**Supplementary Material**

Spectral and computational chemistry studies for the optimization of geometry of dioxomolybdenum(VI) complexes of some unsymmetrical Schiff bases as antimicrobial agent

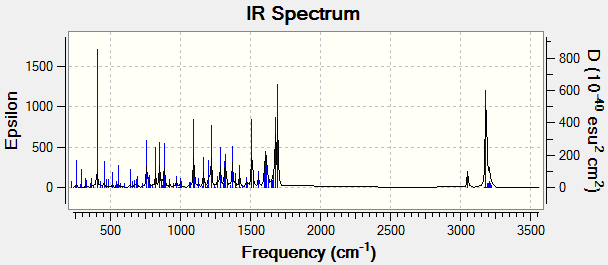
MOHAMMAD NASIR UDDIN\*, D.A. CHOWDHURY, NOBUYUKIMASE, MOHAMMAD FAZLUR RASHID, MONIRUZZAMAN, AMRIN AHSAN and NOOR MOSTAQ SHAH

|  |  |
| --- | --- |
| A close up of a necklace  Description generated with high confidence  L4 | A close up of a necklace  Description generated with high confidence  C4 |
| A close up of a necklace  Description generated with high confidence  L5 | A picture containing tree, air, accessory, sky  Description generated with very high confidence  C5 |
| L6 | A picture containing air, sky, tree, accessory  Description generated with high confidence  C6 |

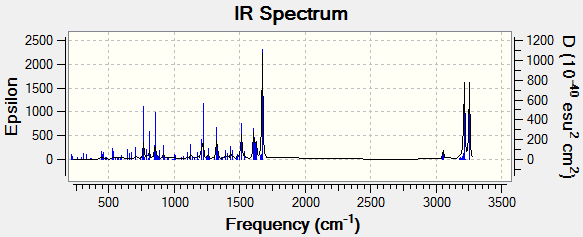
Figure S1. Optimized structure of ligands (L4-L6) and corresponding complexes.

|  |  |  |
| --- | --- | --- |
|  | HOMO | LUMO |
| L4 |  |  |
| L5 |  |  |
| L6 |  | A close up of food  Description generated with high confidence |

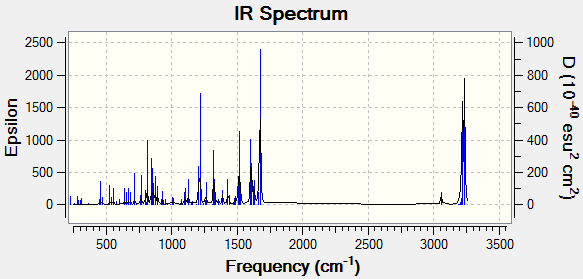
Figure S2. Frontier molecular orbitals, HOMO–LUMO of ligands, (L4-L6).

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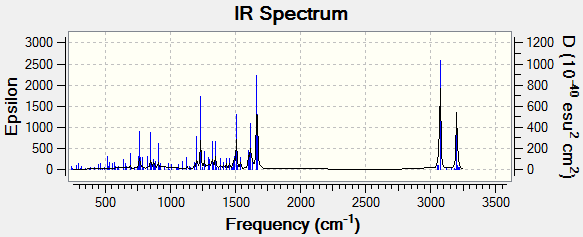
**L1**

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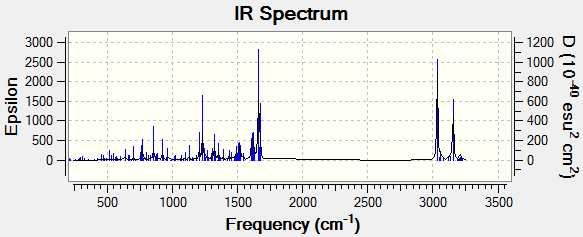
**L2**

****

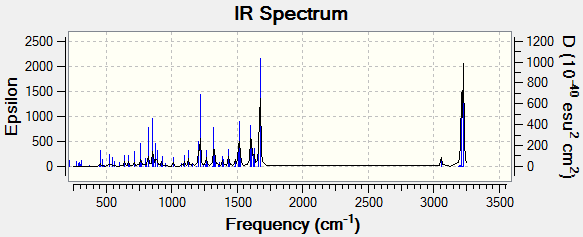
**L3**

****

**L4**

****

**L5**

****

**L6**

Figure S3. IR spectra (calculated by the program) of all ligands.

Figure S4. Quantum chemical calculations of atomic partial charges of all ligands and complexes.

Table S1. Some physical properties of the ligands and their complexes.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sl. No. | Ligands | Color | % Yield | M. P. oC | Sl. No. | Name of the  Complexes | Color | % Yield | M. P.  oC |
| L1 | BrSal-OPD-HNPH2 | Orange | 85 % | 180 | C1 | MoO2(BrSal-  OPD-HNP) | Black | 75 % | >250 |
| L2 | BrSal-OPD-SalH2 | Deep Orange | 75 % | 168-170 | C2 | MoO2(BrSal-  OPD-Sal) | Brownish Black | 90 % | >250 |
| L3 | BrSal-OPD-ClSalH2 | Orange | 70 % | 208 | C3 | MoO2(BrSal-  OPD-ClSal) | Black | 85 % | >250 |
| L4 | BrSal-OPD-HAPH2 | Yellowish Orange | 55 % | 201 | C4 | MoO2(5BrSal-  OPD-HAP) | Black | 75 % | >250 |
| L5 | BrSal-OPD-HPPH2 | Yellow | 70 % | 220 | C5 | MoO2(5BrSal-  OPD-HPP) | Black | 70 % | >250 |
| L6 | BrSal-OPD-BzPH2 | Light Orange | 85 % | 204 | C6 | MoO2(5BrSal-  OPD-BzP) | Greenish Black | 90 % | >250 |

Table S2. FTIR and UV-vis spectral data of the ligands

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Sl. No. | Ligands | Infrared spectral data (cm-1) | | | | | Electronic spectral  bands (nm) |
| ν O-H | ν C=N | ν C-C | νC-N | ν C-O |
| L1 | BrSal-OPD-HNPH2 | 3390 | 1618 vs | 1437 w | 1352 ms | 1276 s | 352, 336, 322, 274, 253 |
| L2 | BrSal-OPD-SalH2 | 3510 | 1616 vs | 1458 s | 1352 ms | 1276 s | 372, 337, 313, 308, 248, 235 |
| L3 | BrSal-OPD-ClSalH2 | 3566 | 1616 vs | 1458 s | 1352 ms | 1277 vs | 385, 335, 313, 300, 249, 238 |
| L4 | BrSal-OPD-HAPH2 | 3420 | 1585ms | 1449 s | 1313 ms | 1275s | 358, 336, 314, 278, 251 |
| L5 | BrSal-OPD-HPPH2 | 3450 | 1612 vs | 1383 s | 1348 ms | 1273 vs | 375, 336, 313, 273, 253, 235 |
| L6 | BrSal-OPD-BzPH2 | 3505 | 1581s | 1381 s | 1346 ms | 1273 vs | 394, 344, 293 (sh), 273 |

* Calculated values are given in parentheses
* vs = very strong, s = strong, ms = medium strong, w = weak, sh = shoulder, flsh = flat shoulder, br = broad
* Electronic spectral bands were carried out in DMF solvent

Table S3. Energy (eV) of HOMO, LUMO, HOMO-LUMO gap, hardness, and softness of ligands and complexes.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Name | HOMO−1 | HOMO | LUMO | LUMO+1 | Gap | Hardness | Softness |
| L1 | -5.687 | -5.387 | -2.395 | -1.768 | 2.99 | 1.49 | 0.67 |
| L2 | -5.714 | -5.496 | -2.340 | -1.687 | 3.15 | 1.58 | 0.63 |
| L3 | -5.905 | -5.687 | -2.639 | -1.796 | 3.05 | 1.52 | 0.66 |
| L4 | -5.986 | -5.469 | -2.285 | -1.442 | 3.18 | 1.59 | 0.63 |
| L5 | -8.626 | -8.245 | -5.823 | -5.306 | 2.42 | 1.21 | 0.83 |
| L6 | -5.768 | -5.578 | -2.530 | -1.796 | 3.05 | 1.52 | 0.66 |
| C1 | -5.850 | -5.387 | -3.864 | -2.748 | 1.52 | 0.76 | 1.31 |
| C2 | -6.231 | -5.768 | -2.476 | -2.394 | 3.29 | 1.65 | 0.60 |
| C3 | -6.689 | -6.122 | -2.966 | -2.557 | 3.15 | 1.58 | 0.63 |
| C4 | -6.122 | -5.333 | -3.129 | -2.802 | 2.20 | 1.10 | 0.91 |
| C5 | -6.068 | -5.714 | -2.449 | -2.204 | 3.26 | 1.63 | 0.61 |
| C6 | -6.394 | -5.932 | -3.319 | -2.639 | 2.61 | 1.32 | 0.77 |

Table S4. Bond distances of all ligands and complexes.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| L1 | | | L2 | |
| Atom number | Distances (Å) | | Atom number | Distances(Å) |
| C3-C4 | 1.3932 | | C5-C6 | 1.3935 |
| C3-C2 | 1.4028 | | C6-C4 | 1.4017 |
| C2-N26 | 1.4106 | | C1-N30 | 1.4120 |
| N26-C28 | 1.3012 | | N30-C33 | 1. 2931 |
| C28-C20 | 1.4428 | | C15-H19 | 1. 0833 |
| C22-C20 | 1.4221 | | C14-C13 | 1. 4271 |
| C22-O30 | 1.3438 | | C13-O35 | 1. 3424 |
| O30-H46 | 1.0188 | | C16-Br36 | 1. 9310 |
| C1-N36 | 1.3977 | | O35-H37 | 1. 0318 |
| C13-O29 | 1.2986 | | C32-N31 | 1.3226 |
| C16-Br35 | 1.9304 | | C32-C24 | 1.4139 |
|  |  | | C25-034 | 1.3046 |
| L3 | | | L4 | |
| Atom number | Distances (Å) | | Atom number | Distances (Å) |
| C5-C6 | 1.3932 | | C5-C6 | 1.3888 |
| C6-C1 | 1.4019 | | C6-C1 | 1.4074 |
| C1-N29 | 1.4120 | | C1-N30 | 1.4009 |
| N29-C32 | 1.2938 | | N30-C32 | 1.2909 |
| C32-C14 | 1.4502 | | C32-H43 | 1.0918 |
| C16-Br33 | 1.9302 | | C13-035 | 1.3559 |
| C13-O35 | 1.3443 | | C16-Br37 | 1.9338 |
| O45-H39 | 1.9579 | | C33-N31 | 1.3260 |
| C25-O36 | 1.3004 | | C25-O36 | 1.3246 |
| N30-C31 | 1.3213 | | O36-H39 | 1.4693 |
| C22-Cl34 | 1.8327 | |  |  |
| L5 | | L6 | | |
| C5-C6 | 1.3913 | | C5-C6 | 1.3933 |
| C6-C1 | 1.4021 | | C6-C1 | 1.4018 |
| C1-N31 | 1.4730 | | C1-N30 | 1.4122 |
| N31-C33 | 1.3349 | | N30-C32 | 1.2935 |
| C14-C13 | 1.4649 | | C16-Br33 | 1.9304 |
| C13-O35 | 1.2944 | | C13-O35 | 1.3439 |
| O35-H33 | 1.5564 | | O35-H39 | 1.0269 |
| C2-N32 | 1.4208 | | C22-Br34 | 1.9299 |
| C26-O30 | 1.3437 | | C25-O36 | 1.3015 |
| O36-H38 | 1.0646 | | O36-H40 | 1.5292 |
| C1 | | | C2 | |
| C6-C1 | 1.4490 | | C5-C6 | 1.3961 |
| C1-N30 | 1.4836 | | C1-N31 | 1.4307 |
| N30-C27 | 1.2850 | | N31-N30 | 1.3182 |
| N36-Mo47 | 2.0112 | | C2-N32 | 1.4225 |
| 029- Mo47 | 1.9723 | | 037-Mo35 | 1.7377 |
| Mo47-037 | 1.7503 | | Mo35-O33 | 2.1526 |
| O38- Mo47 | 1.7512 | | C13-O33 | 1.3131 |
| C22-O30 | 1.4439 | | C16-Br38 | 2.9291 |
| C2-N26 | 1.4808 | | C25-O34 | 2.3417 |
| C26-N26 | 1.2749 | | C40-N32 | 1.2989 |
| C10-Br35 | 1.9085 | |  |  |
| C3 | | | C4 | |
| C5-C6 | 1.3893 | | C5-C6 | 1.3956 |
| C6-C1 | 1.4035 | | C6-C1 | 1.3961 |
| C1-N29 | 1.4147 | | C1-N30 | 1.4203 |
| N29-C37 | 1.3232 | | N30-C32 | 1.2967 |
| C16-Br31 | 1.9272 | | C16-Br39 | 1.9279 |
| C13-O32 | 1.3166 | | C13-O35 | 1.3380 |
| Mo34-O32 | 2.1062 | | N30-Mo34 | 2.3564 |
| Mo34O36 | 1.7327 | | O38- Mo34 | 1.7398 |
| C38-N30 | 1.3227 | | C33-N31 | 1.3255 |
| C38-N30 | 1.3227 | | C25-O36 | 1.3249 |
| C5 | | | C6 | |
| C4-C3 | 1.3982 | | C10-C11 | 1.3869 |
| C3-C2 | 1.3929 | | C11-C12 | 1.4090 |
| C2-N31 | 1.4420 | | C12-N30 | 1.4048 |
| N31-C33 | 1.3214 | | N30-C32 | 1.2890 |
| C25-O36 | 1.3279 | | N29-Mo39 | 2.1548 |
| O36-Mo47 | 2.1168 | | Mo39-O30 | 1.7143 |
| Mo47-O38 | 1.7291 | | C24-O34 | 1.7354 |
| N30- Mo47 | 2.3655 | | C21-Br38 | 1.9211 |
| C16-Br43 | 1.9281 | | C29-C31 | 1.2436 |
| C32-N30 | 1.2964 | | C5-Br27 | 1.9264 |

Table S5. Bond angles of all ligands and complexes.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| L1 | | | C1 | |
| Atom number | Angles (0) | | Atom number | Angles (0) |
| C4-C3-C2 | 120.92 | | C5-C6-C1 | 119.17 |
| C3-C2-N26 | 125.65 | | C6-C1-N36 | 126.25 |
| C2-N26-C28 | 120.57 | | C1-N36-C27 | 127.70 |
| C22-O30-H46 | 119.16 | | C1-N36-Mo47 | 114.45 |
| C15-C16-Br35 | 120.79 | | N36-Mo47-O29 | 98.12 |
| C14-C13-O29 | 121.16 | | O29-Mo47-O30 | 81.68 |
|  |  | | C15-C16-Br35 | 119.86 |
| L2 | | | C2 | |
| C5-C6-C1 | 120.85 | | C5-C6-C1 | 119.76 |
| C1-N30-C33 | 121.28 | | 1-N31-C30 | 121.44 |
| C2-N31-C32 | 131.92 | | N31-Mo35-N33 | 70.05 |
| C14-C13-O35 | 128.01 | | O33-Mo35-O39 | 86.10 |
| C13-O35-H37 | 121.21 | | O33-Mo35-O39 | 107.96 |
| C15-C16-Br36 | 120.55 | | C24-C25-O34 | 123.67 |
|  |  | | C15-C16-Br38 | 120.73 |
| L3 | | C3 | | |
| C5-C6-C1 | 120.82 | | C5-C6-C1 | 120.44 |
| C6-C1-C29 | 125.35 | | C1-N29-C35 | 121.38 |
| C1-C29-C32 | 121.08 | | C13-O32-Mo34 | 122.66 |
| C15-C16-Br33 | 121.54 | | N29-Mo34-N30 | 70.99 |
| C14-C13-O35 | 127.85 | | O32-Mo34-O33 | 161.38 |
| C23-C22-Cl34 | 119.76 | | N35-Mo34-O36 | 115.08 |
|  |  | | C15-C16-Br31 | 120.65 |
|  |  | | C23-C22-Cl41 | 119.65 |
| L4 | | | C4 | |
| C5-C6-C1 | 121.60 | | C5-C6-C1 | 120.22 |
| C1-N30-C32 | 124.61 | | C6-C1-N30 | 124.75 |
| N30-C32-H43 | 122.57 | | C1-N30-C32 | 124.08 |
| C14-C13-O35 | 124.54 | | C14-C13-O35 | 123.93 |
| C13-O35-H38 | 114.91 | | O35-Mo34-O36 | 85.34 |
| C15-C16-Br37 | 120.47 | | N30-Mo34-N31 | 70.27 |
|  |  | | O38-Mo34-O37 | 101.68 |
|  |  | | C15-C16-Br39 | 120.39 |
| L5 | | | C5 | |
| C5-C6-C1 | 120.82 | | C5-C6-C1 | 120.11 |
| C1-N31-C33 | 128.80 | | C1-N30-C32 | 124.26 |
| N31-C33-C14 | 121.27 | | C14-C13-O35 | 124.01 |
| C14-C13-O35 | 121.81 | | C15-C16-Br34 | 120.40 |
| C13-O35-H37 | 103.35 | | N30-Mo47-N31 | 69.96 |
| C26-O36-H38 | 105.77 | | O35-Mo47-O38 | 108.00 |
|  |  | | O37-Mo47-O38 | 101.91 |
| L6 | | | C6 | |
| Atom number | Angles (0) | | Atom number | Angles (0) |
| C5-C6-C1 | 120.84 | | C10-C11-C12 | 122.42 |
| C6-C1-N30 | 125.37 | | C12-N30-C32 | 124.46 |
| C1-N30-C32 | 121.14 | | C20-C21-Br38 | 120.09 |
| C15-C16-Br33 | 121.56 | | C24-O34-Mo39 | 115.17 |
| C13-O35-H39 | 120.69 | | O34-Mo39-O33 | 87.80 |
| C14-C13-O35 | 127.86 | | N30-Mo39-N29 | 63.03 |
|  |  | | O35-Mo39-O36 | 128.96 |

Table S6. Comparison on experimental and theoretical IR frequencies of all ligands.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Molecules | Experimental  FT-IR | Calculated FT-IR | | | Assignment |
| Scaled | Unscaled | |
| L1 | 3390 | 3664 | | 3812 | υO-H |
| 1618 | 1627 | | 1693 | υC=N |
| 1352 | 1317 | | 1370 | υC-N |
| 1276 | 1271 | | 1322 | υC-O |
| 1437 | 1450 | | 1509 | υC-Ca |
| L2 | 3510 | 3127 | | 3253 | υO-H |
| 1616 | 1606 | | 1671 | υC=N |
| 1352 | 1317 | | 1370 | υC-N |
| 1276 | 1276 | | 1327 | υC-O |
| 1458 | 1453 | | 1511 | υC-Ca |
| L3 | 3566 | 3109 | | 3234 | υO-H |
| 1616 | 1608 | | 1673 | υC=N |
| 1352 | 1333 | | 1387 | υC-N |
| 1277 | 1267 | | 1318 | υC-O |
| 1458 | 1454 | | 1513 | υC-Ca |
| L4 | 3420 | 3098 | | 3223 | υO-H |
| 1585 | 1606 | | 1671 | υC=N |
| 1313 | 1336 | | 1390 | υC-N |
| 1275 | 1271 | | 1322 | υC-O |
| 1449 | 1450 | | 1509 | υC-Ca |
| L5 | 3450 | 3098 | | 3223 | υO-H |
| 1612 | 1606 | | 1671 | υC=N |
| 1348 | 1336 | | 1390 | υC-N |
| 1273 | 1271 | | 1322 | υC-O |
| 1383 | 1457 | | 1516 | υC-Ca |
| L6 | 3505 | 3102 | | 3227 | υO-H |
| 1614 | 1608 | | 1673 | υC=N |
| 1346 | 1335 | | 1389 | υC-N |
| 1273 | 1269 | | 1320 | υC-O |
| 1449 | 1455 | | 1514 | υC-Ca |

To scale the theoretical IR intensities scaling factor 0.9613 is applied in gas phase at B3LYP with 6-31G (d) basis set (*J. Phys. Chem. B*, **113**, 6378–6396 (2009)).

Table S7. Selected pharmacokinetic parameters of all ligands and complexes.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Name | Blood brain barrier | Human intestinal absorption | P-glyco  protein inhibitor | Human ether –a-go-go-related gene inhibition | Carcinogen | Rat acute toxicity  LD50  (mol/kg) | Acute oral toxicity |
| L1 | + (0.7702) | + (0.5348) | NI (0.7133) | WI (0.8675) | NC (0.6466) | 2.2149 | III |
| L2 | + (0.7739) | + (0.6682) | NI (0.7920) | WI (0.8841) | NC (0.5883) | 2.3355 | III |
| L3 | + (0.8077) | + (0.5000) | NI (0.8082) | WI (0.8314) | NC (0.5466) | 2.3470 | III |
| L4 | + (0.9774) | + (0.9912) | NI (0.9717) | WI (0.8808) | NC (0.7874) | 2.3727 | III |
| L5 | + (0.6680) | + (0.5000) | NI (0.8327) | WI (0.7922) | NC (0.5204) | 2.0988 | III |
| L6 | + (0.7739) | + (0.6682) | NI (0.7920) | WI (0.8841) | NC (0.5883) | 2.3355 | III |
| C1 | + (0.7129) | + (0.5140) | NI (0.9740) | WI (0.9205) | NC (0.7239) | 2.3209 | III |
| C2 | + (0.7141) | + (0.6230) | NI (0.9719) | WI (0.9089) | NC (0.6903) | 2.4214 | III |
| C3 | + (0.7503) | + (0.4988) | NI (0.9827) | WI (0.9100) | NC (0.6571) | 2.4410 | III |
| C4 | + (0.8604) | + (0.9030) | NI (0.8974) | WI (0.9372) | NC (0.8130) | 2.4702 | III |
| C5 | + (0.6002) | + (0.4808) | NI (0.9003) | WI (0.9034) | NC (0.6329) | 2.2017 | III |
| C6 | + (0.7302) | + (0.5368) | NI (0.8975) | WI (0.9403) | NC (0.6603) | 2.4178 | III |

* NI = non inhibitor, wide inhibition, NC = non carcinogenic, LD50 = lethal dose 50; Toxicity category III indicates slightly toxic and slightly irritating.