# Supplementary Materials

# Novel Tetranuclear Heterometallic $Mn_3Ni$ Complex and Mononuclear Ni Complexes with an *ONO* Schiff Base Ligand: Synthesis, Crystal Structures, and Magnetic Properties

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**Table S1 Crystal data and structure refinement for 1.**

| | |
|---|---|
| Empirical formula | $C_{30}H_{32}N_2NiO_6$ |
| Formula weight | 575.28 |
| Temperature/K | 113.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 10.716(5) |
| b/Å | 20.271(8) |
| c/Å | 13.487(6) |
| α/° | 90 |
| β/° | 112.614(6) |
| γ/° | 90 |
| Volume/Å$^3$ | 2704(2) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.413 |
| μ/mm$^{-1}$ | 0.765 |
| F(000) | 1208.0 |
| Crystal size/mm$^3$ | 0.29 × 0.19 × 0.18 |
| Radiation | MoKα (λ = 0.71075) |
| 2Θ range for data collection/° | 6.25 to 54.974 |
| Index ranges | $-13 \le h \le 11$, $-26 \le k \le 26$, $-17 \le l \le 14$ |
| Reflections collected | 22107 |
| Independent reflections | 6058 [$R_{int}$ = 0.0329, $R_{sigma}$ = 0.0312] |
| Data/restraints/parameters | 6058/0/359 |
| Goodness-of-fit on $F^2$ | 1.071 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0404, $wR_2$ = 0.1056 |
| Final R indexes [all data] | $R_1$ = 0.0476, $wR_2$ = 0.1123 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.65/-0.55 |

**Table S2 Bond Lengths for 1.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Ni1 | O1 | 2.1064(15) | C9 | C10 | 1.409(3) |
| Ni1 | O2 | 2.0113(15) | C9 | C14 | 1.420(3) |
| Ni1 | O3 | 2.1103(16) | C10 | C11 | 1.379(3) |
| Ni1 | O4 | 2.0319(15) | C11 | C12 | 1.396(4) |
| Ni1 | N1 | 2.0531(17) | C12 | C13 | 1.382(3) |
| Ni1 | N2 | 2.0486(17) | C13 | C14 | 1.416(3) |
| O1 | C1 | 1.441(3) | C15 | C16 | 1.509(3) |
| O2 | C14 | 1.311(2) | C16 | C17 | 1.391(3) |
| O3 | C15 | 1.443(2) | C16 | C21 | 1.406(3) |
| O4 | C28 | 1.337(2) | C17 | C18 | 1.390(3) |
| N1 | C7 | 1.419(3) | C18 | C19 | 1.386(3) |
| N1 | C8 | 1.291(2) | C19 | C20 | 1.390(3) |
| N2 | C21 | 1.426(3) | C20 | C21 | 1.392(3) |
| N2 | C22 | 1.287(3) | C22 | C23 | 1.444(3) |
| C1 | C2 | 1.509(3) | C23 | C24 | 1.409(3) |
| C2 | C3 | 1.390(3) | C23 | C28 | 1.418(3) |
| C2 | C7 | 1.408(3) | C24 | C25 | 1.379(3) |
| C3 | C4 | 1.393(4) | C25 | C26 | 1.394(3) |
| C4 | C5 | 1.374(4) | C26 | C27 | 1.381(3) |
| C5 | C6 | 1.396(3) | C27 | C28 | 1.404(3) |
| C6 | C7 | 1.384(3) | O5 | C29 | 1.412(4) |
| C8 | C9 | 1.447(3) | O6 | C30 | 1.400(4) |

**Table S3 Bond Angles for 1.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O1 | Ni1 | O3 | 85.54(6) | C6 | C7 | C2 | 121.05(19) |
| O2 | Ni1 | O1 | 95.38(6) | N1 | C8 | C9 | 123.62(18) |
| O2 | Ni1 | O3 | 173.67(6) | C10 | C9 | C8 | 117.79(19) |
| O2 | Ni1 | O4 | 89.90(7) | C10 | C9 | C14 | 120.26(19) |
| O2 | Ni1 | N1 | 85.16(7) | C14 | C9 | C8 | 121.68(17) |
| O2 | Ni1 | N2 | 94.18(6) | C11 | C10 | C9 | 121.1(2) |
| O4 | Ni1 | O1 | 89.93(6) | C10 | C11 | C12 | 118.9(2) |
| O4 | Ni1 | O3 | 96.37(6) | C13 | C12 | C11 | 121.4(2) |
| O4 | Ni1 | N1 | 174.39(6) | C12 | C13 | C14 | 120.8(2) |
| O4 | Ni1 | N2 | 85.88(7) | O2 | C14 | C9 | 123.27(18) |
| N1 | Ni1 | O1 | 87.89(6) | O2 | C14 | C13 | 119.25(19) |
| N1 | Ni1 | O3 | 88.61(7) | C13 | C14 | C9 | 117.47(18) |
| N2 | Ni1 | O1 | 169.56(6) | O3 | C15 | C16 | 109.17(16) |
| N2 | Ni1 | O3 | 85.43(6) | C17 | C16 | C15 | 121.61(18) |
| N2 | Ni1 | N1 | 97.12(7) | C17 | C16 | C21 | 118.35(18) |
| C1 | O1 | Ni1 | 115.63(11) | C21 | C16 | C15 | 120.01(18) |
| C14 | O2 | Ni1 | 117.35(13) | C18 | C17 | C16 | 120.9(2) |
| C15 | O3 | Ni1 | 120.97(12) | C19 | C18 | C17 | 120.2(2) |
| C28 | O4 | Ni1 | 117.54(12) | C18 | C19 | C20 | 120.05(19) |
| C7 | N1 | Ni1 | 119.03(12) | C19 | C20 | C21 | 119.61(19) |
| C8 | N1 | Ni1 | 121.77(14) | C16 | C21 | N2 | 116.82(17) |
| C8 | N1 | C7 | 119.19(17) | C20 | C21 | N2 | 122.06(18) |

**Table S3 Bond Angles for 1.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C21 | N2 | Ni1 | 116.02(12) | C20 | C21 | C16 | 120.90(18) |
| C22 | N2 | Ni1 | 123.16(14) | N2 | C22 | C23 | 123.75(18) |
| C22 | N2 | C21 | 120.56(17) | C24 | C23 | C22 | 117.54(18) |
| O1 | C1 | C2 | 112.99(17) | C24 | C23 | C28 | 119.25(19) |
| C3 | C2 | C1 | 122.0(2) | C28 | C23 | C22 | 123.09(18) |
| C3 | C2 | C7 | 118.2(2) | C25 | C24 | C23 | 121.8(2) |
| C7 | C2 | C1 | 119.70(18) | C24 | C25 | C26 | 118.7(2) |
| C2 | C3 | C4 | 120.7(2) | C27 | C26 | C25 | 120.7(2) |
| C5 | C4 | C3 | 120.2(2) | C26 | C27 | C28 | 121.6(2) |
| C4 | C5 | C6 | 120.3(2) | O4 | C28 | C23 | 122.61(18) |
| C7 | C6 | C5 | 119.4(2) | O4 | C28 | C27 | 119.48(18) |
| C2 | C7 | N1 | 115.77(18) | C27 | C28 | C23 | 117.87(18) |
| C6 | C7 | N1 | 123.17(19) | | | | |

**Table S4 Hydrogen Bonds for 1.**

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|---|---|---|---|---|---|---|
| O1 | H1 | O4[1] | 0.84 | 1.86 | 2.686(2) | 165.6 |
| O3 | H3 | O4[1] | 0.84 | 1.87 | 2.641(2) | 152.9 |
| O5 | H5A | O2 | 0.84 | 1.88 | 2.678(2) | 158.2 |
| O6 | H6A | O5 | 0.84 | 1.92 | 2.763(3) | 175.8 |

[1]1-X,1-Y,1-Z

**Table S5. Crystal data and structure refinement for 2.**

| | |
|---|---|
| Empirical formula | $C_{60}H_{56}Cl_2Mn_3N_4NiO_{10}$ |
| Formula weight | 1287.51 |
| Temperature/K | 113.00 |
| Crystal system | orthorhombic |
| Space group | *Aea*2 |
| a/Å | 12.180(6) |
| b/Å | 22.558(11) |
| c/Å | 19.913(11) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 5471(5) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.563 |
| μ/mm$^{-1}$ | 1.178 |
| F(000) | 2644.0 |
| Crystal size/mm$^3$ | 0.2 × 0.2 × 0.2 |
| Radiation | MoKα (λ = 0.71075) |
| 2Θ range for data collection/° | 6.402 to 55.02 |
| Index ranges | -15 ≤ h ≤ 15, -28 ≤ k ≤ 28, -25 ≤ l ≤ 25 |
| Reflections collected | 22017 |
| Independent reflections | 6184 [$R_{int}$ = 0.0301, $R_{sigma}$ = 0.0352] |
| Data/restraints/parameters | 6184/1/365 |
| Goodness-of-fit on F$^2$ | 1.077 |

| | |
|---|---|
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0218, $wR_2$ = 0.0546 |
| Final R indexes [all data] | $R_1$ = 0.0220, $wR_2$ = 0.0548 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.30/-0.29 |
| Flack parameter | 0.010(4) |

**Table S6. Bond Lengths for 2.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Ni1 | Ni1[1] | 0.0000(8) | C14 | C9 | 1.420(3) |
| Ni1 | Mn1[1] | 3.1004(10) | C14 | C13 | 1.401(3) |
| Ni1 | O2[1] | 2.0453(18) | C8 | C9 | 1.456(3) |
| Ni1 | O2 | 2.0454(18) | C9 | C10 | 1.404(3) |
| Ni1 | O1[1] | 2.0937(18) | C13 | C12 | 1.387(3) |
| Ni1 | O1 | 2.0937(18) | C21 | C16 | 1.396(3) |
| Ni1 | N1 | 2.022(2) | C21 | C20 | 1.402(3) |
| Ni1 | N1[1] | 2.022(2) | C2 | C7 | 1.398(3) |
| Mn1 | O3 | 1.8761(17) | C2 | C1 | 1.524(3) |
| Mn1 | O2 | 2.1820(17) | C2 | C3 | 1.399(3) |
| Mn1 | O1 | 1.9756(16) | C24 | C23 | 1.414(3) |
| Mn1 | O4 | 1.8607(17) | C24 | C25 | 1.370(3) |
| Mn1 | O5 | 2.2587(18) | C22 | C23 | 1.425(3) |
| Mn1 | N2 | 2.0431(19) | C16 | C17 | 1.390(3) |
| Mn2 | Cl1[1] | 2.4560(10) | C16 | C15 | 1.515(3) |
| Mn2 | Cl1 | 2.4560(10) | C23 | C28 | 1.418(4) |
| Mn2 | O3[1] | 2.1765(18) | C7 | C6 | 1.394(3) |
| Mn2 | O3 | 2.1765(18) | C28 | C27 | 1.407(3) |
| Mn2 | O1[1] | 2.3145(18) | C12 | C11 | 1.390(3) |
| Mn2 | O1 | 2.3145(18) | C18 | C17 | 1.392(3) |
| O3 | C15 | 1.418(3) | C18 | C19 | 1.378(3) |
| O2 | C14 | 1.335(3) | C11 | C10 | 1.377(3) |
| O1 | C1 | 1.428(2) | C26 | C27 | 1.381(3) |
| O4 | C28 | 1.323(3) | C26 | C25 | 1.403(4) |
| O5 | C29 | 1.432(3) | C3 | C4 | 1.382(3) |
| N2 | C21 | 1.431(3) | C6 | C5 | 1.386(3) |
| N2 | C22 | 1.298(3) | C19 | C20 | 1.395(3) |
| N1 | C8 | 1.279(3) | C29 | C30 | 1.517(4) |
| N1 | C7 | 1.432(3) | C4 | C5 | 1.384(4) |

[1]1-X,1-Y,+Z

**Table S7. Bond Angles for 2.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| Ni1[1] | Ni1 | Mn1[1] | 0(8) | Ni1[1] | O1 | Ni1 | 0.000(15) |
| Ni1[1] | Ni1 | O2[1] | 0(10) | Ni1[1] | O1 | Mn2 | 96.98(7) |
| Ni1[1] | Ni1 | O2 | 0(10) | Ni1 | O1 | Mn2 | 96.98(7) |
| Ni1[1] | Ni1 | O1[1] | 0(10) | Mn1 | O1 | Ni1 | 99.22(7) |
| Ni1[1] | Ni1 | O1 | 0(10) | Mn1 | O1 | Ni1[1] | 99.22(7) |
| Ni1[1] | Ni1 | N1 | 0(10) | Mn1 | O1 | Mn2 | 97.09(6) |
| Ni1[1] | Ni1 | N1[1] | 0(10) | C1 | O1 | Ni1[1] | 120.02(13) |
| O2[1] | Ni1 | Mn1[1] | 44.57(4) | C1 | O1 | Ni1 | 120.02(13) |
| O2 | Ni1 | Mn1[1] | 135.91(5) | C1 | O1 | Mn1 | 118.39(12) |

**Table S7. Bond Angles for 2.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O2[1] | Ni1 | O2 | 179.32(9) | C1 | O1 | Mn2 | 120.25(13) |
| O2 | Ni1 | O1[1] | 96.96(6) | C28 | O4 | Mn1 | 127.11(15) |
| O2[1] | Ni1 | O1[1] | 83.53(6) | C29 | O5 | Mn1 | 125.35(14) |
| O2[1] | Ni1 | O1 | 96.96(6) | C21 | N2 | Mn1 | 120.62(14) |
| O2 | Ni1 | O1 | 83.53(6) | C22 | N2 | Mn1 | 120.86(15) |
| O1[1] | Ni1 | Mn1[1] | 38.97(4) | C22 | N2 | C21 | 118.51(18) |
| O1 | Ni1 | Mn1[1] | 93.77(5) | Ni1[1] | N1 | Ni1 | 0.000(17) |
| O1[1] | Ni1 | O1 | 88.09(10) | C8 | N1 | Ni1 | 124.48(16) |
| N1[1] | Ni1 | Mn1[1] | 83.32(6) | C8 | N1 | Ni1[1] | 124.48(16) |
| N1 | Ni1 | Mn1[1] | 137.89(6) | C8 | N1 | C7 | 118.50(19) |
| N1 | Ni1 | O2[1] | 93.65(7) | C7 | N1 | Ni1[1] | 117.01(14) |
| N1 | Ni1 | O2 | 85.91(7) | C7 | N1 | Ni1 | 117.01(14) |
| N1[1] | Ni1 | O2[1] | 85.91(7) | O2 | C14 | C9 | 122.53(19) |
| N1[1] | Ni1 | O2 | 93.66(7) | O2 | C14 | C13 | 119.46(19) |
| N1 | Ni1 | O1 | 85.24(8) | C13 | C14 | C9 | 117.9(2) |
| N1 | Ni1 | O1[1] | 172.41(7) | N1 | C8 | C9 | 123.8(2) |
| N1[1] | Ni1 | O1[1] | 85.24(8) | C14 | C9 | C8 | 122.63(19) |
| N1[1] | Ni1 | O1 | 172.41(7) | C10 | C9 | C14 | 119.3(2) |
| N1 | Ni1 | N1[1] | 101.63(11) | C10 | C9 | C8 | 117.42(19) |
| O3 | Mn1 | O2 | 87.67(7) | C12 | C13 | C14 | 121.4(2) |
| O3 | Mn1 | O1 | 85.36(7) | C16 | C21 | N2 | 119.80(18) |
| O3 | Mn1 | O5 | 84.01(8) | C16 | C21 | C20 | 120.1(2) |
| O3 | Mn1 | N2 | 93.46(7) | C20 | C21 | N2 | 120.10(19) |
| O2 | Mn1 | O5 | 171.54(6) | C7 | C2 | C1 | 127.70(19) |
| O1 | Mn1 | O2 | 82.93(6) | C7 | C2 | C3 | 117.5(2) |
| O1 | Mn1 | O5 | 94.89(7) | C3 | C2 | C1 | 114.61(19) |
| O1 | Mn1 | N2 | 175.19(7) | C25 | C24 | C23 | 120.9(2) |
| O4 | Mn1 | O3 | 171.21(7) | N2 | C22 | C23 | 126.7(2) |
| O4 | Mn1 | O2 | 100.21(8) | C21 | C16 | C15 | 121.50(19) |
| O4 | Mn1 | O1 | 91.70(7) | C17 | C16 | C21 | 118.5(2) |
| O4 | Mn1 | O5 | 88.00(8) | C17 | C16 | C15 | 120.0(2) |
| O4 | Mn1 | N2 | 90.12(7) | C24 | C23 | C22 | 118.9(2) |
| N2 | Mn1 | O2 | 92.36(7) | C24 | C23 | C28 | 118.6(2) |
| N2 | Mn1 | O5 | 89.62(7) | C28 | C23 | C22 | 122.5(2) |
| Cl1[1] | Mn2 | Cl1 | 103.66(5) | C2 | C7 | N1 | 118.31(19) |
| O3 | Mn2 | Cl1 | 99.84(5) | C6 | C7 | N1 | 120.9(2) |
| O3[1] | Mn2 | Cl1 | 96.56(5) | C6 | C7 | C2 | 120.8(2) |
| O3[1] | Mn2 | Cl1[1] | 99.85(5) | O1 | C1 | C2 | 118.79(18) |
| O3 | Mn2 | Cl1[1] | 96.56(5) | O4 | C28 | C23 | 122.3(2) |
| O3[1] | Mn2 | O3 | 153.32(9) | O4 | C28 | C27 | 118.0(2) |
| O3 | Mn2 | O1[1] | 88.04(6) | C27 | C28 | C23 | 119.7(2) |
| O3[1] | Mn2 | O1 | 88.04(6) | C13 | C12 | C11 | 120.5(2) |
| O3 | Mn2 | O1 | 71.05(5) | C19 | C18 | C17 | 119.5(2) |
| O3[1] | Mn2 | O1[1] | 71.05(5) | C10 | C11 | C12 | 119.1(2) |
| O1[1] | Mn2 | Cl1 | 162.96(4) | C27 | C26 | C25 | 120.4(2) |
| O1 | Mn2 | Cl1 | 90.28(6) | C4 | C3 | C2 | 121.7(2) |
| O1 | Mn2 | Cl1[1] | 162.96(4) | C26 | C27 | C28 | 120.1(2) |
| O1[1] | Mn2 | Cl1[1] | 90.28(6) | C5 | C6 | C7 | 120.4(2) |
| O1 | Mn2 | O1[1] | 77.94(9) | C16 | C17 | C18 | 121.7(2) |
| Mn1 | O3 | Mn2 | 105.13(7) | O3 | C15 | C16 | 112.42(17) |
| C15 | O3 | Mn1 | 118.25(13) | C24 | C25 | C26 | 120.3(2) |

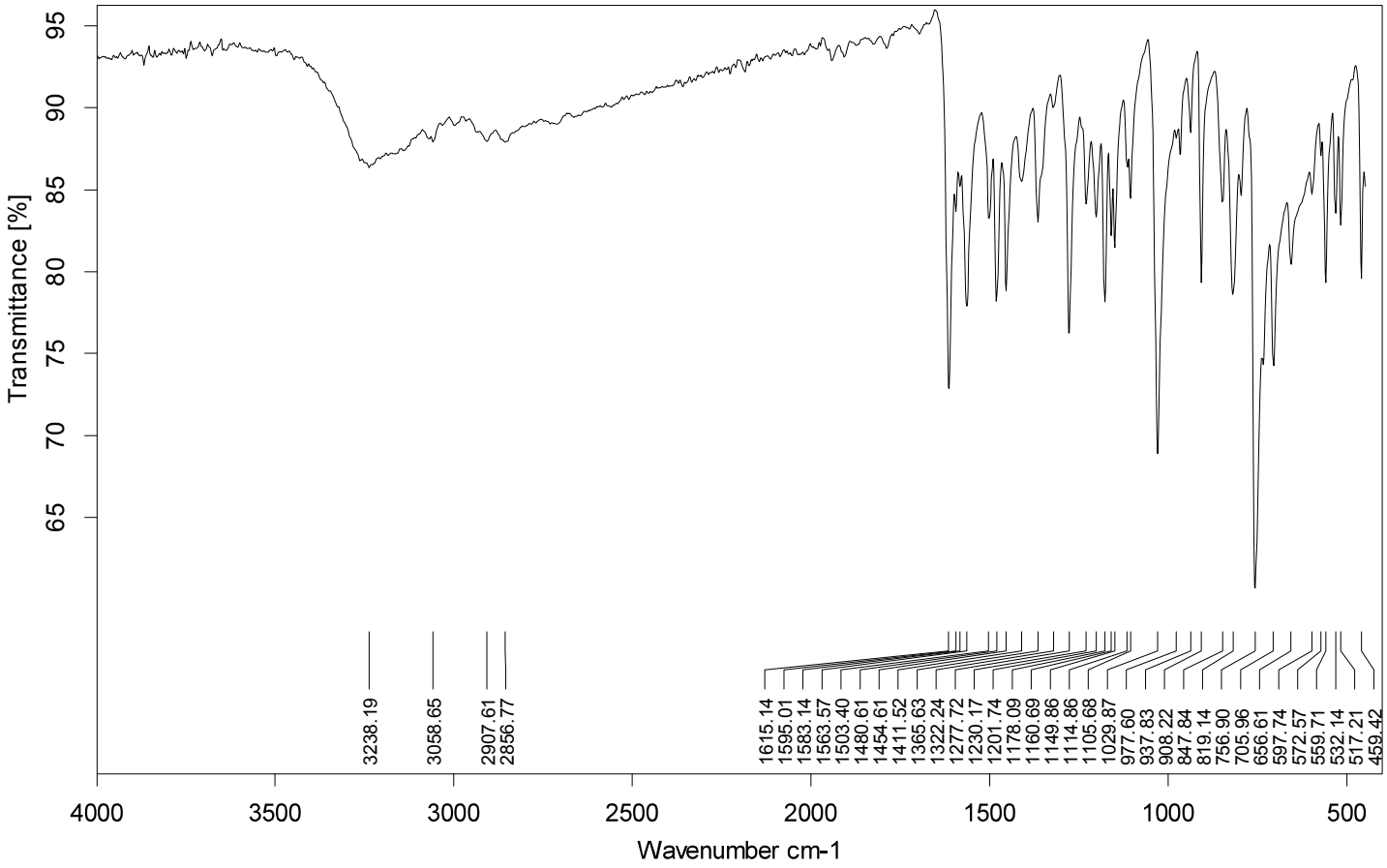
**Table S7. Bond Angles for 2.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C15 | O3 | Mn2 | 130.74(13) | C11 | C10 | C9 | 121.6(2) |
| Ni1[1] | O2 | Ni1 | 0.00(2) | C18 | C19 | C20 | 120.1(2) |
| Ni1 | O2 | Mn1 | 94.29(6) | C19 | C20 | C21 | 120.0(2) |
| Ni1[1] | O2 | Mn1 | 94.29(6) | O5 | C29 | C30 | 109.5(2) |
| C14 | O2 | Ni1 | 118.10(13) | C3 | C4 | C5 | 120.1(2) |
| C14 | O2 | Ni1[1] | 118.10(13) | C4 | C5 | C6 | 119.4(2) |
| C14 | O2 | Mn1 | 125.02(13) | | | | |

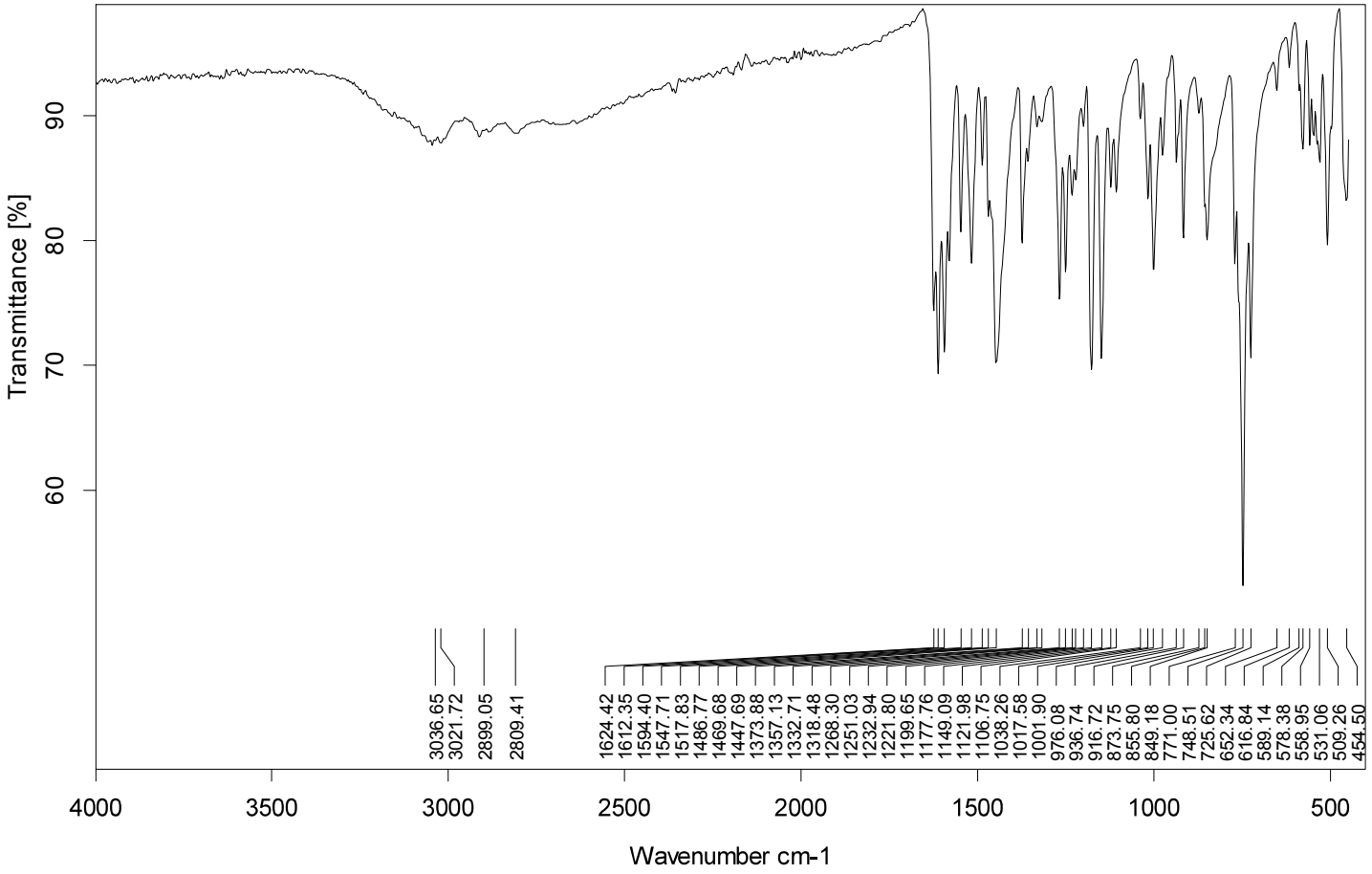
[1]1-X,1-Y,+Z

**Table S8. Hydrogen Bonds for 2.**

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|---|---|---|---|---|---|---|
| O5 | H5 | Cl1 | 0.84 | 2.25 | 3.0745(19) | 169.1 |




| | |
|---|---|
| **Figure S1.** IR spectrum of H2L1-H [N-(2-hydroxymethylphenyl)salicylideneiminesalicylideneimine] | 20/04/2018 |




| | |
|---|---|
| **Figure S2.** IR spectrum of **1**. | 24/01/2019 |

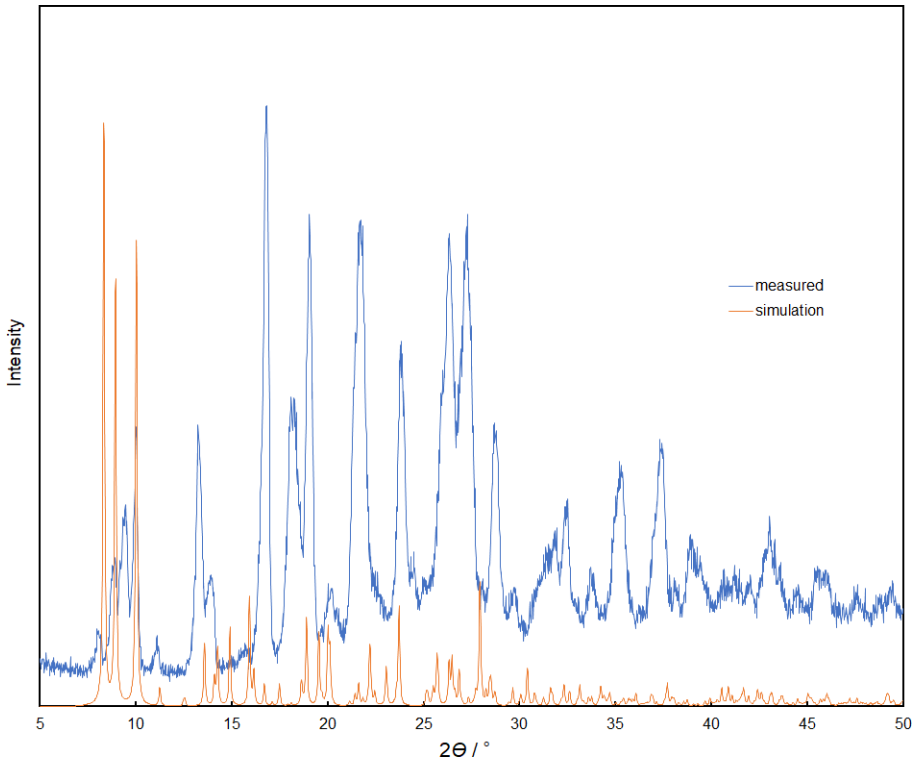



**Figure S3**. XRD patterns for **1**; measuremental data at 25°C. (blue), simulation (orange).

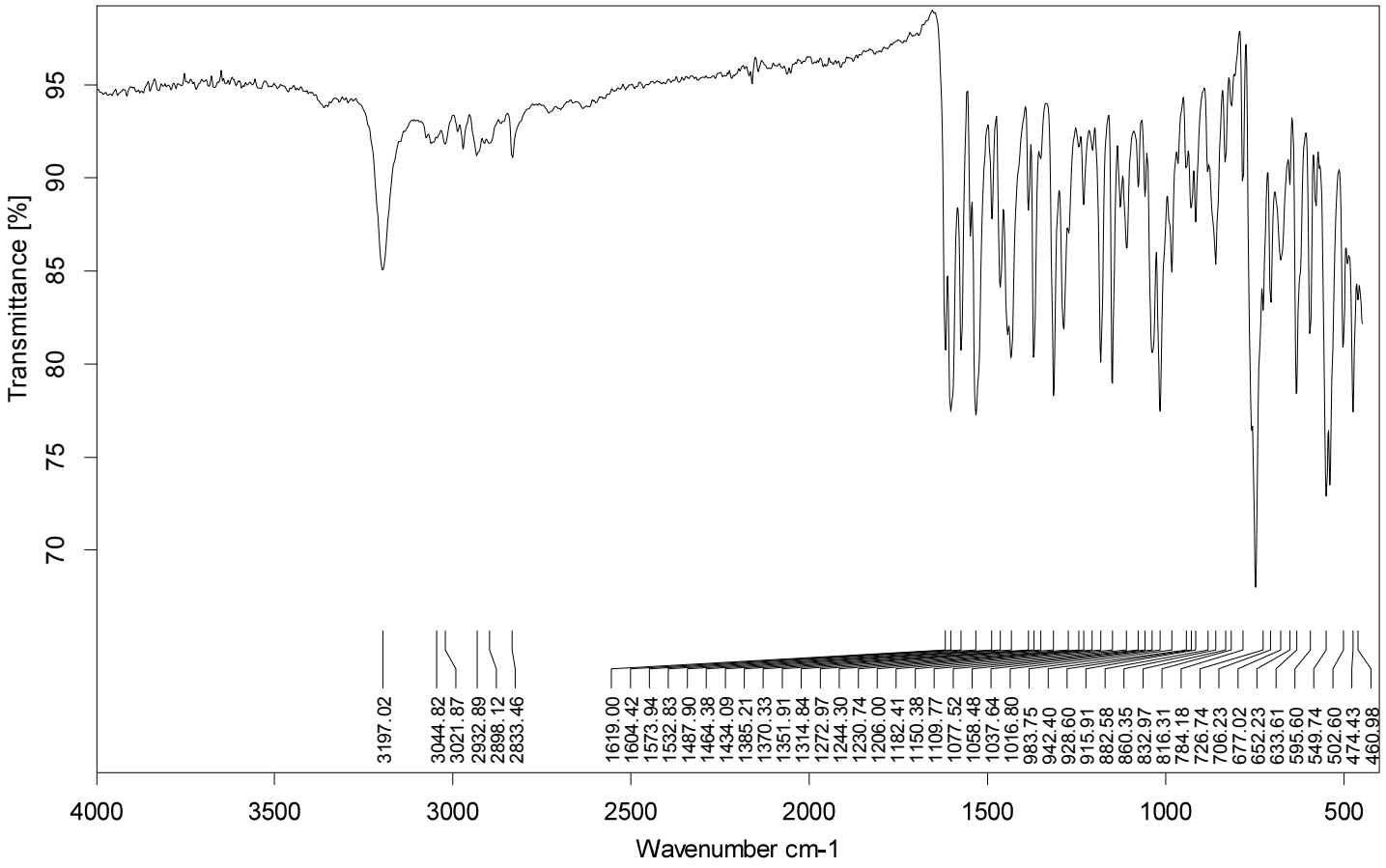



**Figure S4.** IR spectrum of **2.**

05/06/2017

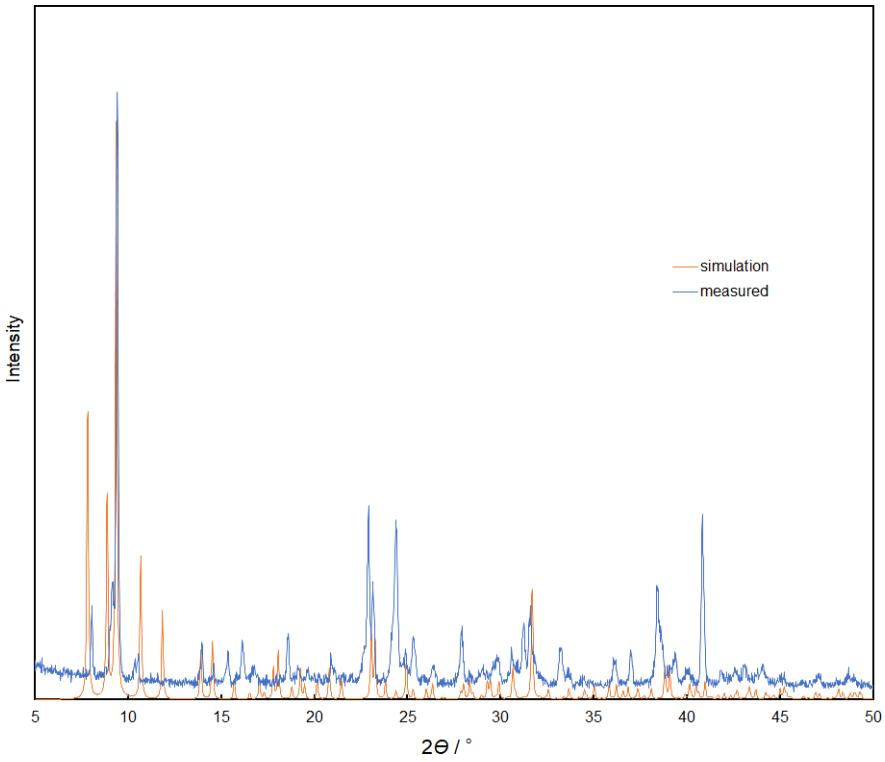



**Figure S5**. XRD patterns for **2**; measuremental data at 25°C (blue), simulation (orange).

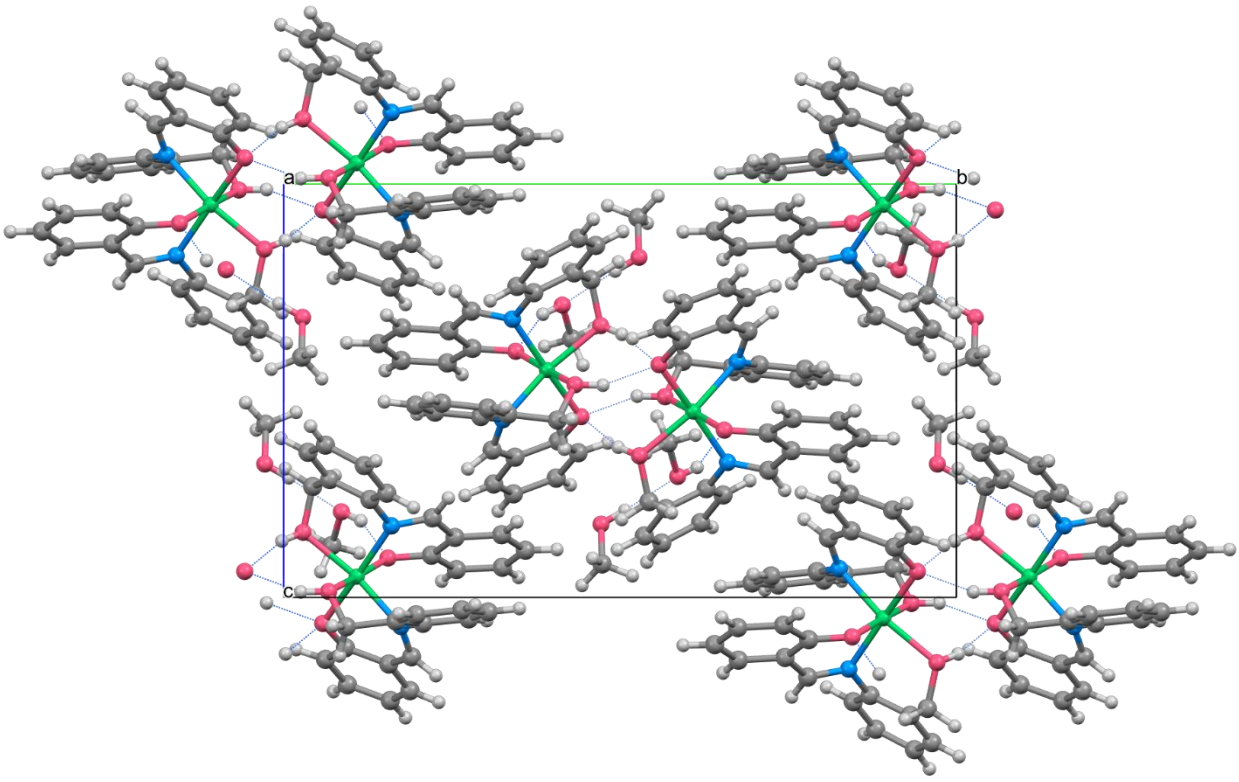



**Figure S6.** Crystal Packing diagram of **1**.

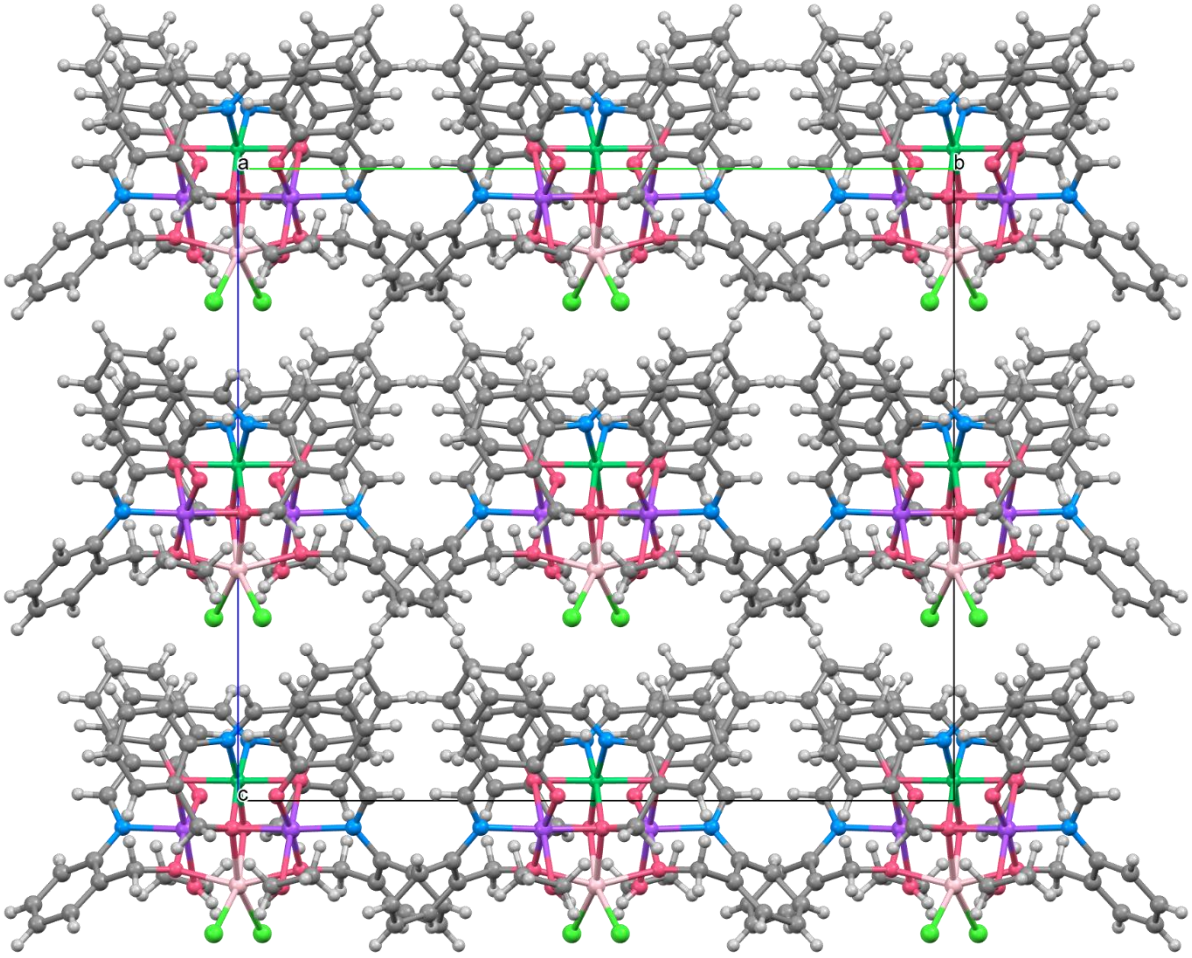



**Figure S7.** Crystal Packing diagram of **2**.

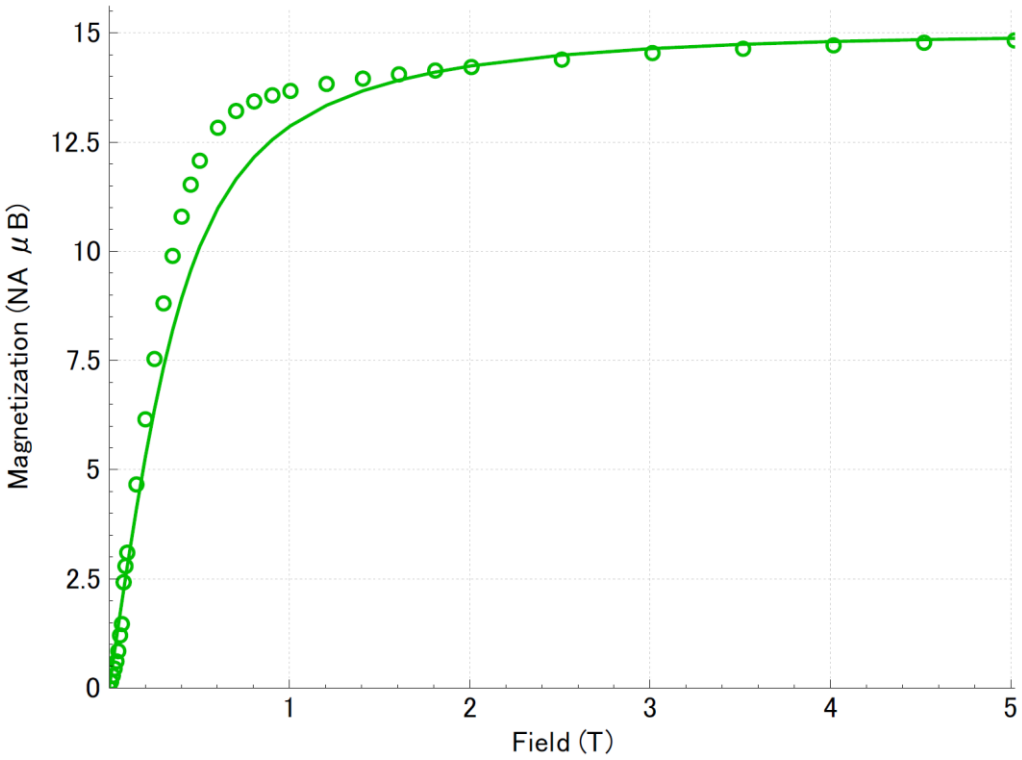



**Figure S8**. The plots of M−H for **2**. The line represents the fitting results by PHI.