Unprecedented tetranuclear complexes "weighing balance shaped" topology: Single crystal structures, unusual EPR spectra, magnetic properties and antioxidant activity

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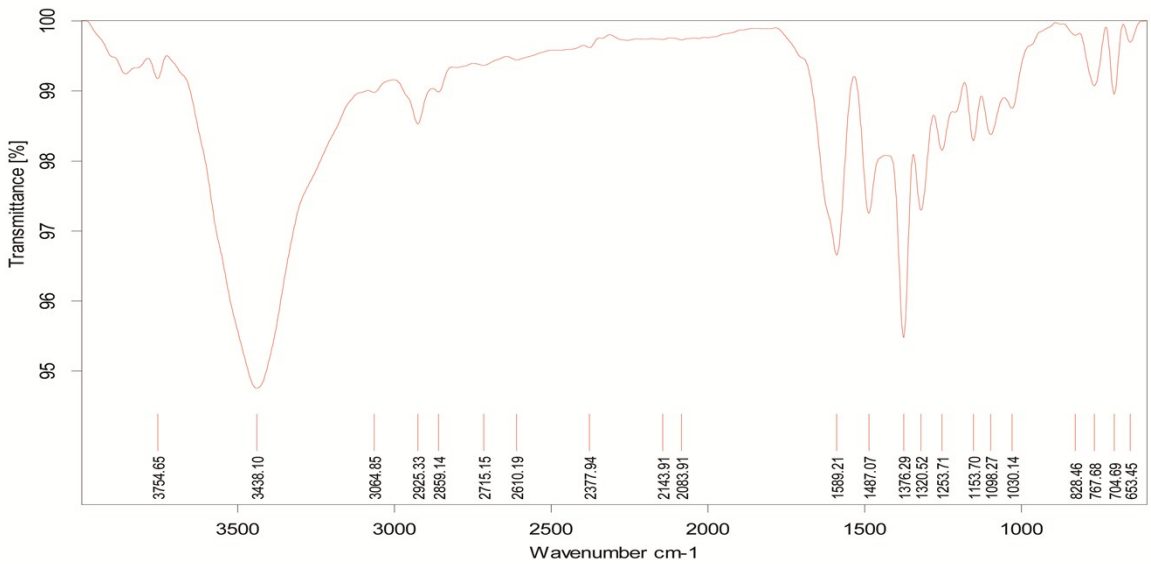

Fig. S1 IR spectra of complex **1.**

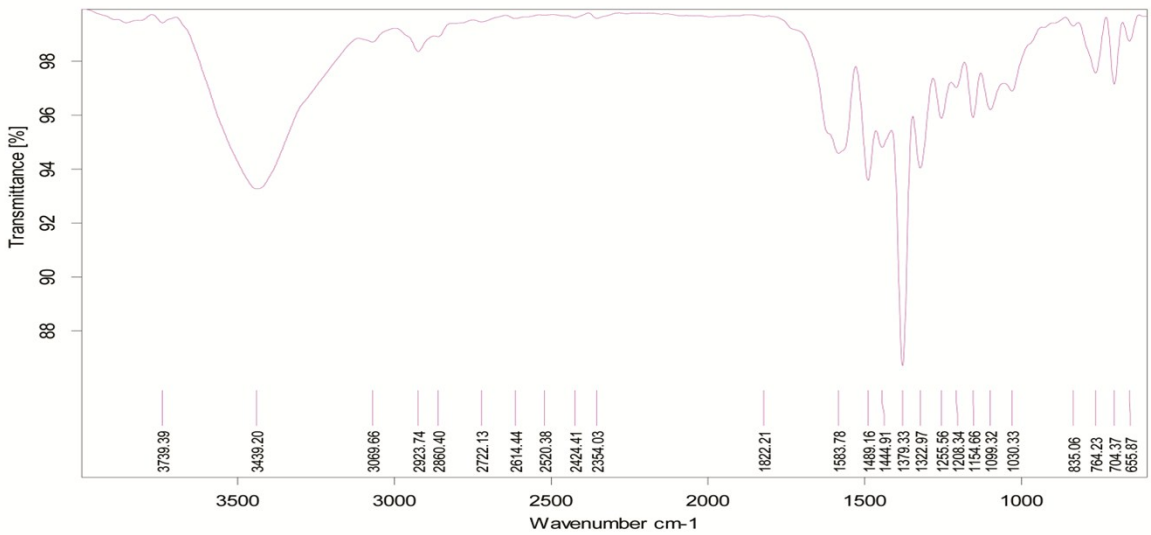

Fig. S2 IR spectra of complex **2.**

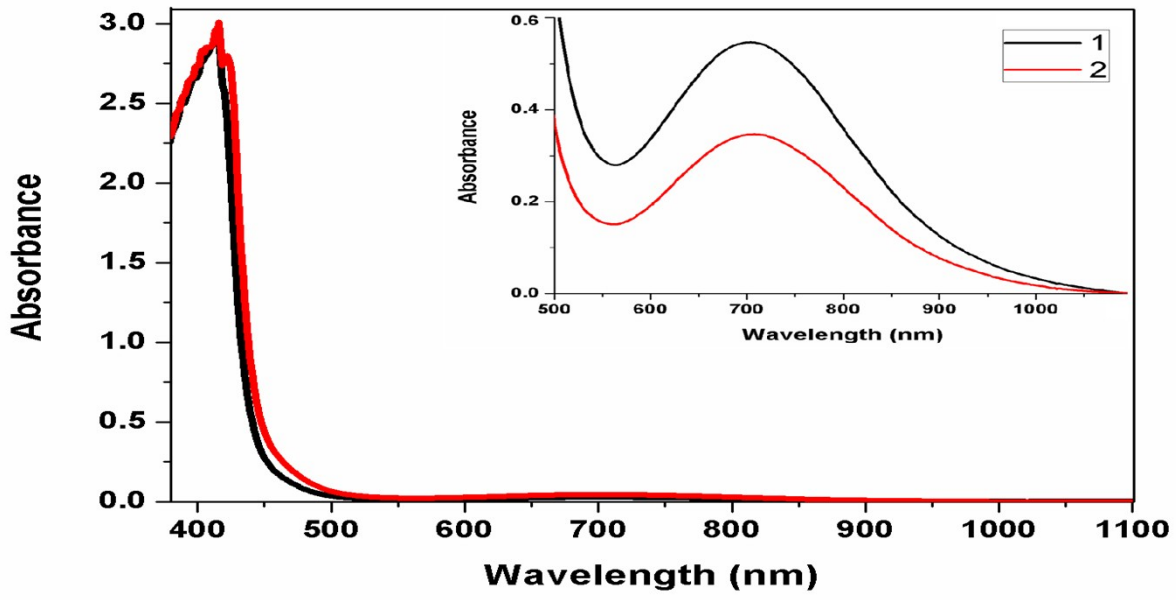

Fig. S3 UV-visible spectra of complexes **1** and **2** in DMSO (6.0×10^{-3} M). Inset: UV-visible spectra of complexes **1** and **2** in DMSO (3.0×10^{-3} M).

Table S1. Selected bond lengths [Å] and angles [°] for complex **1**.

Parameters	XRD data	Theoretical data*	Parameters	XRD data	Theoretical data*
1					
Bond length					
Cu(1)-O(1)	1.9153(19)	2.178	Cu(1)-N(2A)	1.921(2)	2.189
Cu(1)-O(1A)	1.968(2)	2.168	Cu(1)-N(1A)	1.983(2)	2.178
Cu(1)-O(1B)	2.484(2)	2.586	Cu(2)-O(2)	1.915(2)	2.125
Cu(2)-N(2B)	1.915(2)	2.185	Cu(2)-O(1B)	2.0074(19)	2.108
Cu(2)-N(1B)	2.010(2)	2.105	Cu(2)-O(1W)	2.304	2.308
Cu(3)-N(2C)	1.921(3)	2.108	Cu(3)-O(3)	1.929(2)	2.145
Cu(3)-O(1C)	1.978(2)	2.148	Cu(3)-N(1C)	1.995(3)	2.156
Cu(3)-O(2W)	2.368(3)	2.154	Cu(3)-O(1D)	2.790(2)	2.865
Cu(4)-O(4)	1.910(2)	2.186	Cu(4)-N(2D)	1.919(2)	2.156
Cu(4)-O(1D)	2.000(2)	2.187	Cu(4)-N(1D)	2.007(3)	2.168
Cu(4)-O(3W)	2.290(3)	2.369			
Bond angle					
O(1)-Cu(1)-N(2A)	171.40(9)	172.46	O(1)-Cu(1)-O(1A)	102.76(9)	103.78
N(2A)-Cu(1)-(1A)	80.17(9)	81.20	O(1)-Cu(1)-N(1A)	95.83(9)	96.49
O(1)-Cu(1)-N(1A)	95.83(9)	96.85	N(2A)-Cu(1)-N(1A)	80.97(10)	81.98
O(1A)-Cu(1)-(1A)	161.13(9)	162.85	O(1)-Cu(1)-O(1B)	90.67(8)	91.78
N(2A)-Cu(1)-(1B)	97.36(8)	98.38	O(1A)-Cu(1)-O(1B)	91.59(7)	92.49
N(1A)-Cu(1)-(1B)	91.42(8)	92.50			
O(2)-Cu(2)-N(2B)	172.20(10)	173.42	O(2)-Cu(2)-O(1B)	101.60(8)	102.62
N(2B)-Cu(2)-O(1B)	79.18(9)	80.16	O(2)-Cu(2)-N(1B)	97.31(10)	98.33
N(2B)-Cu(2)-N(1B)	80.62(10)	81.64	O(1B)-Cu(2)-N(1B)	158.16(9)	159.15
O(2)-Cu(2)-O(1W)	87.79(11)	88.78	N(2B)-Cu(2)-O(1W)	99.91(11)	100.89
O(1B)-Cu(2)-(1W)	94.75(10)	95.65	N(1B)-Cu(2)-O(1W)	96.81(11)	97.48
O(2)-Cu(2)-O(1A)	87.74(8)	88.75	N(2B)-Cu(2)-O(1A)	84.71(8)	85.88
O(1B)-Cu(2)-(1A)	81.13(7)	82.11	N(1B)-Cu(2)-O(1A)	88.85(8)	89.78
O(1W)-Cu(2)-(1A)	173.20(9)	174.25	N(2C)-Cu(3)-O(3)	171.81(11)	172.89
N(2C)-Cu(3)-O(1C)	80.19(10)	81.20	O(3)-Cu(3)-O(1C)	100.44(9)	101.45
N(2C)-Cu(3)-N(1C)	80.56(11)	81.60	O(3)-Cu(3)-N(1C)	98.17(10)	99.65
O(1C)-Cu(3)-N(1C)	160.50(10)	161.56	N(2C)-Cu(3)-O(2W)	95.88(12)	96.78
O(3)-Cu(3)-O(2W)	92.29(11)	93.38	O(1C)-Cu(3)-O(2W)	89.18(11)	90.42
N(1C)-Cu(3)-(2W)	95.87(12)	96.78	N(2C)-Cu(3)-O(1D)	83.93(9)	84.92
O(3)-Cu(3)-O(1D)	87.92(9)	88.92	O(1C)-Cu(3)-O(1D)	88.60(8)	89.66
N(1C)-Cu(3)-(1D)	86.29(9)	87.27	O(2W)-Cu(3)-O(1D)	177.77(10)	178.78
O(4)-Cu(4)-N(2D)	177.50(11)	178.55	O(4)-Cu(4)-O(1D)	101.23(9)	102.45
N(2D)-Cu(4)-(1D)	79.90(10)	80.87	O(4)-Cu(4)-N(1D)	98.18(10)	99.20
N(2D)-Cu(4)-(1D)	80.44(10)	81.45	O(1D)-Cu(4)-N(1D)	159.41(9)	160.40
O(4)-Cu(4)-O(3W)	91.25(10)	92.30	N(2D)-Cu(4)-O(3W)	90.98(11)	91.98
O(1D)-Cu(4)-(3W)	89.77(11)	90.78	N(1D)-Cu(4)-O(3W)	96.66(11)	97.67
O(4)-Cu(4)-O(1C)	85.99(8)	86.98	N(2D)-Cu(4)-O(1C)	91.82(9)	92.88
O(1D)-Cu(4)-O(1C)	88.62(8)	89.62	N(1D)-Cu(4)-O(1C)	85.92(9)	86.94
O(3W)-Cu(4)-(1C)	176.47(9)	177.50			

*Optimized bond lengths and angles obtained from DFT calculations to compare XRD data.

Table S2. Selected bond lengths [Å] and angles [°] for complex **1**.

Parameters	XRD data	Theoretical data*	Parameters	XRD data	Theoretical data*
2					
Bond length					
Cu(1)-O(1)	1.915(8)	2.185	Cu(1)-N(2A)	1.924(9)	2.1896
Cu(1)-O(1A)	2.007(8)	2.178	Cu(1)-N(1A)	2.007(10)	2.112
Cu(1)-O(1W)	2.278(10)	2.365	Cu(1)-O(1B)	2.792(7)	2.845
Cu(2)-O(2)	1.877(6)	1.976	Cu(2)-N(2B)	1.916(8)	2.471
Cu(2)-N(1B)	1.983(8)	2.128	Cu(2)-O(1B)	1.996(7)	2.145
Cu(3)-O(3)	1.899(7)	2.134	Cu(3)-N(2C)	1.921(8)	2.165
Cu(3)-O(1C)	1.973(7)	2.165	Cu(3)-N(1C)	1.981(8)	2.145
Cu(3)-O(1D)	2.483(7)	2.543	Cu(4)-O(4)	1.872(8)	1.986
Cu(4)-N(1H)	1.948(12)	2.165	Cu(4)-O(1D)	1.967(7)	2.145
Cu(4)-N(1D)	1.982(10)	2.187			
Bond angle					
O(1)-Cu(1)-N(2A)	171.2(4)	172.3	O(1)-Cu(1)-O(1A)	105.4(3)	106.5
N(2A)-Cu(1)-O(1A)	79.4(4)	80.6	O(1)-Cu(1)-N(1A)	93.5(4)	94.6
N(2A)-Cu(1)-N(1A)	80.8(4)	81.9	O(1A)-Cu(1)-N(1A)	159.5(4)	160.6
O(1)-Cu(1)-O(1W)	89.8(4)	90.9	N(2A)-Cu(1)-O(1W)	97.8(4)	98.9
O(1A)-Cu(1)-O(1W)	88.2(4)	89.4	N(1A)-Cu(1)-O(1W)	100.0(4)	101.08
O(1)-Cu(1)-O(1B)	85.2(3)	86.4	N(2A)-Cu(1)-O(1B)	89.4(3)	90.78
O(1A)-Cu(1)-O(1B)	71.9(3)	72.8	N(1A)-Cu(1)-O(1B)	102.4(3)	103.6
O(1W)-Cu(1)-O(1B)	157.3(3)	158.5	O(2)-Cu(2)-N(2B)	175.0(3)	176.1
O(2)-Cu(2)-N(1B)	95.4(3)	96.5	N(2B)-Cu(2)-N(1B)	79.6(3)	80.7
O(2)-Cu(2)-O(1B)	103.8(3)	104.9	N(2B)-Cu(2)-O(1B)	81.0(3)	82.4
N(1B)-Cu(2)-O(1B)	157.4(3)	158.7	O(2)-Cu(2)-O(1A)	88.8(3)	89.6
N(2B)-Cu(2)-O(1A)	93.5(3)	94.5	N(1B)-Cu(2)-O(1A)	112.1(3)	113.2
O(1B)-Cu(2)-O(1A)	80.5(3)	81.6	N(2C)-Cu(3)-O(1C)	80.9(3)	82.0
O(3)-Cu(3)-N(2C)	177.1(3)	178.2	O(3)-Cu(3)-O(1C)	100.2(3)	101.3
O(3)-Cu(3)-N(1C)	97.5(3)	98.6	N(2C)-Cu(3)-N(1C)	81.2(3)	82.3
O(1C)-Cu(3)-N(1C)	161.9(3)	162.8	O(3)-Cu(3)-O(1D)	90.2(3)	91.3
N(2C)-Cu(3)-O(1D)	92.7(3)	93.4	O(1C)-Cu(3)-O(1D)	83.3(3)	84.4
N(1C)-Cu(3)-O(1D)	100.6(3)	101.7	N(2C)-Cu(3)-O(1C)	80.9(3)	81.8
O(4)-Cu(4)-N(2D)	173.2(3)	174.3	O(4)-Cu(4)-N(1H)	90.1(5)	91.8
N(2D)-Cu(4)-N(1H)	86.3(5)	87.4	O(4)-Cu(4)-O(1D)	103.3(3)	104.3
N(2D)-Cu(4)-O(1D)	79.9(3)	80.9	N(1H)-Cu(4)-O(1D)	165.6(5)	166.7
O(4)-Cu(4)-N(1D)	98.9(4)	99.9	N(2D)-Cu(4)-N(1D)	77.7(4)	78.8
O(1D)-Cu(4)-N(1D)	157.5(4)	158.6	O(4)-Cu(4)-O(1C)	86.7(3)	87.8
N(2D)-Cu(4)-O(1C)	99.7(3)	100.8	N(1H)-Cu(4)-O(1C)	103.2(5)	104.4
O(1D)-Cu(4)-O(1C)	83.1(3)	84.1	N(1D)-Cu(4)-O(1C)	101.1(4)	102.2

*Optimized bond lengths and angles obtained from DFT calculations to compare XRD data.

Table S3. Shape geometries for Cu ions in **1** and **2**

Coordination 5	**JTBPY***	**SPY***	**TBPY***	**VOC***	**PP***
Cu1 **1**	8.629	1.567	5.777	2.237	30.234
Cu2 **1**	9.315	1.575	6.483	1.732	27.645
Cu2 **2**	9.983	2.833	6.295	3.444	23.936
Cu3 **2**	9.844	1.809	6.906	2.170	27.663
Cu4 **2**	9.978	2.588	7.176	3.202	25.143
Coordination 6	**JPPY****	**TPR****	**OC****	**PPY****	**HP****
Cu3 **1**	28.466	15.623	2.629	25.575	32.742
Cu4 **1**	28.339	14.153	2.605	25.445	33.396
Cu1 **1**	27.624	10.948	4.099	23.642	32.437

* JTBPY = Johnson trigonal bipyramid; SPY = Spherical square pyramid; TBPY = Trigonal bipyramid; VOC = Vacant octahedron; PP = Pentagon
** JPPY = Johnson pentagonal pyramid; TPR = Trigonal prism; OC = Octahedron; PPY = Pentagonal pyramid; HP = Hexagon