Structural, Photophysical and Magnetic Properties of Transition Metal Complexes Based on the Dipicolylamino-chloro-1,2,4,5-tetrazine Ligand

Iuliia Nazarenko, Flavia Pop, Quichao Sun, Andreas Hauser, Francesc Lloret, Miguel Julve, Abdelkrim El-Ghayoury, and Narcis Avarvari*

SUPPORTING INFORMATION

X-ray structures

Coordination geometry polyhedra in the solid state structures of **2a-2d**

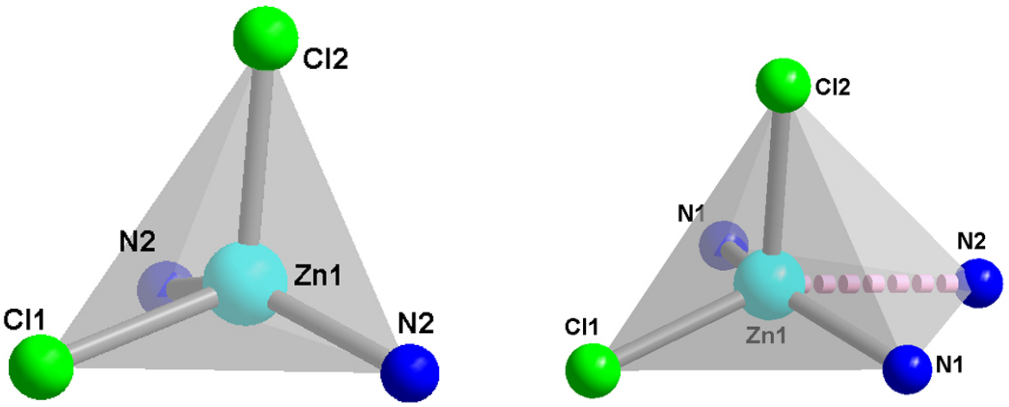


Fig. S1 Complex **2a** with Zn(II) either in tetrahedral (left) or square pyramid (right) environment.

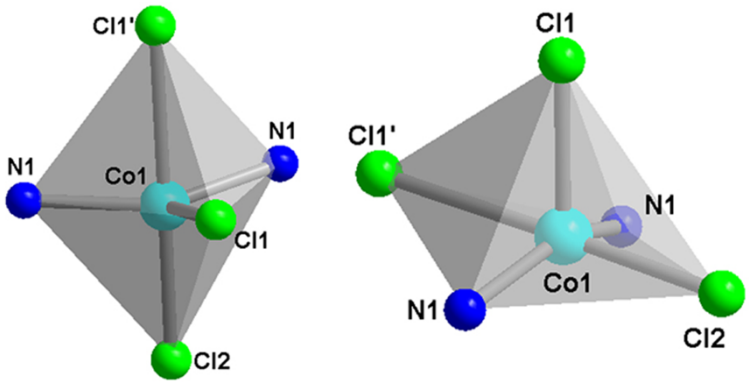


Fig. S2 Complex **2d** with Co(II) penta-coordinated.

Compound **2a**

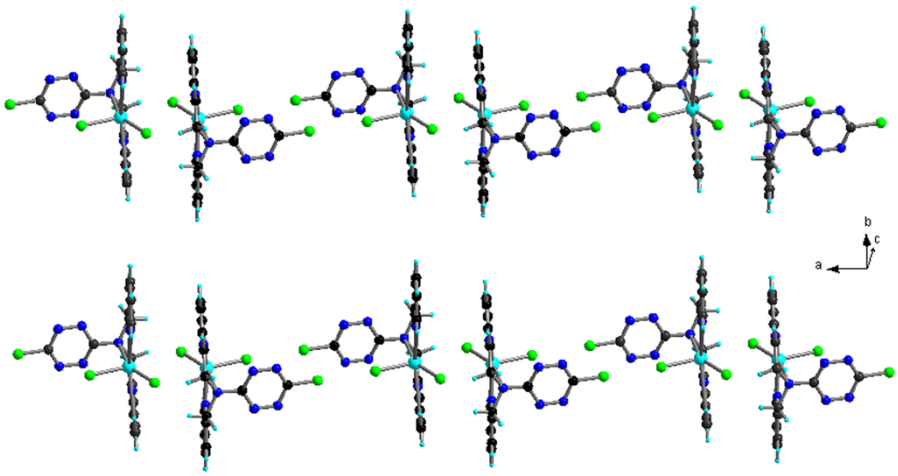


Fig. S3 Packing diagram for **2a**.

Compound **2b**

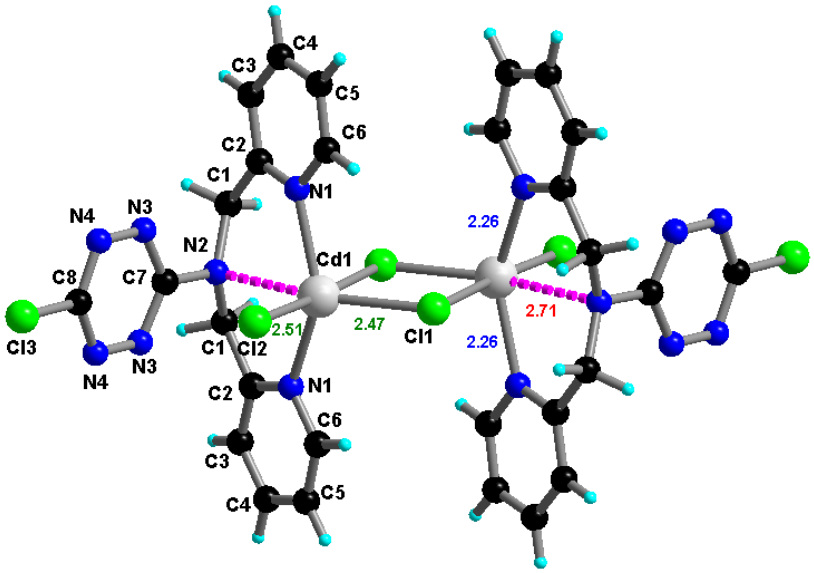


Fig. S4 Molecular structure of **2b** along with the numbering scheme.

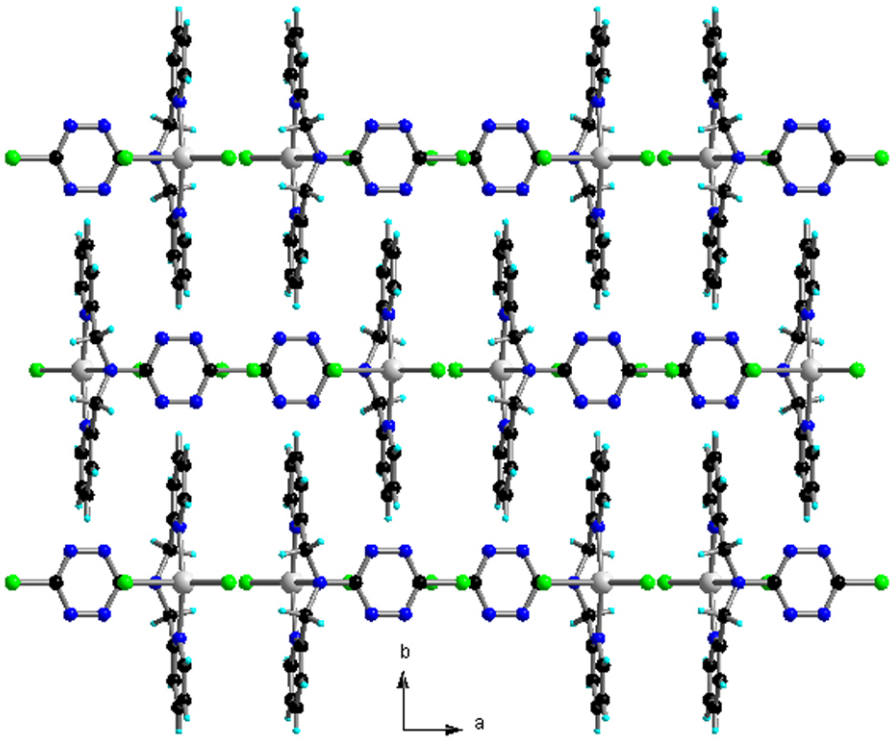


Fig. S5 Packing diagram for **2b**.

Compound **2c**

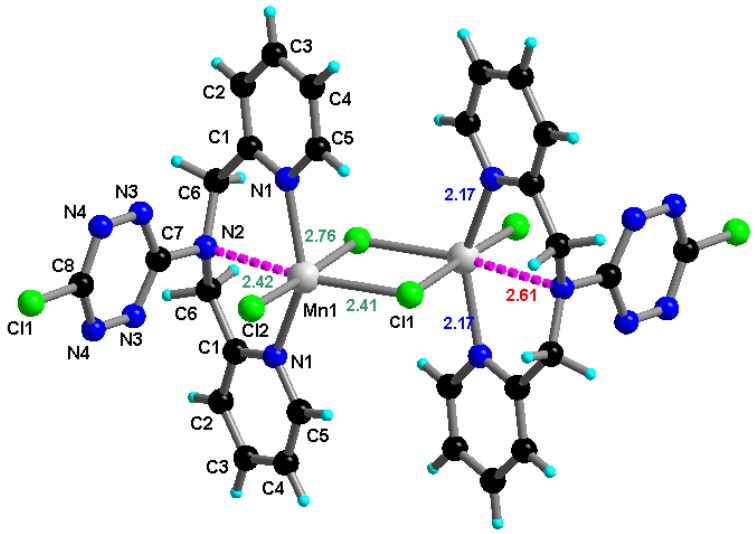


Fig. S6 Molecular structure of **2c** along with the numbering scheme.

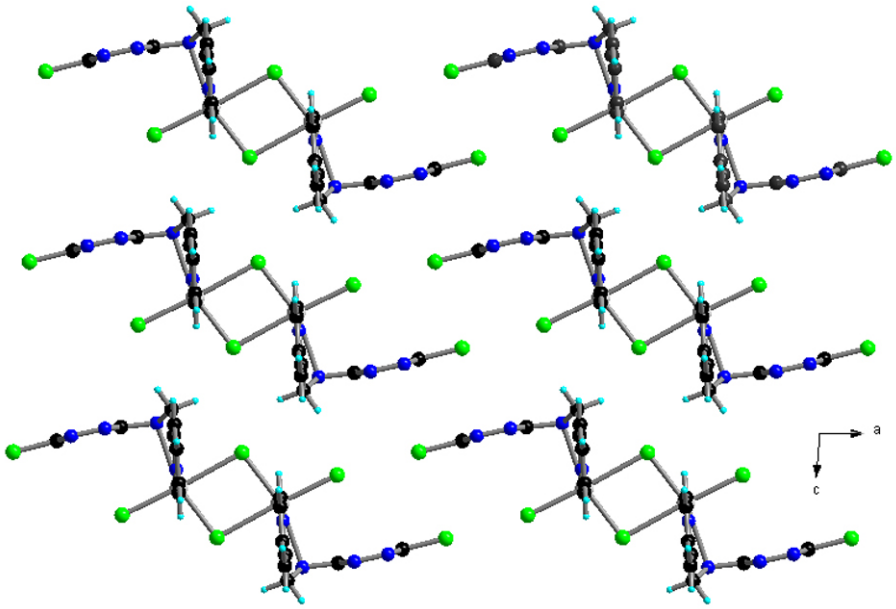


Fig. S7 Packing diagram for **2c**.

Titration studies

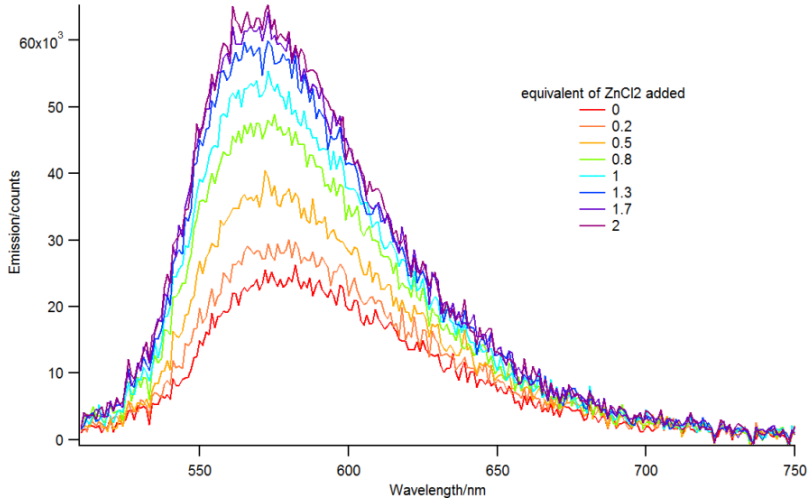


Fig. S8 Evolution of the emission spectrum on adding $ZnCl_2$ solution to the ligand **1** solution in acetonitrile. The molar ration of $ZnCl_2$: **1** from 0 to 2. Excitation and emission slits are all 5 nm.

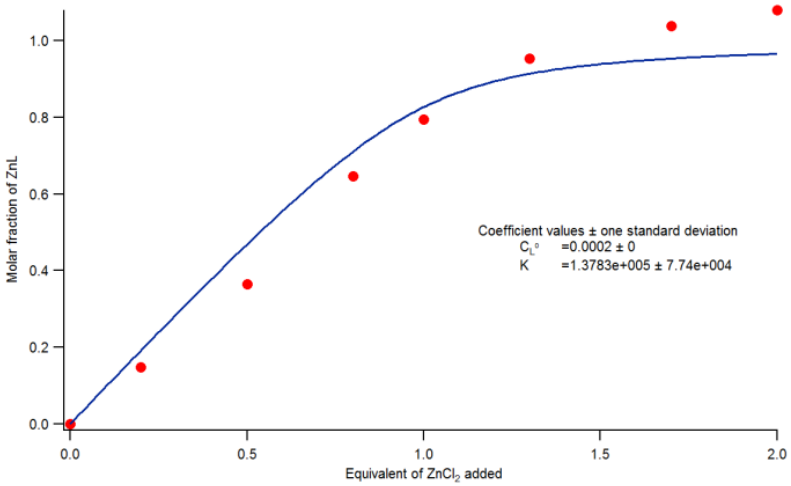
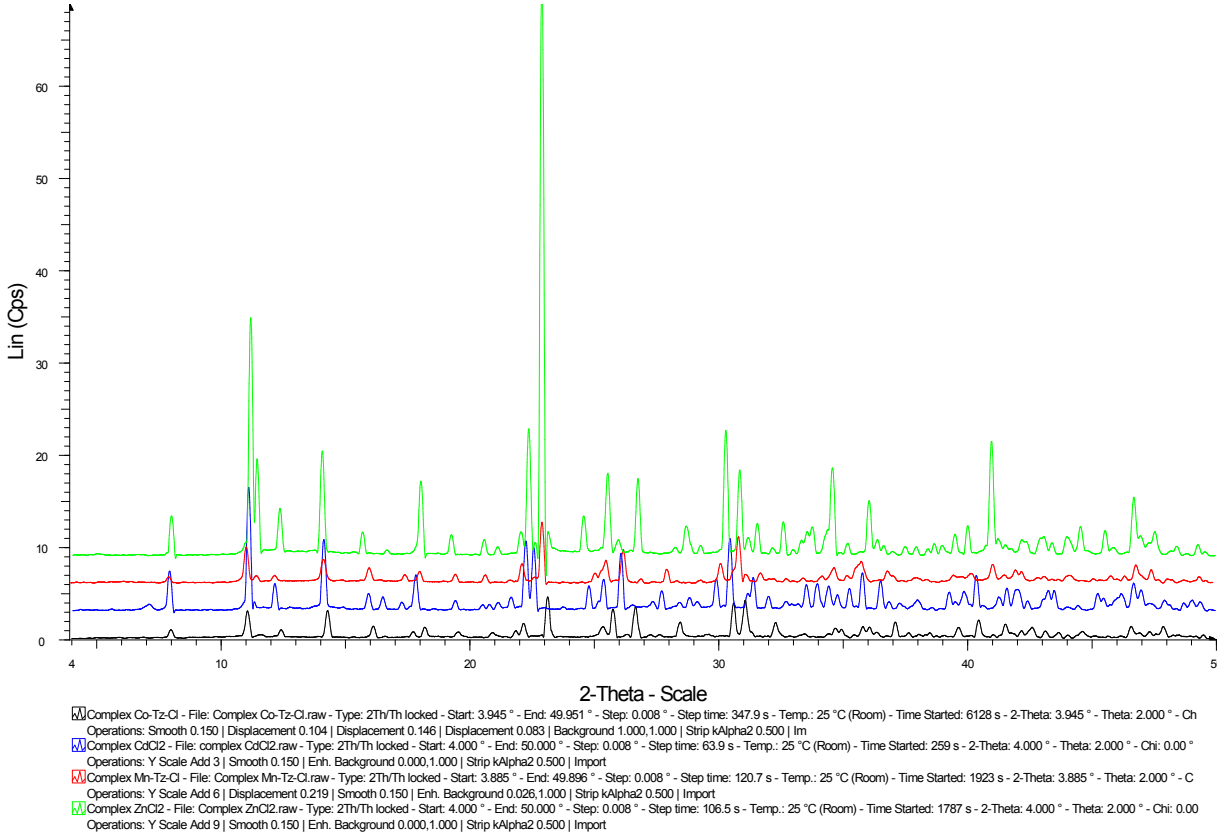
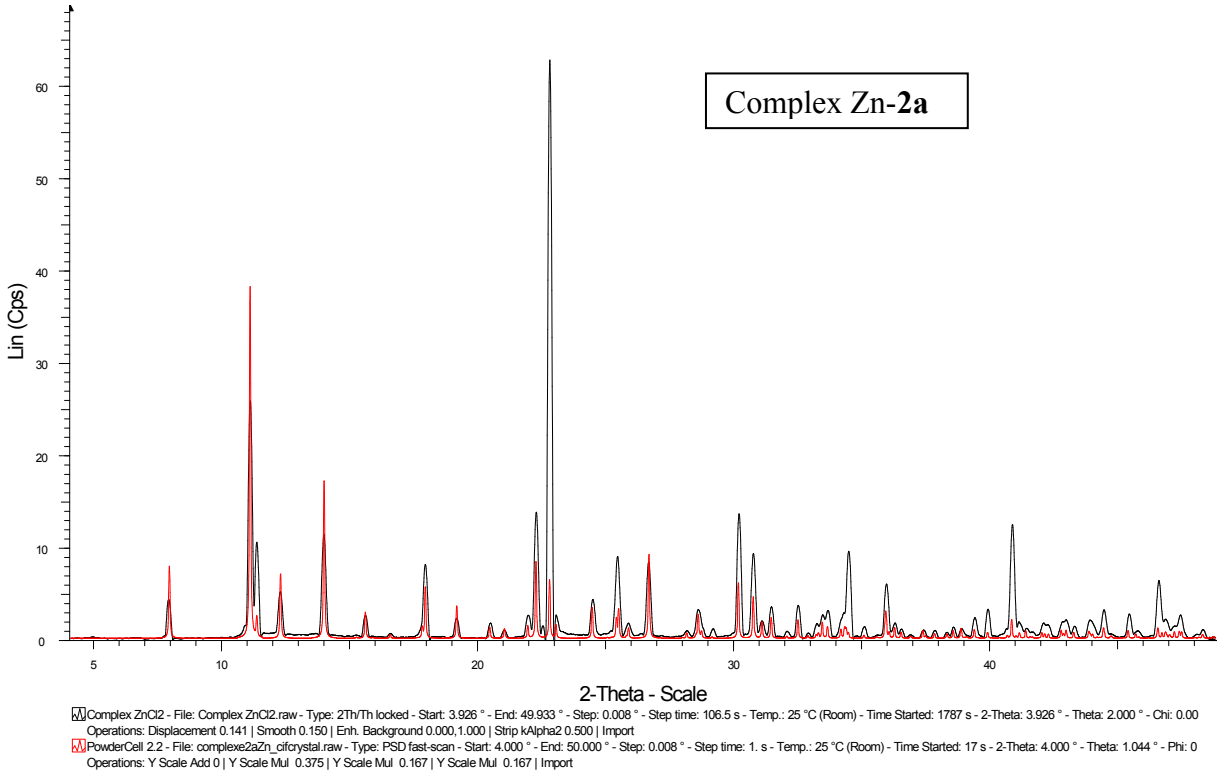


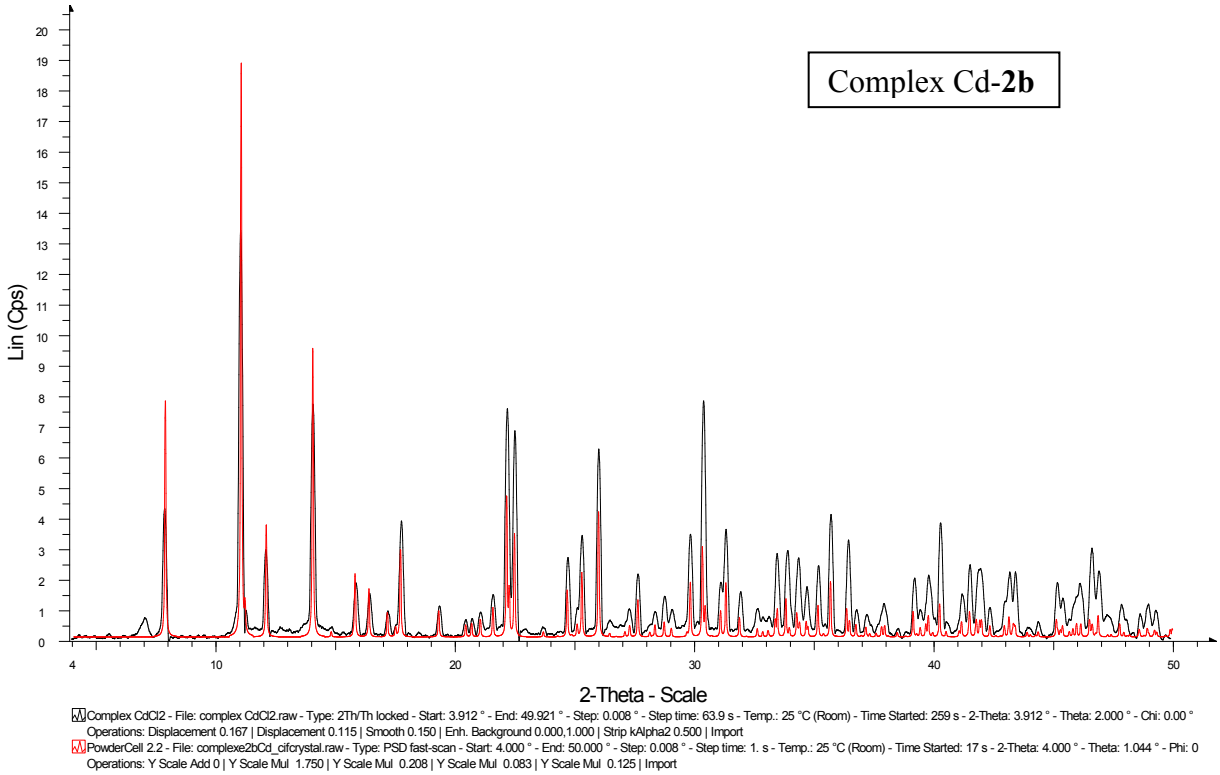
Fig. S9 Normalized evolution of the emission spectrum on adding $ZnCl_2$ solution to the ligand **1** solution in acetonitrile at an initial concentration of $2x10^{-4}$ M (●), least squares fit with $K = 1.4x10^5$ (—).

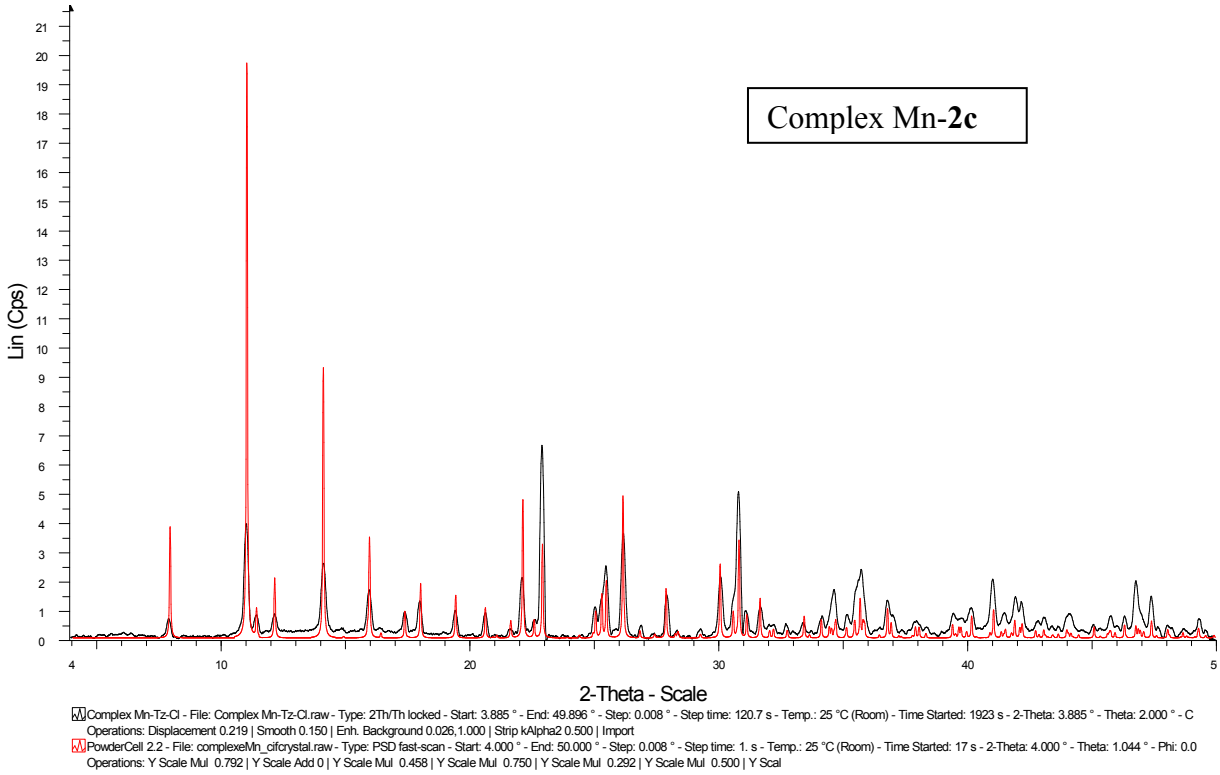
PXRD measurements

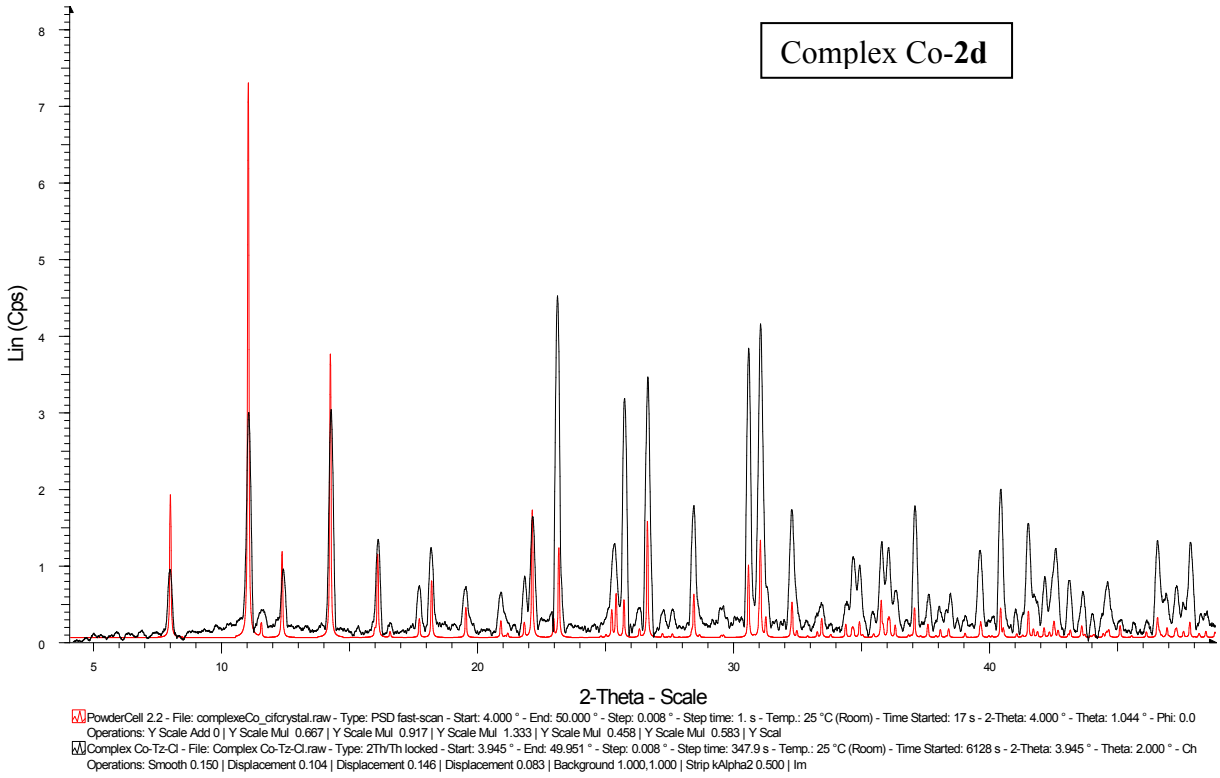
X-ray powder diffraction measurements were carried out on a D8 BRUKER diffractometer using Cu-Kα1,2 radiation, equipped with a linear Vantec super speed detector. The X-ray powder diffraction (XRPD) patterns of all complex (**2a**, **2b**, **2c**, **2d**) show that all the observed reflections (black color) can be indexed in the unit cell parameters obtained from single crystal X-ray diffraction experiments (red color).




Complex Zn-**2a**
Lin (Cps)
2-Theta - Scale
Complex ZnCl2 - File: Complex ZnCl2.raw - Type: 2Th/Th locked - Start: 3.926 ° - End: 49.933 ° - Step: 0.008 ° - Step time: 106.5 s - Temp.: 25 °C (Room) - Time Started: 1787 s - 2-Theta: 3.926 ° - Theta: 2.000 ° - Chi: 0.00
Operations: Displacement 0.141 | Smooth 0.150 | Enh. Background 0.000,1.000 | Strip kAlpha2 0.500 | Import
PowderCell 2.2 - File: complexe2aZn_cifcrystal.raw - Type: PSD fast-scan - Start: 4.000 ° - End: 50.000 ° - Step: 0.008 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 17 s - 2-Theta: 4.000 ° - Theta: 1.044 ° - Phi: 0
Operations: Y Scale Add 0 | Y Scale Mul 0.375 | Y Scale Mul 0.167 | Y Scale Mul 0.167 | Import


Complex Cd-**2b**
Lin (Cps)
2-Theta - Scale
Complex CdCl2 - File: complex CdCl2.raw - Type: 2Th/Th locked - Start: 3.912 ° - End: 49.921 ° - Step: 0.008 ° - Step time: 63.9 s - Temp.: 25 °C (Room) - Time Started: 259 s - 2-Theta: 3.912 ° - Theta: 2.000 ° - Chi: 0.00 °
Operations: Displacement 0.167 | Displacement 0.115 | Smooth 0.150 | Enh. Background 0.000,1.000 | Strip kAlpha2 0.500 | Import
PowderCell 2.2 - File: complexe2bCd_cifcrystal.raw - Type: PSD fast-scan - Start: 4.000 ° - End: 50.000 ° - Step: 0.008 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 17 s - 2-Theta: 4.000 ° - Theta: 1.044 ° - Phi: 0
Operations: Y Scale Add 0 | Y Scale Mul 1.750 | Y Scale Mul 0.208 | Y Scale Mul 0.083 | Y Scale Mul 0.125 | Import


Complex Mn-**2c**
Lin (Cps)
2-Theta - Scale
Complex Mn-Tz-Cl - File: Complex Mn-Tz-Cl.raw - Type: 2Th/Th locked - Start: 3.885 ° - End: 49.896 ° - Step: 0.008 ° - Step time: 120.7 s - Temp.: 25 °C (Room) - Time Started: 1923 s - 2-Theta: 3.885 ° - Theta: 2.000 ° - C
Operations: Displacement 0.219 | Smooth 0.150 | Enh. Background 0.026,1.000 | Strip kAlpha2 0.500 | Import
PowderCell 2.2 - File: complexeMn_cifcrystal.raw - Type: PSD fast-scan - Start: 4.000 ° - End: 50.000 ° - Step: 0.008 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 17 s - 2-Theta: 4.000 ° - Theta: 1.044 ° - Phi: 0.0
Operations: Y Scale Mul 0.792 | Y Scale Add 0 | Y Scale Mul 0.458 | Y Scale Mul 0.750 | Y Scale Mul 0.292 | Y Scale Mul 0.500 | Y Scal


Complex Co-**2d**
Lin (Cps)
2-Theta - Scale
PowderCell 2.2 - File: complexeCo_cifcrystal.raw - Type: PSD fast-scan - Start: 4.000 ° - End: 50.000 ° - Step: 0.008 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 17 s - 2-Theta: 4.000 ° - Theta: 1.044 ° - Phi: 0.0
Operations: Y Scale Add 0 | Y Scale Mul 0.667 | Y Scale Mul 0.917 | Y Scale Mul 1.333 | Y Scale Mul 0.458 | Y Scale Mul 0.583 | Y Scal
Complex Co-Tz-Cl - File: Complex Co-Tz-Cl.raw - Type: 2Th/Th locked - Start: 3.945 ° - End: 49.951 ° - Step: 0.008 ° - Step time: 347.9 s - Temp.: 25 °C (Room) - Time Started: 6128 s - 2-Theta: 3.945 ° - Theta: 2.000 ° - Ch
Operations: Smooth 0.150 | Displacement 0.104 | Displacement 0.146 | Displacement 0.083 | Background 1.000,1.000 | Strip kAlpha2 0.500 | Im

TGA measurements

Thermogravimetric studies (TGA) were performed on a Q500 TA INSTRUMENTS analyzer under nitrogen flow. The two complexes **2b** (up) and **2d** (bottom) are stable till about 250 °C and then start to decompose.