

Constructing two 1D–coordination polymers and one mononuclear complex by pyrazine- and pyridinedicarboxylic acids under mild and sonochemical conditions: Magnetic and CSD studies

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Supporting Information

Table S1. Selected bond lengths [Å] and angles [°] for compounds **1**, **2** and **3**.

Symmetry codes: (i) $-x, -y+1, -z+1$ for **1**, (i) $-x+1, -y+1, -z$ for **2**

Compound			
1			
Cu1–O1	1.951(15)	O1–Cu1–N1	83.53(7)
Cu1–N1	1.967(19)	O1–Cu1–N1 ⁱ	96.47(7)
Cu1–O4	2.546(16)	O1 ⁱ –Cu1–N1 ⁱ	83.53(7)
N1 ⁱ –Cu1–N1	180.0	O1–Cu1–O1 ⁱ	180.0
O1 ⁱ –Cu1–N1	96.47(7)		
2			
Cu1–O1	1.953(12)	O1–Cu1–N1	83.31(6)
Cu1–N1	1.958(15)	O1–Cu1–N1 ⁱ	96.69(6)
Cu1–O4	2.609(1)	O1 ⁱ –Cu1–N1 ⁱ	83.31(6)
O1–Cu1–O1 ⁱ	180.0	N1 ⁱ –Cu1–N1	180.0
O1 ⁱ –Cu1–N1	96.70(6)		
3			
Cu1–O1	2.018(17)	N1–Cu1–O1	80.66(8)
Cu1–O3	2.046(18)	N1–Cu1–O3	79.82(8)
Cu1–O5	2.311(19)	N1–Cu1–O5	94.52(8)
Cu1–N1	1.913(2)	N1–Cu1–N2	171.60(9)
Cu1–N2	1.940(2)	N2–Cu1–O1	97.69(8)
O1–Cu1–O3	159.86(7)	N2–Cu1–O3	100.91(8)
O1–Cu1–O5	93.56(7)	N2–Cu1–O5	93.80(8)
O3–Cu1–O5	92.87(5)		

Table S2 Some of the hydrogen bonding interactions present in **1-3**.

D-H...A	d(D-H)/Å	D(H-A)/Å	d(D-A)/Å	D-H-A/°
1				
N3-H3N...O3	0.87	1.87	2.74(2)	171.60
N4-H4NA...O3	0.88	1.97	2.89(3)	169.59
N4-H4NB...O4	0.88	2.02	2.85(3)	175.43
2				
N2-H2N...O4	0.86	1.86	2.72(2)	176.27
N3-H3NA...O4	0.82	1.98	2.84(2)	172.07
N3-H3NB...O3	0.87	2.06	2.85(2)	164.07
3				
O5-H5OA...O4	0.84	1.96	2.79(3)	165.77
O5-H5OB...O4	0.84	1.97	2.79(3)	164.23
N3-H3NA...O3	0.86	2.04	2.82(3)	151.08
N3-H3NB...O2	0.85	2.01	2.83(3)	160.82

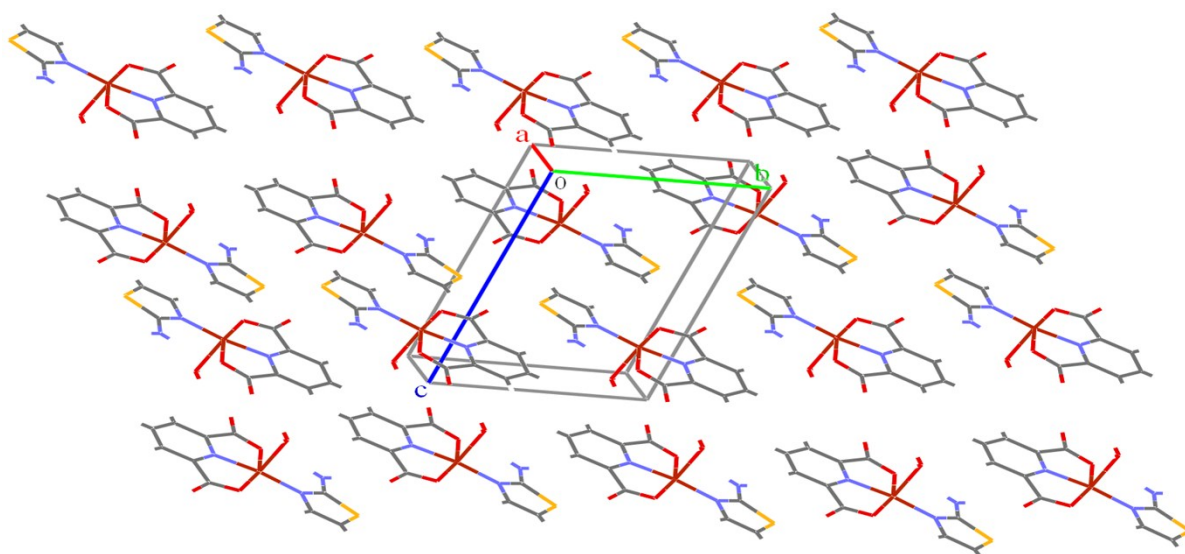


Figure S1. Crystal packing of compound **3** showing the antiparallel arrangement of complex in adjacent layers

CSD search

There are 246, 258 and 1253 examples of coordination compounds of the H₂pyz-2,3-dc, H₂py-2,3-dc and H₂py-2,6-dc ligands in the Cambridge Structural Database (CSD ver. 5.38 updates (Feb 2017)). Those complexes containing first row transition metals in the metal center are the most reported structures while those with main group metal centers are less reported (Figure S2). Looking at the diagram (Figure S2b) clearly shows that for all three ligands, abundance of the metal complexes with the first row transition metals significantly increases from left to right (Sc–Zn) and most abundant corresponds to Cu, Zn, and Co metals while those containing Sc and Cr are the least. This is likely due to the high activity and reactivity of these metallic ions. Therefore, these metals particularly copper are excellent candidates for the preparation of new coordination compounds with dicarboxylate ligands.

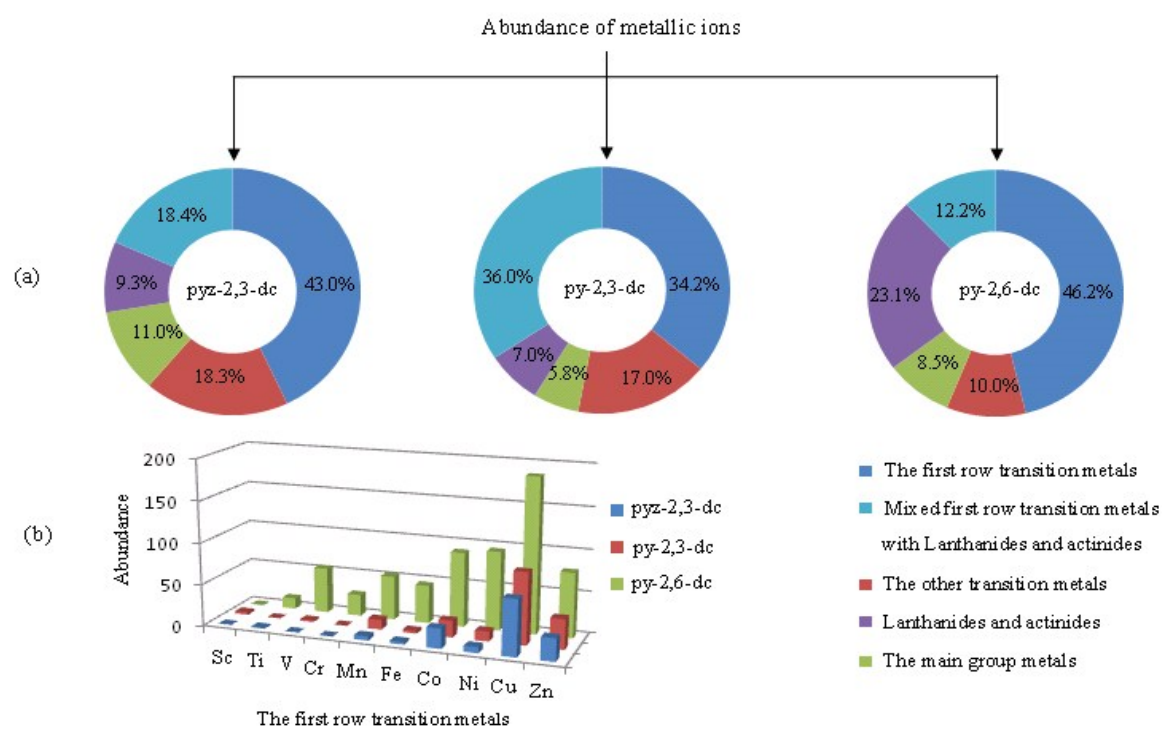


Figure S2 Abundance of reported coordination compounds containing pyz-2,3-dc, py-2,3-dc and py-2,6-dc ligands a) with various metal centres b) with the first row transition metals.

Furthermore, three analyses based on the CSD data have been performed to explore the ligand isomerism and co-ligand roles in determination of the overall structures. To acquire knowledge on the role of ligand isomerism and position of functional groups on the final product, we have extracted all reported coordination modes for these three ligands (Figures S3, S4 and S5). There are 56, 46 and 66 coordination modes for H₂pyz-2,3-dc, H₂py-2,3-dc and H₂py-2,6-dc ligands,

respectively. In 2, 6 isomer, due to the specific situation of the carboxylate groups toward N-ring and its high symmetry compared to isomer of H₂pyridine-2,3-dc, the variety and number of coordination modes are more observed. In addition, the presence of excess nitrogen in aromatic ring increases the number of coordination modes for H₂pyz-2,3-dc compared to H₂pyridine-2,3-dc. Scheme S1 illustrates that more than 80% of prepared compounds by H₂pyz-2,3-dc and H₂pyridine-2,3-dc ligands are polymer while use of H₂pyridine-2,6-dc ligand Leads to mononuclear complex in most cases. Coordination modes 9, 2 and 1 have the most abundance for H₂pyz-2,3-dc, H₂py-2,3-dc and H₂py-2,6-dc ligands, respectively. Two coordination polymers **1**, **2** and mononuclear complex **3** adopt these coordination modes in accordance with the usual behavior of their ligands (diagrams 1, 2 and 3 in Figure S6). Reported structures containing above-mentioned ligands are divided into three general categories: (1) neutral complexes containing ancillary ligand, (2) anionic complexes with counter cation and (3) cationic complexes with counter anion. The most structures for each ligand belong to the first and second categories (Figure S7). Coordination behavior of co-ligand to form structures of first or second category is influenced by several factors such as, nature of the ligand, co-ligand and their substituents. For clarification, a statistical study was performed on the behavior of the co-ligand in the presence of -2,3- and -2,6-dicarboxylate isomers (Figures S8, S9 and S10). The obtained results suggest the following interesting issues. First, all auxiliary ligands with various hetero-atoms (O, S, P and C) coordinate to the metal centre to construct neutral mixed ligand complexes except, those containing nitrogen as heteroatom (green column). Second, auxiliary ligands with N-donor sites show dual behavior and coordinate to the metal centre to form neutral complexes or act as base by the acceptance of acidic protons to form anionic complexes with counter cation. Auxiliary ligands with two N-donor sites tend to coordinate in most cases ($\approx 60\%$) while numbers of neutral and anionic structures are equal approximately for ones with one N-donor site (compare green and pink columns). Actually, the most important point in the formation of mixed-ligand complexes is the competition between the nucleophilicity and basicity of the organic ligands and it depends on type and position of the hetero atoms in the aromatic ring and their substituents. For example, the presence of sulfur hetero-atom in the aromatic ring increases basicity of the ligand significantly. Therefore, ligands containing N, S as hetero-atom tend to accept the acidic proton and act as a counter cation (6 of 7 reported structures) confirmed by the synthesis of two coordination polymers **1** and **2** with H₂-atz counter cation. Unexpectedly, 2-atz in complex **3** acts as an ancillary ligand and coordinates to Cu (II) metal centre. This is likely due to strong chelating effect of H₂py-2,6-dc and demand to fill empty sites to achieve five coordination number (one of the common

coordination number for Cu/py-2,6-dc complexes). These results clearly demonstrate the effect of ligand isomerism on behavior of co-ligand and final structure.

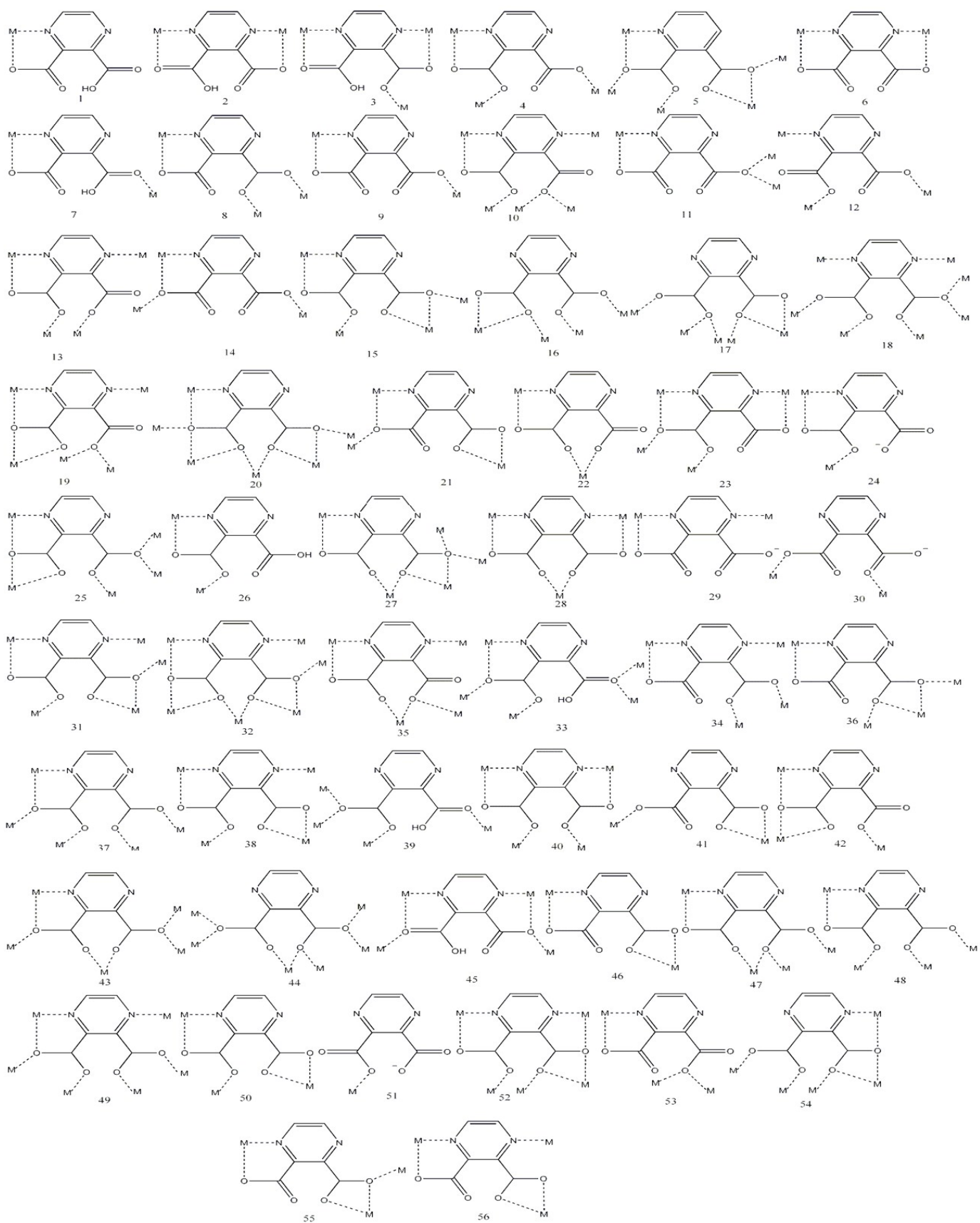


Figure S3 All observed coordination modes for H₂pyz-2,3-dc ligand

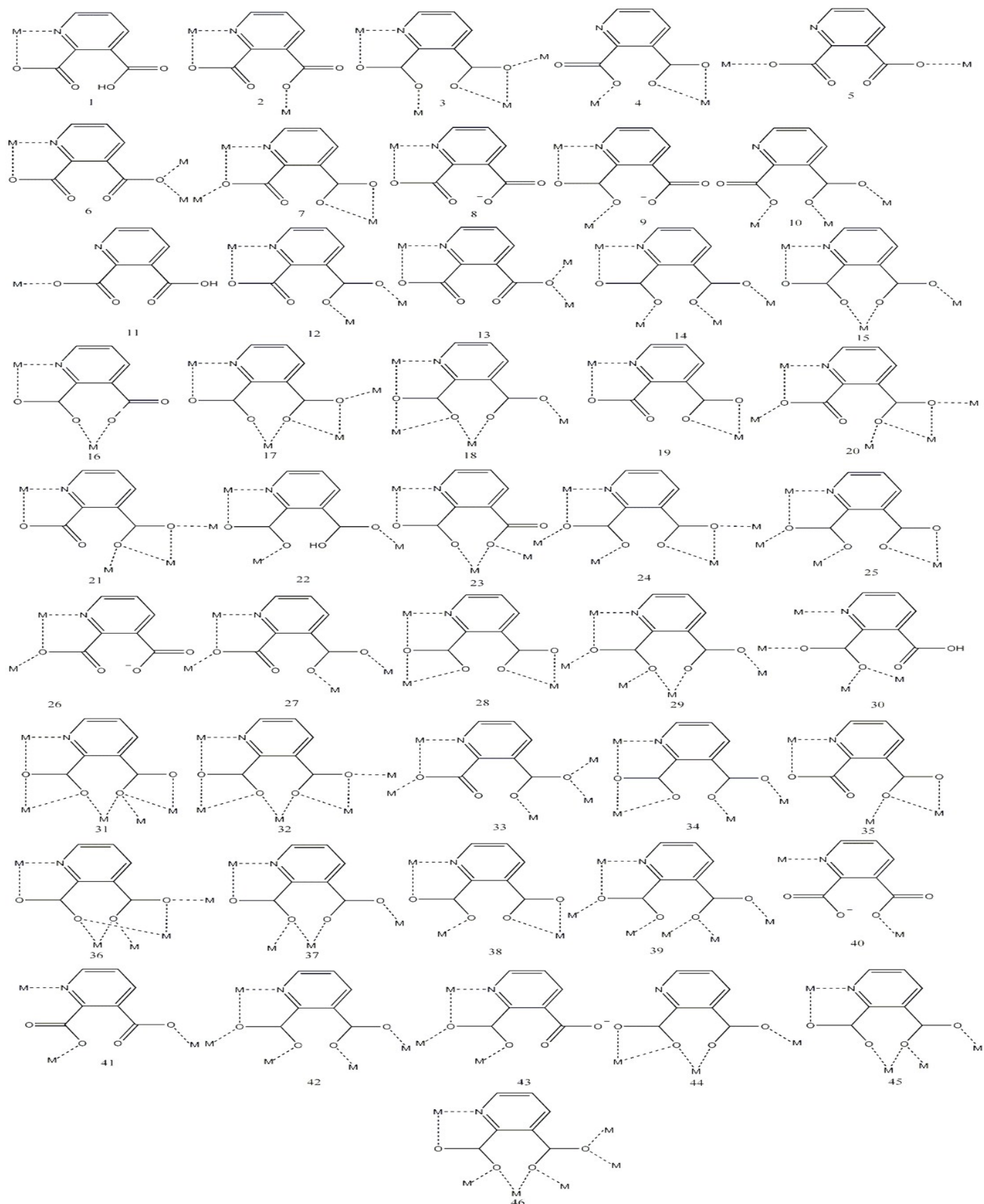


Figure S4. All observed coordination modes for H₂py-2,3-dc ligand

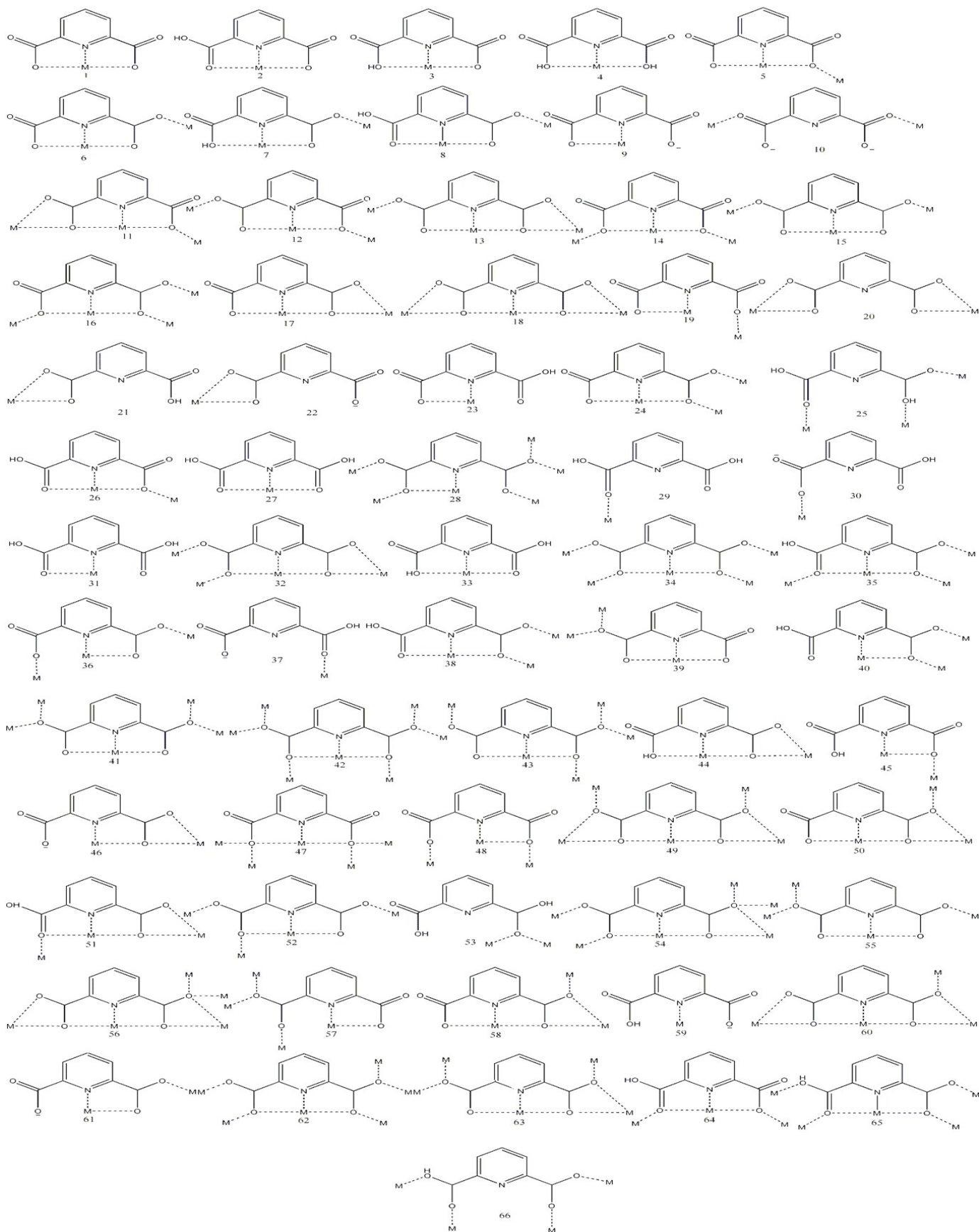
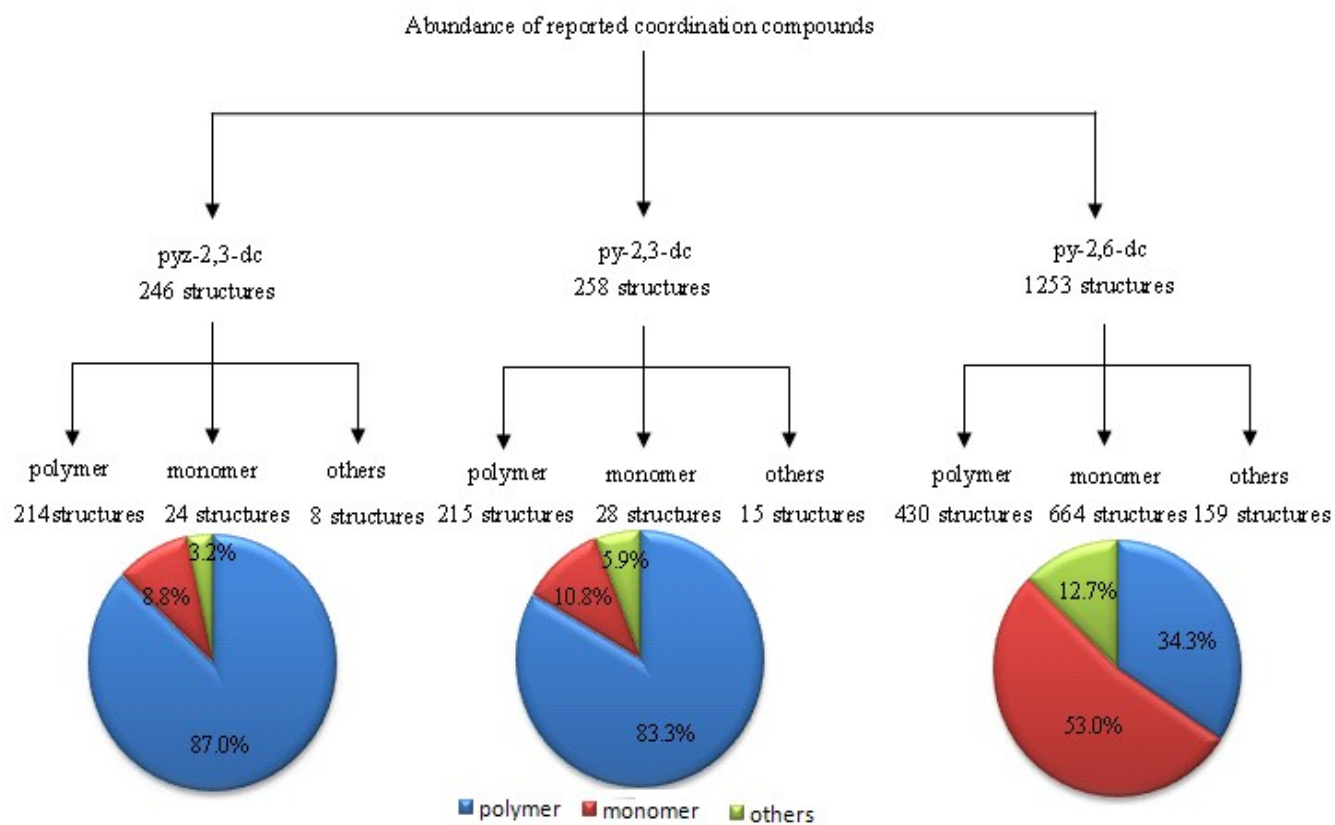


Figure S5. All observed coordination modes for H₂py-2,6-dc ligand



Scheme S1. Abundance of monomer and polymer complexes containing pyz-2,3-dc, py-2,3-dc and py-2,6-dc ligands

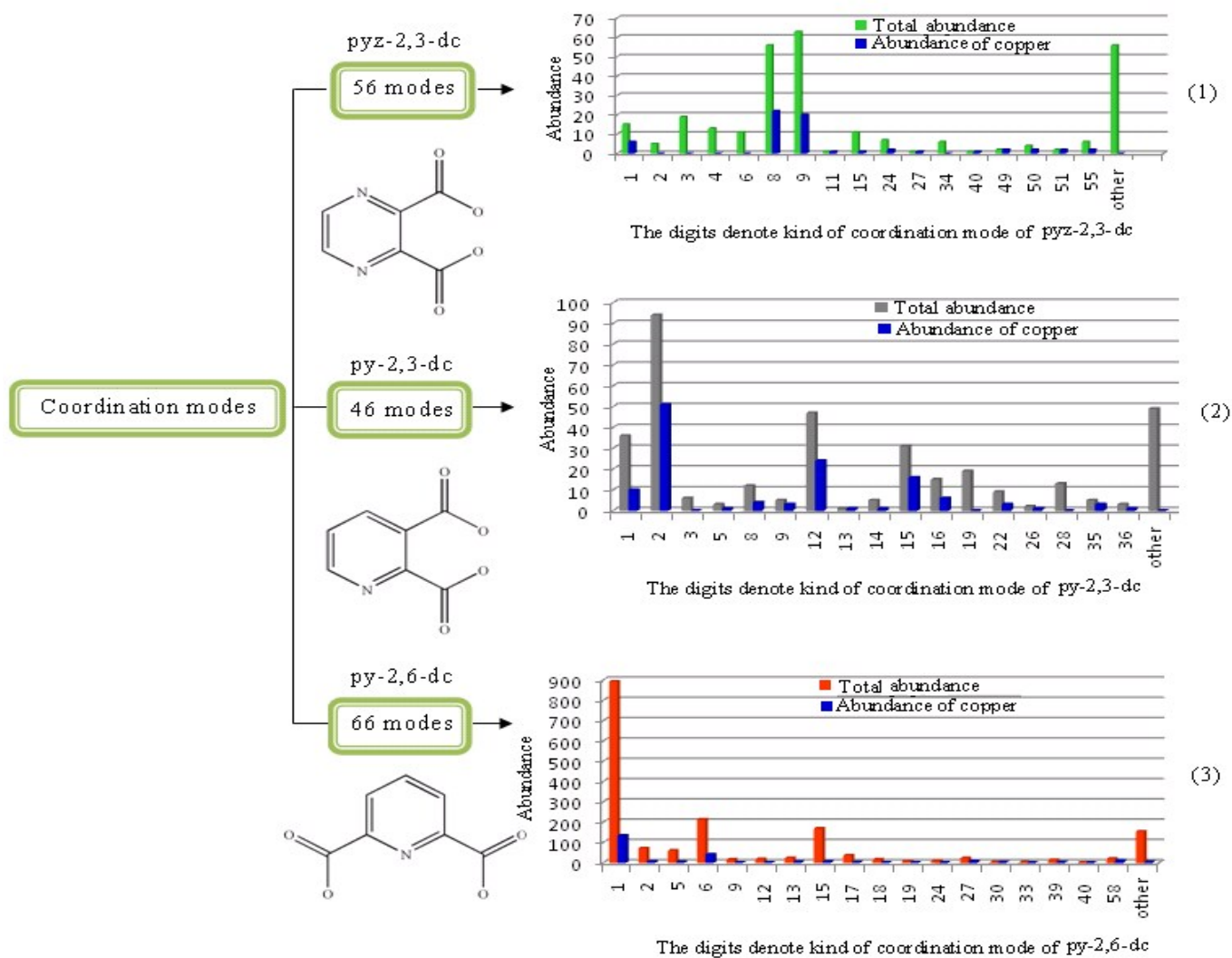


Figure S6. Abundance of coordination compounds in various modes for (1) pyz-2,3-dc, (2) py-2,3-dc and (3) py-2,6-dc ligands

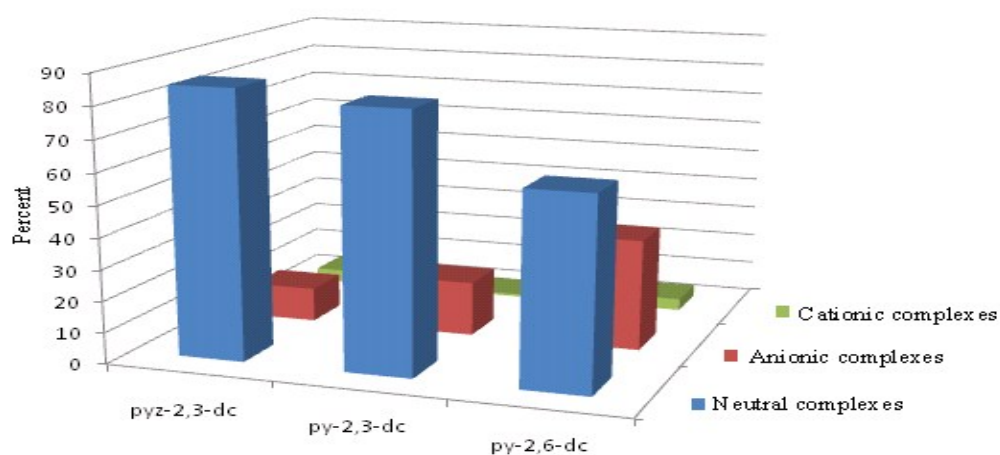


Figure S7. Comparison of abundance of neutral, anionic and cationic complexes containing pyz-2,3-dc, py-2,3-dc and py-2,6-dc ligands

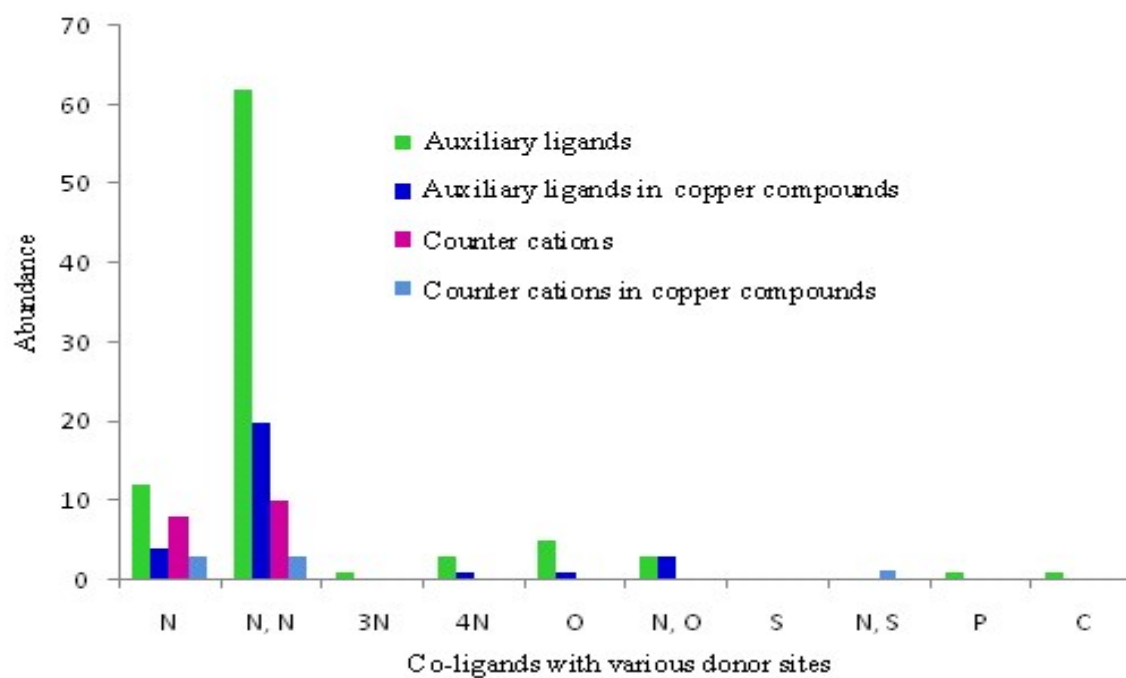


Figure S8. Abundance of complexes containing pyz-2,3-dc ligand with various co-ligands

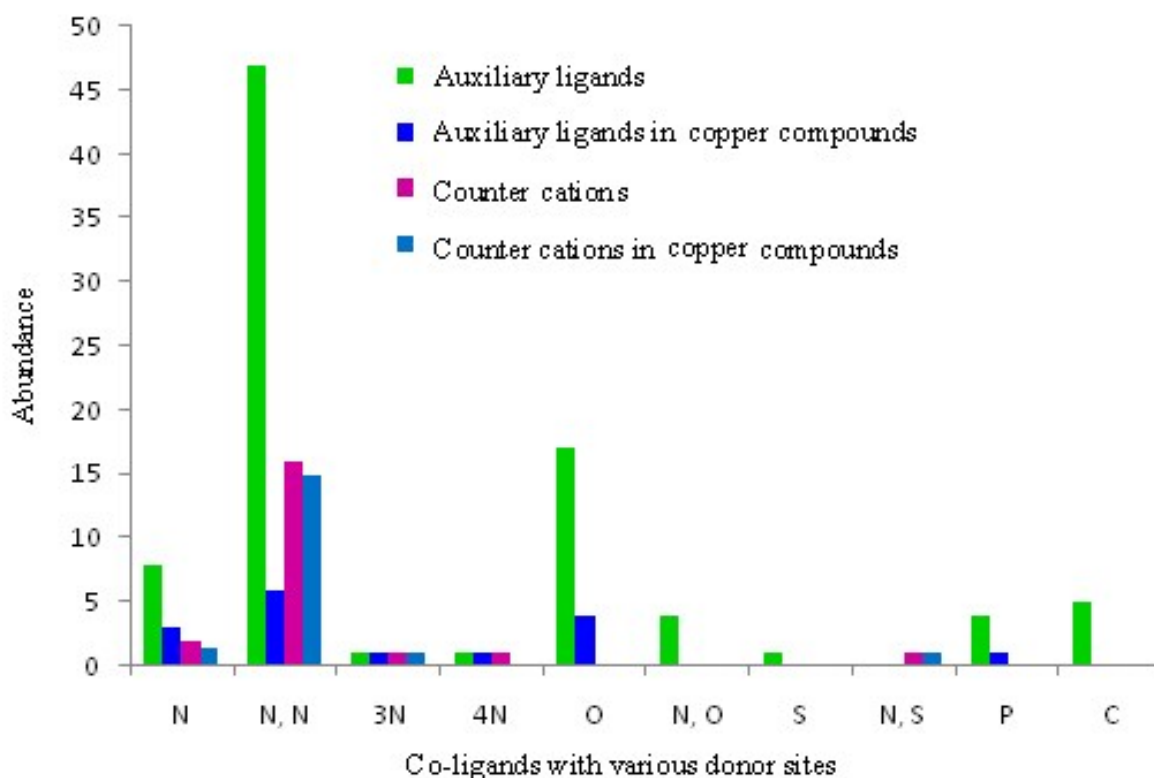


Figure S9. Abundance of complexes containing py-2,3-dc ligand with various co-ligands

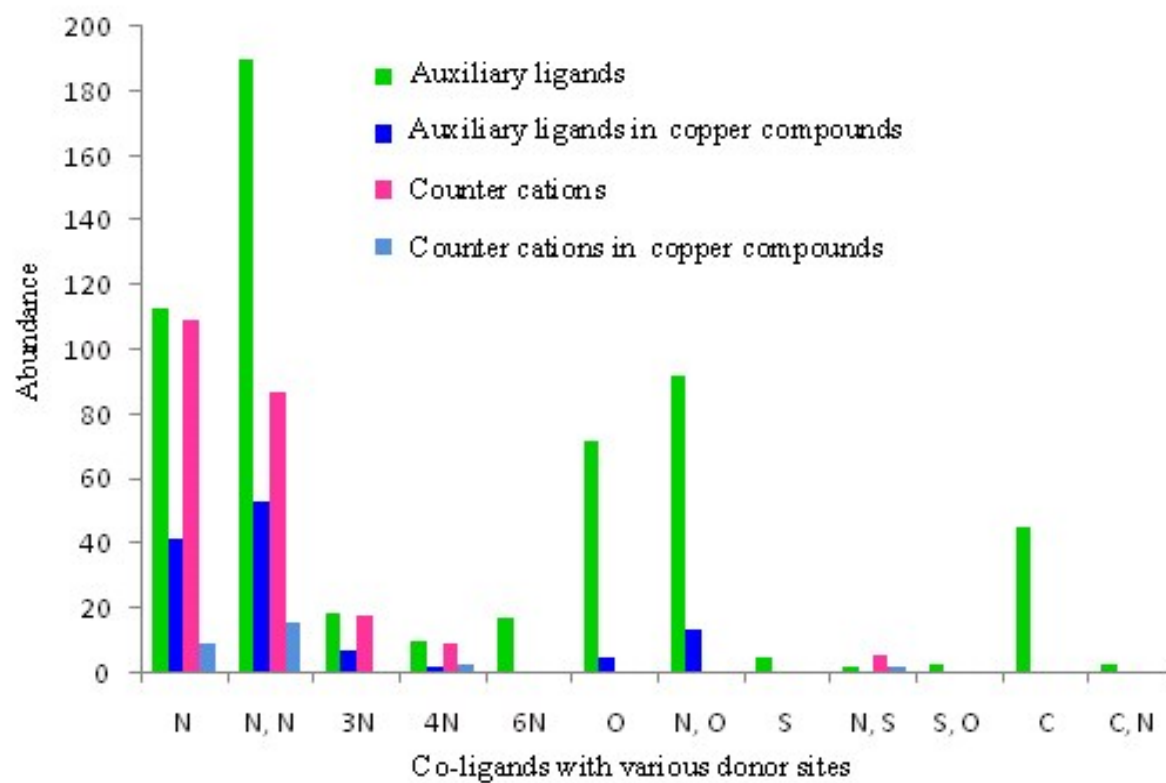


Figure S10. Abundance of complexes containing py-2,6-dc ligand with various co-ligands

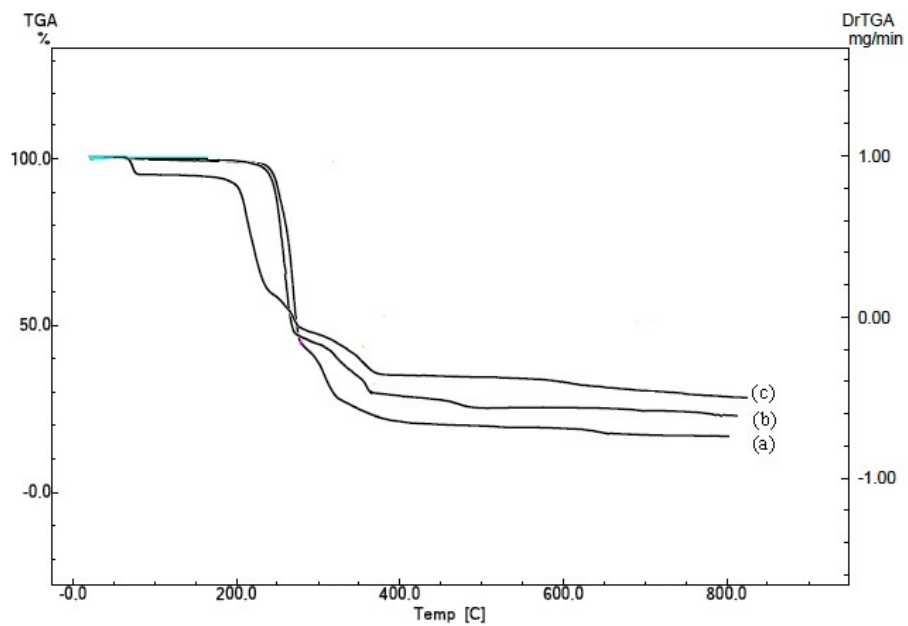


Figure S11. TGA diagrams of 1, 2 and 3

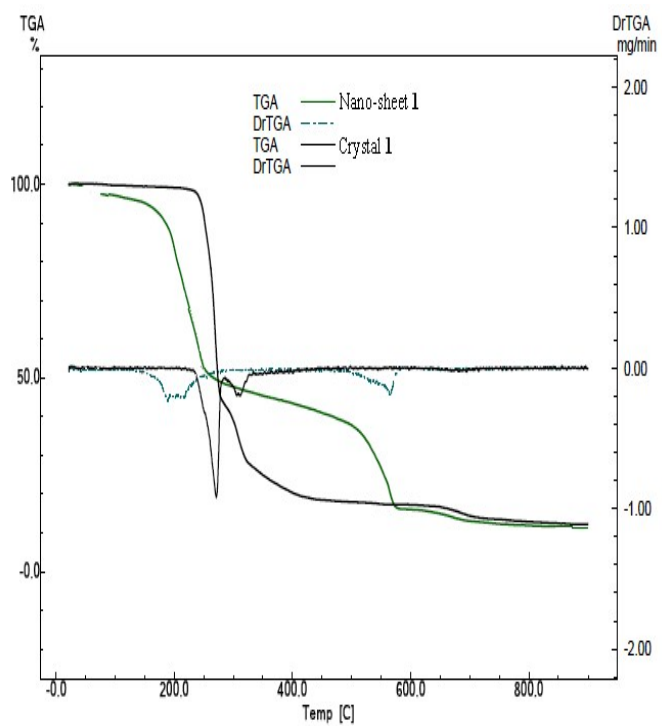


Figure S12. Thermal behavior of compound 1 as bulk and nanosheets

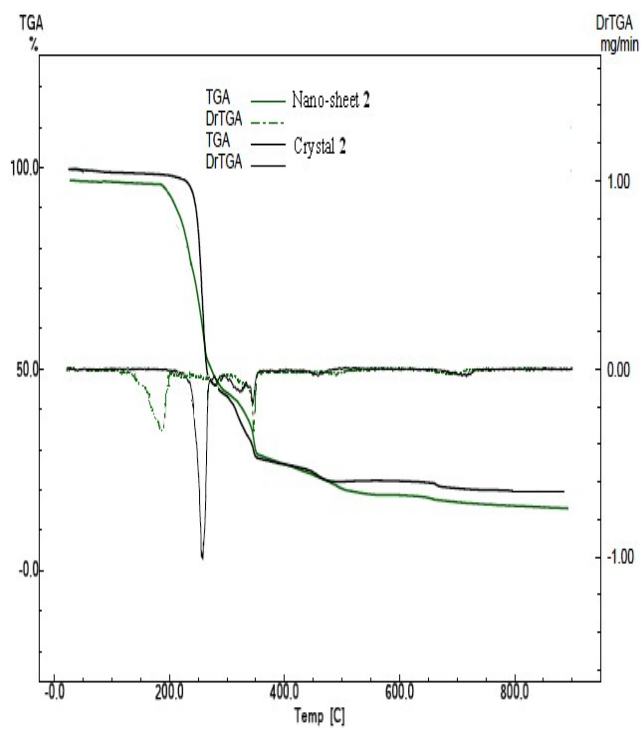


Figure S13. Thermal behavior of compound 2 as bulk and nanosheets

