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Electronic Supplementary Information

Nuclearity dependent solvent contribution on the catechol oxidase activity of novel Copper(II) complexes derived from Mannich-base ligand platforms: synthesis, crystal structure and mechanism†

Ria Sanyal,[a,b] Sergey Ketkov,[c,d] Suranjana Purkait,[a] Franz A. Mautner[e], Grigory Zhigulin[c], and Debasis Das*[,a]

[a]*Department of Chemistry, University of Calcutta, 92, A.P.C. Road, Kolkata 700 009, India*

[b]*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India*

[c]*G.A.Razuvaev Institute of Organometallic Chemistry RAS, 49 Tropinin St.,603950 Nizhny Novgorod, Russian Federation*

[d]*N.I. Lobachevsky Nizhny Novgorod State University, Gagarin ave. 23, 603950 Nizhny Novgorod, Russian Federation*

[e]*Institut fuer Physikalische und Theoretische Chemie, Technische Universitaet Graz, A-8010 Graz, Austria.*

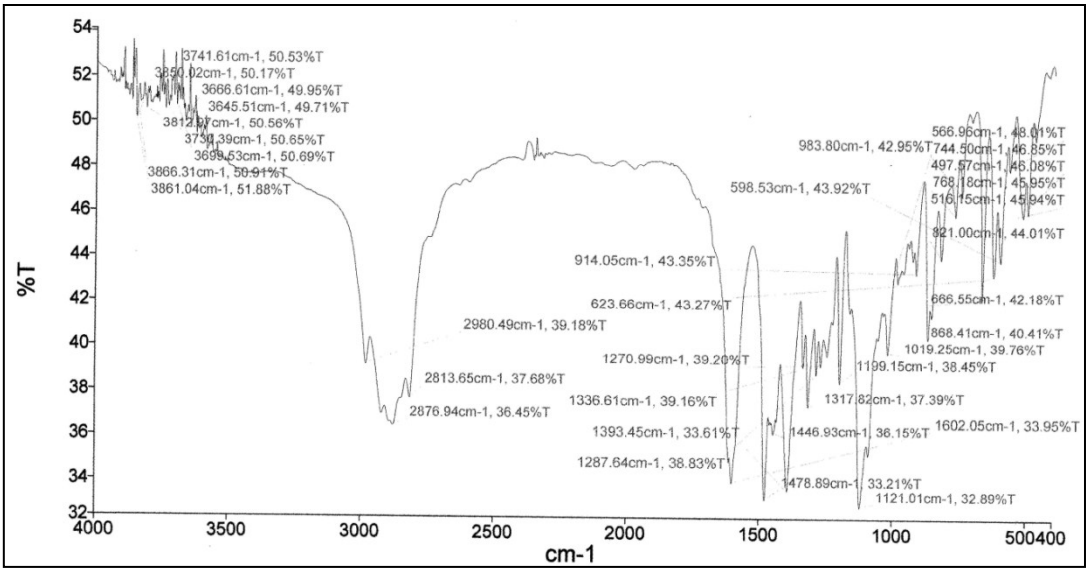

Figure **S1**. FTIR spectrum of complex **1**.

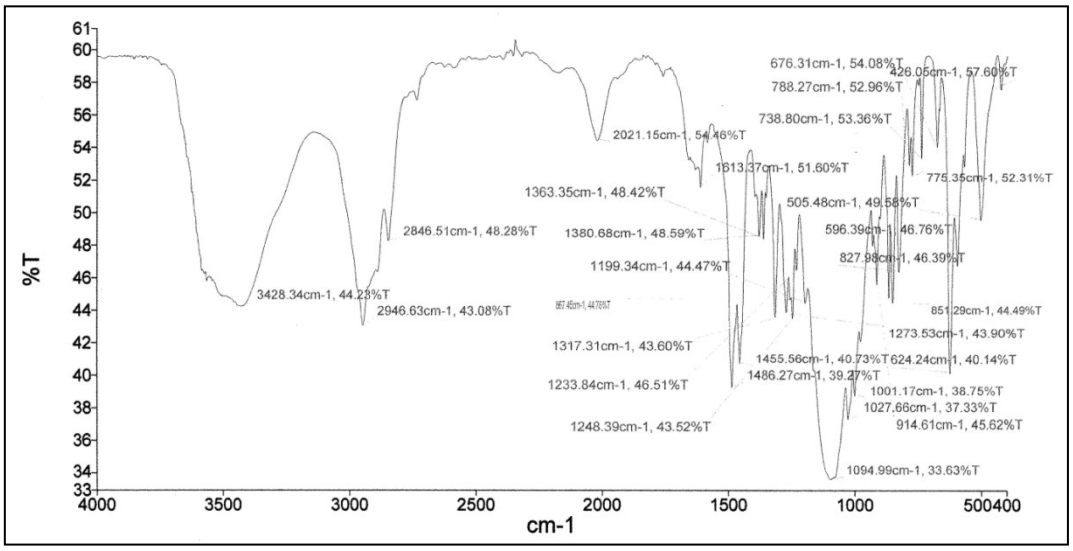

Figure **S2**. FTIR spectrum of complex **2**.

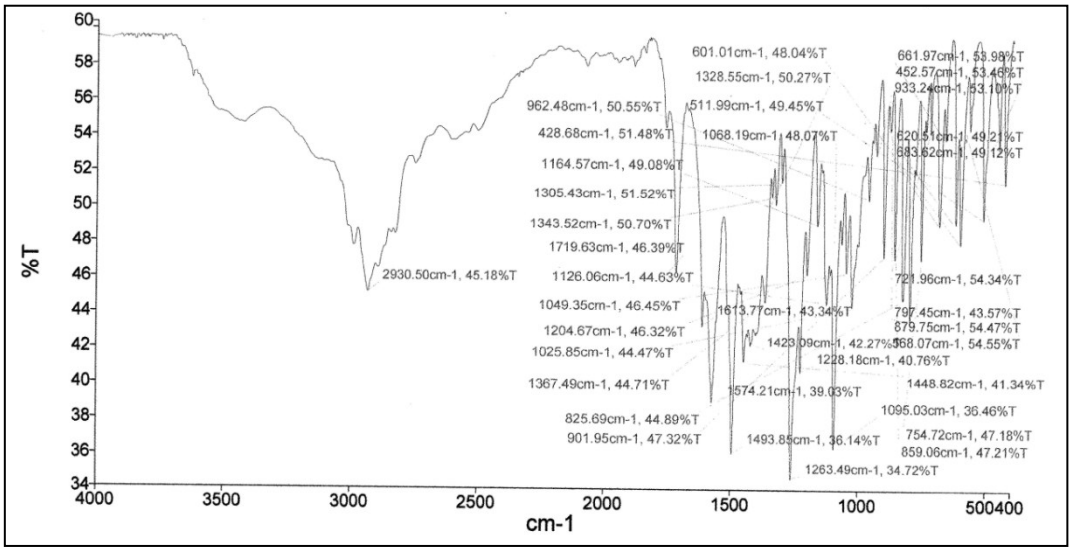

Figure **S3**. FTIR spectrum of complex **3**.

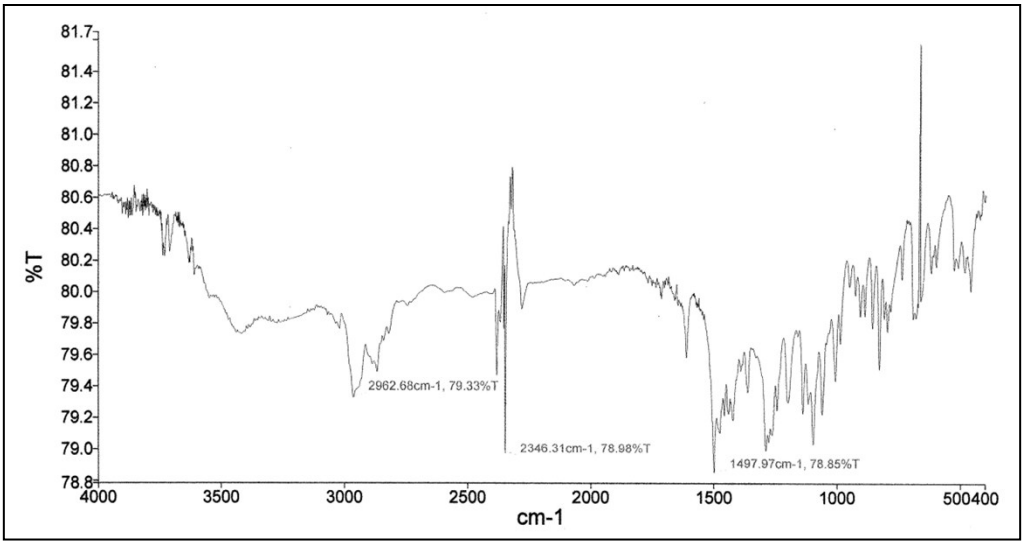

Figure **S4**. FTIR spectrum of complex **4**.

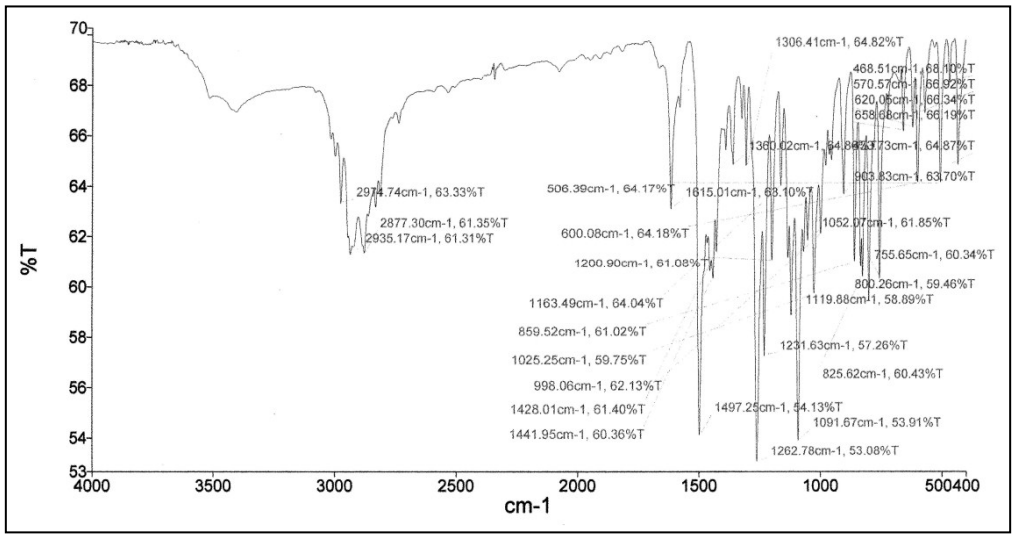

Figure **S5**. FTIR spectrum of complex **5**.

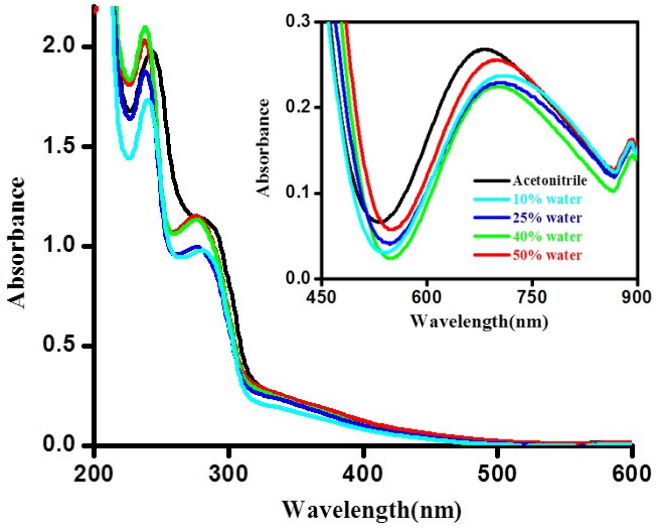

Figure S6. Electronic spectra of 10^{-4} (M) complex **1** showing charge-transfer band. Inset shows the d-d transition for 10^{-3} (M) solution in 5 different solvents.

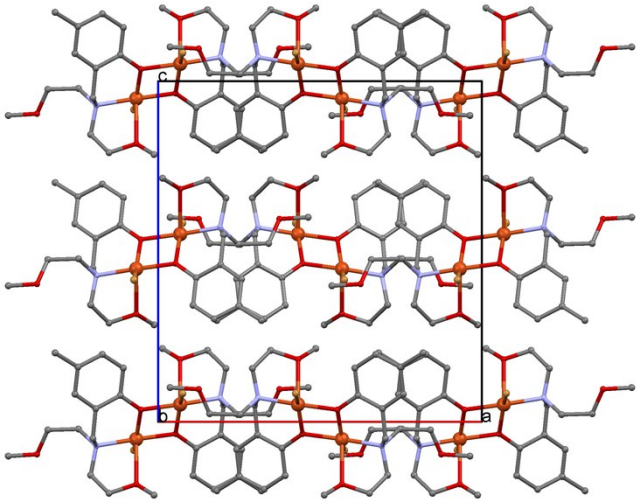

Figure S7. Packing plot of **4.**

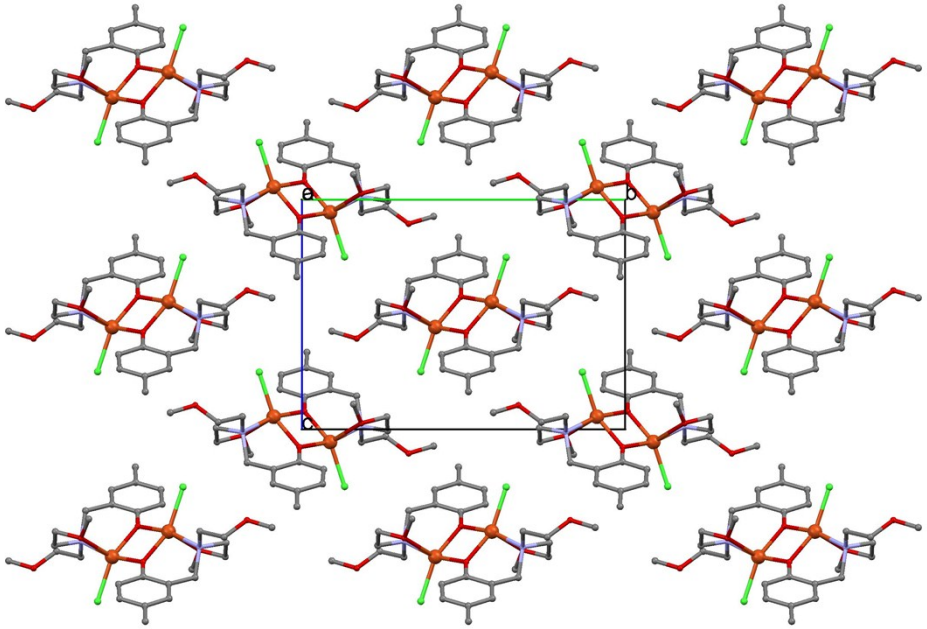

Figure S8. Packing plot of **5.**

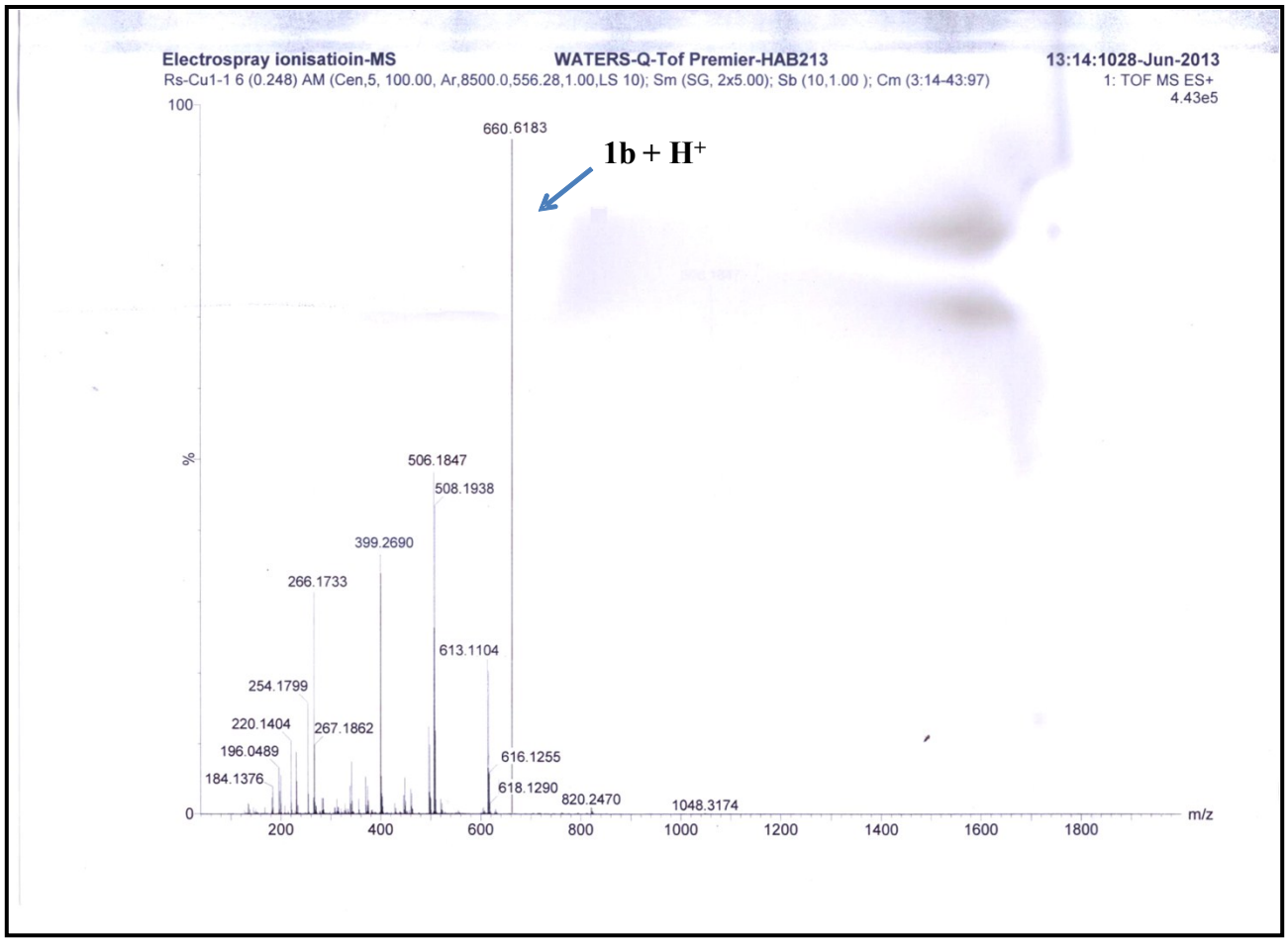

Figure S9. ESI-MS spectrum of complex **1** in acetonitrile (base peak at m/z 660.6183 amu).

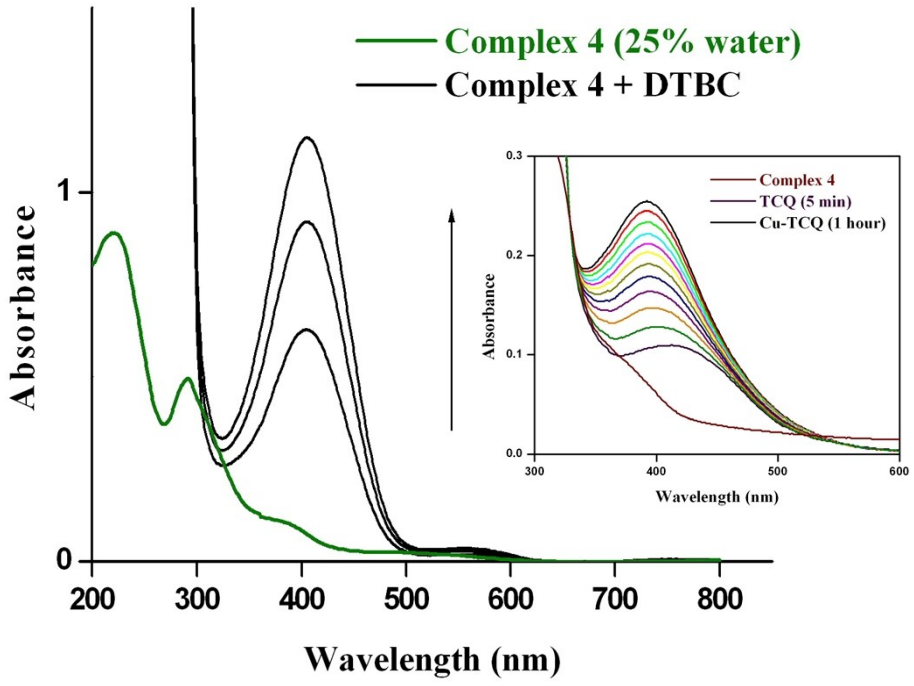

Figure S10. Wavelength scan of complex **4** with 3,5-DTBC. Inset shows the wavelength scan for complex **4** and TCC. Conditions : [3,5-DTBC / TCC] = 10^{-2} (M), [complex **4**] = 10^{-4} (M), Temp = 273 K.

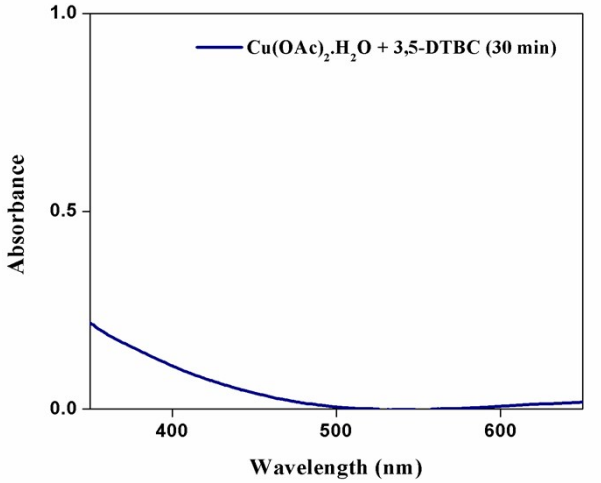

Figure S11. Control experiment with $Cu(OAc)_2.H_2O$. Conditions : [3,5-DTBC] = 10^{-2} (M), [Cu^{II}-salt] = 10^{-4} (M), Solvent = MeCN, Temp = 273 K. Control for free HL^1 and HL^2 have been reported in Ref 38.

Table S1. Selected bond lengths (Å) and angles (°) for **1**.

Complex **1**:			
Cu(1)-O(11)	1.936(5)	Cu(1)-O(12)	1.954(5)
Cu(1)-O(1)	1.975(5)	Cu(1)-N(1)	2.097(7)
Cu(1)-O(19)	2.282(7)	Cu(2)-O(11)	1.949(5)
Cu(2)-O(16)	1.945(6)	Cu(2)-O(1)	1.969(5)
Cu(2)-N(2)	2.119(6)	Cu(2)-O(15)	2.273(7)
Cu(3)-O(11)	1.908(5)	Cu(3)-O(14)	1.938(6)
Cu(3)-O(2)	1.991(6)	Cu(3)-N(3)	2.065(7)
Cu(3)-O(13)	2.258(6)	Cu(4)-O(11)	1.910(5)
Cu(4)-O(18)	1.952(5)	Cu(4)-O(2)	1.981(5)
Cu(4)-N(4)	2.055(7)	Cu(4)-O(17)	2.291(6)
O(11)-Cu(1)-O(12)	98.4(2)	O(11)-Cu(1)-O(1)	78.7(2)
O(12)-Cu(1)-O(1)	176.8(2)	O(11)-Cu(1)-N(1)	161.2(2)
O(12)-Cu(1)-N(1)	92.2(2)	O(1)-Cu(1)-N(1)	91.0(2)
O(11)-Cu(1)-O(19)	95.5(2)	O(12)-Cu(1)-O(19)	90.0(2)
O(1)-Cu(1)-O(19)	89.1(3)	N(1)-Cu(1)-O(19)	100.0(2)
O(11)-Cu(2)-O(16)	97.7(2)	O(11)-Cu(2)-O(1)	78.5(2)
O(16)-Cu(2)-O(1)	176.1(2)	O(11)-Cu(2)-N(2)	162.5(2)
O(16)-Cu(2)-N(2)	92.6(2)	O(1)-Cu(2)-N(2)	91.3(2)
O(11)-Cu(2)-O(15)	96.5(2)	O(16)-Cu(2)-O(15)	91.4(3)
O(1)-Cu(2)-O(15)	88.2(3)	N(2)-Cu(2)-O(15)	97.5(2)
O(11)-Cu(3)-O(14)	94.6(2)	O(11)-Cu(3)-O(2)	79.6(2)
O(14)-Cu(3)-O(2)	174.1(2)	O(11)-Cu(3)-N(3)	162.0(2)

O(14)-Cu(3)-N(3)	94.6(3)	O(2)-Cu(3)-N(3)	91.3(2)
O(11)-Cu(3)-O(13)	99.5(2)	O(14)-Cu(3)-O(13)	91.2(3)
O(2)-Cu(3)-O(13)	88.7(3)	N(3)-Cu(3)-O(13)	95.7(2)
O(11)-Cu(4)-O(18)	94.5(2)	O(11)-Cu(4)-O(2)	79.8(2)
O(18)-Cu(4)-O(2)	174.3(2)	O(11)-Cu(4)-N(4)	162.8(2)
O(18)-Cu(4)-N(4)	95.7(3)	O(2)-Cu(4)-N(4)	89.7(2)
O(11)-Cu(4)-O(17)	98.6(2)	O(18)-Cu(4)-O(17)	92.5(3)
O(2)-Cu(4)-O(17)	88.8(3)	N(4)-Cu(4)-O(17)	94.8(3)
C(21)-O(2)-Cu(4)	130.9(5)	C(21)-O(2)-Cu(3)	130.7(5)
Cu(4)-O(2)-Cu(3)	97.6(2)	C(13)-O(4)-C(12)	109.8(9)
C(17)-O(5)-C(16)	111.8(9)	C(19)-O(6)-C(20)	111.3(9)
C(30)-O(7)-C(29)	112.2(10)	C(32)-O(8)-C(33)	113.8(13)
C(39)-O(9)-C(40)	111.8(10)	C(36)-O(10)-C(37)	111.8(10)
Cu(3)-O(11)-Cu(4)	103.0(2)	Cu(3)-O(11)-Cu(1)	111.4(2)
Cu(4)-O(11)-Cu(1)	115.8(2)	Cu(3)-O(11)-Cu(2)	113.7(2)
Cu(4)-O(11)-Cu(2)	111.0(2)	Cu(1)-O(11)-Cu(2)	102.4(2)
C(1)-O(1)-Cu(2)	128.9(5)	C(1)-O(1)-Cu(1)	130.3(5)
Cu(2)-O(1)-Cu(1)	100.3(2)	C(9)-O(3)-C(10)	111.0(10)

Table S2. Selected bond lengths (Å) and angles (°) for compound **2** - **5**.

Compound **2**			
Cu(1)-N(1')	1.982(5)	Cu(1)-O(3)	2.155(6)
Cu(1)-O(1)	1.922(5)	Cu(1)-O(4)	2.046(6)
Cu(1)-O(2)	1.887(5)		
N(1)-Cu(1)-O(2)	174.3(2)	O(1)-Cu(1)-O(4)	144.0(2)
Cu(1)-O(1)-Cu(1')	98.7(3)	Cu(1)-O(2)-Cu(1')	101.3(4)
Compound **3**			
Cu(1)-N(1')	2.0666(14)	Cu(1)-O(3')	2.3480(13)
Cu(1)-O(1)	1.9747(11)	Cu(1)-O(4)	1.9272(13)
Cu(1)-O(1')	1.9429(11)		
N(1')-Cu(1)-O(1)	167.99(5)	O(1')-Cu(1)-O(4)	165.40(6)
Cu(1)-O(1)-Cu(1')	102.57(5)	O(1)-Cu(1)-O(1')	77.43(5)
Compound **4**			
Cu(1)-N(1')	2.032(3)	Cu(1)-O(3')	2.407(3)
Cu(1)-O(1)	1.946(2)	Cu(1)-Br(1)	2.3923(6)
Cu(1)-O(1')	1.978(2)		
N(1')-Cu(1)-O(1)	163.69(12)	O(1')-Cu(1)-Br(1)	145.81(8)
Cu(1)-O(1)-Cu(1')	103.88(11)	O(1)-Cu(1)-O(1')	76.12(11)
Compound **5**			
Cu(1)-N(1)	2.049(3)	Cu(1)-O(3)	2.331(3)
Cu(1)-O(1)	1.963(3)	Cu(1)-Cl(1)	2.2386(11)
Cu(1)-O(1')	1.961(3)		
N(1)-Cu(1)-O(1')	165.86(12)	O(1)-Cu(1)-Cl(1)	153.91(9)
Cu(1)-O(1)-Cu(1')	103.29(12)	O(1)-Cu(1)-O(1')	76.71(12)

Symmetry code for **2**: (') -x,-y,-z+2; for **3**: (') x,y,-z+1;
for **4**: (') -x,-y,1-z; for **5**: (') 2-x,2-y,-z.

Table S3. Selected experimental (X-ray diffraction) and calculated (PBE/TZVP in the gas phase, B3LYP/DGDZVP in MeCN solution) Cu-Cu, Cu-O and Cu-N interatomic distances in high-spin complexes **1, 3, 5**.

Atoms[a]	Experiment	PBE/TZ2P	B3LYP/DGDZVP
Complex **1**			
Cu1-Cu2	3.027	3.077	3.065
Cu1-Cu3	3.176	3.248	3.311
Cu1-Cu4	3.257	3.298	3.284
Cu1-O11	1.933	1.972	1.980
Cu2-O11	1.948	1.978	1.979
Cu3-O11	1.907	1.945	1.955
Cu4-O11	1.912	1.967	1.967
Cu1-O1	1.974	2.029	2.014
Cu2-O1	1.968	2.040	2.023
Cu3-O2	1.989	2.081	2.055
Cu4-O2	1.982	2.042	2.031

Cu1-O12	1.954	1.995	1.989
Cu4-O18	1.946	2.004	2.004
Cu1-N1	2.102	2.138	2.162
Cu2-N2	2.121	2.179	2.195
Cu3-N3	2.063	2.118	2.140
Cu4-N4	2.057	2.131	2.139
Complex **3**			
Cu1-Cu1'	3.057	3.083	3.120
Cu1-O1'	1.969	1.982	1.994
Cu1-O4	1.941	1.972	1.972
Cu1'-N1	2.067	2.128	2.114
Complex **5**			
Cu1-Cu1'	3.089	3.143	3.127
Cu1-O1'	1.963	2.015	2.042
Cu1-N1	2.049	2.110	2.103
Cu1-Cl1	2.238	2.236	2.315

[a] Atom notations correspond to those in Figures 1, 5, 8.