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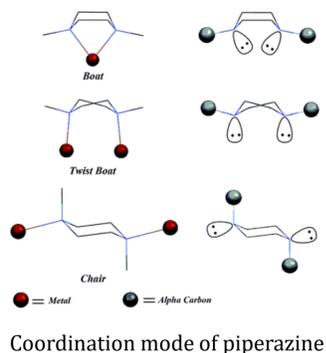
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Introduction

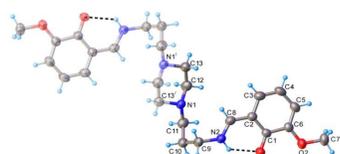
The formation of polynuclear coordination complexes is controlled by the nature of the metal ions, the preorganizing ability of the ligands, as well as the experimental conditions [1]. Based on the Salen pattern, ligands with greater rigidity [2] or flexibility [3] are obtained when the ethylene-bridge was replaced with appropriate "fragments" of molecules. Among these, the bis-N,N-alkylamine piperazine moiety leads to ligands with donor groups disposed symmetrically on each side of piperazine ring, thus offering a large variety of binding possibilities controlled by the conformation of piperazine moiety, as well as the length of the alkyl chain [4].



Results and discussions

1. Crystal structure of $H_2L \cdot 2DMSO$

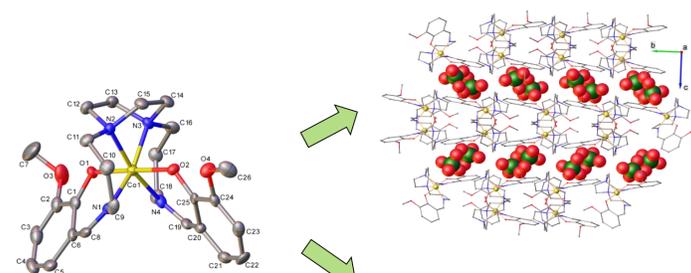
- The Schiff base proligand crystallizes in the zwitterionic form with co-crystallized DMSO molecules in 1:2 ratio.



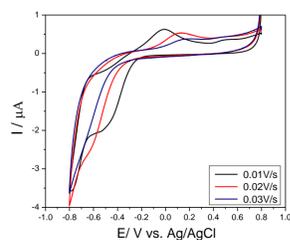
Molecular structure of H_2L (DMSO molecules are not shown) [symmetry code: $i = -x, 1 - y, 1 - z$].

2. Crystal structure of $[CoL]ClO_4$ (1)

- L^{2-} anion acts as a hexadentate ligand and wrap the Co^{III} ion in a distorted octahedral coordination geometry. The oxidation of Co^{II} to Co^{III} occurs and the coordination of L^{2-} stabilizes the high oxidation state.
- Cyclic voltammogram studies show a quasi-reversible behavior of Co^{III}/Co^{II} .



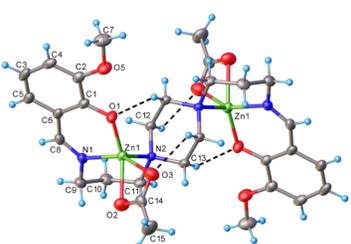
Molecular structure of 1. H - atoms and perchlorate anion are omitted for clarity.



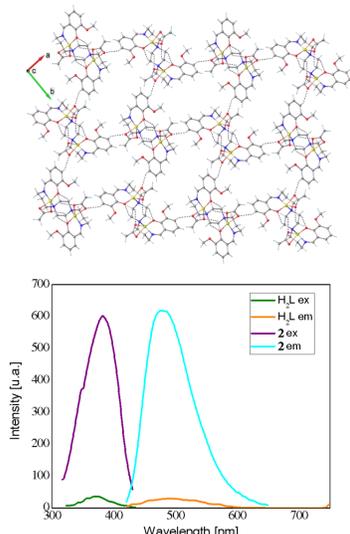
Cyclic voltammogram recorded at GC electrode for 1 in DMSO 10^{-3} M and 0.1 M TBAC within.

3. Crystal structure of $[Zn_2L(CH_3COO)_2] \cdot 2H_2O$ (2)

- The L^{2-} ligand acts bis-tridentate accommodating two Zn^{II} ions with square pyramidal geometry.
- The luminescent investigation shows a strong emission band centered at 476 nm, hypsochromic shifted compared to the emission band observed for the free ligand at 492 nm.



Molecular structure of 2 (water molecules are omitted for clarity) [symmetry code: $i = 1 - x, -y, 1 - z$].

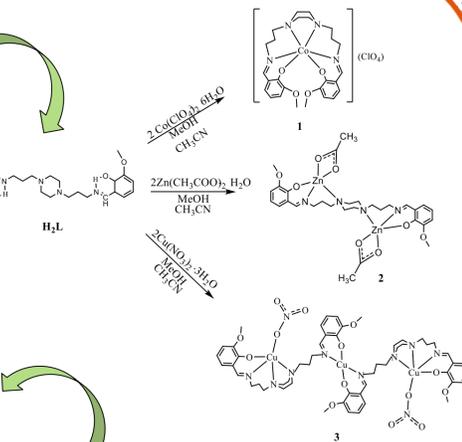
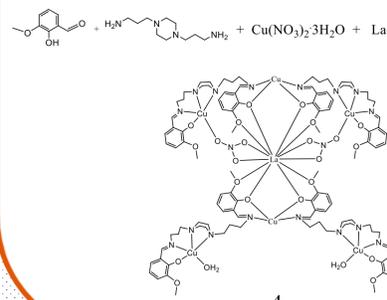


2D supramolecular network viewed along c axis.

The emission spectra for H_2L and complex 2 recorded on DMSO 10^{-4} M.

Experimental

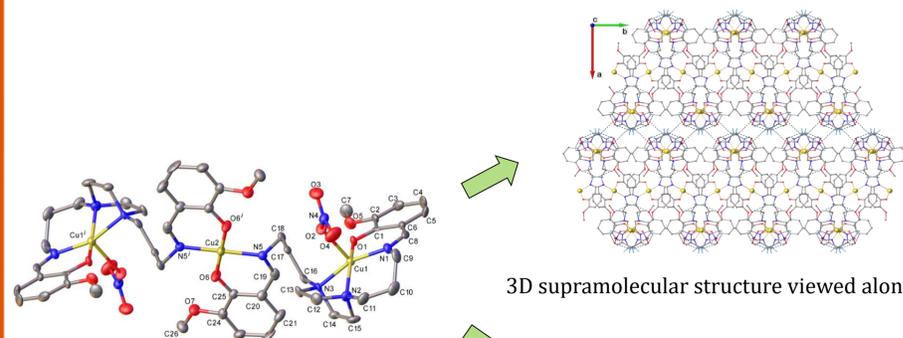
The direct metal - ligand reactions between H_2L (N,N'-bis[(3-methoxysalicylideneamino)-propyl]-piperazine) and corresponding metal salts afford the formation of $[CoL](ClO_4)$ (1), $[Zn_2L(CH_3COO)_2] \cdot 2H_2O$ (2) and $[Cu_3L_2(NO_3)_2]$ (3).



The *in-situ* reaction between *o*-vanillin, 1,4-bis(3-amino-propyl)-piperazine and corresponding metal salts led to the polynuclear complex $[LaCu_6L_4(H_2O)_2](NO_3)_2(NO_3)_5 \cdot 15H_2O$ (4).

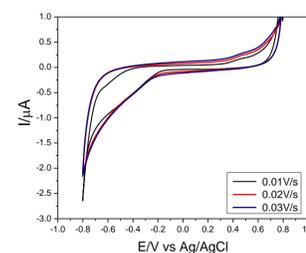
4. Crystal structure of $[Cu_3L_2(NO_3)_2]$ (3)

- Compound 3 is a trinuclear complex generated by two L^{2-} ligands in a bridging coordination mode. The peripheral Cu^{II} atoms present square pyramidal geometry, while the central Cu^{II} atom, exhibits a square planar geometry.
- Cyclic voltammogram studies show an irreversible behavior for Cu^{II}/Cu^I .



X-ray molecular structure of 3. H-atoms are omitted [symmetry code: $i = 1 - x, -y, 1 - z$].

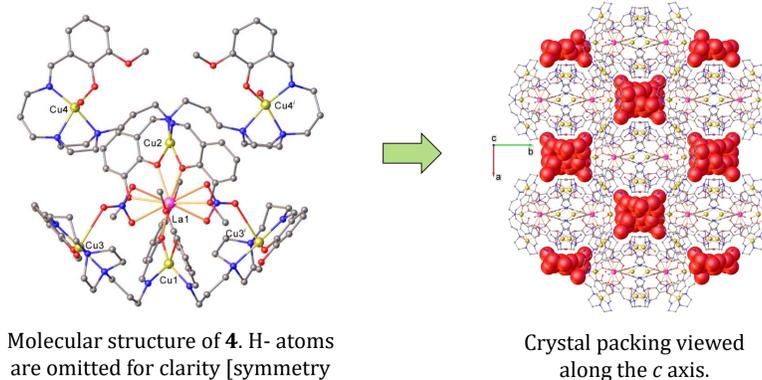
3D supramolecular structure viewed along c axis.



Cyclic voltammogram recorded at GC electrode for 3 in DMSO 10^{-3} M and 0.1 M TBAC

5. Crystal structure of $[LaCu_6L_4(NO_3)_2(H_2O)_2](NO_3)_5 \cdot 15H_2O$ (4)

- L^{2-} acts as compartmental ligand by accommodating the Cu^{II} ion in the inner NO site and the La^{III} ion in the external OO' coordination site.



Molecular structure of 4. H - atoms are omitted for clarity [symmetry code: $i = 1 - x, y, 1.5 - z$].

Crystal packing viewed along the c axis.

References

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