

# Syntheses, structural variation and characterization of a series of crystalline coordination compounds with 4-benzene-1,2,4-triazole: Polymorph, Incomplete spin transition and Single Crystal to Single Crystal Transformation

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Based on the 4-substituted triazole ligand 4-benzene-1,2,4-triazole (L), a series of crystalline coordination complexes varying from mononuclear to trinuclear species, namely [Zn(L)<sub>2</sub>Br<sub>2</sub>] (**1**), [Zn(L)<sub>2</sub>Br<sub>2</sub>] (**2**), [Fe(L)<sub>4</sub>(NCS)<sub>2</sub>]<sub>2</sub> (**3**), [Fe<sub>2</sub>(μ<sub>2</sub>-L)<sub>3</sub>(L)<sub>2</sub>(NCS)<sub>4</sub>]·CH<sub>3</sub>OH·CH<sub>3</sub>CH<sub>2</sub>OH (**4**), [Fe<sub>2</sub>(μ<sub>2</sub>-L)<sub>3</sub>(L)<sub>2</sub>(NCS)<sub>4</sub>]·2CH<sub>3</sub>CH<sub>2</sub>OH (**5**), [Fe<sub>2</sub>(μ<sub>2</sub>-L)<sub>3</sub>(L)<sub>2</sub>(NCS)<sub>4</sub>]·2CH<sub>3</sub>CH<sub>2</sub>OH·1.5H<sub>2</sub>O (**6**) and [Ni<sub>3</sub>(μ<sub>2</sub>-L)<sub>6</sub>(L)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>6</sub>·15.5H<sub>2</sub>O (**7**) have been isolated. **1** and **2** present temperature induced polymorphic phenomenon of two Zinc(II) coordination complexes with L. Solvent effect is quite important for the assembly and magnetic properties of these iron(II) compounds **3-6**: **3** contains mononuclear Fe(L)<sub>4</sub>(NCS)<sub>2</sub> units without spin transition behavior while both **4** and **5** present dinuclear iron(II) complexes with three N<sub>1</sub>,N<sub>2</sub>-1,2,4-triazole bridges behaving incomplete spin transition phenomenon. Low temperature structural analysis (100 K) of **4** is consistent with one of the Fe(II) centers within the dinuclear complex at low spin (LS) state and the other at high-spin (HS) state resulting in a [LS:HS] species. Interestingly when the dinuclear iron(II) complex **5** was exposed in the water atmosphere, solvent induced single crystal to single crystal transformation can be observed, dinuclear iron(II) complex **6** behaving antiferromagnetic interactions can be isolated. Further a trinuclear crystalline compound is isolated when Nickel(II) salts were used to react with L. Variable temperature magnetic susceptibility measurement (2-300K) reveals antiferromagnetic interactions in **7**. The polymorphic phenomenon (**1** and **2**), incomplete spin transition phenomenon (**4** and **5**) and single crystal to single crystal transformation (from **5** to **6**) also reveal great potential in the construction of these novel functional materials with L.

