Mononuclear and Polynuclear Cobalt(II) or Cobalt(III) Complexes Bearing Multidentate Hydrazonato Ligands with Pyridyl and Imidazolyl Donor Groups: Synthesis, Crystal Structures and Properties.

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2-Picolinoylhydrazones having a *N*-heterocyclic (2-pyridyl or 4-imidazolyl) substituents (**Scheme 1:** HLpy or H₂Lim) are promising multidentate ligands, because their neutral and deprotonated forms (Lpy⁻, HLim⁻ and Lim²⁻) have a variety of donor atoms and are possible to act as both multidentate chelating and bridging ligands. In this study, we have prepared a series of cobalt(II or III) complexes bearing such monoanionic ligands (Lpy⁻ or HLim⁻), and their molecular and crystal structures were investigated.

Two types of mononuclear cobalt(III) complexes with

$$R = N$$

$$HLpy$$

$$H_2Lim$$

Scheme 1 Hydrazones used in this research.

Lpy⁻, $[Co(Lpy)_2]BF_4$ and mer- $[Co(Lpy)_3]$, were obtained by reactions of HLpy with $Co(BF_4)_2 \cdot 6H_2O$ and $[Co(acac)_3]$, respectively, in an appropriate molar ratio. In these complexes, the ligand Lpy⁻ coordinated to a Co^{III} center in a tridentate $\kappa^3 N, N', N''$ or a bidentate $\kappa^2 N, N'$ mode. In addition, a trinuclear Co^{III} – Co^{III} complex bridged by Lpy⁻, $[\{Co(Lpy)_2\}_2Co(H_2O)_2](BF_4)_4$ (**Fig. 1a**) was prepared. In the case of the imidazole-based ligand, HLim⁻, both mononuclear and dinuclear Co^{III} complexes, $[Co(HLim)_2]BF_4$ and $[Co_2(\mu-HLim)_3](BF_4)_3$ (**Fig. 1b**), respectively, were isolated and characterized.

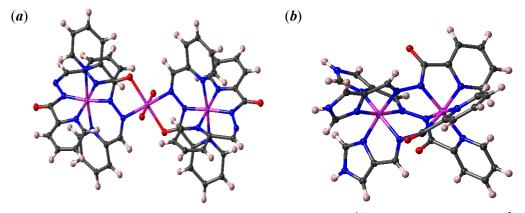


Fig. 1 Perspective views of (a) $[{Co(Lpy)}_2Co(H_2O)_2]^{4+}$ and (b) $[Co_2(\mu-HLim)_3]^{3+}$ (color codes: Co, purple; O, red; N, blue; C, black; H, pale pink).