# Two distinct tetranuclear motifs, rectangular vs extended, are observed for complexes of a bis-tetradentate pyrimidine-based ligand

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## X-ray crystallography

Single crystal X-ray diffraction data for all complexes were collected on a Bruker Kappa Apex II area detector diffractometer at a temperature between 89-92 K. In all cases graphite monochromated Mo Kα radiation (λ = 0.71073 Å) was used. All data sets were corrected for absorption. The structures were solved by direct using SHELXS-97[1-3] and refined against $F^2$ using all data by full matrix least-squares techniques with SHELXL-97.[1-3] All non-hydrogen atoms were modelled anisotropically except where noted. Hydrogen atoms were inserted at calculated positions and rode on the non-H atoms to which they are attached (including isotropic thermal parameters which were equal to 1.2 times to the attached non-hydrogen atom), except where noted, when hydrogen atoms were instead either located from the difference map or inserted at positions suggested by SHELXL-97 and then their coordinates fixed.

**$[Mn^{II}_4(L^{Me})_2Cl_8]\cdot MeOH\cdot 2H_2O$ (1')**: All non-hydrogen atoms were refined anisotropically but DELU and SIMU applied to all atoms (default standard deviations) and 4 atoms required strong ISOR restraints too. All hydrogen atoms were placed at calculated positions and refined using a riding model except for those water molecules where they were found from a difference map and the O-H bonds made equal to 0.85 A before the positions of the hydrogen atoms were fixed (AFIX 01), and also for methanol molecule where AFIX 147 was used to locate the hydrogen atom but then to fix the position of the hydrogen atom, AFIX 01 was applied.

**$[Ni^{II}_4(L^{Me})_2(Cl)_4]Cl_4\cdot 6.4MeOH\cdot ½H_2O$ (3')**: All hydrogen atoms were placed at calculated positions and refined using a riding model, except for the water molecule (O90), where they were inserted using HADD 2 “instruction” and fixed using AFIX 01. Two of the methanol molecules of solvation are of full occupancy (i.e. O50, C50 and O60, C60), one is half occupancy (O70, C70), and one is disordered over two sites in the same region of space with 0.3:0.4 occupancy, for O80 C80 and O81 C81, respectively. All of them were restrained to be similar to the well behaved methanol (O50 C50) by “SAME” instruction.

**$[Cu^{II}_4(L^{Me})_2(Cl)_6]Cl_2\cdot MeOH\cdot {}^7/_2H_2O$ (4')**: All hydrogen atoms were placed at calculated positions and refined using a riding model, except those on O of water which were found from a difference map and the O-H bonds made equal to 0.85 A before the positions of the hydrogen atoms were fixed (AFIX 01). Lattice chloride ion was disordered over three sites with occupancy ratios of 0.50:0.25:0.25 for Cl22, Cl21 Cl20, respectively. Water and methanol molecules are all partial occupancy and disordered. This region of solvent was modelled as well as possible, in preference to resorting to SQUEEZE, however the residual peaks occur in this region.

**Table S1: Interatomic distances (Å) and angles (°) relevant to manganese(II) coordination spheres in $[Mn^{II}_4(L^{Me})_2Cl_8]\cdot MeOH\cdot 2H_2O$ (1')**

| | | | |
|---|---|---|---|
| Mn(1)-N(13) | 2.217(9) | Mn(2)-N(18) | 2.273(10) |
| Mn(1)-N(14) | 2.277(9) | Mn(2)-N(17) | 2.277(10) |
| Mn(1)-Cl(2) | 2.416(3) | Mn(2)-N(16) | 2.324(9) |
| Mn(1)-N(12) | 2.434(8) | Mn(2)-Cl(4) | 2.434(4 |
| Mn(1)-Cl(1a) | 2.554(4) | Mn(2)-Cl(3) | 2.445(4) |
| Mn(1)-Cl(1) | 2.559(3) | Mn(2)-N(15) | 2.507(9) |
| | | | |
| N(13)-Mn(1)-N(14) | 98.7(3) | N(18)-Mn(2)-N(17) | 99.6(4) |
| N(13)-Mn(1)-Cl(2) | 95.1(2) | N(18)-Mn(2)-N(16) | 76.8(3) |
| N(14)-Mn(1)-Cl(2) | 96.3(2) | N(17)-Mn(2)-N(16) | 72.2(3) |
| N(13)-Mn(1)-N(12) | 73.7(3) | N(18)-Mn(2)-Cl(4) | 93.9(3) |
| N(14)-Mn(1)-N(12) | 71.0(3) | N(17)-Mn(2)-Cl(4) | 95.4(3) |
| Cl(2)-Mn(1)-N(12) | 161.0(2) | N(16)-Mn(2)-Cl(4) | 162.6(3) |
| N(13)-Mn(1)-Cl(1a) | 88.3(3) | N(18)-Mn(2)-Cl(3) | 156.4(3) |
| N(14)-Mn(1)-Cl(1a) | 164.2(2) | N(17)-Mn(2)-Cl(3) | 94.8(3) |
| Cl(2)-Mn(1)-Cl(1a) | 97.15(11) | N(16)-Mn(2)-Cl(3) | 90.1(3) |
| N(12)-Mn(1)-Cl(1a) | 97.7(2) | Cl(4)-Mn(2)-Cl(3) | 103.34(14) |
| N(13)-Mn(1)-Cl(1) | 162.7(2) | N(18)-Mn(2)-N(15) | 73.6(3) |
| N(14)-Mn(1)-Cl(1) | 86.2(2) | N(17)-Mn(2)-N(15) | 143.3(3) |
| Cl(2)-Mn(1)-Cl(1) | 100.91(11) | N(16)-Mn(2)-N(15) | 71.1(3) |
| N(12)-Mn(1)-Cl(1) | 92.5(2) | Cl(4)-Mn(2)-N(15) | 120.8(2) |
| Cl(1a)-Mn(1)-Cl(1) | 83.15(11) | Cl(3)-Mn(2)-N(15) | 83.7(2) |

Symmetry operation used to generate equivalent atoms: a = -x+2,-y+1,-z+1

**Table S2. Hydrogen bonds for $[Mn_4(L^{Me})_2Cl_8]\cdot MeOH\cdot 2H_2O$ (1'): [Å and °].**

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(60)-H(60Y)...O(50) | 0.84 | 2.39 | 3.19(4) | 158.9 |
| O(70)-H(70X)...Cl(1a) | 0.86 | 2.61 | 3.472(11) | 178.0 |
| O(70)-H(70Y)...Cl(3) | 0.86 | 2.45 | 3.311(12) | 179.1 |

Symmetry transformations used to generate equivalent atoms: a = x-1,y+1,z

**Table S3: Selected interatomic distances (Å) and angles (°) for [Ni$^{II}_4$(L$^{Me}$)$_2$(Cl)$_4$]Cl$_4$·6.4MeOH·½H$_2$O (3’)**

| | | | |
|---|---|---|---|
| Ni(1)-N(14) | 2.061(6) | Ni(2)-N(18) | 2.032(6) |
| Ni(1)-N(13) | 2.086(6) | Ni(2)-N(16) | 2.082(5) |
| Ni(1)-N(12) | 2.092(5) | Ni(2)-N(17) | 2.096(6) |
| Ni(1)-N(11) | 2.192(5) | Ni(2)-Cl(2a) | 2.3766(17) |
| Ni(1)-Cl(1) | 2.3638(17) | Ni(2)-N(15) | 2.380(5) |
| Ni(1)-Cl(2) | 2.449(2) | Ni(2)-Cl(1a) | 2.4238(19) |

| | | | |
|---|---|---|---|
| N(14)-Ni(1)-N(13) | 84.8(2) | N(18)-Ni(2)-N(16) | 85.9(2) |
| N(14)-Ni(1)-N(12) | 83.4(2) | N(18)-Ni(2)-N(17) | 90.6(2) |
| N(13)-Ni(1)-N(12) | 82.6(2) | N(16)-Ni(2)-N(17) | 80.5(2) |
| N(14)-Ni(1)-N(11) | 95.6(2) | N(18)-Ni(2)-Cl(2a) | 97.87(17) |
| N(13)-Ni(1)-N(11) | 159.8(2) | N(16)-Ni(2)-Cl(2a) | 172.66(16) |
| N(12)-Ni(1)-N(11) | 77.41(19) | N(17)-Ni(2)-Cl(2a) | 93.15(16) |
| N(14)-Ni(1)-Cl(1) | 97.71(15) | N(18)-Ni(2)-N(15) | 82.4(2) |
| N(13)-Ni(1)-Cl(1) | 96.80(16) | N(16)-Ni(2)-N(15) | 73.68(19) |
| N(12)-Ni(1)-Cl(1) | 178.66(16) | N(17)-Ni(2)-N(15) | 153.6(2) |
| N(11)-Ni(1)-Cl(1) | 103.14(14) | Cl(2a)-Ni(2)-N(15) | 112.96(13) |
| N(14)-Ni(1)-Cl(2) | 175.76(16) | N(18)-Ni(2)-Cl(1a) | 173.75(17) |
| N(13)-Ni(1)-Cl(2) | 91.54(17) | N(16)-Ni(2)-Cl(1a) | 91.77(16) |
| N(12)-Ni(1)-Cl(2) | 94.02(16) | N(17)-Ni(2)-Cl(1a) | 94.79(17) |
| N(11)-Ni(1)-Cl(2) | 87.11(15) | Cl(2a)-Ni(2)-Cl(1a) | 85.09(6) |
| Cl(1)-Ni(1)-Cl(2) | 84.80(6) | N(15)-Ni(2)-Cl(1a) | 91.33(14) |

Symmetry operation used to generate equivalent atoms: a = -x,-y+1,-z+1

**Table S4. Hydrogen bonds for [Ni$^{II}_4$(L$^{Me}$)$_2$(Cl)$_4$]Cl$_4$·6.4MeOH·½H$_2$O (3’) [Å and °].**

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(50)-H(50)...Cl(4) | 0.84 | 2.33 | 3.088(8) | 149.8 |
| O(60)-H(60)...Cl(3) | 0.84 | 2.27 | 3.100(6) | 170.5 |
| O(80)-H(80)...O(60) | 0.84 | 1.60 | 2.400(17) | 158.0 |
| O(70)-H(70)...O(81) | 0.84 | 2.15 | 2.890(15) | 146.5 |
| O(81)-H(81)...Cl(4) | 0.84 | 2.15 | 2.974(11) | 166.7 |
| O(90)-H(90X)...Cl(4) | 0.87 | 2.29 | 3.16(2) | 179.2 |

**Table S5: Selected interatomic distances (Å) and angles (°) for $[Cu^{II}_4(L^{Me})_2(Cl)_6]Cl_2\cdot MeOH\cdot {}^7/_2H_2O$ (4')**

| | | | |
|---|---|---|---|
| Cu(1)-N(14) | 1.981(4) | Cu(2)-N(17) | 1.993(4) |
| Cu(1)-N(13) | 1.985(4) | Cu(2)-N(18) | 1.998(4) |
| Cu(1)-N(12) | 2.040(4) | Cu(2)-N(16) | 2.065(4) |
| Cu(1)-Cl(3) | 2.232(1) | Cu(2)-Cl(4) | 2.2321(13) |
| Cu(1)- N(11) | 2.703(1) | Cu(2)-Cl(5) | 2.6480(13) |
| Cu(1)-Cl(3a) | 2.8742(4) | | |
| N(14)-Cu(1)-N(13) | 165.64(16) | N(17)-Cu(2)-N(18) | 163.54(16) |
| N(14)-Cu(1)-N(12) | 82.33(15) | N(17)-Cu(2)-N(16) | 81.38(14) |
| N(13)-Cu(1)-N(12) | 83.35(15) | N(18)-Cu(2)-N(16) | 82.23(15) |
| N(14)-Cu(1)-Cl(3) | 97.02(12) | N(17)-Cu(2)-Cl(4) | 97.44(11) |
| N(13)-Cu(1)-Cl(3) | 97.32(11) | N(18)-Cu(2)-Cl(4) | 97.99(12) |
| N(12)-Cu(1)-Cl(3) | 178.59(12) | N(16)-Cu(2)-Cl(4) | 164.83(11) |
| N(11)-Cu(1)-Cl(3a) | 159.47(10) | N(17)-Cu(2)-Cl(5) | 89.29(11) |
| N(11)-Cu(1)-Cl(3) | 101.69(13) | N(18)-Cu(2)-Cl(5) | 92.83(10) |
| N(11)-Cu(1)- N(12) | 77.20(6) | N(16)-Cu(2)-Cl(5) | 92.33(10) |
| N(11)-Cu(1)- N(13) | 78.83(4) | Cl(4)-Cu(2)-Cl(5) | 102.80(4) |
| N(11)-Cu(1)- N(13) | 98.99(4) | | |
| N(12)-Cu(1)-Cl(3a) | 87.21(4) | | |
| N(13)-Cu(1)-Cl(3a) | 86.26(5) | | |
| N(14)-Cu(1)-Cl(3a) | 91.95(13) | | |
| Cl(3)-Cu(1)-Cl(3a) | 94.07(11) | | |

Symmetry operation used to generate equivalent atoms: a = -x+2,-y+1,-z+1

**Table S6. Hydrogen bonds for $[Cu_4(L^1)2(Cl)_6]Cl_2\cdot MeOH\cdot {}^7/_2H_2O$ (4') [Å and °].**

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(80)-H(80Y)...O(60) | 0.84 | 1.73 | 2.570(16) | 178.6 |
| O(90)-H(90X)...Cl(22) | 0.85 | 2.46 | 3.131(10) | 136.6 |
| O(70)-H(70)...Cl(5) | 0.85 | 2.26 | 3.108(7) | 178.9 |
| O(50)-H(50X)...Cl(21) | 0.87 | 2.31 | 3.169(16) | 167.9 |
| O(50)-H(50Y)...Cl(20b) | 0.85 | 2.36 | 3.209(14) | 173.8 |
| O(50)-H(50Y)...Cl(21b) | 0.85 | 2.18 | 3.006(14) | 165.5 |
| O(80)-H(80X)...Cl(21b) | 0.87 | 2.09 | 2.956(17) | 179.1 |
| O(90)-H(90X)...O(90c) | 0.85 | 1.72 | 2.566(18) | 177.8 |

Symmetry transformations used to generate equivalent atoms: b = -x+1,-y-1,-z ; c = -x+1,-y,-z+1

## References

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