Electronic supporting information (ESI)

# Heterocyclic-2-thione derivatives of metals incorporating cyclopalladated azobenzenes of variable nuclearity and N, S-bridged 1D polymer of [bis(pyridine-2-thiolato)mercury(II)]

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Ψ Deceased (dated April 13, 2021)

1S. X-ray structures

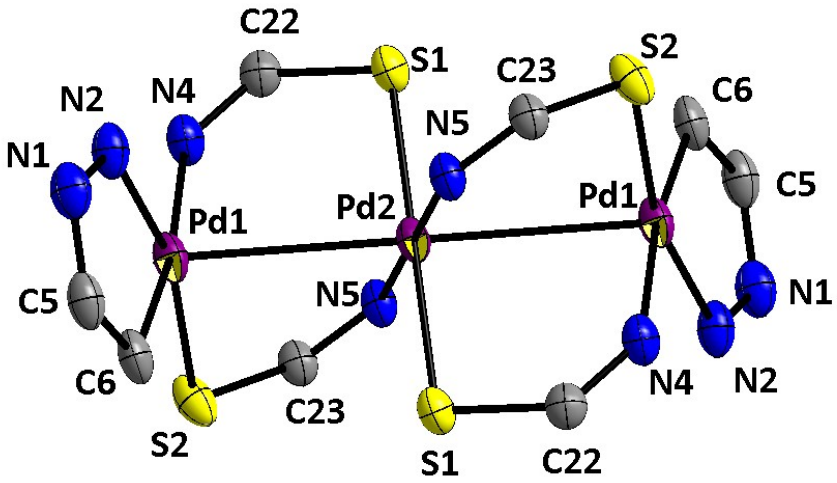


Fig.S1. Structure of trinuclear cluster **4.**

2S.UV-visible spectra (Fig. S2, S3 and S4)

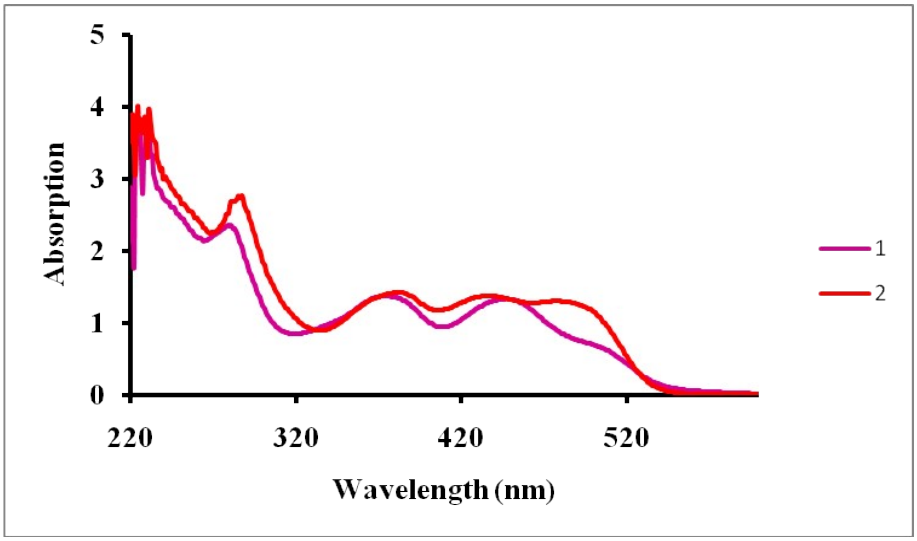


**Fig. S2**. UV-visible absorption spectra of **1** and **2** in $10^{-4}$ M solution in $CH_2Cl_2$ solvent

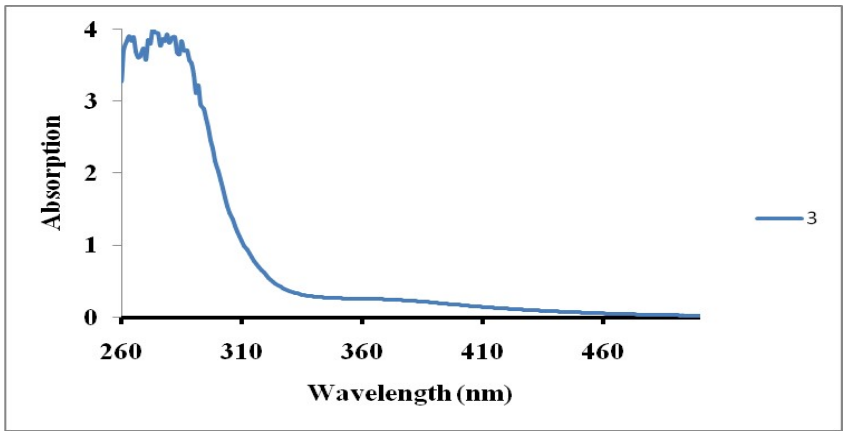


**Fig. S3.** UV-visible absorption spectrum of **3** in $10^{-5}$ M solution in DMSO solvent

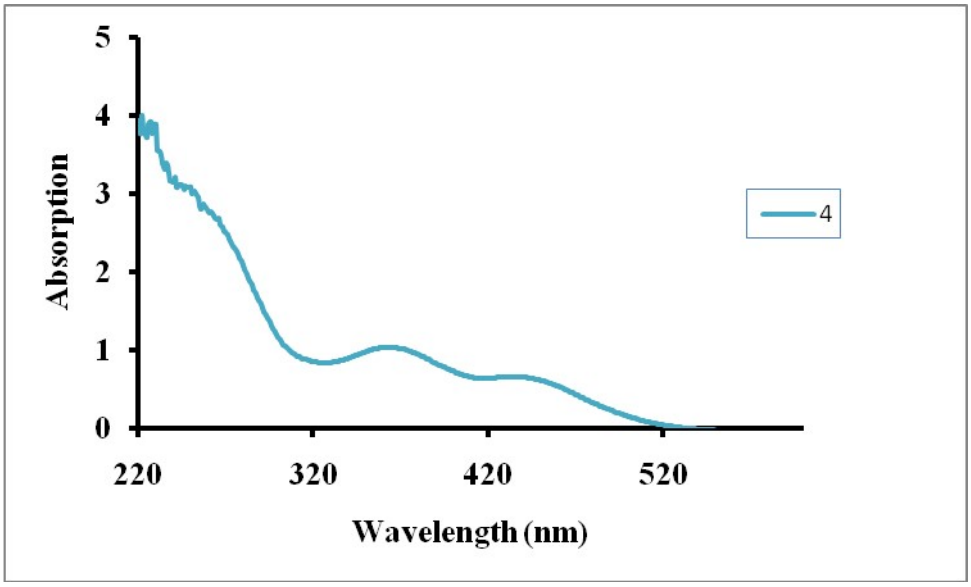


Fig. S4. Electronic absorption spectrum of complex **4**

**2S. NMR spectra**

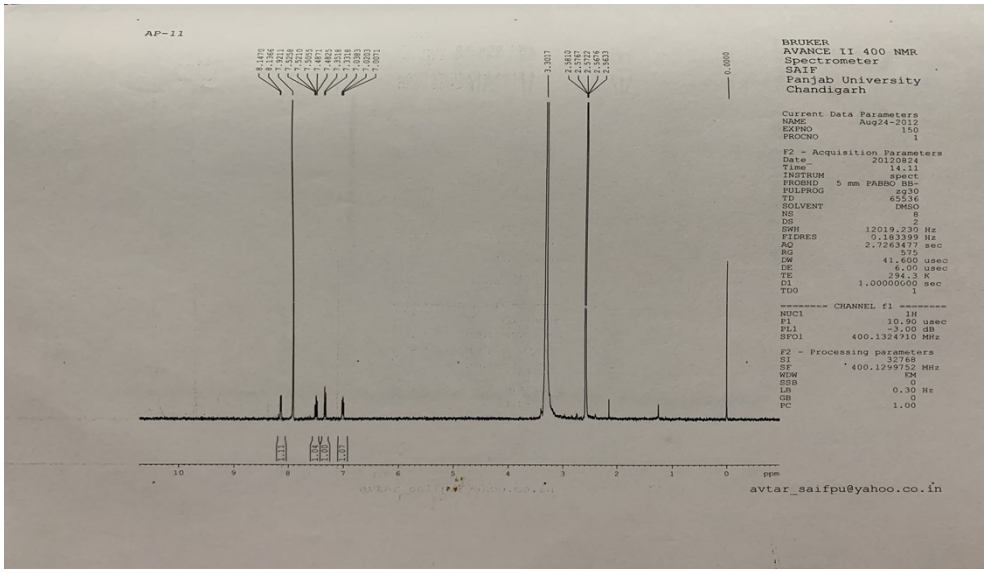


Fig. S5. Proton NMR of Hg complex **5**

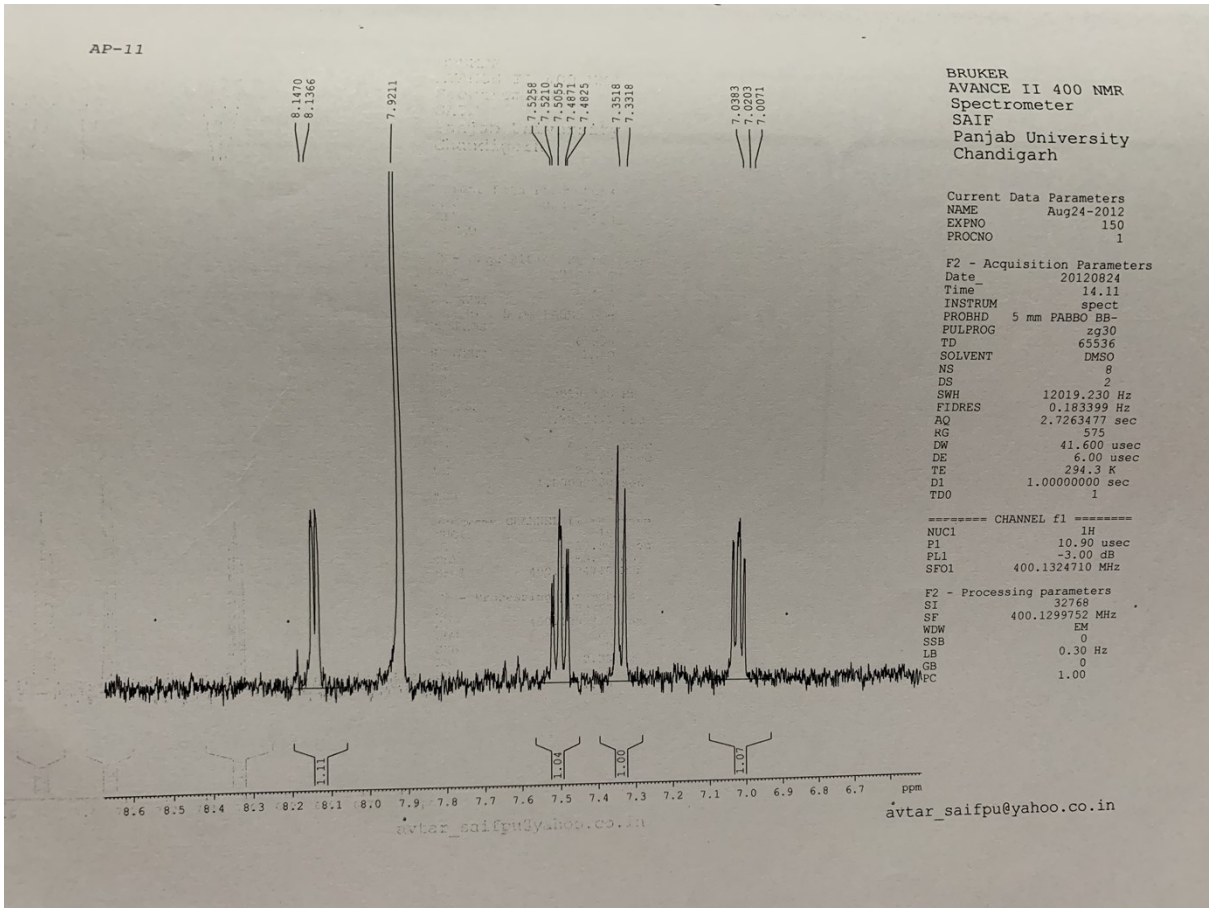


Fig. S6. Expanded Proton NMR spectrum of Hg complex **5**

3S. Bond parameters

**Table S1.** Selected bond distances (Å) and angles (°) of compounds (**1-5**)

| **Compound 1** | | | | | |
|---|---|---|---|---|---|
| Pd1-S1 | 2.294(2) | Pd1-N1 | 2.093(5) | Pd1-N3 | 2.157(6) |
| Pd1-C2 | 1.975(7) | Pd1-Pd1 | 2.876(1) | S1- C21 | 1.741(7) |
| N1-N2 | 1.277(8) | C4-O1 | 1.374(9) | C12-O2 | 1.376(8) |
| N1-Pd1-S1 | 170.1(2) | C2-Pd1-N3 | 177.8(2) | N3-Pd1-S1 | 89.8(2) |
| C2-Pd1-S1 | 91.4(2) | C2-Pd1-N1 | 79.0(2) | N1-Pd1-N3 | 99.8(2) |
| **Compound 2** | | | | | |
| Pd1-S1 | 2.2920(7) | Pd1-N1 | 2.082(2) | S1- C19 | 1.735(3) |
| Pd1-C7 | 1.970(3) | Pd1-Pd1 | 2.8527(4) | N1-N2 | 1.280(3) |
| Pd1-N3 | 2.154(2) | O1-C4 | 1.366(3) | | |
| N1-Pd1-S1 | 170.05(6) | C7-Pd1-N3 | 177.2(1) | C7-Pd1-S1 | 91.84(8) |

| | | | | | |
|---|---|---|---|---|---|
| N3-Pd1-S1 | 89.78(6) | N1-Pd1-N3 | 99.77(9) | C7-Pd1-N1 | 78.74(10) |
| **Compound 3** | | | | | |
| Pd1-S1 | 2.3012(7) | Pd1-Cl1 | 2.3977(7) | Pd1-C1 | 1.994(2) |
| Pd1-N2 | 2.062(2) | C13-S1 | 1.717(3) | N1-N2 | 1.269(3) |
| N2-Pd1-S1 | 165.43(6) | Cl1-Pd1-C1 | 170.46(9) | Cl1-Pd1-S1 | 101.45(3) |
| Cl1-Pd1-N2 | 92.93(6) | N2-Pd1-C1 | 78.80(10) | C1-Pd1-S1 | 86.67(8) |
| **Compound 4** | | | | | |
| Pd1-C6 | 1.973(3) | Pd1-S2 | 2.298(1) | Pd1-N2 | 2.061(3) |
| Pd1-N2 | 2.061(3) | Pd2 – Pd1 | 3.0432(7) | Pd2-S1 | 2.3296(11) |
| Pd2-N5 | 2.023(2) | N1-N2 | 1.273(4) | C1-O1 | 1.439(9) |
| C22-S1 | 1.723(3) | C23-S2 | 1.722(3) | | |
| S2-Pd1-N4 | 94.27(8) | S2-Pd1-C6 | 91.22(11) | C6-Pd1-N4 | 171.19(12) |
| N2-Pd1-N4 | 94.12(11) | N2-Pd1-C6 | 79.5(14) | N2-Pd1-S2 | 164.67(84) |
| N5-Pd2-N5* | 180.0 | S1-Pd2-S1* | 180.0 | N5-Pd2-S1 | 88.18(8) |
| N5-Pd2-S1* | 91.82(8) | N5*-Pd2-S1* | 88.18(8) | N5*-Pd2-S1 | 91.82(8) |
| **Compound 5** | | | | | |
| Hg1-S1,S* | 2.3533(19) | S1-C1 | 1.927(5) | S1-Hg1-S1* | 111.4(1) |
| Hg1-S1-C1 | 106.39(15) | S1-C1-C2 | 94.1(3) | S1-C1-N1 | 128.8(3) |
| All pyridyl ring angles | 120.0 | | | | |

* -x,y,-z