Some new nano-sized mononuclear Cu(II) Schiff base complexes: design, characterization, molecular modeling and catalytic potentials in benzyl alcohol oxidation

Laila H. Abdel Rahman[a]*, Ahmed M. Abu-Dief[a], Mohamed Shaker S. Adam and Samar Kamel Hamadan[a]

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Table S1: Crystal data and structure refinements details for npap.

Formula	$C_{32}H_{24}N_4O_2$
Formula weight	496.57
Crystal system	Monoclinic
Space group	P1 $2_1/c_1$
Crystal colour/ shape	Yellow/ needle
Temperature	293K
Crystal dimensions (mm)	0.15× 0.20× 0.34
Unit cell dimensions	a = 5.83 (9) Å, b = 17.47 (3) Å, c = 24.29 (4) Å $\alpha = 90.00^o$, $\beta = 91.92\ (6)^o$, $\gamma = 90.00^o$
Cell volume $(Å)^3$	2473.10 (7) $Å^3$
Formula units/ unit cell	4
D cal (mg m^{-3})	1.33
μ cal (mm^{-1})	0.085
Reflections measured	4173
$\theta_{max}(^o)$	16.88
Range of h, k, l	-4< h >4, -13< k >13, -11< l >19
Data collection method	φ and ω scans
S	1.06
R-factor	0.048
weighted R-factor	0.127
Δρmin	-0.24 e $Å^{-3}$
Δρmax	0.24 e $Å^{-3}$
Refinement on	F^2
Weight function	$1/[\sigma^2(F_{obs}^2) + (0.100 \times P)^2 + 0.000 \times P + 0.000 + 0.000 \times \sin\theta]$, $P = 0.333 \times \max(F_{obs}^2,0) + 0.667 \times Fcalc^2$
Parameters refined	181

Table S2: Selected bond lengths (X, Y, Z) and bond angles (^{o}) of npap.

Label	X(Å)	Y(Å)	Z(Å)
Bond length (Å)			
O1	0.6674(7)	0.4074(2)	0.28612(17)
C2	0.7862(11)	0.4656(3)	0.2779(2)
C3	0.7239(8)	0.5205(3)	0.2366(2)
C4	0.5328(8)	0.5068(3)	0.2023(2)
N5	0.4060(7)	0.4465(3)	0.20744(19)
C6	0.2184(10)	0.4321(3)	0.1735(3)
C7	0.0970(9)	0.3660(4)	0.1843(2)
C8	-0.0920(11)	0.3462(3)	0.1533(3)
C9	-0.1623(9)	0.3921(4)	0.1111(3)
C10	-0.0384(9)	0.4576(4)	0.1015(2)
N11	0.1531(8)	0.4789(3)	0.1315(2)
C12	0.8631(9)	0.5874(3)	0.2308(2)
Bond angles (^{o})			
C2- O1- H11	165.153°	C30- C31- C32	119.100(5)°
O1 - C2- C19	121.200(6)°	C32- C31- C34	118.300(5)°
C4- C3- C12	121.800(5)°	C32 - C33- C1	119.800(5)°
C3- C4- H41	119.900(13)°	C1- C33- H331	119.600(13)°
C4- N5- C6	122.500(6)°	C31 - C34- H341	119.300(13)°
N5- C6- N11	122.800(5)°	C34 - C35- C36	118.900(6)°
C6- C7- C8	121.300(7)°	C36- C35- H351	120.200(13)°
C8- C7- H71	119.900(13)°	C35- C36- H361	119.600(13)°
C7- C8- H81	120.500(13)°	C30- C37- C36	121.700(5)°
C8- C9- C10	118.200(6)°	C36 -C37- H371	118.900(13)°
C10- C9- H91	121.300(14)°	O20 - C1- C33	119.700(5)°
C9- C10 - H101	118.300(13)°	O1- C2- C3	122.000(6)°

Table S4: Characteristic IR bands of Schiff base ligands and their metal complexes (in KBr disc 400 - 4000 cm^{-1})

Compounds	$\upsilon(OH)/H_2O$	$\upsilon(NH)$	$\upsilon(CH)_{ar}$	$\upsilon(C=O)$	$\upsilon(C=N)$	$\upsilon(C=N)py$	$\upsilon\ (C-O)_{ph}$	$\upsilon(M-N)$	$\upsilon(M-O)$
npap	3426 (sh)	-	3000 (w)	-	1630 (vs)	1585 (s)	1315 (m)	-	-
Cunpap	3455 (b)	-	3050 (w)	-	1614 (vs)	1563 (s)	1285 (m)	615 (w)	482 (w)
bsisnph	3464 (b)	3196 (w)	3068 (w)	1736 (s)	1627 (vs) 1607 (s)	-	1308 (m)	-	-
Cubsisnph	-	3199 (w)	3080 (w)	1695 (s)	1603 (vs) 1573 (s)	-	1267 (m)	535 (w)	442 (w)
npisnph	3437 (b)	3199 (m)	3021(w) 3070 (w)	1740 (s)	1634 (vs) 1599 (s)	-	1212 (m)	-	-
Cunpisnph	3451(w)	3199 (m)	3039 (w) 3050 (w)	1689 (s)	1600 (vs) 1573 (s)	-	1172 (m)	641 (w)	581 (w)

sh = shrap, vs = very strong, s = strong, m = medium, b = broad, w = weak, ar = aromatic, py= pyridine, ph = phenoli

Table S6: Energetic of the studied ligand and its anions using B3LYP/ LANL2DZ

	bsisnph	$bsisnph^{-1}$	Cubsisnph	npisnph	$npisnph^{-1}$	Cunpisnph
E_T, au	-	-	1841.33	-	-	- 1982.41
$E_{HOMO,au}$	- 0.2299	- 0.1337	- 0.2124	- 0.2892	- 0.1290	0.2084
$E_{LUMO,au}$	0.1049	0.1362	- 0.1352	0.0347	0.1358	- 0.1275
Eg, ev	9.100	7.3000	2.0900	8.800	7.200	2.2000
μ, D	7.250	8.9100	7.6500	7.8100	6.48	8.1700
Net charge						
N27	- 0.468	- 0.8720	-	- 0.7270	- 0.8170	-
O35	- 0.605	- 0.7430	-	- 0.7490	- 0.7300	-
N7	- 0.553	- 0.7600	-	- 0.7420	- 1.0320	-
O13	- 0.541	- 0.5970	-	- 0.6050	- 0.6050	-

Table S7: The optimized bond length (Å), bond angles (^{o}) and dihedral angles of the metals in coordination sphere using B3LYP/ LANL2DZ.

Selected bond length (Å)			**Selected bond angle (^{o})**		
	Cubsisnph	**Cunpisnph**		**Cubsisnph**	**Cunpisnph**
Cu-N11	2.397	2.750	Cu-N11-C12	117.5	132.8
N11-C29	1.400	1.412	N11-C12-C13	115.2	119.2
C29-C28	1.439	1.432	C12-C13-O14	125.6	128.2
Cu-O14	2.559	3.835	Cu -O14-C13	108.2	95.1
O14-C13	1.247	1.240	Cu -O10-C7	120.9	129.2
C13-C12	1.534	1.543	O10-C9-C4	123.7	123.3
C12-N11	1.292	1.481	C9-C4-C3	121.4	122.3
Cu-O23	2.048	1.956	Cu -N2-C3	120.7	124.3
Cu-N2	2.190	2.010	Cu -N2-C28	114.0	115.2
N2-C3	1.317	1.338	Cu -N11-C29	45.90	96.3
C3-C4	1.437	1.417	N2-C28-C29	114.6	117.8
C4-C9	1.454	1.443	Cu -O23-N24	128.1	127.6
C9-O10	1.325	1.310	Cu -O27-H46	106.6	105.5
M-O10	1.932	1.957	Cu -O10-C9-C4	42.5	11.3
M-O27	1.980	1.991	Cu - N2-C28-C30	37.9	47.2
			Cu -O14-C13-N14	- 104.8	- 157.7
			Cu -O23-N24-O25	- 177.8	- 163.4

Table S8: Net charge on chelating centers of the ligands and their complexes using B3LYP/ LANL2DZ

	bsisnph	npisnph	Cubsisnph	Cunpisnph
Cu	-	-	0.5680	0.6772
N2	- 0.8720	- 0.8170	- 0.2135	- 0.3284
N11	- 0.7600	- 0.7940	- 0.0599	0.0071
O10	- 0.7430	0.7300	- 0.4202	- 0.4329
O14	- 0.5970	0.6050	- 0.2336	- 0.2094
O23	-	-	- 0.4452	- 0.4252
O25	-	-	-	-
O26	-	-	-	-
O27	-	-	- 0.7584	- 0.7859
Br	0.0900	-	- 0.0501	-
Cu $\rightarrow$ L(bsisnph or npisnph)	-	-	1.4438	1.3228