Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. *82* (6) S268–S271 (2017) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Zinc, copper and nickel complexes of a macrocycle synthesized from pyridinedicarboxylic acid: A spectroscopic, thermal and theoretical study

ESMAIEL SOLEIMANI, SAYED ALI NAGHI TAHERI* and MOHSEN SARGOLZAEI

Faculty of Chemistry, Shahrood University of Technology, Shahrood, Iran

J. Serb. Chem. Soc. *82* (6) (2017) 665–680

Macrocycle ***1***. IR, $\tilde{\nu}$ /cm^{-1}: 3245 (N–H), 3025 (C–H), 2880 (C–H), 1720, 1685 (C=O), 1595 (C=N), 1455 (C=C), 1275 (C–O), 1145 (C–N); ^{1}H–NMR (DMSO-d_6, δ / ppm): 8.18 (*t*, 1H, CH_{py}), 7.86 (*d*, 2H, $2CH_{py}$), 4.82 (*b*, 2H, 2NH), 3.82 (*t*, 4H, $2CH_2N$), 3.41 (*s*, 4H, NCH_2CH_2N), 2.62 (*t*, 4H, $2CH_2O$); ^{13}C–NMR (DMSO-d_6, δ / ppm): 48.72 (2C, NCH_2CH_2N), 63.83 (2C, $2CH_2N$), 75.66 (2C, $2CH_2O$), 124.68 (1C, CH_{py}), 136.26 (2C, $2CH_{py}$), 155.12 (2C, $2C_{py}$), 176.38 (C=O); UV–Vis (DMSO, 25 °C), λ_{max} / nm (ε): 258 (9685).

Ni(II) complex ***2***. IR, $\tilde{\nu}$ /cm^{-1}: 3225 (N–H), 3030 (C–H), 2885 (C–H), 1725, 1680 (C=O), 1582 (C=N), 1453 (C=C), 1258 (C–O), 1142 (C–N), 482 (Ni–O), 457 (Ni–N); UV–Vis (DMSO, 25 °C), λ_{max} / nm (ε): 255 (8865), 470 (287), 778 (284).

Cu(II) complex ***3***. IR, $\tilde{\nu}$ /cm^{-1}: 3225 (N–H), 3022 (C–H), 2888 (C–H), 1715, 1678 (C=O), 1580 (C=N), 1450 (C=C), 1260 (C–O), 1155 (C–N), 485 (Cu–O), 458 (Cu–N); UV–Vis (DMSO, 25 °C), λ_{max} / nm (ε): 262 (8560), 522 (470), 655 (253).

Zn(II) complex ***4***. IR, $\tilde{\nu}$ /cm^{-1}: 3220 (N–H), 3018 (C–H), 2875 (C–H), 1720, 1682 (C=O), 1583 (C=N), 1452 (C=C), 1262 (C–O), 1147 (C–N), 487 (Zn–O), 451 (Zn–N); ^{1}H-NMR (DMSO-d_6, δ / ppm): 8.16 (*t*, 1H, CH_{py}), 7.83 (*d*, 2H, $2CH_{py}$), 4.76 (*b*, 2H, 2NH), 3.78 (*t*, 4H, $2CH_2N$), 3.38 (*s*, 4H, NCH_2CH_2N), 2.68 (*t*, 4H, $2CH_2O$); ^{13}C-NMR (DMSO-d_6, δ / ppm): 45.25 (2C, NCH_2CH_2N), 58.76 (2C, $2CH_2N$), 71.24 (2C, $2CH_2O$), 123.36 (1C, CH_{py}), 137.61 (2C, $2CH_{py}$), 159.67 (2C, $2C_{py}$), 172.44 (C=O); UV–Vis (DMSO, 25 °C), λ_{max} / nm (ε): 258 (9685).

* Corresponding author. E-mail: sayedalinaghitaheri@yahoo.com

TABLE S-I. Selected optimized geometry parameters of **1** (L) and its complexes (bond length in Å and bong angle in degrees)

Bond	L	$[Ni(L)Cl_2]$	$[Cu(L)Cl_2]$	$[Zn(L)Cl_2]$
		Bond lengths		
N1–C2	1.350	1.365	1.357	1.354
N1–C6	1.350	1.365	1.357	1.354
C2–C8	1.505	1.508	1.503	1.501
C6–C7	1.505	1.508	1.503	1.501
C7–O9	1.246	1.243	1.241	1.240
C8–O10	1.246	1.243	1.241	1.240
C7–O11	1.362	1.404	1.384	1.378
C8–O12	1.362	1.404	1.384	1.378
C13–O11	1.404	1.425	1.462	1.451
C20–O12	1.404	1.425	1.462	1.451
C13–C14	1.529	1.532	1.534	1.530
C19–C20	1.529	1.532	1.534	1.530
C14–N15	1.468	1.485	1.482	1.488
C19–N16	1.468	1.485	1.482	1.488
C17–N15	1.471	1.488	1.486	1.490
C18–N16	1.471	1.488	1.486	1.490
C17–C18	1.550	1.546	1.544	1.545
N1–M	-	2.005	2.160	2.215
O11–M	-	2.176	2.424	2.321
O12–M	-	2.180	2.428	2.325
N15–M	-	2.349	2.340	2.351
N16–M	-	2.345	2.340	2.348
Cl39–M	-	2.534	2.512	2.521
Cl40–M	-	2.530	2.514	2.524
		Bond angles		
N1–M–O11	-	73.71	71.48	70.77
N1–M–O12	-	76.08	71.48	70.13
N15–M–O11	-	71.20	71.27	72.25
N16–M–O12	-	78.25	72.40	72.21
N15–M–N16	-	71.70	75.30	74.87
Cl39–M–Cl40	-	178.90	177.26	176.38

TABLE S-II. Energy of some bonding molecular orbital for the ligand and considered complexes. The unit of energy is a.u.

Atoms	L	$[Ni(L)Cl_2]$	$[Cu(L)Cl_2]$	$[Zn(L)Cl_2]$
N1–C2	–0.848	–0.880	–0.874	–0.882
C2–C8	–0.676	–0.702	–0.698	–0.707
C8–O12	–0.913	–0.944	–0.940	–0.941
O12–C20	–0.788	–0.824	–0.819	–0.821
C20–C19	–0.260	–0.649	–0.636	–0.640
C19–N16	–0.707	–0.720	–0.719	–0.720
N16–C18	–0.696	–0.717	–0.717	–0.717
C18–C17	–0.581	–0.611	–0.613	–0.615

TABLE S-II. Continued

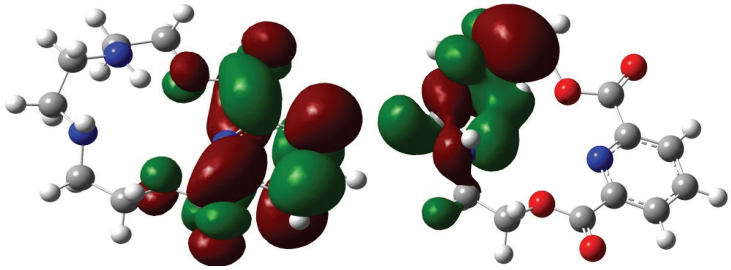
Atoms	L	$[Ni(L)Cl_2]$	$[Cu(L)Cl_2]$	$[Zn(L)Cl_2]$
C17–N15	–0.682	–0.697	–0.716	–0.717
N15–C14	–0.684	–0.706	–0.714	–0.717
C14–C13	–0.610	–0.611	–0.626	–0.634
C13–O11	–0.782	–0.800	–0.801	–0.812
O11–C7	–0.915	–0.942	–0.932	–0.939
C7–C6	–0.675	–0.700	–0.696	–0.705
C6–N1	–0.847	–0.889	–0.875	–0.881

TABLE S-III. Calculated energies (eV) of HOMO and LUMO, chemical potential (μ), electronegativity (χ) and global hardness (η) for macrocycle 1 (L) and its complexes

Parameter	L	$[Ni(L)Cl_2]$	$[Cu(L)Cl_2]$	$[Zn(L)Cl_2]$
E_{LUMO}	–0.241	–2.820	–3.225	–2.892
E_{HOMO}	–0.863	–6.232	–6.125	–5.558
Gap energy	0.622	3.412	2.900	2.666
EA	0.241	2.820	3.225	2.892
IE	0.863	6.232	6.125	5.558
μ	–0.552	–4.526	–4.675	–4.225
η	0.311	1.706	1.450	1.333
χ	0.552	4.526	4.675	4.225

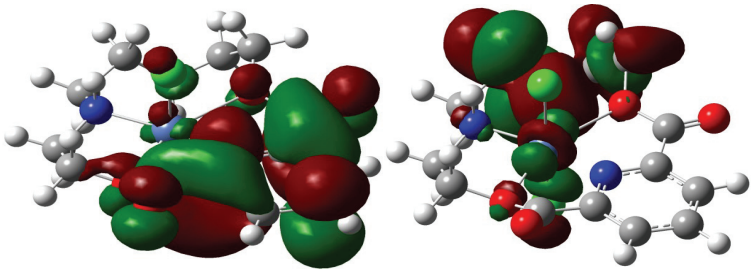
TABLE S-IV. Selected AIM atomic charges for macrocycle L (1) and its complexes

Atom	L (**1**)	$[Ni(L)Cl_2]$ (**2**)	$[Cu(L)Cl_2]$ (**3**)	$[Zn(L)Cl_2]$ (**4**)
N1	–0.796	–0.902	–0.875	–0.887
C2	–0.399	0.388	0.516	0.417
C3	–0.300	–0.400	–0.382	–0.320
C4	–0.270	–0.250	–0.210	–0.200
C5	–0.400	–0.630	–0.681	–0.626
C6	–0.380	0.404	0.381	0.324
C7	1.157	1.188	1.471	1.173
C8	1.126	1.173	1.459	1.186
O9	–0.907	–0.883	–0.891	–0.894
O10	–0.915	–0.893	–0.882	–0.891
O11	–0.816	–0.889	–0.928	–0.902
O12	–0.825	–0.894	–0.937	–0.894
C13	0.320	0.307	0.352	0.309
C14	0.312	0.277	0.263	0.261
N15	–0.718	–0.932	–0.948	–0.916
N16	–0.712	–0.938	–0.947	–0.913
C17	0.221	0.302	0.314	0.247
C18	0.220	0.291	0.317	0.242
C19	0.317	0.277	0.262	0.266
C20	0.320	0.303	0.351	0.308
Cl39	–	–0.672	–0.647	–0.602
Cl40	–	–0.679	–0.650	–0.606
M	–	1.027	1.420	1.405

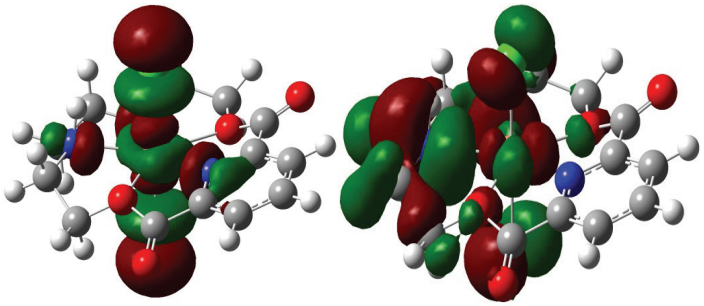


LUMO 1 HOMO 1

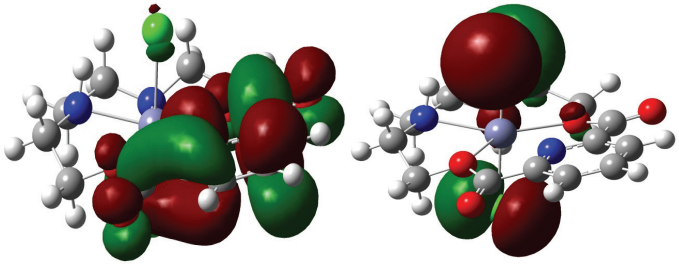
Fig. S-1. The graphical presentation of LUMO and HOMO orbitals of **1**.



LUMO 2 HOMO 2



LUMO 3 HOMO 3



LUMO 4 HOMO 4

Fig. S-2. The graphical presentation of LUMO and HOMO orbitals for complexes **2**–**4**.