ in Fig. 3, each of the three copper ions has a distorted square-planar N₂O₂ coordination geometry. Consequently, the conformation of the six-membered ring formed by the three Cu ions and the three coordinated O-atoms assumes a slightly chair-shaped twist. The Cu-O distances are all similar with

average parameters Cu-O = 1.93 Å. The Cu(1)-O(1)-Cu(3) angle of 142.4° is greater than the Cu(1 or 3)-O(2 or 3)-Cu(2) angles of 132.1° and 130.2°, respectively. The Cu-Cu distances reveal that the plane encompassing the three copper ions is an isosceles triangle, with the Cu(1)-Cu(2) and Cu(2)-Cu(3) distances being 3.50 Å and 3.52 Å, respectively, but the Cu(1)-Cu(3) distance at the base is longer, 3.65 Å.

It should be noted that we have used racemic epichlorohydrin in the preparation of **7-Me** and **7-Et** in this preliminary study. Thus, the ligands synthesized should be a 1:1 mixture of the enantiomeric (RR or SS) and meso (RS) forms. Inasmuch as the chiral centers introduced are located on the periphery of the complex, the stereochemistry of the ligands should not impact the reactivity toward O-atom transfer. More importantly, the conformation of the six-membered ring formed by the three Cu ions and the three coordinated O-atoms is almost planar, assuming only a slightly chair-shaped twist. DFT calculations have shown that the reactivity is related only to the core structure of $[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}(\mu\text{-O})_2]^{3+}$ and its ability to harness the highly reactive "singlet oxene," and this reactivity is extremely robust, primarily sensitive to the Cu-O and Cu-Cu distances and the electronic distribution within the tricopper cluster (6).

Although oxygenation of $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{L})]^{1+}(\text{X})$ (**L** = **7-Me** or **7-Et**; **X** = ClO_4^- or BF_4^-) complexes resulted in the formation of at least two species according to mass spectrometry analysis, it is unlikely that the two distinct trinuclear Cu(II) complexes observed in the ESI-MS (one with two glycolonitrile ligands and the other with two weakly coordinating anions) arise from the heterogeneity of the starting ligand and the differential reactivity of the Cu(I) complexes created. We surmise that the two trinuclear Cu(II) complexes seen in the ESI-MS, $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{L})(\text{O})]^{2+}(\text{X})_2 + \text{H}\}^+$ and $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{L})(\text{O})]^{2+}(\text{X}) + 2(\text{CH}_2\text{OHCN})\}^+$, are related to the details of the chemistry associated with the system. For every glycolonitrile generated, two putative $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}(\mu\text{-O}_2)$ intermediates must be involved. One $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}(\mu\text{-O}_2)$ is directly involved in oxo-transfer to the CH_3CN , and the second participates in subsequent intercluster electron transfer to extract the remaining reducing equivalent from the product $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{O})$ species. In this manner, two trinuclear Cu(II) complexes are produced per glycolonitrile generated. Because one of the two trinuclear Cu(II) complexes seen in the MS is coordinated by two glycolonitriles, stoichiometry dictates that the $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{X}) + 2(\text{CH}_2\text{OHCN})\}^+$

detected in the MS must be accompanied maximally by three trinuclear Cu(II) complexes with the two weakly coordinating anions alone, namely, $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{X})_2 + \text{H}\}^+$. This theoretical limit is close to the intensity ratio observed for the two distinct trinuclear Cu(II) complexes in the ESI-MS when the counterion was ClO_4^- . When the counterion was BF_4^- , the observed intensity ratio of the $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{BF}_4^-)_2$ and $\{[\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}(\text{7-Et})(\text{O})]^{2+}(\text{BF}_4^-) + 2(\text{CH}_2\text{OHCN})\}^+$ mass peaks was ~1. We expect the intensity ratio of the mass peaks associated with these two species to be influenced principally by the coordinating counterion (ClO_4^- or BF_4^-) and the nature of the solvent.

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