

## Supplementary Information

### **Blocking and bridging ligands direct the structure and magnetic properties of dimers of pentacoordinate nickel(II)**

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Table S1. Crystallographic data for complexes **1** – **5**.

| Complex                                       | 1            | 2            | 3            | 4.CH <sub>2</sub> Cl <sub>2</sub> | 5                           |
|-----------------------------------------------|--------------|--------------|--------------|-----------------------------------|-----------------------------|
| Formula                                       |              |              |              | C45 H54 B2 Cl4<br>Ni14 Ni2 O2     | C26 H50 F12 N6<br>Ni2 O4 P2 |
| <u>M</u>                                      |              |              |              | 1103.86                           | 918.08                      |
| Crystal system                                | orthorhombic | orthorhombic | orthorhombic | monoclinic                        | monoclinic                  |
| Space group                                   | Pnmm         | Pnmm         | Pnmm         | C2/c                              | P21/n                       |
| <u>Z</u>                                      |              |              |              | 4                                 | 2                           |
| <i>a</i> / Å                                  | 17.1572(2)   | 17.24479(18) | 17.3543(2)   | 17.9483(17)                       | 8.1736(4)                   |
| <i>b</i> / Å                                  | 13.65435(14) | 13.66574(12) | 13.69393(14) | 19.1658(18)                       | 15.1274(8)                  |
| <i>c</i> / Å                                  | 7.88214(7)   | 7.88513(6)   | 7.89244(8)   | 15.6504(15)                       | 14.9948(8)                  |
| $\alpha$ / °                                  | 90           | 90           | 90           | 90                                | 90                          |
| $\beta$ / °                                   | 90           | 90           | 90           | 103.780(2)                        | 90.6130(10)                 |
| $\gamma$ / °                                  | 90           | 90           | 90           | 90                                | 90                          |
| <i>V</i> / Å <sup>3</sup>                     | 1846.55(3)   | 1858.23(3)   | 1875.63(4)   | 5228.7(9)                         | 1853.93(17)                 |
| <i>T</i> / K                                  |              |              |              | 100(2)                            | 100(2)                      |
| $\lambda$ / Å                                 | 0.82449      | 0.82449      | 0.82449      | 0.71073                           | 0.71073                     |
| $\mu$ / mm <sup>-1</sup>                      |              |              |              | 1.402                             | 1.203                       |
| Reflections collected                         |              |              |              | 6409                              | 4329                        |
| Independent reflections                       |              |              |              | 5622 (326)                        | 4026 (235)                  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>      |              |              |              | 1.085                             | 1.243                       |
| Final <i>R</i> indices                        |              |              |              | 0.0865                            | 0.0588                      |
| [ <i>I</i> > 2σ( <i>I</i> )] <sup>[a,b]</sup> |              |              |              | 0.0946                            | 0.0646                      |
| <i>R</i> indices (all data) <sup>[a,b]</sup>  |              |              |              | 0.2423                            | 0.1243                      |
|                                               |              |              |              | 0.2506                            | 0.1274                      |
| Max /min                                      |              |              |              | 5.220                             | 0.641                       |
| $\Delta\rho$ [e· Å <sup>-3</sup> ]            |              |              |              | -1.185                            | -0.506                      |

<sup>[a]</sup>  $R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$  for reflections with  $I > 2\sigma I$ . <sup>[b]</sup>  $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$  for all reflections;  
 $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$ , in which  $P = (2F_c^2 + F_o^2)/3$  and *a* and *b* are constants set by the program.

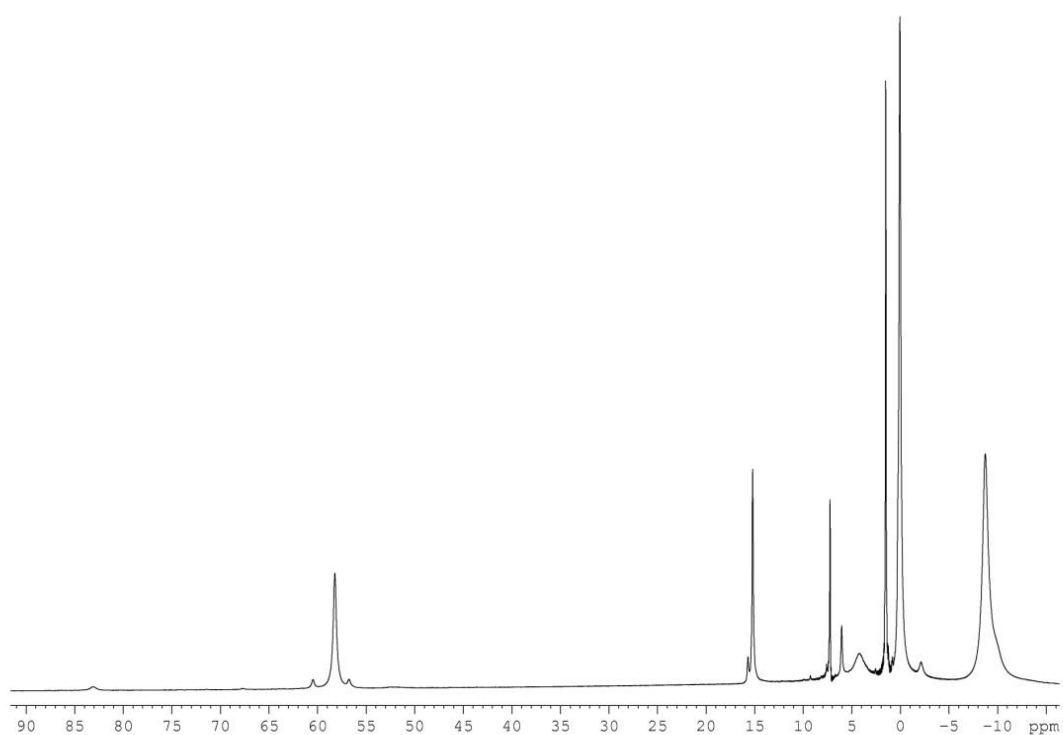


Figure S1.  $^1\text{H}$  NMR spectrum of **4** in  $\text{CDCl}_3$  solution at r.t.

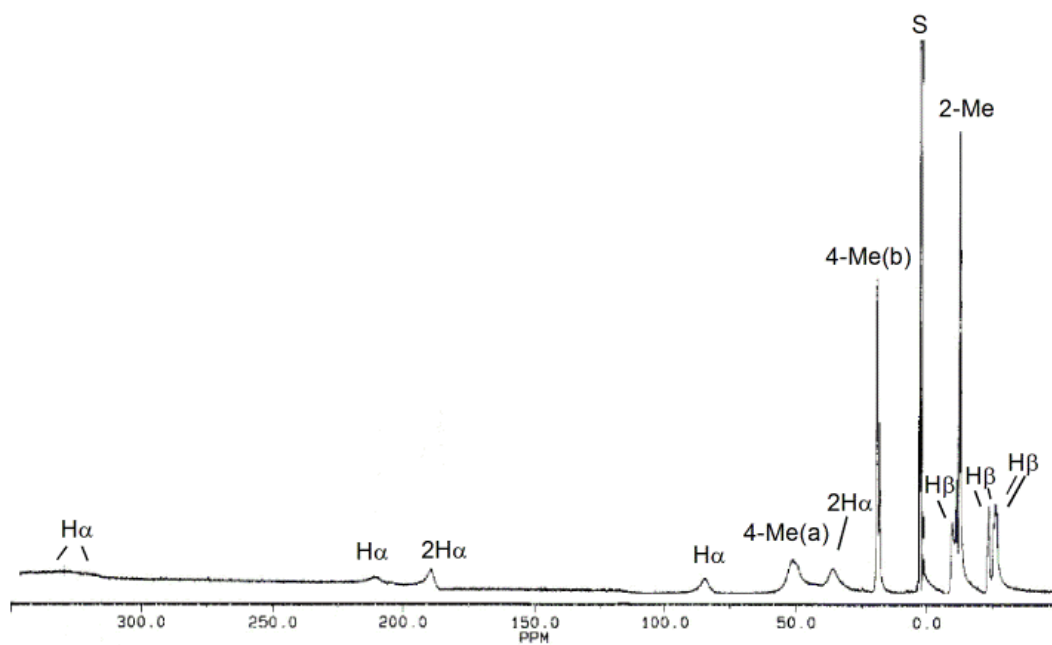
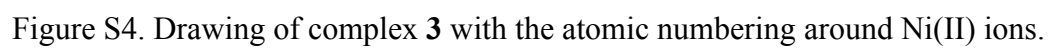
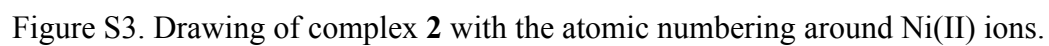


Figure S2.  $^1\text{H}$  NMR spectrum of **5** in  $(\text{CD}_3)_2\text{CO}$  solution at r.t.



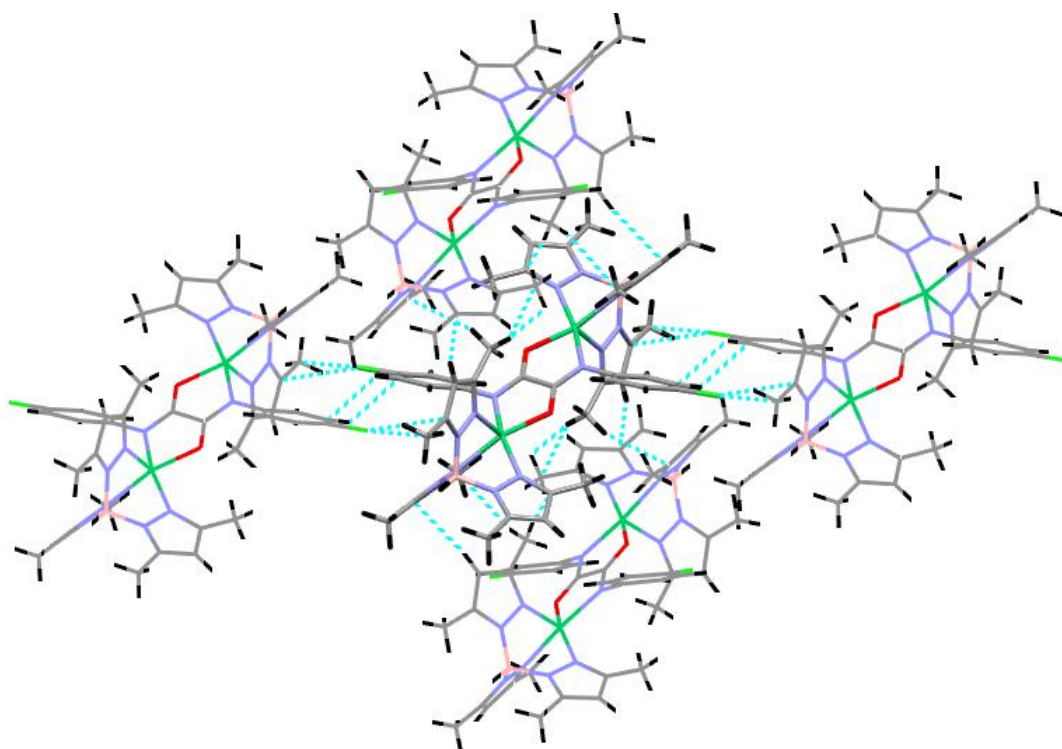


Figure S6. Molecular packing of complex **4** showing CH $\cdots$  $\pi$  interactions.

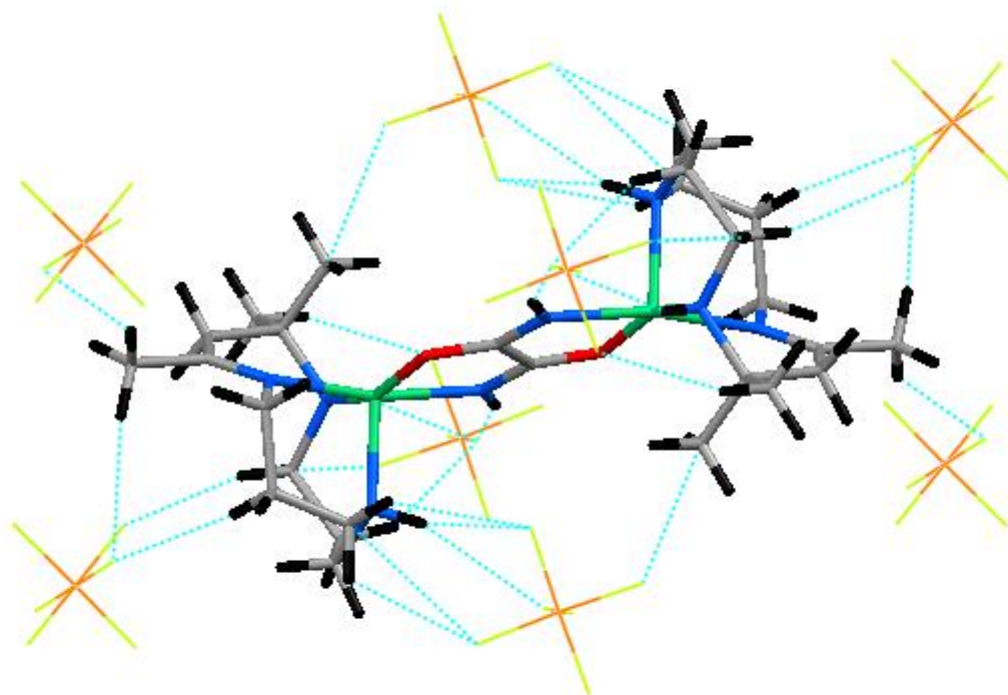


Figure S7. Molecular packing of {[Ni(N<sub>3</sub>-mc)]<sub>2</sub>(μ-*oa*)}(PF<sub>6</sub>)<sub>2</sub> showing supramolecular interactions.

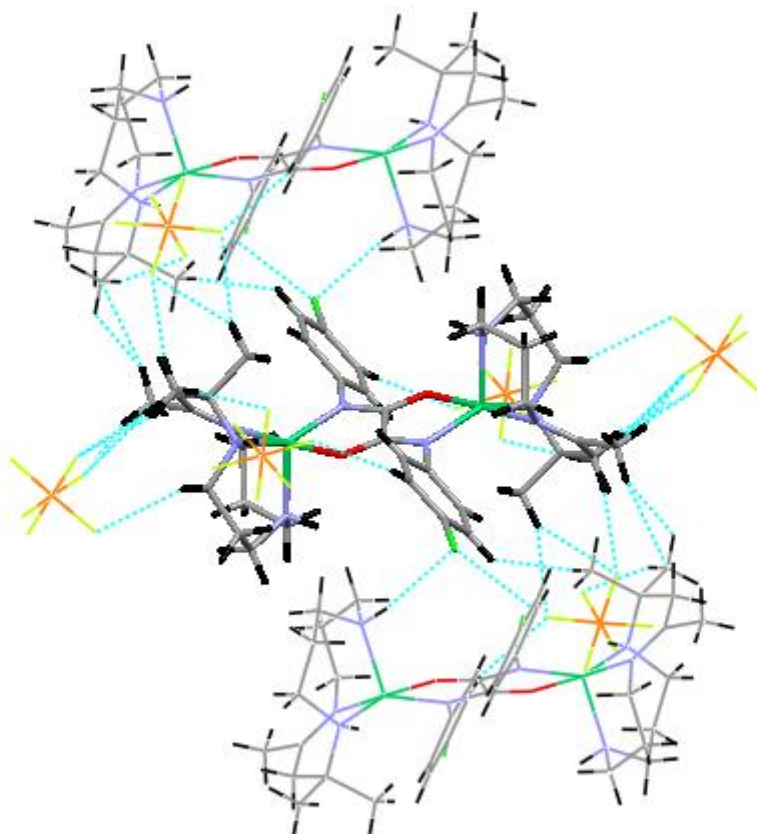


Figure S8. Molecular packing of  $\{[\text{Ni}(\text{N}_3\text{-mc})]_2[\mu\text{-CO}(4\text{-Cl-C}_6\text{H}_4\text{-N})]_2\}(\text{PF}_6)_2$  showing supramolecular interactions.

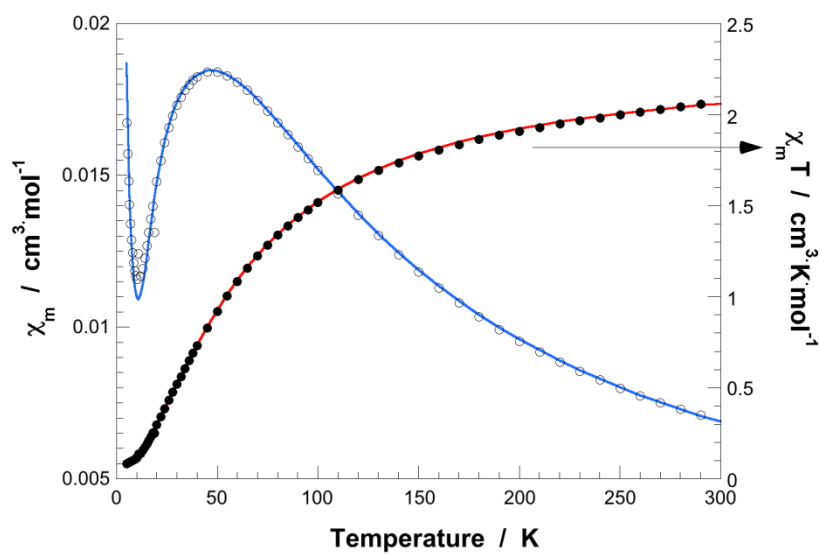


Figure S9. Thermal variation of  $\chi_m$  and  $\chi_m T$  for complex **1**. The solid lines correspond to the best fits obtained with Eq. 1.

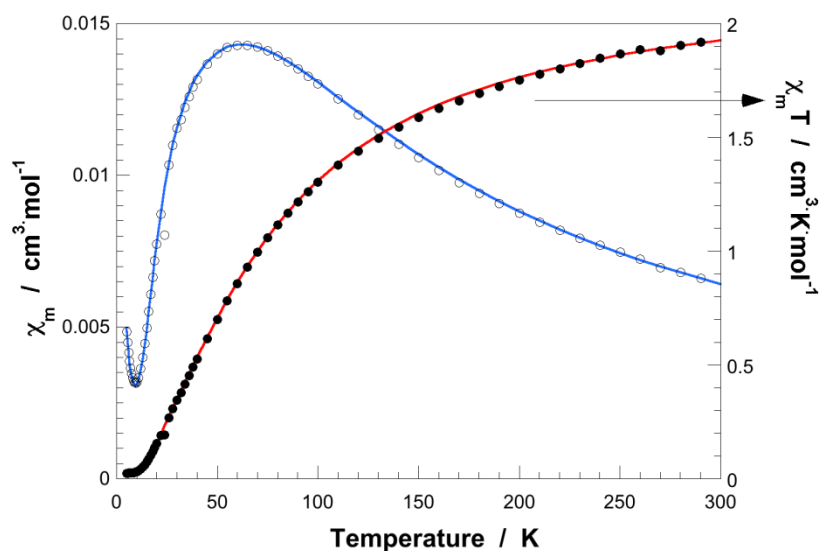


Figure S10. Thermal variation of  $\chi_m$  and  $\chi_m T$  for complex **2**. The solid lines correspond to the best fits obtained with Eq. 1.

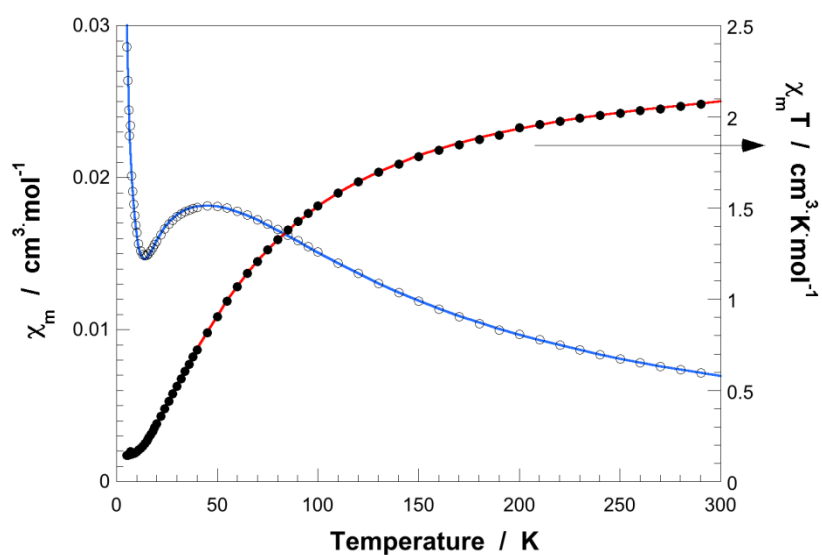


Figure S11. Thermal variation of  $\chi_m$  and  $\chi_m T$  for complex **4**. The solid lines correspond to the best fits obtained with Eq. 1.

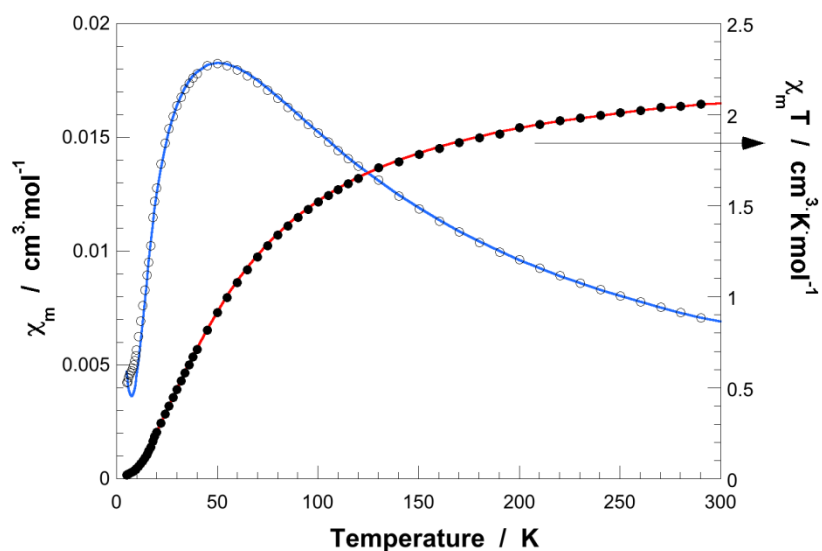


Figure S12. Thermal variation of  $\chi_m$  and  $\chi_m T$  for complex **5**. The solid lines correspond to the best fits obtained with Eq. 1.

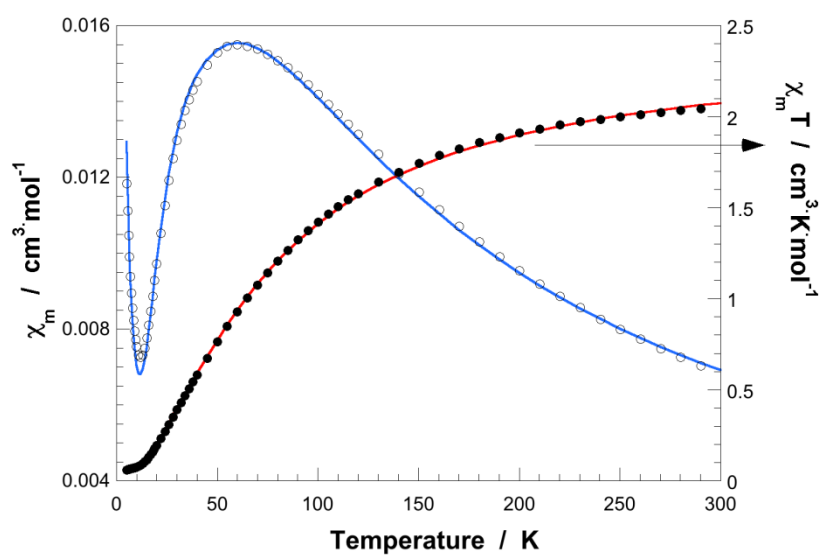


Figure S13. Thermal variation of  $\chi_m$  and  $\chi_m T$  for complex **6**. The solid lines correspond to the best fits obtained with Eq. 1.

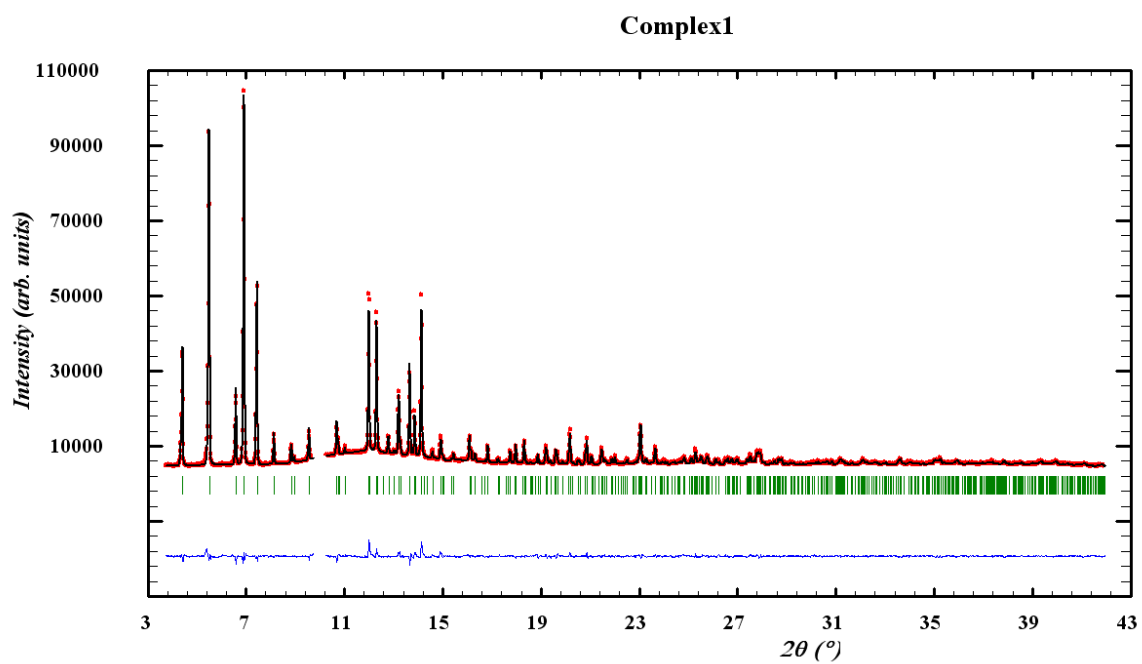


Figure S14: Plot for the Rietveld refinement of **1**

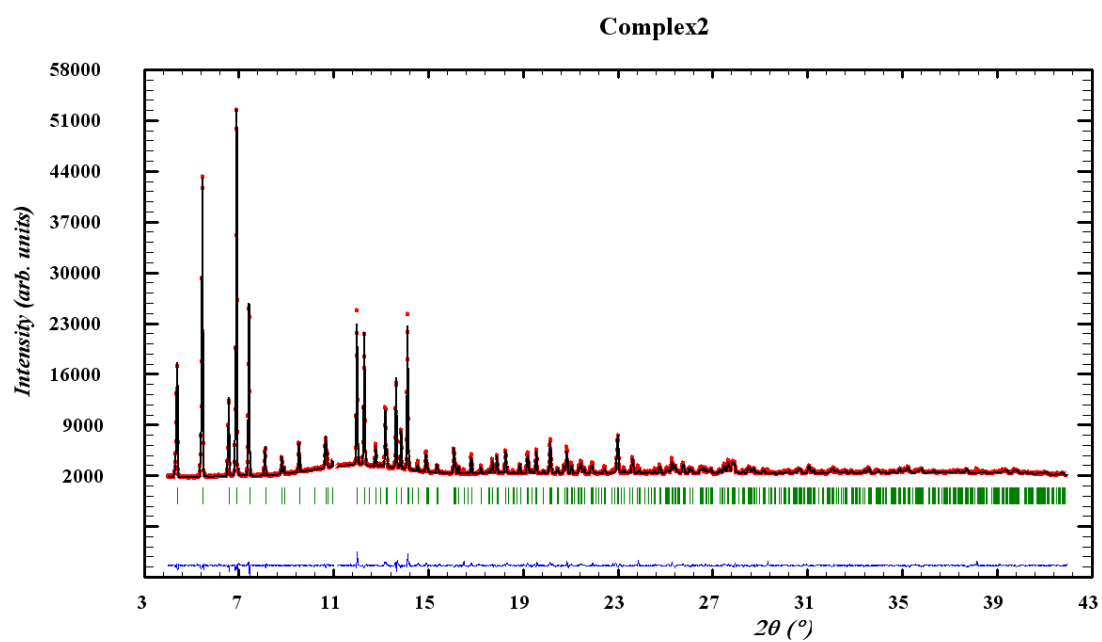


Figure S15: Plot for the Rietveld refinement of **2**

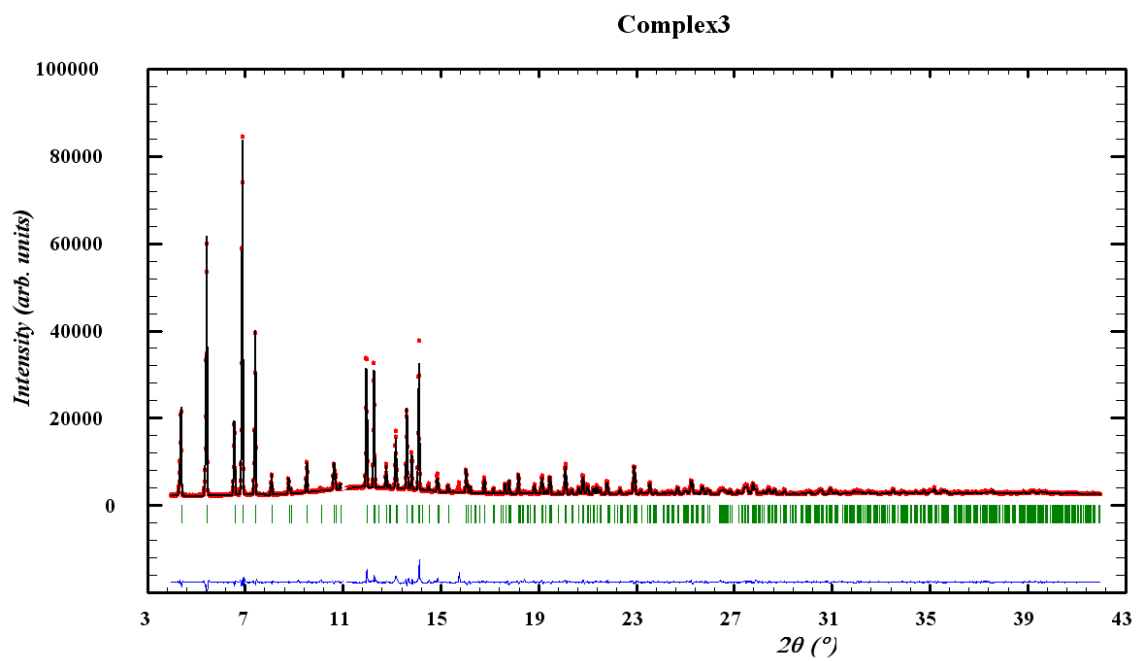


Figure S16: Plot for the Rietveld refinement of **3**