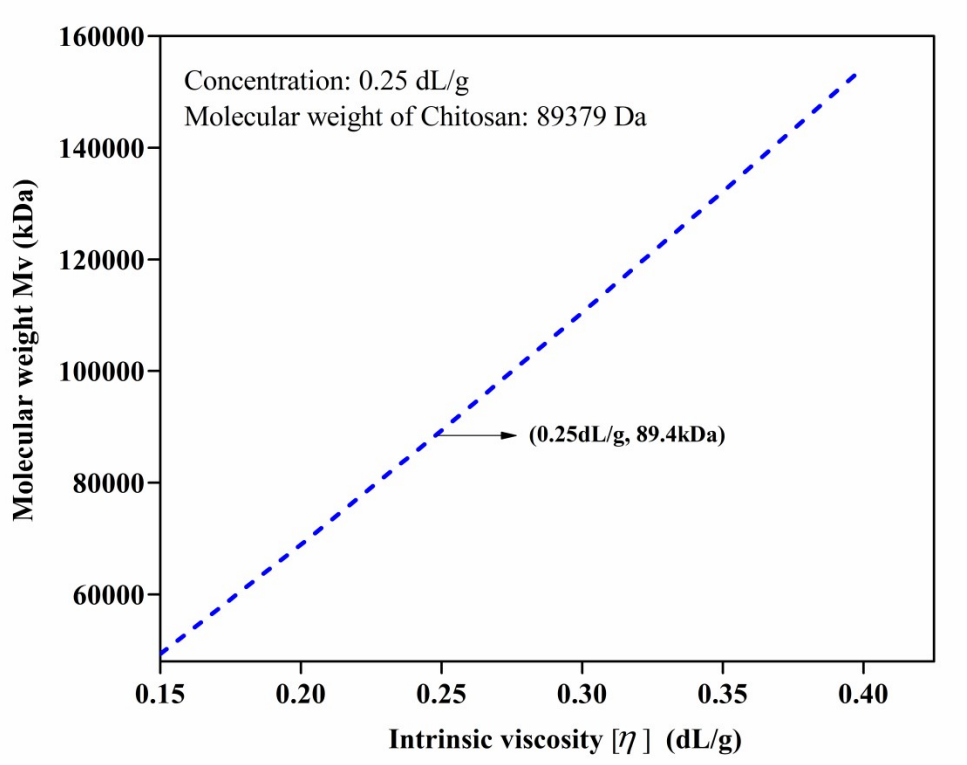
# Antimicrobial efficacies and molecular 3D-modeling of novel biopolymer derivatives extracted from bio-waste using a solid-state mechanochemical technique

Murugaiyan Manimohan [1]*, Mohamed Aboobucker Sithique [1].

[1]PG & Research Department of Chemistry, Islamiah College (Autonomous), Vaniyambadi, Tirupattur District, Tamil Nadu– 635 752, India.




**S.fig.1** Viscosity-average molecular weight of chitosan

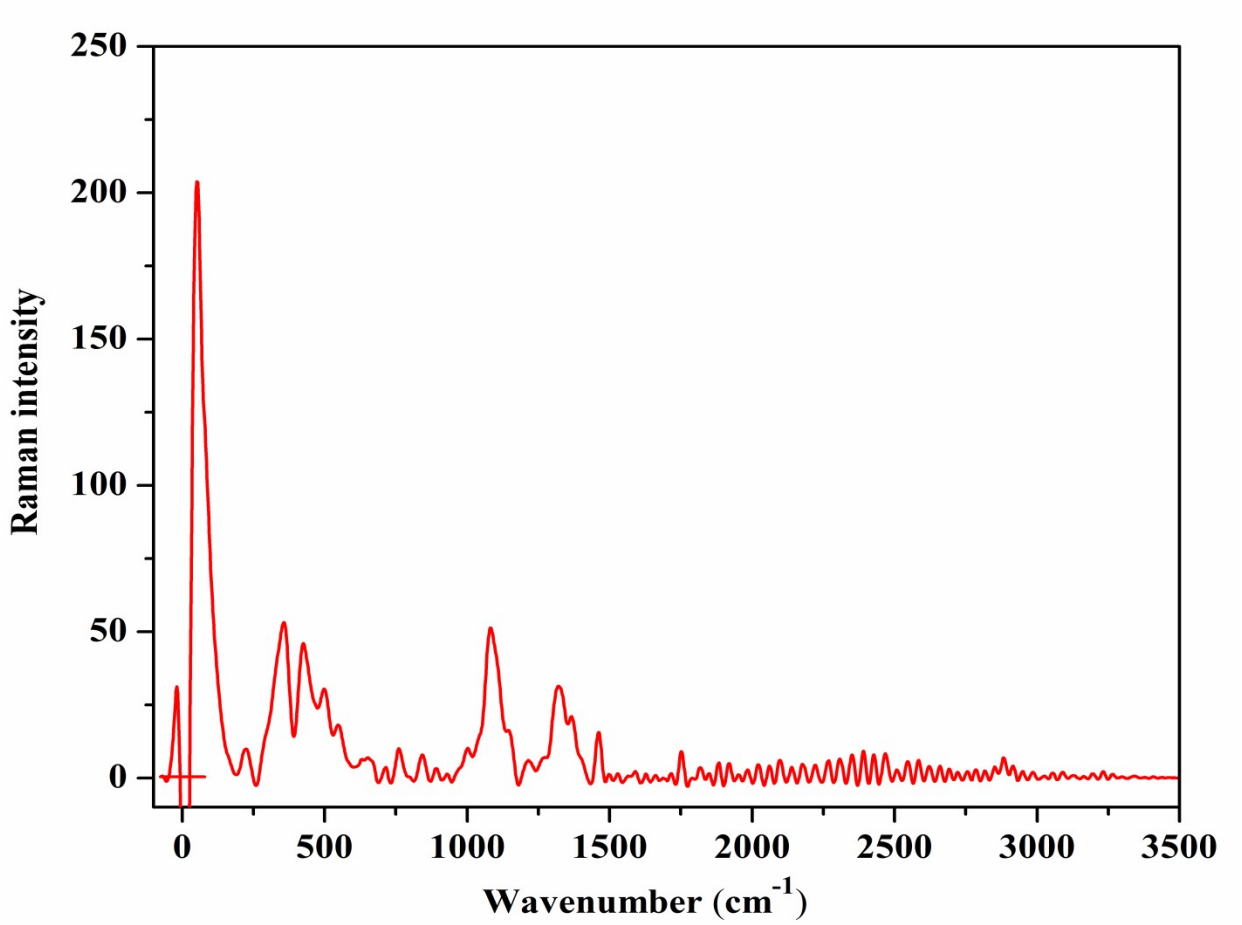
The viscosity-average molecular weight of chitosan was calculated as follows

K = $1.38\times10^{-5}$ and α = 0.86 substituted in Mark–Houwink equation $M = ((\eta)/k)^{1/\alpha}$

= $(0.25 / 1.38\times10^{-5})^{1/0.86}$

~ 89379 Da

~ 89 kDa




**S.fig.2** FT-Raman spectrum of hydrazide incorporated O-carboxymethyl chitosan Schiff base copper (II) metal complexes.

The obtained quantities of product for all synthesized metal complexes were found with good yield and are shown below in S. table 1.

| Name of the ligand/complex | Quantity of the reactant (g) | Yield of the product (g) | Weight of the product in (%) |
|---|---|---|---|
| [(IA-OCMCS)-Co(OAc)$_2$] | 0.80 | 0.46 | 57.50 |
| [(BHA-OCMCS)-Co(OAc)$_2$] | 0.80 | 0.47 | 58.75 |
| [(HBA-OCMCS)-Co(OAc)$_2$] | 0.80 | 0.39 | 48.75 |
| [(ID-OCMCS)-Co(OAc)$_2$] | 0.80 | 0.41 | 51.25 |
| [(BHD-OCMCS)-Co(OAc)$_2$] | 0.80 | 0.43 | 53.75 |
| [(HBD-OCMCS)-Co(OAc)$_2$] | 0.80 | 0.38 | 47.50 |
| [(IA-OCMCS)-Cu(OAc)$_2$] | 0.80 | 0.42 | 52.50 |
| [(BHA-OCMCS)-Cu(OAc)$_2$] | 0.80 | 0.43 | 53.75 |
| [(HBA-OCMCS)-Cu(OAc)$_2$] | 0.80 | 0.48 | 60.00 |
| [(ID-OCMCS)-Cu(OAc)$_2$] | 0.80 | 0.51 | 63.75 |
| [(BHD-OCMCS)-Cu(OAc)$_2$] | 0.80 | 0.38 | 47.50 |
| [(HBD-OCMCS)-Cu(OAc)$_2$] | 0.80 | 0.49 | 61.25 |
| [(IA-OCMCS)-Zn(OAc)$_2$] | 0.80 | 0.35 | 43.75 |
| [(BHA-OCMCS)-Zn(OAc)$_2$] | 0.80 | 0.37 | 46.25 |
| [(HBA-OCMCS)-Zn(OAc)$_2$] | 0.80 | 0.43 | 53.75 |
| [(ID-OCMCS)-Zn(OAc)$_2$] | 0.80 | 0.38 | 47.50 |
| [(BHD-OCMCS)-Zn(OAc)$_2$] | 0.80 | 0.35 | 43.75 |
| [(HBD-OCMCS)-Zn(OAc)$_2$] | 0.80 | 0.41 | 51.25 |

**S.table. 1**. The yields in percentage for Co(II), Cu(II), and Zn(II) complexes of substituted O-CMCS Schiff bases.

The biopolymer Schiff base ligands fully dissolved in water. The biopolymer Schiff base metal complexes dissolved in hot water, DMF, DMSO, and toluene, but did not dissolve in AcOH, MeOH, and EtOH. The solubility results of the prepared compounds are represented below in S.table 2.

| Name of the compound / ligand / complex | Solubility in solvents | | | | | | |
|---|---|---|---|---|---|---|---|
| | >1% AcOH | Water | MeOH | EtOH | DMSO | DMF | Toluene $\times 10^{-3}$ M |
| **DCS** | + | - | - | - | - | - | - |
| **Biopolymer Schiff base ligand** | - | + | - | - | - | - | - |
| **[(O-CMCS)-Co(OAc)$_2$]** | - | ± | - | - | + | + | + |
| **[(O-CMCS)-Cu(OAc)$_2$]** | - | ± | - | - | + | + | + |
| **[(O-CMCS)-Zn(OAc)$_2$]** | - | ± | - | - | + | + | + |

**Note: [Soluble: +, Partially Soluble: ±, Insoluble: -]**

**S.table. 2.** Solubility of the DCS, Schiff base ligand and their Co(II), Cu(II), and Zn(II) metal complexes

| S.No. | Name of the compound | Responsible functional groups in 2$\theta$ (Degree) | | |
|---|---|---|---|---|
| | | Schiff base imine (-C=N) | Carboxymethyl moieties | After complexation |
| **1** | IA-OCMCS | 23.08 | 25.62, 31.14 | - |
| **2** | BHA-OCMCS | 23.11 | 27.95, 30.12 | - |
| **3** | HBA-OCMCS | 22.20 | 30.49, 34.08 | - |
| **4** | ID-OCMCS | 22.12 | 27.02, 30.59 | - |
| **5** | BHD-OCMCS | 23.63 | 27.17, 35.93 | - |
| **6** | HBD-OCMCS | 21.93 | 26.82, 31.11 | - |
| **7** | [(IA-OCMCS) Co $(OAc)_2$] | - | 32.17, 39.78 | 16.29 |
| **8** | [(BHA-OCMCS) Co $(OAc)_2$] | - | 32.12, 68.23 | 16.10 |
| **9** | [(HBA-OCMCS) Co $(OAc)_2$] | - | 33.36, 39.62 | 16.23 |
| **10** | [(ID-OCMCS) Co $(OAc)_2$] | - | 32.37, 37.36 | 16.29 |
| **11** | [(BHD-OCMCS) Co $(OAc)_2$] | - | 33.27, 49.46 | 15.91 |
| **12** | [(HBD-OCMCS) Co $(OAc)_2$] | - | 32.80, 39.63 | 16.09 |
| **13** | [(IA-OCMCS) Cu $(OAc)_2$] | - | 32.64, 38.67 | 15.98 |
| **14** | [(BHA-OCMCS) Cu $(OAc)_2$] | - | 32.54, 39.66 | 16.12 |
| **15** | [(HBA-OCMCS) Cu $(OAc)_2$] | - | 33.11, 38.93 | 16.19 |
| **16** | [(ID-OCMCS) Cu $(OAc)_2$] | - | 32.24, 39.21 | 16.23 |
| **17** | [(BHD-OCMCS) Cu $(OAc)_2$] | - | 31.31, 39.43 | 15.96 |
| **18** | [(HBD-OCMCS) Cu $(OAc)_2$] | - | 32.67, 39.58 | 16.15 |
| **19** | [(IA-OCMCS) Zn $(OAc)_2$] | - | 32.82, 39.28 | 16.09 |
| **20** | [(BHA-OCMCS) Zn $(OAc)_2$] | - | 32.23, 39.31 | 15.90 |
| **21** | [(HBA-OCMCS) Zn $(OAc)_2$] | - | 32.25, 38.54 | 16.22 |
| **22** | [(ID-OCMCS) Zn $(OAc)_2$] | - | 32.18, 38.86 | 16.27 |
| **23** | [(BHD-OCMCS) Zn $(OAc)_2$] | - | 32.24, 38.63 | 16.21 |
| **24** | [(HBD-OCMCS) Zn $(OAc)_2$] | - | 33.18, 39.93 | 16.18 |

**S.table. 3.** X-ray diffraction peaks of 4-Bromo benzohydrazide, Isoniazid, and 4-Amino benzohydrazide based biopolymer O-carboxymethyl chitosan Schiff base ligand and their Co (II), Cu (II) and Zn (II) complexes.

**a) Chitosan (CS)**

Weight %

| | C | N | O | Mg |
|---|---|---|---|---|
| ***Base(4)_pt1*** | 32.40 | 14.10 | 53.33 | 0.17 |

Atom %

| | C | N | O | Mg |
|---|---|---|---|---|
| ***Base(4)_pt1*** | 38.29 | 14.29 | 47.32 | 0.10 |

**b) Deacetylated chitosan (DCS)**

Weight %

| | C | N | O | Mg |
|---|---|---|---|---|
| ***Base(4)_pt1*** | 32.40 | 14.10 | 53.33 | 0.17 |

Atom %

| | C | N | O | Mg |
|---|---|---|---|---|
| ***Base(4)_pt1*** | 38.29 | 14.29 | 47.32 | 0.10 |

**c) Biopolymer Schiff base (O-CMCS) ligand**

Weight %

| | C | N | O | Cl | Fe |
|---|---|---|---|---|---|
| ***Base(7)_pt1*** | 31.71 | 9.71 | 40.20 | 18.23 | 0.15 |

Atom %

| | C | N | O | Cl | Fe |
|---|---|---|---|---|---|
| ***Base(7)_pt1*** | 41.49 | 10.90 | 39.49 | 8.08 | 0.04 |

**d) Biopolymer Schiff base ligand Cu(II) metal complex (O-CMCS-$Cu(OAc)_2$)**

Weight %

| | C | N | O | Ca | Cl | Cu |
|---|---|---|---|---|---|---|
| ***Base(5)_pt1*** | 26.31 | 16.63 | 52.84 | 0.38 | 0.00 | 3.85 |

Atom %

| | C | N | O | Ca | Cl | Cu |
|---|---|---|---|---|---|---|
| ***Base(5)_pt1*** | 32.57 | 17.65 | 49.10 | 0.14 | 0.00 | 0.54 |

**e) Biopolymer Schiff base ligand Cu(II) metal complex (O-CMCS-$Co(OAc)_2$)**

Weight %

| | C | N | O | Ca | Cl | Co |
|---|---|---|---|---|---|---|
| ***Base(5)_pt1*** | 26.39 | 16.99 | 51.25 | 0.30 | 0.07 | 2.98 |

Atom %

| | C | N | O | Ca | Cl | Co |
|---|---|---|---|---|---|---|
| ***Base(5)_pt1*** | 30.63 | 16.89 | 51.37 | 0.10 | 0.08 | 0.72 |

**f) Biopolymer Schiff base ligand Zn(II) metal complex (O-CMCS-$Zn(OAc)_2$)**

Weight %

| | C | N | O | Ca | Cl | Zn |
|---|---|---|---|---|---|---|
| ***Base(5)_pt1*** | 29.12 | 13.29 | 50.48 | 0.29 | 0.00 | 3.10 |

Atom %

| | C | N | O | Ca | Cl | Zn |
|---|---|---|---|---|---|---|
| ***Base(5)_pt1*** | 30.77 | 14.61 | 49.18 | 0.18 | 0.00 | 0.58 |

**S.table. 4a.** EDAX elemental composition of a) CS, b) DCS, c) O-CMCS Schiff base ligand, d) O-CMCS-$Cu(OAc)_2$ e) O-CMCS-$Co(OAc)_2$, and f) O-CMCS-$Zn(OAc)_2$

| Name of the compounds | Theoretical value in (%) | | | Observed value in (%) | | |
|---|---|---|---|---|---|---|
| | C | H | N | C | H | N |
| **IA-OCMCS** | 47.20 | 6.04 | 7.86 | 50.96 | 6.08 | 7.42 |
| **BHA-OCMCS** | 52.62 | 7.07 | 12.27 | 51.91 | 7.18 | 11.88 |
| **HBA-OCMCS** | 53.61 | 7.28 | 11.91 | 54.08 | 7.03 | 10.77 |
| **ID-OCMCS** | 56.54 | 5.51 | 6.38 | 60.71 | 5.48 | 6.11 |
| **BHD-OCMCS** | 62.06 | 6.25 | 9.65 | 62.76 | 6.61 | 9.54 |
| **HBD-OCMCS** | 62.61 | 6.44 | 9.42 | 63.86 | 6.48 | 9.61 |
| **[(IA-OCMCS) Co $(OAc)_2$]** | 42.39 | 4.98 | 5.36 | 43.68 | 5.16 | 5.96 |
| **[(BHA-OCMCS) Co $(OAc)_2$]** | 45.72 | 5.60 | 8.89 | 45.13 | 5.77 | 8.78 |
| **[(HBA-OCMCS) Co $(OAc)_2$]** | 46.59 | 5.79 | 8.69 | 45.49 | 5.64 | 8.55 |
| **[(ID-OCMCS) Co $(OAc)_2$]** | 50.49 | 4.72 | 5.05 | 51.21 | 4.88 | 4.96 |
| **[(BHD-OCMCS) Co $(OAc)_2$]** | 54.12 | 5.21 | 7.42 | 53.73 | 5.78 | 7.26 |
| **[(HBD-OCMCS) Co $(OAc)_2$]** | 54.69 | 5.38 | 7.29 | 54.93 | 5.24 | 7.12 |
| **[(IA-OCMCS) Cu $(OAc)_2$]** | 42.11 | 4.95 | 5.89 | 41.38 | 4.61 | 5.76 |
| **[(BHA-OCMCS) Cu $(OAc)_2$]** | 45.39 | 5.55 | 8.82 | 46.68 | 5.73 | 8.71 |
| **[(HBA-OCMCS) Cu $(OAc)_2$]** | 46.26 | 5.75 | 8.63 | 47.27 | 5.62 | 8.66 |
| **[(ID-OCMCS) Cu $(OAc)_2$]** | 50.22 | 4.70 | 5.02 | 51.63 | 4.84 | 4.93 |
| **[(BHD-OCMCS) Cu $(OAc)_2$]** | 53.79 | 5.18 | 7.38 | 52.92 | 5.47 | 7.19 |
| **[(HBD-OCMCS) Cu $(OAc)_2$]** | 54.36 | 5.34 | 7.25 | 53.19 | 5.39 | 7.13 |
| **[(IA-OCMCS) Zn $(OAc)_2$]** | 42.01 | 4.94 | 5.88 | 43.18 | 4.88 | 5.86 |
| **[(BHA-OCMCS) Zn $(OAc)_2$]** | 45.26 | 5.54 | 8.80 | 46.87 | 6.08 | 8.87 |
| **[(HBA-OCMCS) Zn $(OAc)_2$]** | 46.13 | 5.73 | 8.61 | 45.29 | 5.73 | 8.52 |
| **[(ID-OCMCS) Zn $(OAc)_2$]** | 50.11 | 4.69 | 5.01 | 51.51 | 4.86 | 5.09 |
| **[(BHD-OCMCS) Zn $(OAc)_2$]** | 53.66 | 5.17 | 7.36 | 52.04 | 5.63 | 7.27 |
| **[(HBD-OCMCS) Zn $(OAc)_2$]** | 54.24 | 5.33 | 7.23 | 52.07 | 5.45 | 7.11 |

**S.table. 4b.** Elemental analysis of synthesized water soluble hydrazide based O-carboxymethyl chitosan Schiff base and their Co (II), Cu (II) and Zn (II) metal complexes.

| Functional group | Name of the Schiff base ligand | | | | | |
|---|---|---|---|---|---|---|
| | IA-OCMCS | BHA-OCMCS | HBA-OCMCS | ID-OCMCS | BHD-OCMCS | HBD-OCMCS |
| | Chemical shift (ppm) | | | | | |
| **Methyl ($-CH_3$) group Protons** | 1.91 3H(s)<br>2.22 3H(s)<br>2.16 3H(s) | 2.11 3H(s)<br>2.15 3H(s)<br>2.27 3H(s) | 1.93 3H(s)<br>2.01 3H(s)<br>2.29 3H(s) | - | - | - |
| **Methylene ($-CH_2-$) proton** | 3.69 2H(s) | 3.73 2H(s) | 3.76 2H(s) | 3.78 2H(s) | 3.80 3H(s) | 3.70 3H(s) |
| **Imine (-N=C<) proton** | 5.10 NH(s) | 8.10 NH(s) | 6.54NH(s) | 5.36NH(s) | 6.98 NH(s) | 6.39 NH(s) |
| **Aromatic protons** | 8.12 H(d)<br>8.34 H(d)<br>8.55 H(s) | 8.12 H(d)<br>8.06 H(d)<br>8.07 H(s) | 6.97 H(d)<br>6.89 H(d)<br>6.90 H(s) | 7.18 H(d)<br>7.59 H(d)<br>7.41 H(s) | 7.41 H(d)<br>7.84 H(d)<br>7.46 H(s) | 7.04 H(d)<br>7.06 H(d)<br>7.17 H(s) |
| **Hydrazone (>C=N-NH-)** | 8.63 H(s) | 9.01 H(s) | 8.85 H(s) | 9.14 H(s) | 8.55 H(s) | 7.75 H(s) |
| **Carboxylic (-COOH) acidic proton** | 10.41 H(s) | 11.90 H(s) | 10.95 H(s) | 10.45 H(s) | 10.55 H(s) | 11.36 H(s) |

**S.table. 5a** The $^1H$ NMR spectra of IA-OCMCS, BHA-OCMCS, HBA-OCMCS, ID-OCMCS, BHD-OCMCS and HBD-OCMCS compound.

| Functional group | Name of the Schiff base ligand | | | | | |
|---|---|---|---|---|---|---|
| | IA-OCMCS | BHA-OCMCS | HBA-OCMCS | ID-OCMCS | BHD-OCMCS | HBD-OCMCS |
| | Chemical shift (ppm) | | | | | |
| **Carboxy methyl** | 169.18 | 171.16 | 176.37 | 181.20 | 186.58 | 191.43 |
| **Hydrazone (>C=N-NH-)** | 178.91 | 178.45 | 163.75 | 169.85 | 183.32 | 181.26 |
| **Hydrazone (-N=C<)** | 173.97 | 169.57 | 168.26 | 165.15 | 179.18 | 180.98 |
| **Imine** (>C=N-) | 148.97 | 149.56 | 145.67 | 156.65 | 153.19 | 156.00 |
| **Aromatic ring carbon** | 126.86<br>125.92 | 130.32<br>129.88 | 131.92<br>130.25 | 128.91<br>127.07 | 129.88<br>131.28 | 130.95<br>131.25 |
| **Methylene ($-CH_2$)** | 39.73 | 40.68 | 41.45 | 40.91 | 41.50 | 42.48 |

**S.table. 5b.** The $^{13}C$ NMR spectra of IA-OCMCS, BHA-OCMCS, HBA-OCMCS, ID-OCMCS, BHD-OCMCS and HBD-OCMCS compound.

| Assignment | Selected bond length (˚/A) | | | Selected bond angle (˚/A) | | |
|---|---|---|---|---|---|---|
| **IA-OCMCS-Co(OAc)$_2$** | **Atoms** | **Actual (˚/A)** | **Optimal (˚/A)** | **Atoms** | **Actual (˚/A)** | **Optimal (˚/A)** |
| Carbon-bromine linkage | C(3)-Br(29) | 1.881 | 1.881 | C(4)-C(3)-Br(29) | 120.000 | 118.100 |
| Carboxylic group | O(51)-C(52) | 1.208 | 1.208 | O(51)-C(52) | 109.125 | 107.700 |
| Alcoholic group of chain | O(45)-H(88) | 0.972 | 0.972 | H(88)-O(45)-C(43) | 106.099 | 106.100 |
| Cobalt ester linkage | Co(39)-O(50) | 0.600 | 0.600 | C(52)-O(50)-Co(39) | 119.999 | 120.000 |
| Cobalt and imine | N(17)-Co(39) | 1.836 | 1.842 | O(50)-Co(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Co(39)-N(8) | 109.500 | 108.115 |
| Glycosidic linkage | C(20)-O(24) | 2.054 | 1.400 | C(20)-O(24) | 110.375 | 106.700 |
| **BHA-OCMCS-Co(OAc)$_2$** | | | | | | |
| Cobalt ester linkage | Co(39)-O(50) | 0.602 | 0.600 | C(52)-O(50)-Co(39) | 120.000 | 120.000 |
| Isoniazid nitrogen | C(3)-N(4) | 1.351 | 1.358 | C(3)-N(27)-O(40) | 120.000 | 120.000 |
| Methyl group (hydrazide) | C(3)-C(27) | 1.497 | 1.497 | C(27)-C(3)-C(2) | 120.000 | 121.400 |
| Cobalt and imine | N(17)-Co(39) | 1.836 | 1.836 | O(50)-Co(39)-N(17) | 90.000 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.356 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 128.000 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Co(39)-N(8) | 109.500 | 108.115 |
| **HBA-OCMCS-Co(OAc)$_2$** | | | | | | |
| Cobalt ester linkage | Co(39)-O(50) | 0.600 | 0.600 | C(52)-O(50)-Co(39) | 119.999 | 120.000 |
| Free amine at hydrazide | C(3)-N(28) | 1.266 | 1.462 | C(4)-C(3)-N(28) | 120.000 | 120.000 |
| Cobalt and imine | N(17)-Co(39) | 1.836 | 1.842 | O(50)-Co(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Co(39)-N(8) | 109.500 | 108.115 |
| **ID-OCMCS-Co(OAc)$_2$** | | | | | | |
| Carbon-bromine linkage | C(3)-Br(29) | 1.881 | 1.881 | C(4)-C(3)-Br(29) | 120.000 | 118.100 |
| Carboxylic group | O(51)-C(52) | 1.208 | 1.208 | O(51)-C(52) | 109.125 | 107.700 |
| Alcoholic group of chain | O(45)-H(88) | 0.972 | 0.972 | H(88)-O(45)-C(43) | 106.099 | 106.100 |
| Cobalt ester linkage | Co(39)-O(50) | 0.600 | 0.600 | C(52)-O(50)-Co(39) | 119.999 | 120.000 |
| Cobalt and imine | N(17)-Co(39) | 1.836 | 1.842 | O(50)-Co(39)-N(17) | 89.999 | 91.050 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Co(39)-N(8) | 109.500 | 108.115 |
| **BHD-OCMCS-Co(OAc)$_2$** | | | | | | |
| Cobalt ester linkage | Co(39)-O(50) | 0.600 | 0.600 | C(52)-O(50)-Co(39) | 119.999 | 120.000 |
| Isoniazid nitrogen | C(3)-N(4) | 1.351 | 1.358 | C(3)-N(27)-O(40) | 120.000 | 120.000 |
| Methyl group (hydrazide) | C(3)-C(27) | 1.497 | 1.497 | C(27)-C(3)-C(2) | 120.000 | 121.400 |
| Cobalt and imine | N(17)-Co(39) | 1.836 | 1.842 | O(50)-Co(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Co(39)-N(8) | 109.500 | 108.115 |
| **HBD-OCMCS-Co(OAc)$_2$** | | | | | | |
| Cobalt ester linkage | Co(39)-O(50) | 0.600 | 0.600 | C(52)-O(50)-Co(39) | 119.999 | 120.000 |
| Free amine at hydrazide | C(3)-N(28) | 1.266 | 1.462 | C(4)-C(3)-N(28) | 120.000 | 120.000 |
| Cobalt and imine | N(17)-Co(39) | 1.836 | 1.842 | O(50)-Co(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Co(39)-N(8) | 109.500 | 108.115 |

**S.table 6a.** Selected bond length and bond angle of prepared Schiff base cobalt(II) metal complexes.

| **Assignment** | **Selected bond length (˚/A)** | | | **Selected bond angle (˚/A)** | | |
|---|---|---|---|---|---|---|
| **IA-OCMCS-Cu(OAc)$_2$** | **Atoms** | **Actual (˚/A)** | **Optimal (˚/A)** | **Atoms** | **Actual (˚/A)** | **Optimal (˚/A)** |
| Carbon-bromine linkage | C(3)-Br(29) | 1.881 | 1.881 | C(4)-C(3)-Br(29) | 120.000 | 118.100 |
| Carboxylic group | O(51)-C(52) | 1.208 | 1.208 | O(51)-C(52) | 109.125 | 107.700 |
| Alcoholic group of chain | O(45)-H(88) | 0.972 | 0.972 | H(88)-O(45)-C(43) | 106.099 | 106.100 |
| Copper ester linkage | Cu(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Cu(28) | 120.000 | 120.000 |
| Copper-imine | N(17)-Cu(39) | 1.836 | 1.842 | O(50)-Cu(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Cu(39)-N(8) | 109.500 | 108.115 |
| **BHA-OCMCS-Cu(OAc)$_2$** | | | | | | |
| Copper ester linkage | Cu(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Cu(28) | 120.000 | 120.000 |
| Isoniazid nitrogen | C(3)-N(4) | 1.351 | 1.358 | C(3)-N(27)-O(40) | 120.000 | 120.000 |
| Methyl group (hydrazide) | C(3)-C(27) | 1.497 | 1.497 | C(27)-C(3)-C(2) | 120.000 | 121.400 |
| Copper-imine | N(17)-Cu(39) | 1.836 | 1.842 | O(50)-Cu(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Cu(39)-N(8) | 109.500 | 108.115 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **HBA-OCMCS-Cu(OAc)$_2$** | | | | | | |
| Copper ester linkage | Cu(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Cu(28) | 120.000 | 120.000 |
| Free amine at hydrazide | C(3)-N(28) | 1.266 | 1.462 | C(4)-C(3)-N(28) | 120.000 | 120.000 |
| Copper-imine | N(17)-Cu(39) | 1.836 | 1.842 | O(50)-Cu(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Cu(39)-N(8) | 109.500 | 108.115 |
| **ID-OCMCS-Cu(OAc)$_2$** | | | | | | |
| Carbon-bromine linkage | C(3)-Br(29) | 1.881 | 1.881 | C(4)-C(3)-Br(29) | 120.000 | 118.100 |
| Carboxylic group | O(51)-C(52) | 1.208 | 1.208 | O(51)-C(52) | 109.125 | 107.700 |
| Alcoholic group of chain | O(45)-H(88) | 0.972 | 0.972 | H(88)-O(45)-C(43) | 106.099 | 106.100 |
| Copper ester linkage | Cu(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Cu(28) | 120.000 | 120.000 |
| Copper-imine linkage | N(17)-Cu(39) | 1.836 | 1.842 | O(50)-Cu(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Cu(39)-N(8) | 109.500 | 108.115 |
| **BHD-OCMCS-Cu(OAc)$_2$** | | | | | | |
| Copper ester linkage | Cu(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Cu(28) | 120.000 | 120.000 |
| Isoniazid nitrogen | C(3)-N(4) | 1.351 | 1.358 | C(3)-N(27)-O(40) | 120.000 | 120.000 |
| Methyl group (hydrazide) | C(3)-C(27) | 1.497 | 1.497 | C(27)-C(3)-C(2) | 120.000 | 121.400 |
| Copper-imine linkage | N(17)-Cu(39) | 1.836 | 1.842 | O(50)-Cu(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Cu(39)-N(8) | 109.500 | 108.115 |
| **HBD-OCMCS-Cu(OAc)$_2$** | | | | | | |
| Copper ester linkage | Cu(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Cu(28) | 120.000 | 120.000 |
| Free amine at hydrazide | C(3)-N(28) | 1.266 | 1.462 | C(4)-C(3)-N(28) | 120.000 | 120.000 |
| Copper-imine linkage | N(17)-Cu(39) | 1.836 | 1.842 | O(50)-Cu(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Cu(39)-N(8) | 109.500 | 108.115 |

**S.table 6b.** Selected bond length and bond angle of prepared Schiff base Copper(II) metal complexes.

| **Assignment** | **Selected bond length (˚/A)** | | | **Selected bond angle (˚/A)** | | |
|---|---|---|---|---|---|---|
| **IA-OCMCS-Zn(OAc)$_2$** | **Atoms** | **Actual (˚/A)** | **Optimal (˚/A)** | **Atoms** | **Actual (˚/A)** | **Optimal (˚/A)** |
| Carbon-bromine linkage | C(3)-Br(29) | 1.881 | 1.881 | C(4)-C(3)-Br(29) | 120.000 | 118.100 |
| Carboxylic group | O(51)-C(52) | 1.208 | 1.208 | O(51)-C(52) | 109.125 | 107.700 |
| Alcoholic group of chain | O(45)-H(88) | 0.972 | 0.972 | H(88)-O(45)-C(43) | 106.099 | 106.100 |
| Zinc ester linkage | Zn(28)-O(49) | 1.890 | 1.890 | C(51)-O(49)-Zn(28) | 120.000 | 120.000 |
| Zinc-imine linkage | N(17)-Zn(39) | 1.836 | 1.842 | O(50)-Zn(39)- | 89.999 | 91.050 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | N(17) | | |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Zn(39)-N(8) | 109.500 | 108.115 |
| **BHA-OCMCS-Zn(OAc)$_2$** | | | | | | |
| Zinc ester linkage | Zn(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Zn(28) | 120.000 | 120.000 |
| Isoniazid nitrogen | C(3)-N(4) | 1.351 | 1.358 | C(3)-N(27)-O(40) | 120.000 | 120.000 |
| Methyl group (hydrazide) | C(3)-C(27) | 1.497 | 1.497 | C(27)-C(3)-C(2) | 120.000 | 121.400 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Zn(39)-N(8) | 109.500 | 108.115 |
| **HBA-OCMCS-Zn(OAc)$_2$** | | | | | | |
| Zinc ester linkage | Zn(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Zn(28) | 120.000 | 120.000 |
| Free amine at hydrazide | C(3)-N(28) | 1.266 | 1.462 | C(4)-C(3)-N(28) | 120.000 | 120.000 |
| Zinc-imine linkage | N(17)-Zn(39) | 1.836 | 1.842 | O(50)-Zn(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Zn(39)-N(8) | 109.500 | 108.115 |
| **ID-OCMCS-Zn(OAc)$_2$** | | | | | | |
| Carbon-bromine linkage | C(3)-Br(29) | 1.881 | 1.881 | C(4)-C(3)-Br(29) | 120.000 | 118.100 |
| Carboxylic group | O(51)-C(52) | 1.208 | 1.208 | O(51)-C(52) | 109.125 | 107.700 |
| Alcoholic group of chain | O(45)-H(88) | 0.972 | 0.972 | H(88)-O(45)-C(43) | 106.099 | 106.100 |
| Zinc ester linkage | Zn(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Zn(28) | 120.000 | 120.000 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Zn(39)-N(8) | 109.500 | 108.115 |
| **BHD-OCMCS-Zn(OAc)$_2$** | | | | | | |
| Zinc ester linkage | Zn(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Zn(28) | 120.000 | 120.000 |
| Isoniazid nitrogen | C(3)-N(4) | 1.351 | 1.358 | C(3)-N(27)-O(40) | 120.000 | 120.000 |
| Methyl group (hydrazide) | C(3)-C(27) | 1.497 | 1.497 | C(27)-C(3)-C(2) | 120.000 | 121.400 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Zn(39)-N(8) | 109.500 | 108.115 |
| **HBD-OCMCS-Zn(OAc)$_2$** | | | | | | |
| Zinc ester linkage | Zn(28)-O(49) | 1.810 | 1.810 | C(47)-O(45)-Zn(28) | 120.000 | 120.000 |
| Free amine at hydrazide | C(3)-N(28) | 1.266 | 1.462 | C(4)-C(3)-N(28) | 120.000 | 120.000 |
| Zinc-imine linkage | N(17)-Zn(39) | 1.836 | 1.842 | O(50)-Zn(39)-N(17) | 89.999 | 91.050 |
| Hydrazone linkage | N(17)-N(19) | 1.352 | 1.356 | H(69)-N(19)-N(17) | 128.000 | 126.300 |
| Imine linkage | N(8)-C(13) | 1.647 | 1.438 | N(13)-Zn(39)-N(8) | 109.500 | 108.115 |

**S.table 6c.** Selected bond length and bond angle of prepared Schiff base zinc (II) metal complexes.