# Supporting Information

## Structural and insights into the coordination chemistry and reactivity of a 3,3′-*bis*-imine-2,2′-bipyridine ligand

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## Contents

# S-1 Synthesis

**N3,N3′-di-2-hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-diamine (L8)[1]**

Salicylaldehyde (5.81 g, 47 mmol) was added dropwise to a solution of 3,3′-diamino-2,2′-bipyridine **L1** (4.04 g, 21 mmol) in MeOH (160 mL). The resulting yellow mixture was stirred overnight at room temperature, after which time a yellow solid was isolated by filtration. The precipitate was washed with MeOH (3 × 20 mL) and $Et_2O$ (3 × 20 mL) and dried in air. An additional crop of the ligand was obtained by evaporating the filtrate to dryness, affording an additional 2.43 g of the ligand. Combined yield: 7.54 g (88 %). Single crystals suitable for X-ray diffraction were obtained *via* the slow evaporation of a saturated DCM solution, m.p. 213 °C (Lit. 207.5 – 208.5°C)[1b]; $^1$H NMR (600 MHz, $CDCl_3$): $\delta_H$ = 12.11 (2H, s, O*H*), 8.67 (2H, dd, *J* = 4.7, 1.5 Hz, *o*-py, H1 & H10), 8.45 (2H, s, *H*C=N, H11 & H18), 7.57 (2H, dd, *J* = 8.2, 1.5 Hz, *p*-py, H3 & H8), 7.41 (2H, dd, *J* = 8.2, 4.7 Hz, *m*-py, H2 & H9), 7.26 (2H, ddd, *J* = 8.5, 7.1, 1.6 Hz, H15 & H22), 7.05 (2H, dd, *J* = 7.7, 1.6 Hz, H17 & H24), 6.82 (2H, dd, *J* = 8.5, 1.1 Hz, H14 & H21), 6.76 (2H, ddd, *J* = 7.7, 7.1, 1.1 Hz, H16 & H23); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta_C$ = 164.7 (C11 & C18), 160.7 (C13 & C20), 151.7 (C5 & C6), 148.1 (C1 & C10), 143.4 (C4 & C7), 133.7 (C15 & C22), 132.6 (C17 & C24), 126.0 (C3 & C8), 124.6 (C2 & C9), 119.2 (C12 & C19), 119.0 (C14 & C21), 117.1 (C16 & C23); FT-IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3448, 3055, 1612, 1567, 1492, 1419, 1398, 1365, 1278, 1145, 908, 761; UV/Vis (MeCN, nm; $\varepsilon/M^{-1}\cdot cm^{-1}$) $\lambda_{max}$ = 279 (30800), 346 (19510); MS (FAB) *m*/*z* = 395 ($[M+H]^+$, 100%), 394 ($[M]^+$, 35%); Elemental analysis: calc for $C_{22}H_{16}N_4O_2$: C 72.50%, H 4.43%, N 23.07%; found C 71.97%, H 4.43%, N 23.43%.

## S-2 Tables of Bond Lengths and Angles

### Ligand L8 - Selected geometric parameters (Å, º)

| Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|
| N1—C1 | 1.334 (2) | C8—C9 | 1.380 (2) |
| N1—C5 | 1.347 (2) | C9—C10 | 1.387 (2) |
| N2—C10 | 1.340 (2) | C11—C12 | 1.448 (2) |
| N2—C6 | 1.346 (2) | C12—C17 | 1.402 (2) |
| N3—C11 | 1.291 (2) | C12—C13 | 1.415 (2) |
| N3—C4 | 1.418 (2) | C13—C14 | 1.399 (2) |
| N4—C18 | 1.287 (2) | C14—C15 | 1.383 (3) |
| N4—C7 | 1.420 (2) | C15—C16 | 1.389 (3) |
| O1—C13 | 1.355 (2) | C16—C17 | 1.384 (2) |
| O2—C20 | 1.355 (2) | C18—C19 | 1.448 (2) |
| C1—C2 | 1.391 (3) | C19—C24 | 1.401 (2) |
| C2—C3 | 1.378 (3) | C19—C20 | 1.414 (3) |
| C3—C4 | 1.401 (2) | C20—C21 | 1.396 (3) |
| C4—C5 | 1.403 (2) | C21—C22 | 1.385 (3) |
| C5—C6 | 1.498 (2) | C22—C23 | 1.387 (3) |
| C6—C7 | 1.397 (2) | C23—C24 | 1.380 (2) |
| C7—C8 | 1.396 (2) | | |

| Bond | Angle (°) | Bond | Angle (°) |
|---|---|---|---|
| C1—N1—C5 | 117.29 (15) | C17—C12—C13 | 118.58 (16) |
| C10—N2—C6 | 116.86 (15) | C17—C12—C11 | 119.18 (16) |
| C11—N3—C4 | 120.65 (15) | C13—C12—C11 | 122.23 (16) |
| C18—N4—C7 | 122.37 (15) | O1—C13—C14 | 118.84 (16) |
| C13—O1—H1A | 109.5 | O1—C13—C12 | 121.81 (15) |
| C20—O2—H2A | 109.5 | C14—C13—C12 | 119.34 (16) |
| N1—C1—C2 | 123.49 (16) | C15—C14—C13 | 120.27 (17) |
| N1—C1—H1 | 118.3 | C15—C14—H14 | 119.9 |
| C2—C1—H1 | 118.3 | C13—C14—H14 | 119.9 |
| C3—C2—C1 | 119.07 (17) | C14—C15—C16 | 121.28 (17) |
| C3—C2—H2 | 120.5 | C14—C15—H15 | 119.4 |
| C1—C2—H2 | 120.5 | C16—C15—H15 | 119.4 |
| C2—C3—C4 | 119.01 (16) | C17—C16—C15 | 118.70 (16) |
| C2—C3—H3 | 120.5 | C17—C16—H16 | 120.6 |
| C4—C3—H3 | 120.5 | C15—C16—H16 | 120.6 |
| C3—C4—C5 | 117.57 (16) | C16—C17—C12 | 121.77 (17) |
| C3—C4—N3 | 125.76 (15) | C16—C17—H17 | 119.1 |
| C5—C4—N3 | 116.63 (15) | C12—C17—H17 | 119.1 |
| N1—C5—C4 | 123.52 (16) | N4—C18—C19 | 120.80 (16) |
| N1—C5—C6 | 115.51 (15) | N4—C18—H18 | 119.6 |
| C4—C5—C6 | 120.96 (15) | C19—C18—H18 | 119.6 |
| N2—C6—C7 | 123.68 (16) | C24—C19—C20 | 118.94 (16) |

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|---|---|---|---|
| N2—C6—C5 | 115.91 (15) | C24—C19—C18 | 119.34 (16) |
| C7—C6—C5 | 120.39 (14) | C20—C19—C18 | 121.70 (16) |
| C8—C7—C6 | 117.93 (15) | O2—C20—C21 | 118.87 (17) |
| C8—C7—N4 | 125.71 (15) | O2—C20—C19 | 121.73 (16) |
| C6—C7—N4 | 116.29 (15) | C21—C20—C19 | 119.40 (17) |
| C9—C8—C7 | 118.88 (17) | C22—C21—C20 | 120.06 (18) |
| C9—C8—H8 | 120.6 | C22—C21—H21 | 120.0 |
| C7—C8—H8 | 120.6 | C20—C21—H21 | 120.0 |
| C8—C9—C10 | 118.95 (17) | C21—C22—C23 | 121.10 (17) |
| C8—C9—H9 | 120.5 | C21—C22—H22 | 119.4 |
| C10—C9—H9 | 120.5 | C23—C22—H22 | 119.4 |
| N2—C10—C9 | 123.69 (16) | C24—C23—C22 | 119.26 (18) |
| N2—C10—H10 | 118.2 | C24—C23—H23 | 120.4 |
| C9—C10—H10 | 118.2 | C22—C23—H23 | 120.4 |
| N3—C11—C12 | 121.95 (16) | C23—C24—C19 | 121.23 (18) |
| N3—C11—H11 | 119.0 | C23—C24—H24 | 119.4 |
| C12—C11—H11 | 119.0 | C19—C24—H24 | 119.4 |

## Complex 1 - Selected geometric parameters (Å, º)

| Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|
| Sn1—N2 | 2.191 (4) | C2—C3 | 1.354 (8) |
| Sn1—N1 | 2.205 (4) | C3—C4 | 1.416 (8) |
| Sn1—Cl1 | 2.3720 (16) | C4—C5 | 1.421 (7) |
| Sn1—Cl4 | 2.3771 (15) | C5—C6 | 1.479 (7) |
| Sn1—Cl2 | 2.4020 (14) | C6—C7 | 1.416 (7) |
| Sn1—Cl3 | 2.4316 (14) | C7—C8 | 1.409 (8) |
| O1—C13 | 1.360 (7) | C8—C9 | 1.355 (8) |
| O2—C18 | 1.421 (8) | C9—C10 | 1.382 (8) |
| O3—C20A | 1.416 (5) | C11—C12 | 1.515 (7) |
| O3—C20B | 1.422 (5) | C12—C13 | 1.391 (8) |
| N1—C1 | 1.324 (7) | C12—C17 | 1.401 (8) |
| N1—C5 | 1.372 (7) | C13—C14 | 1.403 (8) |
| N2—C10 | 1.335 (7) | C14—C15 | 1.363 (9) |
| N2—C6 | 1.373 (6) | C15—C16 | 1.384 (10) |
| N3—C4 | 1.364 (7) | C16—C17 | 1.380 (8) |
| N3—C11 | 1.435 (7) | C18—C19 | 1.501 (11) |
| N4—C7 | 1.373 (7) | C20A—C21 | 1.497 (5) |
| N4—C11 | 1.450 (7) | C20B—C21 | 1.499 (5) |
| C1—C2 | 1.392 (8) | | |

| Bond | Angle (°) | Bond | Angle (°) |
|---|---|---|---|
| N2—Sn1—N1 | 74.02 (17) | N1—C5—C4 | 117.2 (5) |
| N2—Sn1—Cl1 | 168.55 (12) | N1—C5—C6 | 114.7 (4) |
| N1—Sn1—Cl1 | 94.99 (12) | C4—C5—C6 | 128.0 (5) |

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|---|---|---|---|
| N2—Sn1—Cl4 | 95.61 (12) | N2—C6—C7 | 117.7 (5) |
| N1—Sn1—Cl4 | 169.47 (12) | N2—C6—C5 | 115.5 (4) |
| Cl1—Sn1—Cl4 | 95.46 (6) | C7—C6—C5 | 126.6 (5) |
| N2—Sn1—Cl2 | 88.11 (12) | N4—C7—C8 | 118.6 (5) |
| N1—Sn1—Cl2 | 86.01 (12) | N4—C7—C6 | 123.5 (5) |
| Cl1—Sn1—Cl2 | 94.44 (6) | C8—C7—C6 | 117.8 (5) |
| Cl4—Sn1—Cl2 | 91.87 (5) | C9—C8—C7 | 122.0 (5) |
| N2—Sn1—Cl3 | 85.28 (12) | C8—C9—C10 | 118.3 (5) |
| N1—Sn1—Cl3 | 89.76 (12) | N2—C10—C9 | 121.2 (5) |
| Cl1—Sn1—Cl3 | 91.56 (6) | N3—C11—N4 | 111.1 (4) |
| Cl4—Sn1—Cl3 | 91.27 (5) | N3—C11—C12 | 111.0 (4) |
| Cl2—Sn1—Cl3 | 172.93 (5) | N4—C11—C12 | 108.7 (4) |
| C20A—O3—C20B | 50.3 (10) | C13—C12—C17 | 119.3 (5) |
| C1—N1—C5 | 123.5 (5) | C13—C12—C11 | 119.5 (5) |
| C1—N1—Sn1 | 119.4 (4) | C17—C12—C11 | 121.1 (5) |
| C5—N1—Sn1 | 116.7 (3) | O1—C13—C12 | 117.7 (5) |
| C10—N2—C6 | 122.7 (5) | O1—C13—C14 | 122.4 (5) |
| C10—N2—Sn1 | 119.9 (3) | C12—C13—C14 | 119.8 (5) |
| C6—N2—Sn1 | 117.3 (3) | C15—C14—C13 | 119.5 (6) |
| C4—N3—C11 | 122.4 (4) | C14—C15—C16 | 121.5 (6) |
| C7—N4—C11 | 118.7 (4) | C17—C16—C15 | 119.4 (6) |
| N1—C1—C2 | 121.1 (5) | C16—C17—C12 | 120.4 (6) |
| C3—C2—C1 | 118.2 (5) | O2—C18—C19 | 107.0 (6) |
| C2—C3—C4 | 121.7 (5) | O3—C20A—C21 | 111.9 (10) |
| N3—C4—C3 | 116.7 (5) | O3—C20B—C21 | 111.5 (10) |
| N3—C4—C5 | 125.1 (5) | C20A—C21—C20B | 47.4 (10) |
| C3—C4—C5 | 118.2 (5) | | |

## Complex 2 – Selected geometric parameters (Å, º)

| Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|
| Cu1 -O2 | 1.946(2) | N2 -C10 | 1.328(3) |
| Cu1 -O3 | 1.9142(18) | N3 -C11 | 1.452(3) |
| Cu1 -N1 | 1.964(2) | N3 -C4 | 1.370(3) |
| Cu1 -N2 | 1.977(2) | N4 -C7 | 1.372(3) |
| Cu1 -O3_c | 2.4949(19) | N4 -C11 | 1.451(3) |
| Cl2 -O8 | 1.459(4) | C1-C2 | 1.390(4) |
| Cl2 -O9 | 1.396(4) | C2 -C3 | 1.361(4) |
| Cl2 -O10 | 1.402(5) | C3 -C4 | 1.409(4) |
| Cl2 -O11 | 1.430(4) | N3 -H31 | 0.849(6) |
| Cl2 -O30 | 0.876(5) | C4 -C5 | 1.407(3) |
| Cl2 -C30 | 0.891(9) | N4 -H41 | 0.85(2) |
| Cl2 -H30 | 1.3200 | C5 -C6 | 1.479(3) |
| Cl2-H30A | 1.3000 | C6 -C7 | 1.408(4) |
| Cl2-H30B | 1.3600 | C7 -C8 | 1.411(4) |
| Cl1 -O5 | 1.498(4) | O8 -O8_b | 1.275(5) |

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|---|---|---|---|
| Cl1 -O7 | 1.441(4) | C8 -C9 | 1.371(4) |
| Cl1 -O5_a | 1.498(4) | O9 -C30 | 0.884(10) |
| Cl1 -O7_a | 1.441(4) | C9 -C10 | 1.388(4) |
| Cl1 -O4 | 1.429(3) | O10 -O30 | 0.924(8) |
| `Cl1 -O6 | 1.361(5) | O10 -C30 | 1.457(10) |
| Cl1-O6_a | 1.361(5) | O11-O30 | 1.433(7) |
| O1 -C17 | 1.374(3) | C11 -C12 | 1.514(4) |
| O2 -C24 | 1.245(3) | C12 -C13 | 1.387(4) |
| O3 -C18 | 1.315(3) | C12 -C17 | 1.393(4) |
| N1 -C5 | 1.367(3) | C13 -C14 | 1.382(4) |
| N1 -C1 | 1.330(3) | C14 -C15 | 1.384(4) |
| O1 -H111 | 0.8400 | C15-C16 | 1.383(4) |
| N2 -C6 | 1.368(3) | C16 -C17 | 1.389(4) |
| C18-C19 | 1.404(4) | C18-C23 | 1.417(4) |
| C19-C20 | 1.371(4) | C20 -C21 | 1.401(4) |
| C21 -C22 | 1.360(4) | C22-C23 | 1.422(4) |
| C23 -C24 | 1.418(4) | O30 -C30 | 1.447(10) |

| **Bond** | **Angle (°)** | **Bond** | **Angle (°)** |
|---|---|---|---|
| O4 -Cl1-O6 | 112.4(3) | C4-N3-H31 | 112(2) |
| O6 -Cl1-O7 | 49.3(3) | C7-N4-H41 | 115.7(18) |
| O5_a -Cl1 -O6 | 111.4(3) | C11-N4-H41 | 115.4(17) |
| O4-Cl1-O6_a | 112.4(3) | C3-C4 -C5 | 118.0(2) |
| O6_a-Cl1-O7_a | 49.3(3) | N3-C4-C5 | 123.5(2) |
| O7-Cl1-O7_a | 138.0(3) | N3-C4-C3 | 118.4(2) |
| O4-Cl1-O7 | 111.02(18) | C4-C5-C6 | 127.2(2) |
| O5_a -Cl1-O7 | 64.2(2) | N1-C5-C4 | 119.2(2) |
| O6_a-Cl1-O7 | 112.2(3) | N1-C5-C6 | 113.4(2) |
| O4-Cl1-O5_a | 104.67(18) | C5-C6-C7 | 128.4(2) |
| O5_a-Cl1-O7_a | 104.7(2) | N2-C6-C5 | 112.7(2) |
| Cu1-O2-C24 | 125.65(18) | N2-C6 -C7 | 118.9(2) |
| Cu1_c -O3-C18 | 104.24(15) | C6-C7-C8 | 118.1(2) |
| Cu1-O3-Cu1_c | 99.10(8) | N4 -C7-C6 | 125.2(2) |
| Cu1-O3-C18 | 126.01(17) | N4-C7-C8 | 116.8(2) |
| Cu1-N1-C5 | 116.26(16) | Cl2-O8-O8_b | 146.5(4) |
| C1-N1-C5 | 121.6(2) | C7-C8 -C9 | 120.7(3) |
| C17-O1-H111 | 109.00 | Cl2-O9-C30 | 38.3(6) |
| Cu1-N1-C1 | 122.18(18) | C8-C9-C10 | 118.9(2) |
| C6 -N2-C10 | 122.2(2) | N2-C10-C9 | 121.1(2) |
| Cu1-N2-C10 | 121.68(17) | O30-O10-C30 | 70.9(5) |
| Cu1-N2-C6 | 116.02(16) | Cl2-O10-O30 | 37.6(4) |
| C4-N3-C11 | 120.4(2) | Cl2-O10-C30 | 36.3(4) |
| C7-N4-C11 | 122.7(2) | N4-C11-C12 | 109.7(2) |
| N1-C1-C2 | 121.5(3) | N3-C11-N4 | 110.3(2) |
| C1-C2-C3 | 118.7(3) | Cl2-O11-O30 | 35.6(2) |
| C11-N3-H31 | 117(2) | N3-C11-C12 | 109.4(2) |
| C2-C3-C4 | 121.0(2) | C11-C12-C17 | 120.8(2) |

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|---|---|---|---|
| C13-C12-C17 | 118.1(2) | C3-C2-H2 | 121.00 |
| C11-C12-C13 | 121.0(2) | C1-C2-H2 | 121.00 |
| C12-C13-C14 | 121.8(3) | C2-C3-H3 | 120.00 |
| C13-C14-C15 | 119.5(3) | C4-C3-H3 | 119.00 |
| C14-C15-C16 | 119.8(3) | C9 -C8-H8 | 120.00 |
| C15-C16-C17 | 120.4(3) | O8_b-O8-H30 | 94.00 |
| O1-C17-C12 | 117.8(2) | Cl2-O8-H30 | 57.00 |
| O1-C17-C16 | 121.8(2) | C7-C8-H8 | 120.00 |
| C12-C17-C16 | 120.5(3) | H30A-O9-H30B | 131.00 |
| O3 -C18 -C23 | 122.9(2) | Cl2-O9-H30B | 65.00 |
| C19-C18-C23 | 118.1(2) | C8-C9-H9 | 121.00 |
| O3-C18-C19 | 119.0(2) | C30-O9-H30B | 58.00 |
| C18-C19-C20 | 120.6(3) | Cl2-O9-H30A | 68.00 |
| C19-C20-C21 | 121.8(2) | C10-C9-H9 | 121.00 |
| C20-C21-C22 | 118.9(3) | C30-O9-H30A | 78.00 |
| C21-C22-C23 | 121.0(3) | C9-C10-H10 | 119.00 |
| C18-C23-C22 | 119.6(2) | N2-C10-H10 | 119.00 |
| C18 -C23 -C24 | 22.4(2) | N4-C11-H11 | 109.00 |
| C22-C23-C24 | 118.0(2) | C12 -C11-H11 | 109.00 |
| O2 -C24 -C23 | 127.0(3) | N3-C11-H11 | 109.00 |
| O10 -O30 -O11 | 149.5(5) | C12-C13-H13 | 119.00 |
| Cl2-O30 -C30 | 35.4(4) | C14 -C13-H13 | 119.00 |
| O11-O30 -C30 | 90.0(5) | C15-C14-H14 | 120.00 |
| Cl2-O30 -O11 | 72.0(4) | C13-C14-H14 | 120.00 |
| Cl2-O30 -O10 | 102.3(6) | C14-C15-H15 | 120.00 |
| O10-O30 -C30 | 72.0(5) | C16-C15-H15 | 120.00 |
| C2-C1-H1 | 119.00 | C17-C16-H16 | 120.00 |
| N1-C1-H1 | 119.00 | C15-C16-H16 | 120.00 |
| C20 -C19-H19 | 120.00 | O5_a-O7-O6 | 118.8(4) |
| C18-C19-H19 | 120.00 | O9 -C30-O30 | 137.1(9) |
| C21-C20-H20 | 119.00 | Cl2-C30-O9 | 103.7(9) |
| C19-C20-H20 | 119.00 | Cl2-C30-O10 | 68.5(6) |
| C20-C21-H21 | 121.00 | Cl2-C30-O30 | 34.7(4) |
| C22-C21-H21 | 121.00 | O9-C30-O10 | 169.6(10) |
| C21-C22-H22 | 119.00 | O10 -C30-O30 | 37.1(4) |
| C23-C22-H22 | 120.00 | H30B-C30-H30C | 109.00 |
| C23-C24-H24 | 117.00 | Cl2-C30-H30A | 88.00 |
| O2-C24-H24 | 116.00 | Cl2-C30-H30B | 93.00 |
| O10-O30-H30 | 112.00 | Cl2-C30-H30C | 144.00 |
| C30 -O30-H30 | 122.00 | O9 -C30-H30A | 40.00 |
| Cl2-O30 -H30 | 94.00 | O9-C30 -H30B | 73.00 |
| O11-O30-H30 | 98.00 | O9-C30-H30C | 110.00 |
| Cl1-O5-O7_a | 56.1(2) | O10-C30-H30A | 143.00 |
| Cl1-O5 -O6 | 56.8(3) | O10-C30-H30B | 100.00 |
| O6-O5-O7_a | 105.7(4) | O10-C30-H30C | 80.00 |
| O5-O6 -O7 | 134.4(5) | O30-C30 -H30A | 110.00 |
| Cl1-O6 -O7 | 68.9(4) | O30-C30-H30B | 109.00 |
| Cl1-O6 -O5 | 67.1(3) | O30-C30-H30C | 109.00 |

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|---|---|---|---|
| Cl1-O7-O6 | 61.8(3) | H30A-C30-H30B | 109.00 |

Symmetry code(s):
a =[ 3566.00] = [ 3_566] =x,3/2-y,3/2-z
b =[ 2565.00] = [ 2_565] =1/2-x,1-y,z
c =[ 5567.00] = [ 5_567] =-x,1-y,2-z

## Complex 3 – Selected geometric parameters (Å, º)

| Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|
| Mn1—N1 | 2.1999 (16) | C1—C2 | 1.390 (3) |
| Mn1—N2 | 2.2177 (15) | C2—C3 | 1.371 (3) |
| Mn1—O3 | 2.3427 (14) | C3—C4 | 1.402 (2) |
| Mn1—Cl3 | 2.5218 (5) | C4—C5 | 1.410 (2) |
| Mn1—Cl2 | 2.5343 (6) | C5—C6 | 1.499 (2) |
| Mn1—Cl3$^{i}$ | 2.5359 (5) | C6—C7 | 1.419 (2) |
| Cl3—Mn1$^{i}$ | 2.5359 (5) | C7—C8 | 1.409 (3) |
| O2—C13 | 1.368 (2) | C8—C9 | 1.367 (3) |
| O3—C101 | 1.424 (3) | C9—C10 | 1.391 (3) |
| O3—C201 | 1.442 (5) | C11—C12 | 1.508 (3) |
| N1—C1 | 1.333 (2) | C12—C17 | 1.392 (3) |
| N1—C5 | 1.366 (2) | C12—C13 | 1.394 (3) |
| N2—C10 | 1.326 (2) | C13—C14 | 1.390 (3) |
| N2—C6 | 1.364 (2) | C14—C15 | 1.379 (3) |
| N3—C4 | 1.374 (2) | C15—C16 | 1.387 (3) |
| N3—C11 | 1.454 (2) | C16—C17 | 1.384 (3) |
| N4—C7 | 1.372 (2) | C101—C102 | 1.507 (3) |
| N4—C11 | 1.446 (2) | C201—C202 | 1.515 (5) |

| Bond | Angle (°) | Bond | Angle (°) |
|---|---|---|---|
| N1—Mn1—N2 | 72.11 (6) | N3—C4—C3 | 118.74 (16) |
| N1—Mn1—O3 | 84.83 (5) | N3—C4—C5 | 122.66 (16) |
| N2—Mn1—O3 | 94.77 (5) | C3—C4—C5 | 118.57 (16) |
| N1—Mn1—Cl3 | 159.21 (4) | N1—C5—C4 | 119.22 (16) |
| N2—Mn1—Cl3 | 95.88 (4) | N1—C5—C6 | 114.37 (15) |
| O3—Mn1—Cl3 | 79.22 (4) | C4—C5—C6 | 125.96 (16) |
| N1—Mn1—Cl2 | 101.95 (4) | N2—C6—C7 | 118.75 (16) |
| N2—Mn1—Cl2 | 91.20 (4) | N2—C6—C5 | 113.02 (15) |
| O3—Mn1—Cl2 | 172.10 (4) | C7—C6—C5 | 128.08 (16) |
| Cl3—Mn1—Cl2 | 95.060 (19) | N4—C7—C8 | 116.78 (16) |
| N1—Mn1—Cl3$^{i}$ | 99.41 (4) | N4—C7—C6 | 125.50 (17) |
| N2—Mn1—Cl3$^{i}$ | 171.41 (4) | C8—C7—C6 | 117.71 (17) |

| | | | |
|---|---|---|---|
| O3—Mn1—Cl3$^{i}$ | 85.61 (4) | C9—C8—C7 | 121.36 (17) |
| Cl3—Mn1—Cl3$^{i}$ | 92.622 (16) | C8—C9—C10 | 118.09 (18) |
| Cl2—Mn1—Cl3$^{i}$ | 89.253 (18) | N2—C10—C9 | 121.72 (17) |
| Mn1—Cl3—Mn1$^{i}$ | 87.378 (16) | N4—C11—N3 | 109.87 (15) |
| C101—O3—C201 | 32.9 (3) | N4—C11—C12 | 110.50 (15) |
| C101—O3—Mn1 | 133.45 (14) | N3—C11—C12 | 110.47 (15) |
| C201—O3—Mn1 | 121.3 (5) | C17—C12—C13 | 119.01 (18) |
| C1—N1—C5 | 121.04 (16) | C17—C12—C11 | 121.45 (17) |
| C1—N1—Mn1 | 119.56 (12) | C13—C12—C11 | 119.52 (17) |
| C5—N1—Mn1 | 119.30 (12) | O2—C13—C14 | 121.55 (17) |
| C10—N2—C6 | 122.08 (16) | O2—C13—C12 | 118.55 (17) |
| C10—N2—Mn1 | 118.75 (12) | C14—C13—C12 | 119.90 (18) |
| C6—N2—Mn1 | 118.93 (12) | C15—C14—C13 | 120.26 (19) |
| C4—N3—C11 | 118.61 (15) | C14—C15—C16 | 120.48 (19) |
| C7—N4—C11 | 121.15 (16) | C17—C16—C15 | 119.23 (19) |
| N1—C1—C2 | 122.08 (17) | C16—C17—C12 | 121.06 (19) |
| C3—C2—C1 | 118.29 (17) | O3—C101—C102 | 111.1 (2) |
| C2—C3—C4 | 120.60 (17) | O3—C201—C202 | 108.9 (5) |

Symmetry code(s): (i) −*x*+2, −*y*−1, −*z*+1.

## Complex 4 – Selected geometric parameters (Å, º)

| Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|
| Fe1—O1$^{i}$ | 1.8704 (13) | C3—C4 | 1.377 (3) |
| Fe1—O1 | 1.8704 (13) | C4—C5 | 1.404 (3) |
| Fe1—N3$^{i}$ | 1.9279 (17) | C5—C6 | 1.480 (3) |
| Fe1—N3 | 1.9279 (17) | C6—C7 | 1.416 (3) |
| Fe1—N2 | 1.9865 (17) | C7—C8 | 1.403 (3) |
| Fe1—N2$^{i}$ | 1.9865 (17) | C8—C9 | 1.366 (3) |
| O1—C17 | 1.315 (2) | C9—C10 | 1.384 (3) |
| N1—C1 | 1.337 (3) | C11—C12 | 1.430 (3) |
| N1—C5 | 1.349 (3) | C12—C13 | 1.412 (3) |
| N2—C10 | 1.338 (3) | C12—C17 | 1.420 (3) |
| N2—C6 | 1.365 (3) | C13—C14 | 1.372 (3) |
| N3—C11 | 1.295 (3) | C14—C15 | 1.396 (3) |
| N3—C4 | 1.422 (3) | C15—C16 | 1.378 (3) |
| N4—C7 | 1.364 (3) | C16—C17 | 1.406 (3) |
| C1—C2 | 1.371 (3) | N5—C18 | 1.129 (3) |
| C2—C3 | 1.386 (3) | C18—C19 | 1.459 (4) |

| Bond | Angle (°) | Bond | Angle (°) |
|---|---|---|---|
| O1$^{i}$—Fe1—O1 | 180.00 (8) | C3—C4—N3 | 120.86 (19) |
| O1$^{i}$—Fe1—N3$^{i}$ | 89.83 (7) | C5—C4—N3 | 119.01 (18) |

| | | | |
|---|---|---|---|
| O1—Fe1—N3$^{i}$ | 90.17 (7) | N1—C5—C4 | 120.2 (2) |
| O1$^{i}$—Fe1—N3 | 90.17 (7) | N1—C5—C6 | 116.23 (19) |
| O1—Fe1—N3 | 89.83 (7) | C4—C5—C6 | 123.53 (19) |
| N3$^{i}$—Fe1—N3 | 180.00 (14) | N2—C6—C7 | 119.71 (19) |
| O1$^{i}$—Fe1—N2 | 88.99 (7) | N2—C6—C5 | 118.53 (18) |
| O1—Fe1—N2 | 91.01 (7) | C7—C6—C5 | 121.71 (19) |
| N3$^{i}$—Fe1—N2 | 94.12 (7) | N4—C7—C8 | 118.4 (2) |
| N3—Fe1—N2 | 85.88 (7) | N4—C7—C6 | 123.4 (2) |
| O1$^{i}$—Fe1—N2$^{i}$ | 91.01 (7) | C8—C7—C6 | 118.07 (19) |
| O1—Fe1—N2$^{i}$ | 88.99 (7) | C9—C8—C7 | 120.6 (2) |
| N3$^{i}$—Fe1—N2$^{i}$ | 85.88 (7) | C8—C9—C10 | 118.9 (2) |
| N3—Fe1—N2$^{i}$ | 94.12 (7) | N2—C10—C9 | 122.0 (2) |
| N2—Fe1—N2$^{i}$ | 180.00 (13) | N3—C11—C12 | 123.7 (2) |
| C17—O1—Fe1 | 123.47 (13) | C13—C12—C17 | 119.7 (2) |
| C1—N1—C5 | 118.8 (2) | C13—C12—C11 | 119.0 (2) |
| C10—N2—C6 | 120.62 (18) | C17—C12—C11 | 120.87 (19) |
| C10—N2—Fe1 | 116.41 (14) | C14—C13—C12 | 121.1 (2) |
| C6—N2—Fe1 | 122.93 (14) | C13—C14—C15 | 119.2 (2) |
| C11—N3—C4 | 119.80 (18) | C16—C15—C14 | 121.0 (2) |
| C11—N3—Fe1 | 125.35 (15) | C15—C16—C17 | 121.3 (2) |
| C4—N3—Fe1 | 114.85 (13) | O1—C17—C16 | 119.16 (19) |
| N1—C1—C2 | 123.9 (2) | O1—C17—C12 | 123.06 (19) |
| C1—C2—C3 | 118.0 (2) | C16—C17—C12 | 117.7 (2) |
| C4—C3—C2 | 119.0 (2) | N5—C18—C19 | 178.8 (3) |
| C3—C4—C5 | 120.0 (2) | | |

Symmetry code(s): (i) −*x*+2, −*y*, −*z*

## Complex 5 - Selected geometric parameters (Å, º)

| Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|
| Fe1—O5 | 1.796 (3) | C44—C43 | 1.416 (6) |
| Fe1—O2 | 1.887 (3) | C18—N4 | 1.299 (5) |
| Fe1—O4 | 1.909 (3) | C18—C19 | 1.460 (5) |
| Fe1—N4 | 2.162 (3) | C20—O2 | 1.313 (5) |
| Fe1—N8 | 2.166 (3) | C20—C21 | 1.403 (6) |
| Fe2—O5 | 1.778 (3) | C20—C19 | 1.422 (5) |
| Fe2—O3 | 1.891 (3) | C13—O1 | 1.318 (5) |
| Fe2—O1 | 1.908 (3) | C13—C14 | 1.408 (6) |
| Fe2—N7 | 2.167 (3) | C13—C12 | 1.411 (6) |
| Fe2—N3 | 2.170 (3) | C1—N1 | 1.342 (6) |
| C3—C2 | 1.388 (6) | C1—C2 | 1.373 (6) |
| C3—C4 | 1.390 (5) | C26—C27 | 1.385 (6) |
| C29—N5 | 1.345 (5) | C26—C25 | 1.386 (7) |
| C29—C28 | 1.394 (5) | C11—N3 | 1.292 (5) |
| C29—C30 | 1.502 (5) | C11—C12 | 1.443 (6) |

| | | | |
|---|---|---|---|
| C30—N6 | 1.341 (5) | C12—C17 | 1.405 (6) |
| C30—C31 | 1.397 (5) | C36—C41 | 1.397 (6) |
| C5—N1 | 1.347 (5) | C42—N8 | 1.290 (5) |
| C5—C4 | 1.384 (5) | C42—C43 | 1.434 (6) |
| C5—C6 | 1.496 (5) | C43—C48 | 1.405 (6) |
| C7—C8 | 1.395 (5) | C21—C22 | 1.388 (7) |
| C7—C6 | 1.396 (5) | C10—N2 | 1.333 (5) |
| C7—N4 | 1.423 (5) | C22—C23 | 1.387 (7) |
| C28—C27 | 1.388 (5) | C32—C33 | 1.372 (6) |
| C28—N7 | 1.434 (5) | C41—C40 | 1.379 (6) |
| C37—O3 | 1.313 (5) | C38—C39 | 1.385 (7) |
| C37—C38 | 1.407 (6) | C14—C15 | 1.379 (7) |
| C37—C36 | 1.414 (6) | C40—C39 | 1.380 (7) |
| C35—N7 | 1.289 (5) | C25—N5 | 1.337 (6) |
| C35—C36 | 1.445 (6) | C34—N6 | 1.340 (6) |
| C24—C23 | 1.381 (6) | C34—C33 | 1.388 (6) |
| C24—C19 | 1.381 (6) | C17—C16 | 1.371 (7) |
| C31—C32 | 1.389 (6) | C45—C46 | 1.384 (7) |
| C31—N8 | 1.433 (5) | C47—C48 | 1.380 (7) |
| C4—N3 | 1.431 (5) | C47—C46 | 1.390 (7) |
| C9—C10 | 1.383 (6) | C15—C16 | 1.381 (8) |
| C9—C8 | 1.384 (6) | N9—C49 | 1.135 (9) |
| C6—N2 | 1.350 (5) | C49—C50 | 1.454 (11) |
| C44—O4 | 1.323 (5) | N10—C51 | 1.141 (7) |
| C44—C45 | 1.402 (6) | C52—C51 | 1.449 (7) |

| **Bond** | **Angle** | **Bond** | **Angle** |
|---|---|---|---|
| O5—Fe1—O2 | 123.32 (15) | C24—C19—C20 | 121.3 (4) |
| O5—Fe1—O4 | 117.65 (14) | C24—C19—C18 | 117.2 (3) |
| O2—Fe1—O4 | 119.02 (14) | C20—C19—C18 | 121.6 (4) |
| O5—Fe1—N4 | 95.01 (12) | N1—C1—C2 | 123.2 (4) |
| O2—Fe1—N4 | 86.81 (12) | C9—C8—C7 | 119.1 (4) |
| O4—Fe1—N4 | 89.17 (12) | C27—C26—C25 | 118.7 (4) |
| O5—Fe1—N8 | 95.00 (12) | N3—C11—C12 | 126.2 (4) |
| O2—Fe1—N8 | 88.32 (13) | C17—C12—C13 | 120.0 (4) |
| O4—Fe1—N8 | 85.52 (12) | C17—C12—C11 | 117.9 (4) |
| N4—Fe1—N8 | 169.95 (12) | C13—C12—C11 | 122.2 (4) |
| O5—Fe2—O3 | 118.73 (15) | C41—C36—C37 | 119.7 (4) |
| O5—Fe2—O1 | 114.47 (14) | C41—C36—C35 | 117.1 (4) |
| O3—Fe2—O1 | 126.78 (15) | C37—C36—C35 | 123.1 (4) |
| O5—Fe2—N7 | 99.15 (12) | N8—C42—C43 | 126.1 (4) |
| O3—Fe2—N7 | 86.50 (13) | C48—C43—C44 | 119.4 (4) |
| O1—Fe2—N7 | 86.62 (12) | C48—C43—C42 | 117.4 (4) |
| O5—Fe2—N3 | 98.80 (12) | C44—C43—C42 | 123.1 (4) |
| O3—Fe2—N3 | 86.15 (12) | C22—C21—C20 | 120.7 (4) |

| | | | |
|---|---|---|---|
| O1—Fe2—N3 | 84.67 (12) | N2—C10—C9 | 123.2 (4) |
| N7—Fe2—N3 | 162.00 (12) | C26—C27—C28 | 118.8 (4) |
| Fe2—O5—Fe1 | 148.0 (2) | C23—C22—C21 | 121.7 (4) |
| C2—C3—C4 | 118.8 (4) | C33—C32—C31 | 119.5 (4) |
| N5—C29—C28 | 122.6 (4) | C40—C41—C36 | 121.7 (4) |
| N5—C29—C30 | 114.5 (3) | C1—C2—C3 | 118.7 (4) |
| C28—C29—C30 | 122.7 (3) | C24—C23—C22 | 118.4 (4) |
| N6—C30—C31 | 122.1 (4) | C39—C38—C37 | 120.8 (4) |
| N6—C30—C29 | 114.3 (3) | C15—C14—C13 | 120.7 (5) |
| C31—C30—C29 | 123.6 (3) | C41—C40—C39 | 118.7 (4) |
| N1—C5—C4 | 122.3 (3) | C40—C39—C38 | 121.3 (4) |
| N1—C5—C6 | 114.9 (3) | N5—C25—C26 | 123.3 (4) |
| C4—C5—C6 | 122.7 (3) | N6—C34—C33 | 122.4 (4) |
| C8—C7—C6 | 118.3 (3) | C16—C17—C12 | 120.8 (5) |
| C8—C7—N4 | 120.1 (3) | C32—C33—C34 | 118.9 (4) |
| C6—C7—N4 | 121.5 (3) | C10—N2—C6 | 118.3 (4) |
| C27—C28—C29 | 118.7 (4) | C34—N6—C30 | 118.7 (4) |
| C27—C28—N7 | 120.6 (4) | C18—N4—C7 | 117.4 (3) |
| C29—C28—N7 | 120.7 (3) | C18—N4—Fe1 | 124.8 (3) |
| O3—C37—C38 | 119.0 (4) | C7—N4—Fe1 | 117.2 (2) |
| O3—C37—C36 | 123.3 (4) | C1—N1—C5 | 118.0 (4) |
| C38—C37—C36 | 117.8 (4) | C11—N3—C4 | 116.0 (3) |
| N7—C35—C36 | 125.6 (4) | C11—N3—Fe2 | 123.8 (3) |
| C23—C24—C19 | 121.1 (4) | C4—N3—Fe2 | 120.0 (2) |
| C32—C31—C30 | 118.4 (4) | C35—N7—C28 | 117.1 (3) |
| C32—C31—N8 | 119.3 (3) | C35—N7—Fe2 | 125.5 (3) |
| C30—C31—N8 | 122.3 (3) | C28—N7—Fe2 | 116.9 (2) |
| C5—C4—C3 | 118.9 (3) | C42—N8—C31 | 117.0 (3) |
| C5—C4—N3 | 120.9 (3) | C42—N8—Fe1 | 121.6 (3) |
| C3—C4—N3 | 120.2 (3) | C31—N8—Fe1 | 120.9 (3) |
| C10—C9—C8 | 118.6 (4) | C25—N5—C29 | 117.7 (4) |
| N2—C6—C7 | 122.2 (3) | C44—O4—Fe1 | 129.0 (3) |
| N2—C6—C5 | 113.5 (3) | C13—O1—Fe2 | 131.3 (3) |
| C7—C6—C5 | 124.2 (3) | C37—O3—Fe2 | 134.9 (3) |
| O4—C44—C45 | 119.8 (4) | C20—O2—Fe1 | 134.7 (3) |
| O4—C44—C43 | 122.1 (4) | C46—C45—C44 | 121.1 (4) |
| C45—C44—C43 | 118.1 (4) | C48—C47—C46 | 118.8 (4) |
| N4—C18—C19 | 126.3 (3) | C45—C46—C47 | 121.0 (4) |
| O2—C20—C21 | 119.1 (4) | C14—C15—C16 | 121.1 (4) |
| O2—C20—C19 | 124.1 (4) | C47—C48—C43 | 121.5 (4) |
| C21—C20—C19 | 116.8 (4) | C17—C16—C15 | 119.6 (5) |
| O1—C13—C14 | 119.7 (4) | N9—C49—C50 | 178.4 (7) |
| O1—C13—C12 | 122.5 (4) | N10—C51—C52 | 179.1 (6) |
| C14—C13—C12 | 117.8 (4) | | |

# S3- Magnetic studies

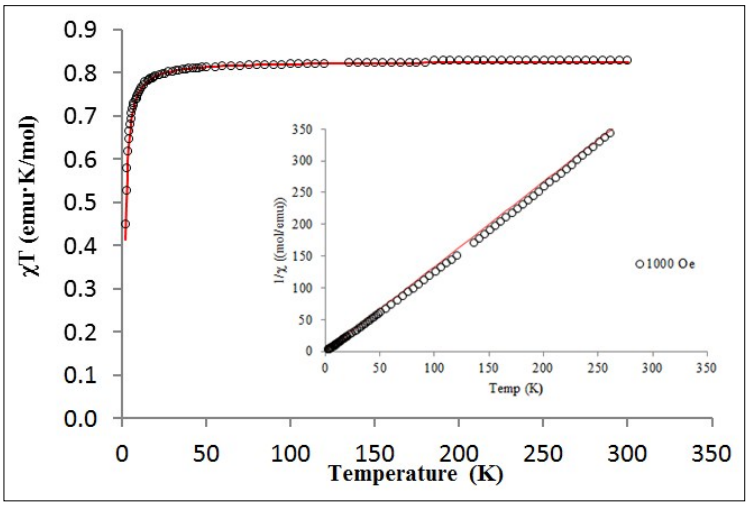



**Fig. 3.1** χT *vs.* T for [Cu(**L8**)sal($ClO_4$)]$_2$ (**2**). The fit to the Bleaney-Bowers equation is shown as a red line.[2] Inset, plot of 1/χ *vs.* T; the fit to the Curie Weiss law is shown as a red line.

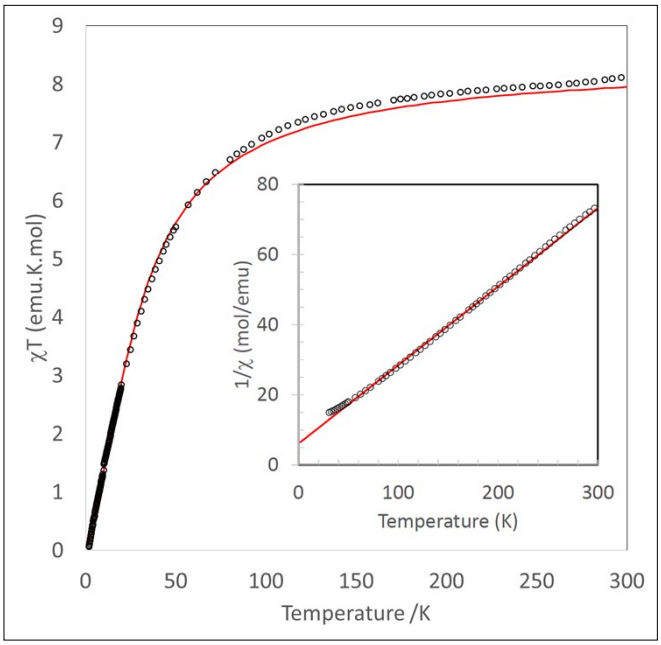



**Fig. 3.2** Temperature dependence of χT (per mole of dimer) for complex [Mn(**L9**)$Cl_2$(EtOH)]$_2$ (**3**). The red line is the fit to the dimer model for two interacting S = 5/2 ions.[27] Inset: Plot of 1/χ *vs*. T (per mole of $Mn^{2+}$; the fit to the Curie Weiss law is shown as a red line).

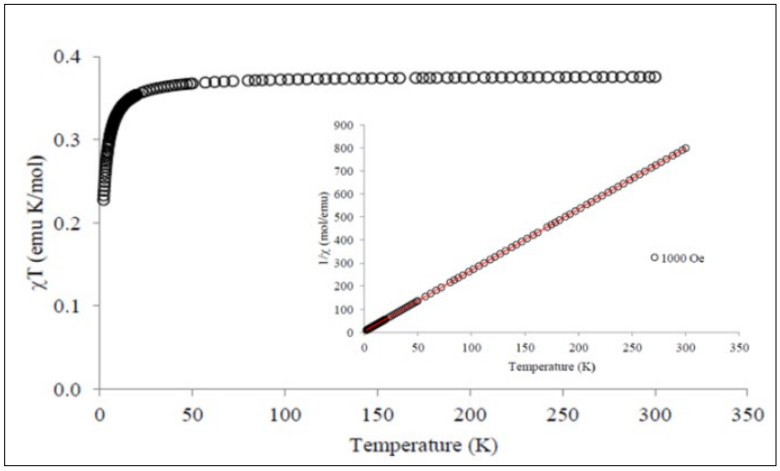
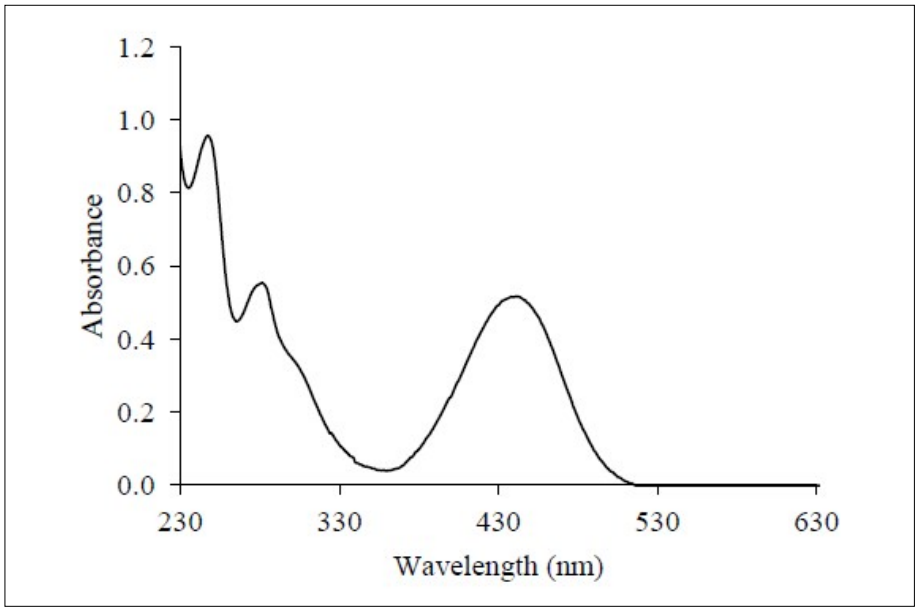
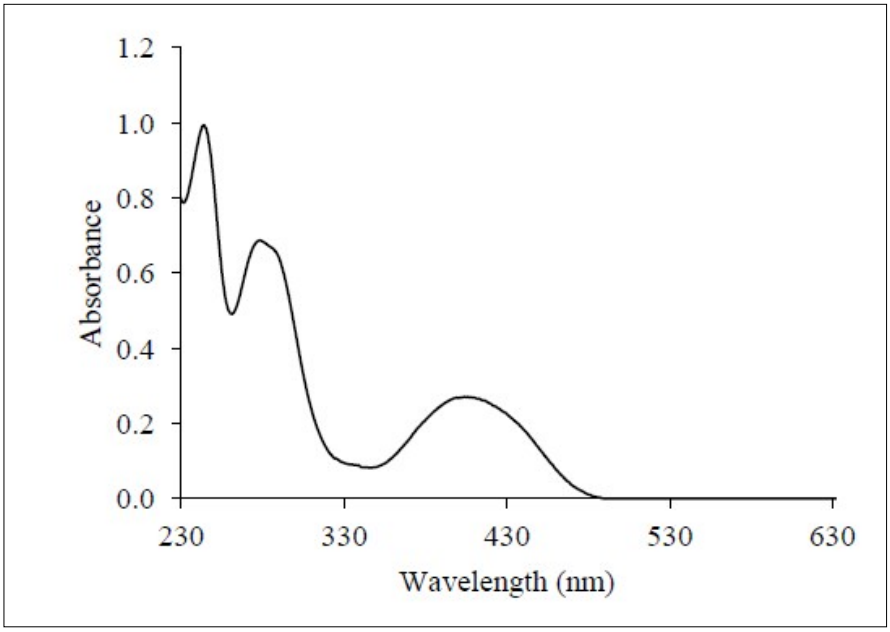



**Fig. 3.1** Variation of the χT product versus temperature for [Fe(**L10**)$_2$Cl]·$CH_3CN$ (**4**) and inset, variation of 1/χ vs. T, the fit to the Curie Weiss Law is shown as a red line.

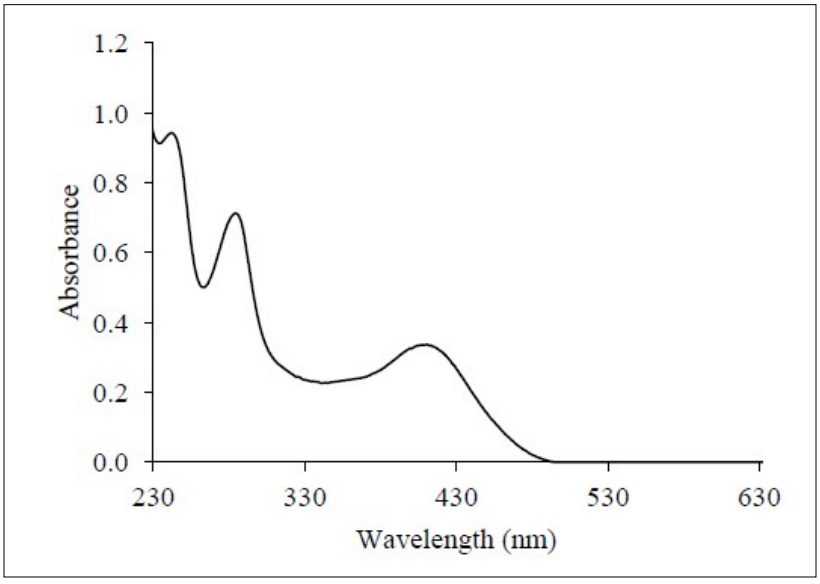
## S4 – UV-Vis data



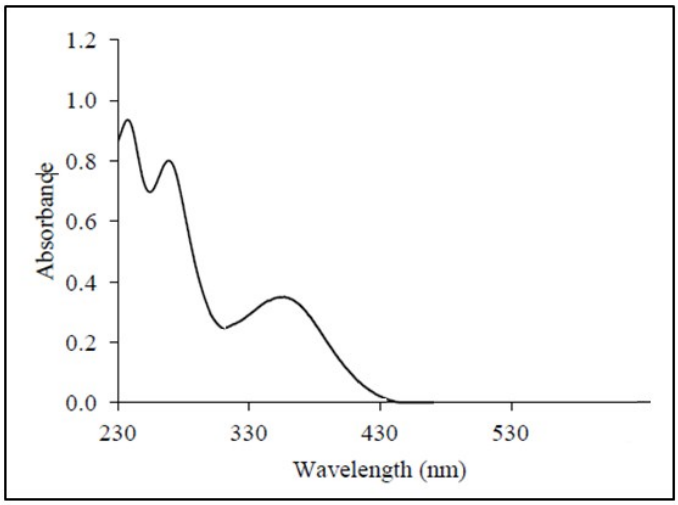

UV-Vis spectrum of a $10^{-5}$ M solution of complex **1** in methanol.



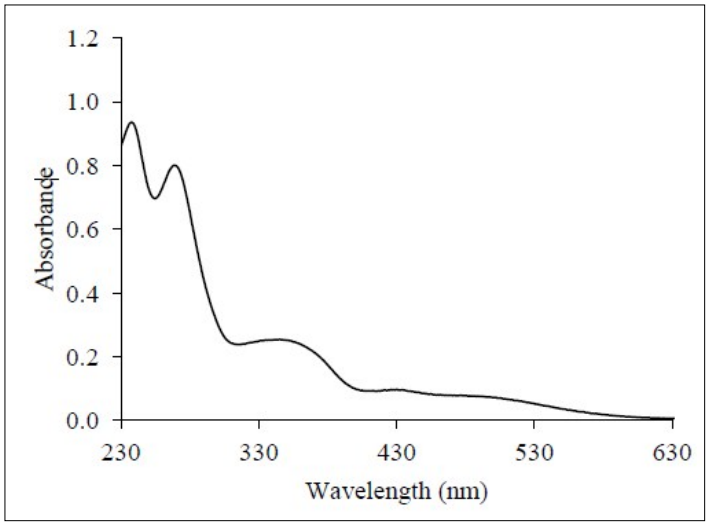

UV-Vis spectrum of a $10^{-5}$ M solution of complex **2** in methanol.




UV-Vis spectrum of a $10^{-5}$ M solution of complex **3** in methanol




UV-Vis spectrum of a $10^{-5}$ M solution of complex **4** in methanol




UV-Vis spectrum of a $10^{-5}$ M solution of complex **5** in methanol

## S5 – References

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