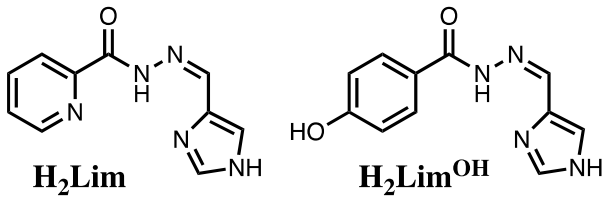
Mononuclear and Dinuclear Transition-Metal Complexes Containing Hydrazonates: Synthesis, Structures, and Spectroscopic and Electrochemical Properties

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Aroylhydrazones or *N*-acylhydrazones are promising versatile ligands in current organic synthesis, coordinate chemistry, macromolecular sciences and drug designs, owing to their modular synthesis from the condensation reaction of relevant carbonyls and organic hydrazines. Having their substituents with coordination donor groups, they can provide variety of coordination modes with transition metals. Also, they have acidic NH proton which can undergo reversible deprotonation, which induces to form hydrazonato-bridged dinuclear metal complexes.[1,2] Hence, complexes of this type have several fascinating properties, i.e., strong catalytic ability, biological activity, fluorescent properties and chromic behavior.[3,4]



Scheme 1 Hydrazones used in this study: H_2Lim and H_2Lim^{OH}.

A reaction of $MnCl_2$•$4H_2O$ or $FeSO_4$•$7H_2O$ and H_2Lim (in 1:2 molar ratio) in EtOH/MeOH under a reflux in air gave orange or green complex of $[Mn(HLim)_2]Cl$ (**1**) and $[Fe(H_2Lim)_2]SO_4$ (**2**) respectively. A similar reaction of $Co(BF_4)_2$•$6H_2O$ and H_2Lim^{OH} in air afforded the corresponding complex of $[Co(H_2Lim^{OH})(HLim^{OH})]BF_4$ (**3**). These complexes were analyzed by X-ray, ^{1}HNMR and UV-vis spectroscopy. Structurally, the complexes showed bis(hydrazone or hydrazonato)-type structure with *meridional* configuration of tridentate H_2Lim^- or $HLim^{OH-}$ ligand in the κ^3*N,N',N"* mode (**Fig. 1**). Because the Co^{II} complex **3** has both possible protonation (H_2Lim^{OH}) and deprotonation ($HLim^{OH-}$) sites in the coordinating ligands, we have examined the acid-base behavior in solution. The results, as well as syntheses and characterization of the corresponding mononuclear and dinuclear complexes, will be reported.

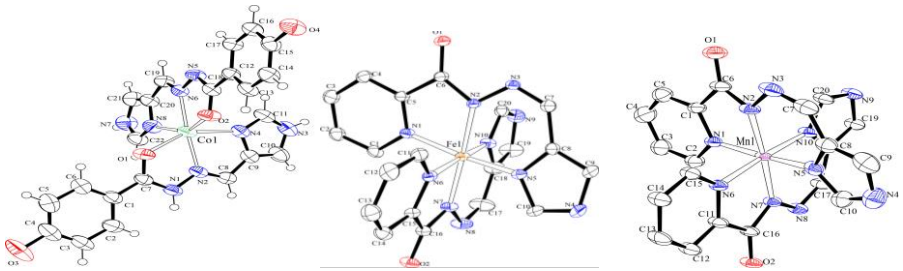


Fig. 1 ORTEP drawings of the cationic complexes in **1, 2** and **3**

[1] E. Pilichos *et al.*, *Magnetochemistry, 5*(3), 39 (**2019**). [2] N. Ribeiro *et al.*, *New J. Chem.,* in the press (**2019**).[3] M. Chang *et* al., *Bull. Chem. Soc. Jpn.,* 83,905-910 (**2010**); *Chem. Lett.,* 40, 1335-1337 (**2011**). [4] S. Rodriguez-Hermida *et al., Chem-Eur.J.*, *21*(17), 6605-6616 (**2015**).

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