

Electronic Supplementary Information

Complexes of copper(II) with 3-(*ortho*-substituted phenylhydrazo)pentane-2,4-diones: syntheses, properties and catalytic activity for cyclohexane oxidation

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Substituent constants

Table S1 Substituent constants

Substituents	σ_p^a	σ_o^b	σ_1^a
-OH	-0.37	-0.24	0.25
-AsO ₃ H ₂	-0.02	-0.01	-
-Cl	0.23	0.15	0.47
-SO ₃ H	0.35	0.23	-
-COOCH ₃	0.45	0.29	0.30
-COOH	0.45	0.29	0.30
-NO ₂	0.78	0.51	0.63
-H	0	0	0

^a C. Hansch, A. Leo, W. R. Taft, *Chem. Rev.* 1991, **91**, 165; C. Laurence, B. Wojtkowiak, *Ann. Chim.* 1970, **5**, 163; B. P. McDaniel, H. C. Brown, *J. Am. Chem. Soc.* 1958, **23**, 420; V. A. Pal'm, *Rus. Chem. Rev.* 1961, **30**, 471;

^b Values were calculated by equation $\sigma_o = 0.65 \cdot \sigma_p$. (A. Beteringhe, *Central Eur. J. Chem.* 2005, **3**, 585).

Computational details

Table S2 Total energies, enthalpies, Gibbs free energies (in Hartree) and entropies (in cal·mol⁻¹K⁻¹) of the calculated structures for gas-phase and water solution

	E _g	E _s	H _g	H _s	S _g	S _s	G _g	G _s
H ₂ O	-76.422572	-76.434146	-76.397694	-76.409268	46.50	25.37	-76.419789	-76.421322
<i>trans</i> - Cu(H ₂ O) ₂ (OH) ₂	-501.889708	-501.913699	-501.802952	-501.826943	94.01	51.02	-501.847621	-501.851184
<i>cis</i> -Cu(H ₂ O) ₂ (OH) ₂	-501.885273	-501.912323	-501.798819	-501.825869	95.83	52.01	-501.844350	-501.850581
L ₁	-761.571563	-761.588873	-761.336899	-761.354209	125.99	68.29	-761.396760	-761.386656
L ₂	-3146.434639		-3146.177179		150.57		-3146.248719	
L ₃	-1145.943481		-1145.722540		128.38		-1145.783535	
L ₄	-1310.147887	-1310.161000	-1309.899940	-1309.913053	143.68	77.85	-1309.968207	-1309.950042
L ₅	-914.235881		-913.958974		144.46		-914.027612	
L ₆	-874.930175		-874.683164		136.81		-874.748167	
L ₇	-890.854244		-890.620086		136.99		-890.685174	
L ₈	-686.351342	-686.361137	-686.121915	-686.131710	121.11	65.66	-686.179456	-686.162907
[Cu(OH)(L ₈) (H ₂ O)](H ₂ O)	-1111.835151	-1111.852626	-1111.544688	-1111.562163	166.92	90.39	-1111.623995	-1111.605110
[Cu(L ₁)(H ₂ O) ₂] (H ₂ O)	-1187.091071	-1187.108453	-1186.795078	-1186.812460	164.32	88.99	-1186.873153	-1186.854742
[Cu(L ₄)(H ₂ O) ₂] (H ₂ O)	-1735.678476	-1735.703365	-1735.368377	-1735.393266	180.58	97.77	-1735.454178	-1735.439720

Thermal behaviours of 1–8 and some of their copper(II) complexes

The thermal properties of the ADB and their copper(II) complexes were investigated by thermogravimetric analysis (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA). The thermodynamic parameters of decomposition of the complexes, namely the activation energy (E_a), enthalpy ($\Delta^\ddagger H$), entropy ($\Delta^\ddagger S$) and free energy ($\Delta^\ddagger G$), as well as the pre-exponential factor (A) were evaluated graphically using the Coats-Redfern relationship [(a) A. W. Coats, J. P. Redfern, *Nature*, 1964, **20**, 68; (b) E. Urbanovici, C. Popescu, E. Segal, *J. Ther. Anal. Calor.*, 1999, **58**, 683]:

$$\ln\{[-\ln(1-\alpha)]/T^2\} = -E_a/RT + \ln[AR/\phi E_a],$$

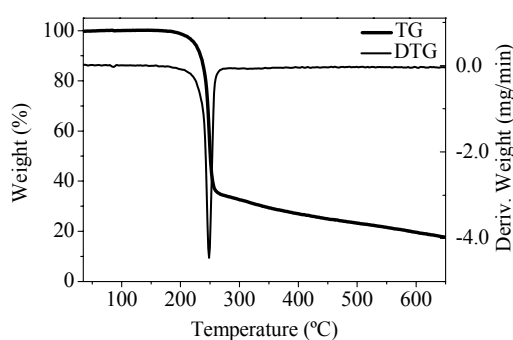
where α is the fraction of the sample decomposed at temperature T , A is the pre-exponential factor, ϕ the heating rate, E_a the activation energy and R the gas constant. A plot of $\ln\{[-\ln(1-\alpha)]/T^2\}$ against $1/T$ gives a slope from which E_a was calculated, and A was determined from the intercept. The activation entropy ($\Delta^\ddagger S$), enthalpy ($\Delta^\ddagger H$) and free energy change ($\Delta^\ddagger G$) were calculated using the following equations:

$$\Delta^\ddagger S = 2.303R \lg(Ah/kT_s),$$

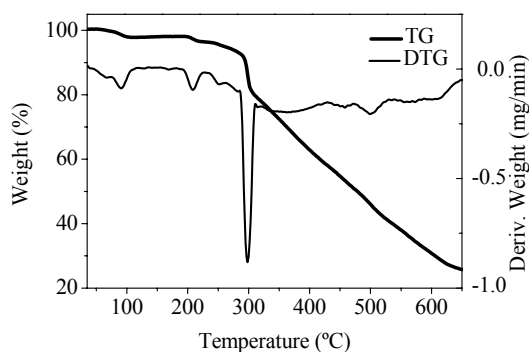
$$\Delta^\ddagger H = E_a - RT_s,$$

$$\Delta^\ddagger G = \Delta^\ddagger H - T_s \Delta^\ddagger S,$$

where k , h and T_s are the Boltzman constant, the Planck constant and the DTG peak temperature, respectively.



1



2

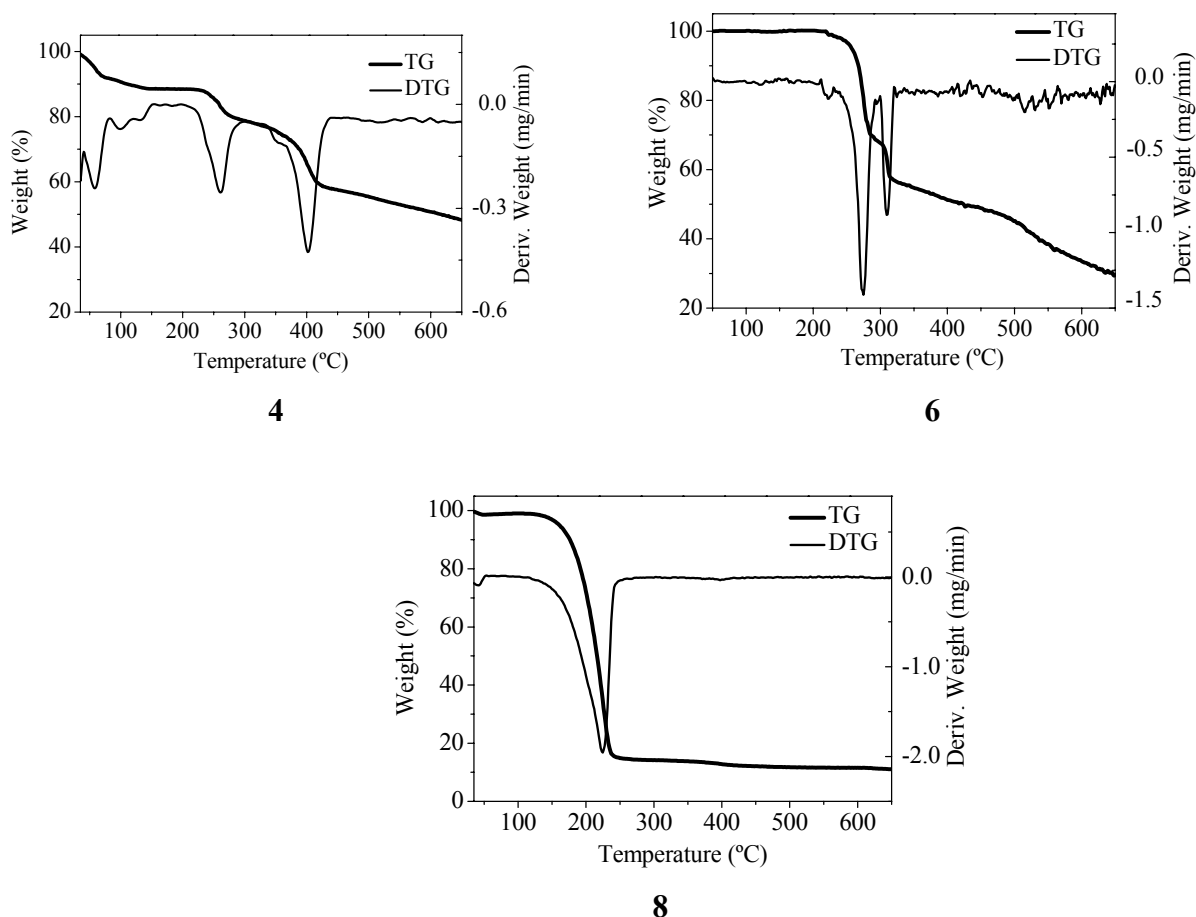


Fig. S1 TG and DTG curves of 1, 2, 4, 6 and 8.

Table S3 Thermal behaviours and kinetic parameters of 1, 2, 4, 6 and 8

Compound	Temperature range (K)	% Weight loss found	DTG peak temperature (K)	A (s^{-1})	E_a ($kJ \cdot mol^{-1}$)	$\Delta^\ddagger H$ ($kJ \cdot mol^{-1}$)	$\Delta^\ddagger S$ ($J \cdot K^{-1} mol^{-1}$)	$\Delta^\ddagger G$ ($kJ \cdot mol^{-1}$)
1	470–568	66.0	527	$3.3 \cdot 10^8$	112	107	–87	153
2	343–388	1.98	368	$9.2 \cdot 10^{-2}$	22.5	19.4	–267	118
	466–504	1.78	484	0.21	31.5	27.5	–262	154
	520–593	17.8	575	62.6	55.8	51.0	–216	175
4	338–377	3.1	356	$5.8 \cdot 10^{-4}$	5.5	2.6	–308	112
	486–561	9.0	536	$1.1 \cdot 10^{-3}$	9.5	5.0	–306	169
	643–701	14.6	684	$4.1 \cdot 10^{-2}$	24.7	19.1	–279	210
6	491–574	31.8	551	$1.1 \cdot 10^7$	105	100	–115	163
	574–620	5.8	585	0.31	28.9	24.0	–260	176
8	414–517	82.5	499	$9.8 \cdot 10^4$	69.2	65.0	–154	142

Example of calculations for the thermal decomposition of 8.

i) Calculation of $1-\alpha$:

The initial sample weight: $m_0 = 5.268$ mg.

8 decomposes at 414– 517 K (Fig. S1, Table S3).

Sample weight upon decomposition at 414 K: $m = 5.147$ mg.

$$5.147 \cdot 100 / 5.268 = 97.7 \%$$

Thus, $1-\alpha = 0.977$ at 414 K.

Sample weight at 466 K: $m = 4.160$ mg.

$$4.160 \cdot 100 / 5.268 = 79.0 \%$$

$1-\alpha = 0.790$ at 466 K.

Sample weight at 495 K: $m = 2.123$ mg.

$$2.123 \cdot 100 / 5.268 = 40.3 \%$$

$1-\alpha = 0.403$ at 495 K.

Sample weight at 499 K: $m = 1.687$ mg.

$$1.687 \cdot 100 / 5.268 = 31.9 \%$$

$1-\alpha = 0.319$ at 499 K.

Sample weight at 517 K: $m = 0.799$ mg.

$$0.799 \cdot 100 / 5.268 = 15.2 \%$$

$1-\alpha = 0.152$ at 517 K.

ii) Calculation of the weight loss:

Sample weight: $m_0 = 5.268$ mg.

$m = 5.147$ mg at 414 K.

$m = 0.799$ mg at 517 K.

Weight loss = $5.147 - 0.799 = 4.348$ mg.

$$4.348 \cdot 100 / 5.268 = 82.53 \%$$

(Table S3).

iii) Calculation of $\ln\{-\ln(1-\alpha)/T^2\}$:

$$\ln\{-\ln(1-\alpha)/T^2\} = \ln\{-\ln(0.977)/414^2\} = -15.81 \text{ at } 414 \text{ K; and } 1/T = 2.415 \cdot 10^{-3}$$

$$\ln\{-\ln(1-\alpha)/T^2\} = \ln\{-\ln(0.790)/466^2\} = -13.73 \text{ at } 466 \text{ K; and } 1/T = 2.150 \cdot 10^{-3}$$

$$\ln\{-\ln(1-\alpha)/T^2\} = \ln\{-\ln(0.403)/495^2\} = -12.50 \text{ at } 495 \text{ K; and } 1/T = 2.020 \cdot 10^{-3}$$

$$\ln\{-\ln(1-\alpha)/T^2\} = \ln\{-\ln(0.319)/499^2\} = -12.29 \text{ at } 499 \text{ K; and } 1/T = 2.000 \cdot 10^{-3}$$

$$\ln\{-\ln(1-\alpha)/T^2\} = \ln\{-\ln(0.152)/517^2\} = -11.86 \text{ at } 517 \text{ K; and } 1/T = 1.930 \cdot 10^{-3}$$

iv) The plot of $\ln\{-\ln(1-\alpha)/T^2\}$ versus $1/T$ (Fig. S2) gives the slope from which E_a can be calculated, and A can be determined from the intercept.

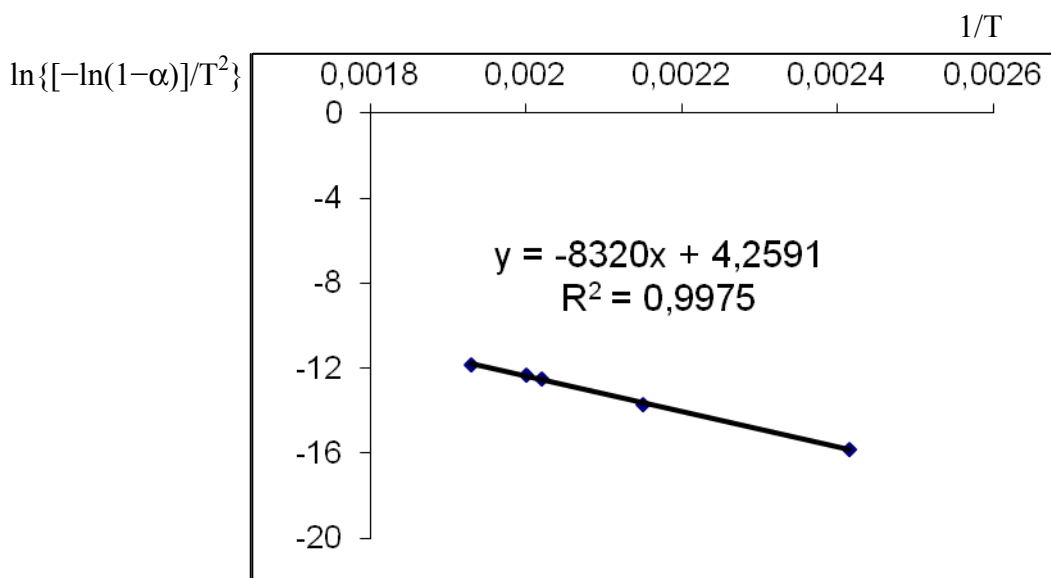


Fig. S2 Plot of $\ln\{-\ln(1-\alpha)/T^2\}$ vs. $1/T$.

v) Calculation of E_a :

$-E_a/R = -8320$ (Fig. S2).

$-E_a/R = -8320 \Rightarrow E_a = 8320 \cdot 8.314 = 69172.48 \text{ J}\cdot\text{mol}^{-1} \approx 69.2 \text{ kJ}\cdot\text{mol}^{-1}$ (Table S3).

vi) Calculation of A:

$\ln[AR/\phi E_a] = +4.2591$ (Fig. S2).

Scan rate was $10.00^\circ\text{C}/\text{min}$ and sample heated from 30.00°C to 800.00°C .

$T = 273.15 + t$ ($^\circ\text{C}$)

For instance, $T_1 = 273.15 + 30 = 303.15 \text{ K}$; $T_2 = 273.15 + 40 = 313.15 \text{ K}$;

$T_3 = 273.15 + 50 = 323.15 \text{ K}$; $T_4 = 273.15 + 60 = 333.15 \text{ K}$;

$\phi = \Delta T/\Delta \text{time} = T_2 - T_1 / \text{time}_2 - \text{time}_1 = 313.15 - 303.15 / 2 \text{ min} - 1 \text{ min} =$
 $= 313.15 - 303.15 / 120 \text{ s} - 60 \text{ s} = 0.16666 \text{ K/s} \approx 0.167 \text{ K/s}$.

$\phi = \Delta T/\Delta \text{time} = T_4 - T_2 / \text{time}_4 - \text{time}_2 = 333.15 - 313.15 / 4 \text{ min} - 2 \text{ min} =$
 $= 333.15 - 313.15 / 240 \text{ s} - 120 \text{ s} = 0.16666 \text{ K/s} \approx 0.167 \text{ K/s}$.

$\phi \approx 0.167 \text{ K/s} = \text{constant}$.

$\ln[AR/\phi E_a] = +4.2591 \Rightarrow \ln[A \cdot 8.314 / 0.167 \cdot 69172] \Rightarrow A = 3.3 \cdot 10^8 \text{ s}^{-1}$ (Table S3).

vii) Calculation of $\Delta^\ddagger H$:

$T_s = 499 \text{ K}$ (Fig. S1, DTG peak, Table S3).

$\Delta^\ddagger H = E_a - RT_s = 69172 - 8.314 \cdot 499 = 65.0 \text{ kJ}\cdot\text{mol}^{-1}$ (Table S3).

viii) Calculation of $\Delta^\ddagger S$:

$\Delta^\ddagger S = 2.303R \lg(Ah/kT_s) = 2.303 \cdot 8.314 \lg(3.3 \cdot 10^8 \cdot 6.626 \cdot 10^{-34} / 1.38 \cdot 10^{-23} \cdot 499) = -154 \text{ J}\cdot\text{K}^{-1} \cdot \text{mol}^{-1}$

(Table S3).

ix) Calculation of $\Delta^\ddagger G$:

$\Delta^\ddagger G = \Delta^\ddagger H - T_s \Delta^\ddagger S = 65.0 - 499 \cdot (-0.1536) = 142 \text{ kJ}\cdot\text{mol}^{-1}$ (Table S3).

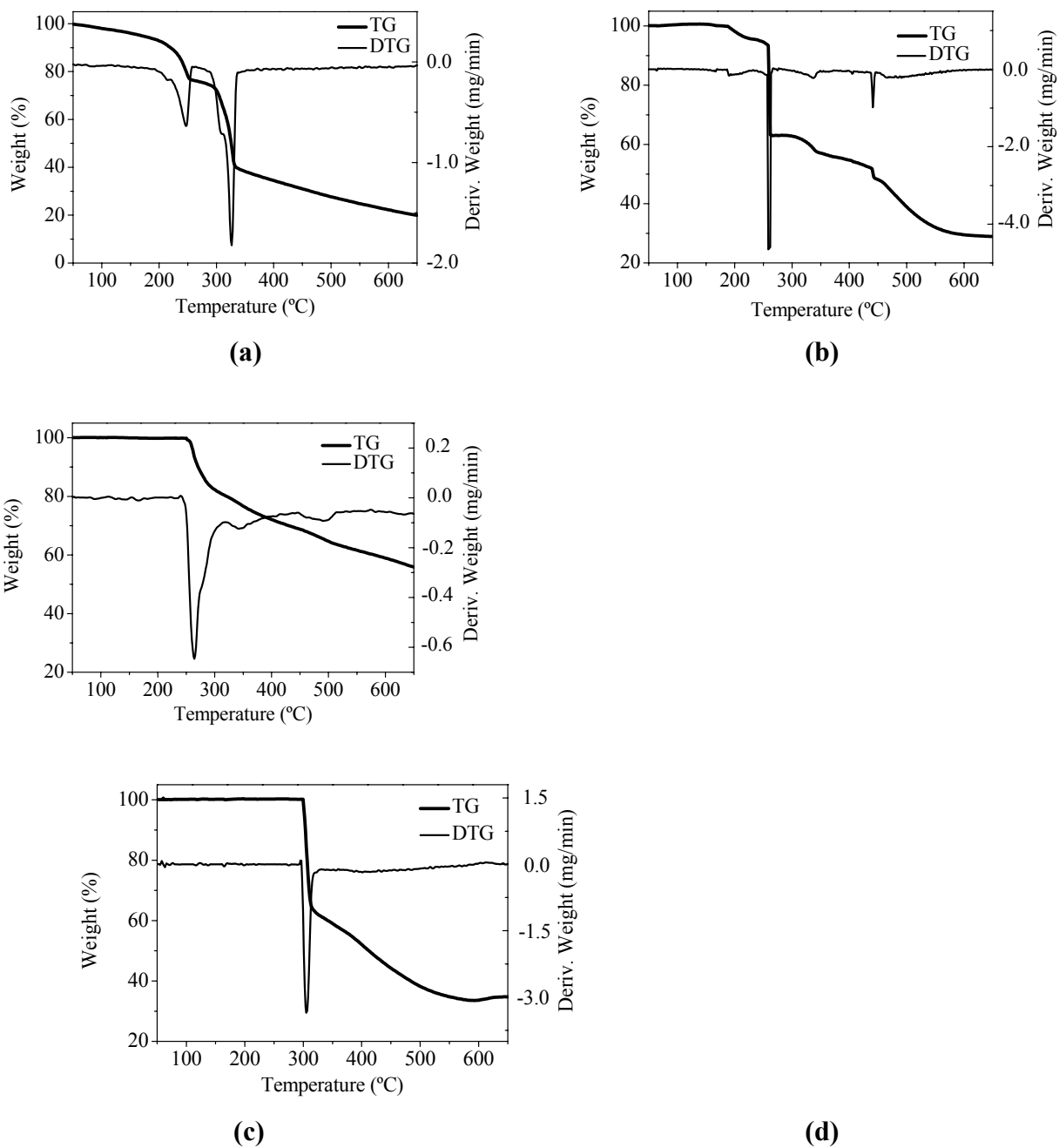
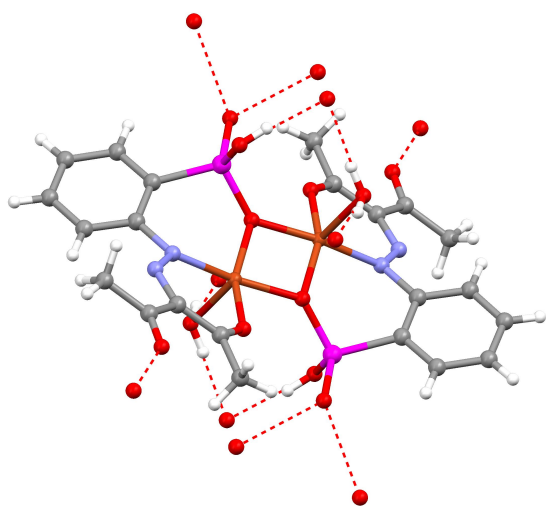
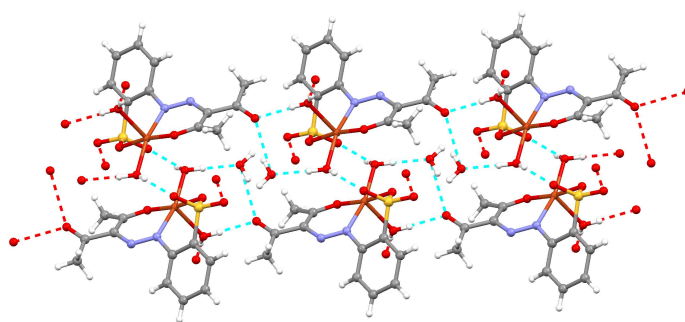


Fig. S3 TG and DTG curves of $[\text{Cu}_2(\mu\text{-L}_1)_2(\text{CH}_3\text{OH})_2]$ (a), **9** (b), **10** (c) and **13** (d).

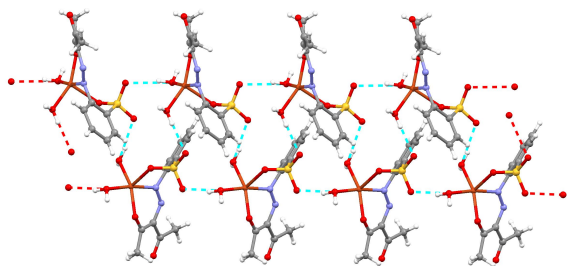
X-ray analyses



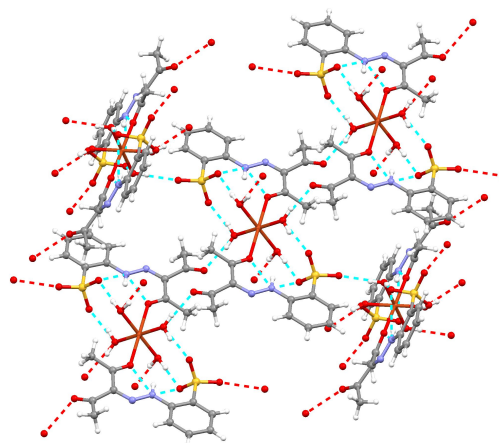
(a)



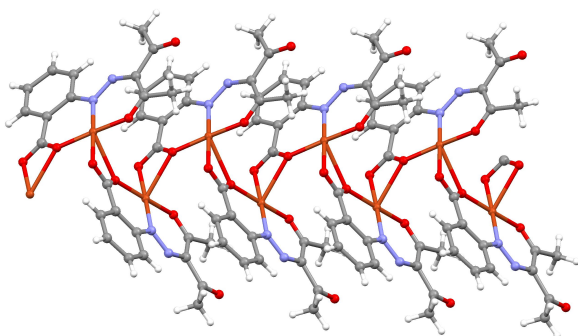
(b)



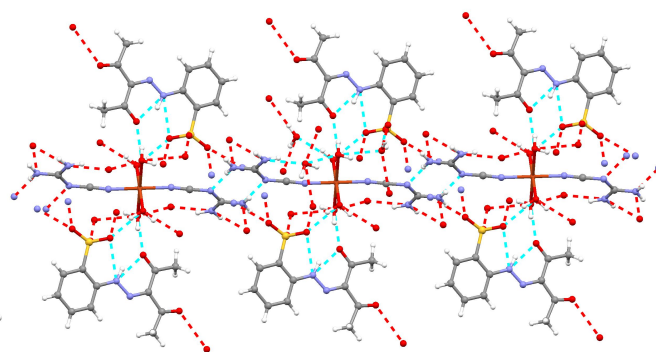
(c)



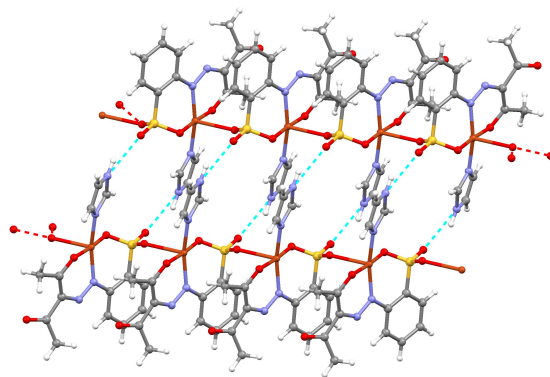
(d)



(e)



(f)



(g)

Fig. S4 Packing diagrams of Cu-ADB complexes **9** (a), **10** (b), **11** (c), **12** (d), **13** (e), **14** (f), **15** (g).

Catalytic activity of the complexes

Table S4 Peroxidative oxidation of cyclohexane to cyclohexanol and cyclohexanone^a

Entry	Cu catalyst	n(H ₂ O ₂)/ n(HNO ₃)/		Yield ^b of products, %			TON ^d
		n(Cat)	n(Cat)	Alcohol	Ketone	Total ^c	
1	9	750	0	5.2	6.5	11.7	23.8
2	9	750	10	5.4	6.5	11.9	24.2
3	9	750	20	4.7	7.6	12.3	25.0
4	9	750	30	4.3	7.2	11.5	23.4
5	9	750	60	4.0	6.3	10.3	21.0
6	9	500	10	3.1	4.6	7.7	15.7
7	9	1000	10	6.9	9.9	16.8	34.2
8	9	1250	10	8.7	10.8	19.5	39.7
9	10	750	0	2.1	2.5	4.6	4.6
10	10	750	10	3.4	4.5	7.9	7.9
11	10	750	20	3.6	4.7	8.3	8.3
12	10	750	30	3.2	5.3	8.5	8.5
13	10	750	60	3.1	5.8	8.9	8.9
14	10	500	10	3.3	3.5	6.8	6.8
15	10	1000	10	4.3	7.1	11.4	11.4
16	10	1250	10	5.7	6.5	12.2	12.2
17	10	1000	10	4.4	7.0	11.4	326
18	12	750	0	2.8	4.1	6.9	12.1
19	12	750	10	6.7	9.1	15.8	27.8
20	12	750	20	6.2	9.2	15.4	27.1
21	12	750	30	6.4	9.2	15.6	27.4
22	12	750	60	5.5	7.5	13.0	22.8
23	12	500	10	4.7	5.7	10.4	18.3
24	12	1000	10	9.3	10.9	20.2	35.5
25	12	1250	10	10.5	12.0	22.5	39.5
26	12	1000	10	8.9	10.9	19.8	566
27	13	750	0	4.2	5.8	10.0	10.3
28	13	750	10	5.3	6.3	11.6	11.9
29	13	750	20	5.3	6.7	12.0	12.3
30	13	750	30	5.2	7.2	12.4	12.7

31	13	750	60	4.8	6.7	11.5	11.8
32	13	500	10	3.8	4.5	8.3	8.5
33	13	1000	10	7.2	9.1	16.3	16.7
34	13	1250	10	7.4	9.5	16.9	17.4
35	$[\text{Cu}_2(\mu\text{-L}^1)_2(\text{CH}_3\text{OH})_2]^{8\text{e}}$	1000	10	7.1	16.6	23.7	23.7
36	$\text{Cu}(\text{NO}_3)_2^{\text{e}}$	1000	10	1.6	3.8	5.4	5.4
37	2,4 or 6 ^e	1000	10	-	-	- ^f	-
38	Blank	1000	10	-	-	- ^f	-

^a Selected data; reaction conditions: C_6H_{12} (1 mmol), Cu-catalyst (0.35-10.0 μmol), MeCN/ H_2O 4 mL, $n(\text{HNO}_3)/n(\text{Cat}) = 0\text{-}60$, H_2O_2 (5.0-12.5 mmol added as an aqueous 30% solution), reaction time: 6 h, 298 K. ^b Moles of product/100 moles of C_6H_{12} (Alcohol = cyclohexanol, Ketone = cyclohexanone). ^c Cyclohexanol + cyclohexanone. ^d Overall TON values (moles of products/mole of catalyst). ^e For comparative purposes, $\text{Cu}(\text{NO}_3)_2$ and ligands **2,4** and **6** were used as catalysts (10.0 μmol). ^f Traces, < 0.3 %.

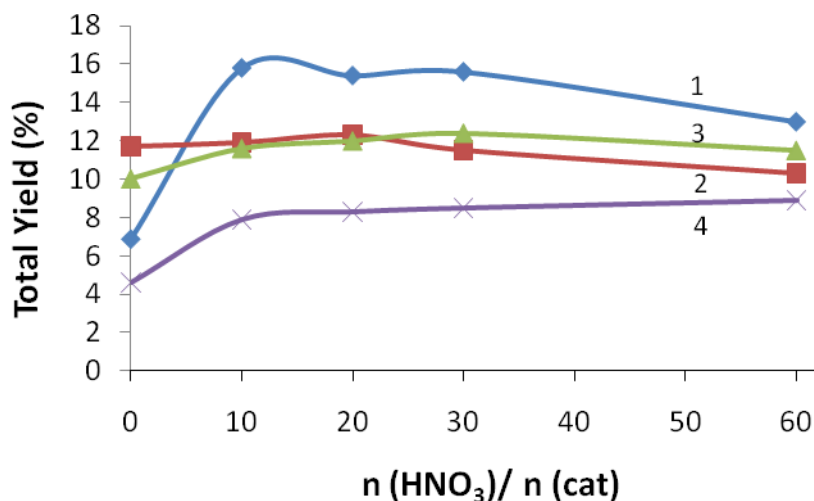


Fig. S5 Effect of the nitric acid-to-catalyst molar ratio on the total yield of products in the cyclohexane oxidation catalyzed by complexes **12** (1), **9** (2), **13** (3) and **10** (4). Reaction conditions are those of Table S4.

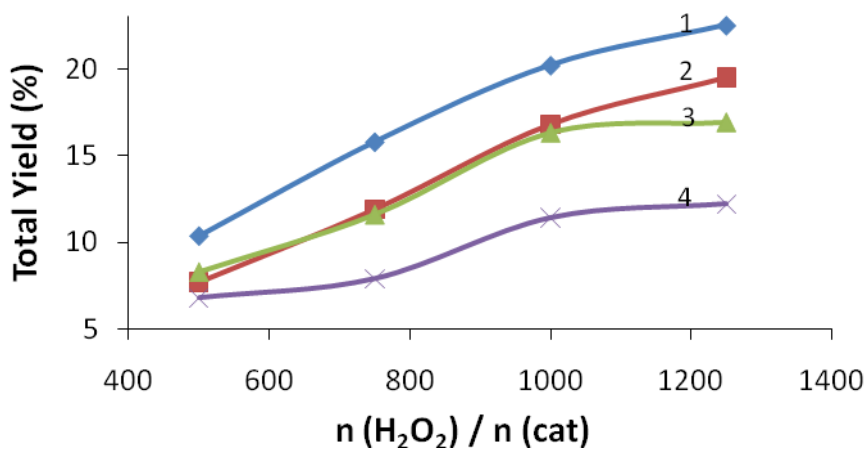


Fig. S6 Effect of the oxidant-to-catalyst molar ratio on the total yield of products in the cyclohexane oxidation catalyzed by complexes **12** (1), **9** (2), **13** (3) and **10** (4). Reaction conditions are those of Table S4.

