Unexpected Ni(II) and Cu(II) polynuclear assemblies – a balance between ligand and metal ion coordination preferences.

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Supplementary material

Ligand syntheses

3,6-Pyridazinebis(carboxylic acid amide). Ammonia was bubbled through a hot solution of 3,6-Dicarbomethoxypyridazine (2.42 g, 0.0123 mol) in 300 ml of methanol for 6 h and white precipitate was collected by filtration, 2.03 g (99 %). LC/MS was not obtained due to low solubility. IR/cm^{-1}: 3421s, 3410s, 3289w, 3203ms, 3093w, 1678vs, 1605m, 1579w, 1561vw, 1332mw, 1170mw, 1163m, 1093mw, 1081mw, 877m, 790mw.

3,6-Pyridazinedicarbonitrile. 3,6-Pyridazinebis-(carboxylic acid amide) (2.06 g, 0.0124 mol) was suspended in 20 ml DMF and 4.0 ml of $POCl_3$ was added dropwise over the course of 30 min. The mixture was stirred at ambient temperature for 11 h and 10 ml of water was added drop-wise while the reaction flask kept in cold water bath. Then another 30 ml of water was added and the reaction mixture extracted with $CHCl_3$, and the residue evaporated until a dark oil was produced. This oil was further concentrated under vacuum using an apparatus where the volatiles were trapped on a cold finger with an attached cup. Recrystallization of the residue from $CHCl_3$ gave 1.1 g (68 %) of 3,6-pyridazine-dicarbonitrile as colorless needles. M. p. 131 – 133^{o}C; LC/MS *m/z*: 129 $[M - H]^+$; IR/cm^{-1}: 3131vw, 3118vw, 3089w, 3062w, 2251w, 2198vw, 1983vw, 1849vw, 1721vw, 1563vs, 1541vs, 1502mw, 1394vs, 1239mw, 1143w, 1126w, 1117m, 1101w, 1041w, 993w, 862vs, 771vw, 677w, 633mw, 581m, 561m.

Ligand L2. 3,6-pyridazinedicarbonitrile (0.40 g, 3.1 mmol) was dissolved in 10 ml of dry methanol, and the pH was adjusted to 8 by addition of sodium. The solution was gently heated for 20 min and neutralized with glacial acetic acid. Then 2-pyridinecarboxalic acid hydrazide (0.95 g, 6.9 mmol) was added as a solution in 20 ml of methanol and the mixture was heated for 2 d until a yellow suspension was produced. The product was collected by filtration, 1.09 g, 87 %. LC/MS (major fragment) *m/z*: 405 $[M + H]^+$. Elem.

Anal. (found/calc.): C, 53.23/53.46; H, 4.01/3.99; N, 34.55/34.64. IR/cm^{-1}: 3421m, 3295s, 3186br, 1679s, 1648vw, 1609vs, 1587vs, 1570ms, 1513vs, 1433s, 1416m, 1300vw, 1287w, 1241w, 1155mw, 1093w, 1077w, 1043mw, 999w, 923vw, 867vw, 815vw, 750m, 695m, 657m, 621ms, 612ms.

Compound 2. Nickel perchlorate hexahydrate (0.16 g, 0.44 mmol) and ligand **L2** (0.10 g, 0.25 mmol) were heated in 20 ml of methanol for 10 min to produce an orange suspension. Then 0.45 ml of 1 M NaOH (aq) was added, the mixture heated for 5 min followed by addition of 8 ml of H_2O and heating for 25 min. The cloudy red-orange solution was filtered and left standing for two weeks, producing a small quantity of red crystalline plates in addition to a bulk red microcrystalline sample (Yield 50 mg; 30 %). Elem. Anal. (found/calc.) for bulk sample $[(C_{18}H_{14}N_{10}O_2)_3Ni_{16}](ClO_4)_2 \cdot 10H_2O$: C, 35.88/35.86; H, 2.89/2.79; N, 23.64/23.23.

2,2'-Bipyridine-3-carboxylic acid hydrazide. 2,2'-bipyridine-3-methylcarboxylate[1] (2.97 g, 13.9 mmol) was dissolved in 125 ml of methanol and hydrazine hydrate (0.88 g, 17.6 mmol) added. The solution was refluxed for 4 h and the volume was reduced to ca. 1/3. The product precipitated after a few hours of standing as pale yellow solid, 1.4 g (47 %). M. p. 162-163 ^{o}C. LC/MS (major fragment) *m/z*: 215 $[M + H]^+$.

Ligand L4. 3,6-pyridazinedicarbonitrile (0.23 g, 1.8 mmol) was dissolved in 10 ml of dry methanol, and the pH was brought to 8 by addition of sodium. The solution was gently heated for 40 min and neutralized with glacial acetic acid. Then 2,2'-bipyridine-3-carboxylic acid hydrazide (0.78 g, 3.6 mmol) was added along with 50 ml of methanol and the mixture was heated for 2 d until a yellow suspension was produced. The product was collected by filtration, 0.85 g, 86 %. LC/MS was not obtained due to low solubility. Elem. Anal. (found/calc.) for $C_{28}H_{22}N_{12}O_2$: C, 60.04/60.21; H, 3.97/3.97; N, 29.99/30.09. IR/cm^{-1}: 3420br, 3318mw, 3177br, 1736vw, 1683m, 1607vs, 1581s, 1562mw, 1518s, 1428ms, 1321vw, 1257vw, 1229vw, 1169w, 1079mw, 1037vw, 993w, 930w, 860vw, 836w, 792mw, 756m, 683m, 634m.

Compound 5. A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.080 g, 0.21 mmol) in $MeOH/H_2O$ (20/5 mL) was added to a suspension of L4 (0.040g, 0.072 mmol) in MeOH (20 mL), and the mixture stirred under reflux for 15 m giving a reddish brown solution. NaOAc (0.1 g, 1.25 mmol) was added, and the colour changed to deep red. The hot solution was filtered and concentrated by slow evaporation to give a dark brown solid. The solid was extracted with $MeOH/CH_3CN$ (3/3 mL) to give dark brown crystals on standing suitable for structural determination (Yield 30 mg, 31%). Elem. Anal. (found/calc.) for bulk air dried sample $(C_{28}H_{18}N_{12}O_2)_3Cu_{11}(ClO_4)_4(CH_3COO)_4Na(OH)(H_2O)_{31}$: C, 30.82/30.74; H, 2.85/3.61; N, 13.81/14.03.

4,6-Pyrimidinebis(carboxylic acid amide). Ammonia was bubbled through a hot solution of 4,6-Dicarbomethoxypyrimidine[2] (3.00 g, 15.3 mmol) in 200 ml of methanol for 18 h and white precipitate was collected by filtration, 1.53 g (60 %). LC/MS was not obtained due to low solubility. IR/cm^{-1}: 3433w, 3406m, 3287br, 3233br, 1706s, 1677ms, 1588m, 1535s, 1402m, 1295m, 1203w, 1191w, 1170w, 1088mw, 997w, 929m, 805w, 774mw, 760w, 638s.

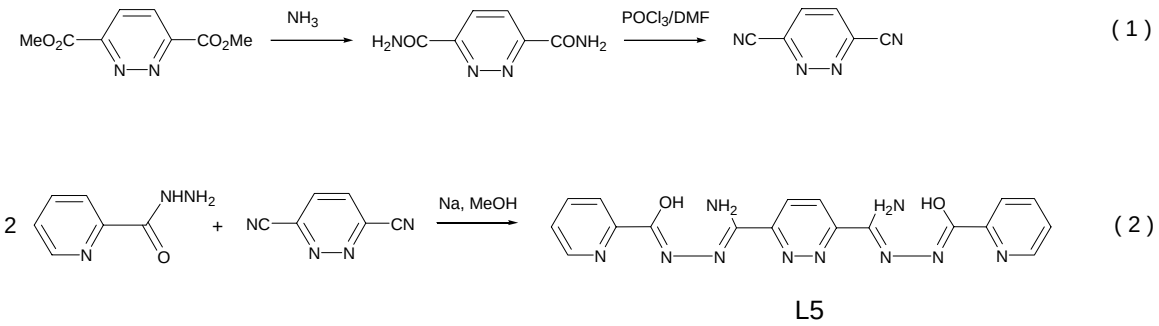
4,6-Pyrimidinedicarbonitrile. 4,6-Pyrimidinebis-(carboxylic acid amide) (2.06 g, 0.0124 mol) was suspended in 20 ml DMF and 4.0 ml of $POCl_3$ was added dropwise over the course of 30 min. The mixture was stirred at ambient temperature for 11 h and 10 ml of water was added drop-wise while the reaction flask kept in cold water bath. Then another 30 ml of water was added and the reaction mixture extracted with $CHCl_3$, and the extract evaporated until yellow oil was produced. This oil was further concentrated using a cold finger under vacuum (vide supra). Recrystallization of the residue from $CHCl_3$ gave 1.1 g (68 %) of 4,6-pyrimidinedicarbonitrile as colorless plates/blocks. Recrystallization was carried out quickly due to slow decomposition of the dinitrile in $CHCl_3$. M. p. 91– 95^oC; IR/cm^{-1}: 3136vw, 3122vw, 3094w, 3069mw, 1815w, 1630w, 1577s, 1563vs, 1526vs, 1331s, 1323s, 1308ms, 1237m, 1227mw, 1172m, 1156mw, 1143w, 1128w, 1116vw, 1010vw, 985m, 910s, 894ms, 877m, 772m, 670vw.

Ligand L6. 4,6-pyrimidinedicarbonitrile (0.37 g, 2.8 mmol) was dissolved in 10 ml of dry methanol, and 1.0 ml of 0.29 M solution of NaOMe in MeOH was added. The solution was heated for 35 min, during which time it changed from very intense purple to orange-red in color. Then the solution was neutralized with 2 drops of glacial acetic acid, 2-pyridinecarboxalic acid hydrazide (0.90 g, 6.6 mmol) added as a solution in 20 ml of methanol and the mixture refluxed for 1 d to give a yellow suspension. It was filtered hot and the product collected by filtration (Yield 0.28 g; 24 %). IR/cm^{-1}: 3442m, 3410m, 3290br, 3190br, 1671vs, 1656ms, 1627vs, 1588vs, 1571ms, 1520vs, 1449vs, 1309mw, 1288mw, 1242mw, 1202w, 1172mw, 1090w, 1047vw, 995mw, 936w, 923mw, 902vw, 810mw, 798w, 742ms, 700m, 675mw, 664w, 619ms.

Compound 6. Nickel nitrate hexahydrate (0.09 g, 0.31 mmol) and ligand **L6** (0.05 g, 0.12 mmol) were heated in 10 ml of methanol for 2 h to produce a dark red solution with some dark red precipitate. 5 ml of water was added but the precipitate remained undissolved. The mixture was filtered and the filtrate was allowed to slowly evaporate for two months, after that the volume of solvent was reduced to ca. 0.5 ml. Then the flask was sealed and left standing for a few weeks producing dark red crystals suitable for structural determination (Yield 50 mg ; 30 %). Elem. Anal. (found/calc.) for bulk sample $[(C_{18}H_{13}N_{10}O_2)_8Ni_{16}(NO_3)_{16}(H_2O)_{40}$: C, 29.67/29.50; H, 2.70/3.16; N, 22.53/22.94.

Results and discussion

To prepare ligands L2 and L4 it was necessary to develop a high yield synthesis of the 3,6-pyridazinedicarbonitrile precursor. Our initial attempts involved extension of the previously reported preparation procedure for 1,4-phthalazinedicarbonitrile,[3] using 1,4-diiodophthalazine and CuCN in pyridine, to 3,6-diiodopyridazine, but the reaction consistently gave low yields. On the other hand, dehydration of the corresponding bis-amide using $POCl_3$ in DMF according to the slightly modified published method for 2,6-pyridinedicarbonitrile[4] gave 3,6-pyridazinedicarbonitrile in 68 % yield (eqn 1, Scheme 1). The latter was converted *in situ* to the corresponding bis-imino ester followed by the reaction with 2-pyridine hydrazone to give L2 in 87 % yield (eqn 2, Scheme 1).



Scheme 1

1. T. Norrby et al., *Acta Chem. Scand.* **1998**, *52*, 77-85.
2.1. R. R. Hunt, J. F. W. McOmie and E. R. Sayer, *J. Chem. Soc.*, 1959, 525.
3. A. Hirsch, D. G. Orphanos, *Can. J. Chem.*, 1966, 44, 1551-1554.
4. Gorbyleva, O. I.; Evstratova, M. I.; Yakhontov, L. N., *Chem. Heterocycl. Comp.*, 1983, 10, 1419.

Eqn. S1

$$H_{ex} = -J1\{ S_2 \cdot S_3 + S_6 \cdot S_7\} -J2\{S_1 \cdot S_2 + S_3 \cdot S_4 + S_5 \cdot S_6 + S_7 \cdot S_8 + S_9 \cdot S_{10}\} + Cu(11)$$

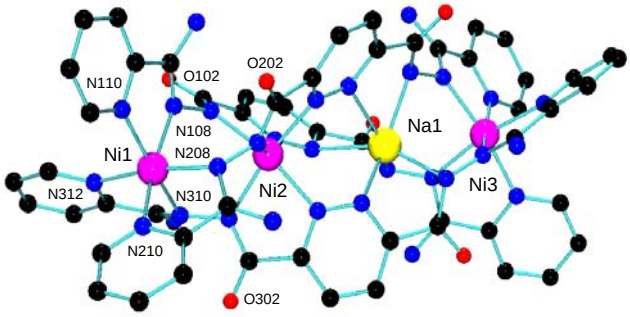


Fig. S1. Structure of **1**.

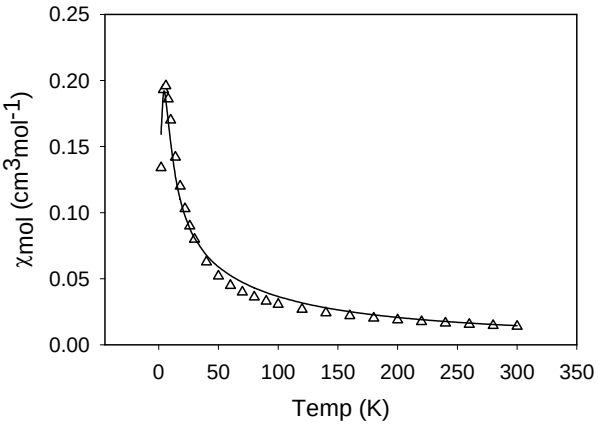


Fig. S2. Magnetic data for **2.** Solid line based on the fitted parameters (see text).

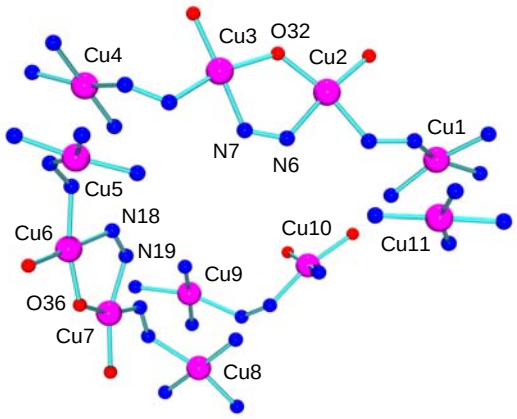
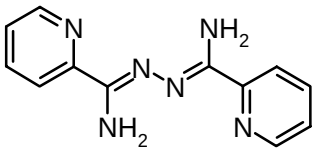
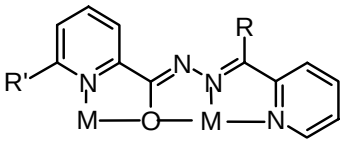


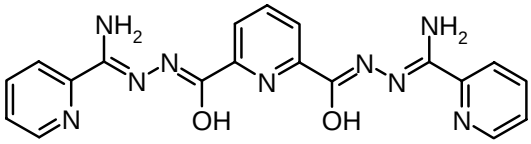
Fig. S3. Core structure for **5,** showing non-orthogonal copper connections



pahap



poap (R=NH_2,R'=H)
pomp (R=CH_3,R'=H)
mpoap (R=NH_2, R'=CH_3)



2poap

Chart S1

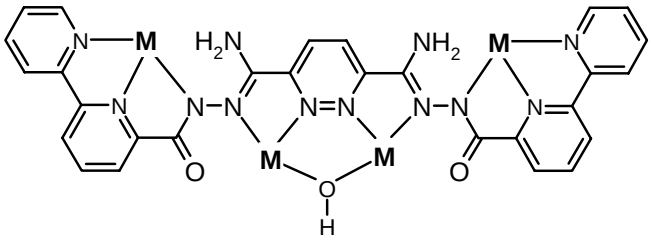


Chart S2