Synthesis and characterization of Ni(III) complex with condensation product of 2-acetylpyridine and Girard's P reagent

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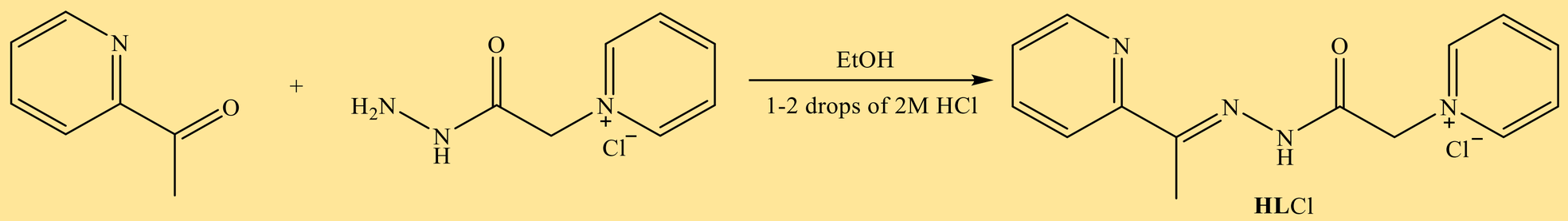
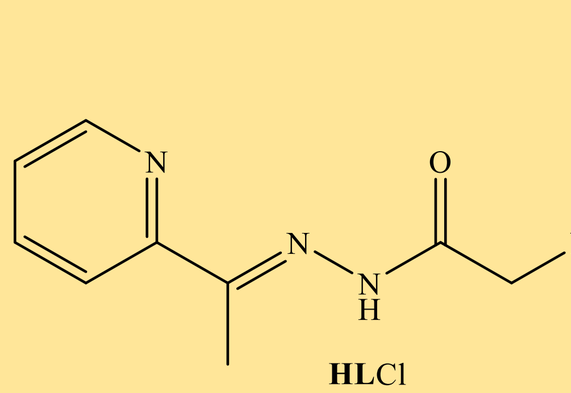
The ligand (**HL**Cl) was synthetized by the reaction of 2-acetylpyridine and Girard's P reagent in molar ratio 1 : 1 in ethanol (1–2 drops of cc. HCl were added, Scheme 1). The reaction of hydrazone ligand with the metal salt $Ni(BF_4)_2 \cdot 6H_2O$ and NaN_3 in a molar ratio 1 : 1 : 4 in methanol/acetonitrile/water mixture results in the formation of Ni(III) complex with composition [Ni**L**$(N_3)_3$] (Scheme 2). The ligand (**HL**Cl) was characterized by elemental analysis, IR and NMR spectroscopy and structure of the complex was defined by X-ray analysis, IR and EPR spectroscopy (**Fig. 2**), molar conductivity and elemental analysis. DFT calculations were performed to determine stability and rationalise formation of Ni(III) complex (**Fig. 3**).



Scheme 1. Synthesis of ligand **HL**Cl.



Scheme 2. Synthesis of complex [Ni**L**$(N_3)_3$].

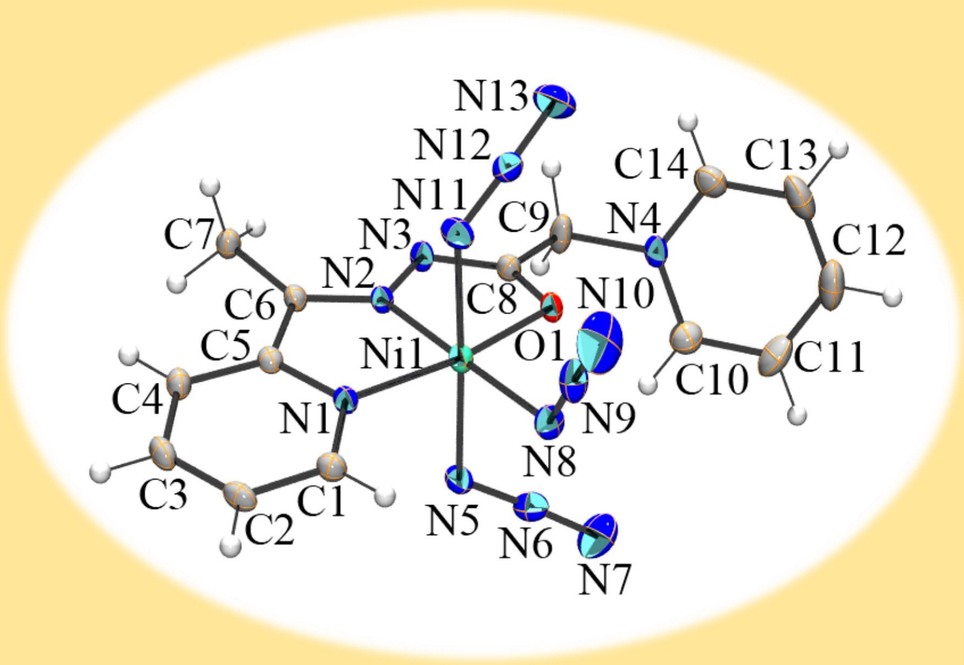


Figure 1. ORTEP representation of the [Ni**L**$(N_3)_3$] complex. Thermal ellipsoids are drawn at the 30% probability level.

Complex crystallizes with one independent molecule in the asymmetric unit of the triclinic *P*–1 space group (No. 2). The molecular structure of complex is displayed in **Fig. 1**. Two nitrogen atoms (N1 and N2) and one oxygen atom (O1) of the tridentate ligand **L** in combination with three nitrogen atoms (N5, N8 and N11) from three azide anions arranged meridionally complete the octahedral coordination of the Ni(III) ion.

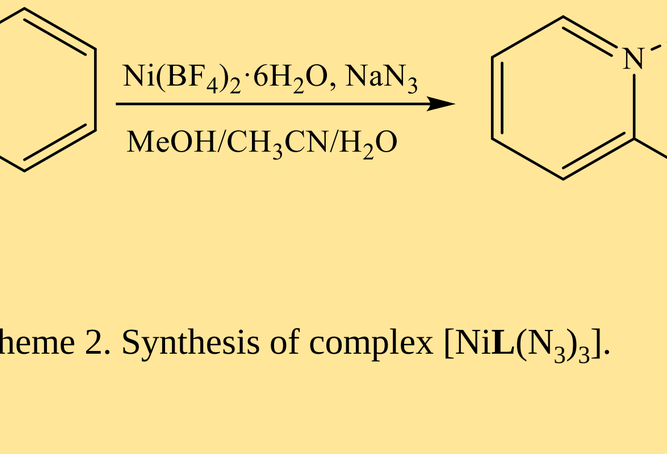


Figure 3. Spin density distribution (orange isosurface with 0.004 $e^-/Å^3$ isovalue) in low-spin Ni(III) complex.

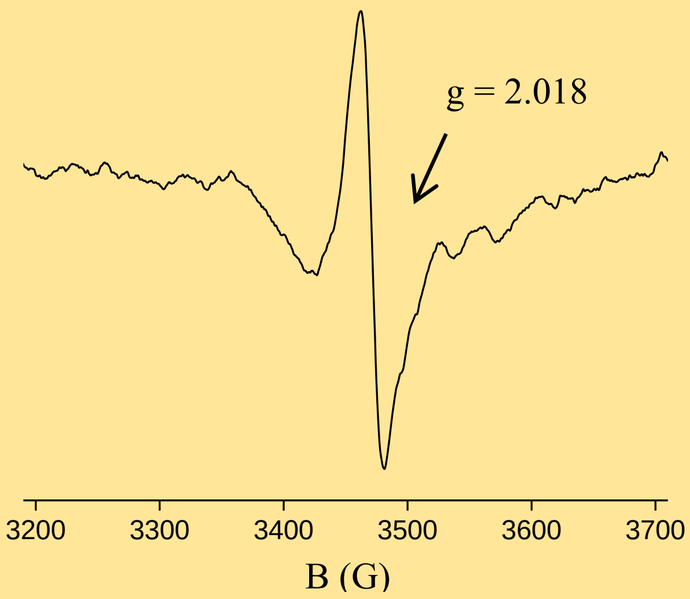


Figure 2. EPR spectra of complex [Ni**L**$(N_3)_3$].

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