C001198

Synthesis and Characterization of Nickel(II) Complex with an Unsymmetric Azine Ligand

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Keywords: Azines, Unsymmetric Azine, Symmetric Azine, Functionality, H-bonding.

Azines (symmetrical or unsymmetrical) are class of organic compounds with a functionality: C=N–N=C. They are conventionally synthesized by the condensation of hydrazine with aldehydes/ketones. Symmetrical azines are easier and readily synthesized, whiles preparation of their unsymmetrical counterparts is more challenging. For instance, during this work, several attempts were made to synthesize the desired unsymmetrical azine ligand spontaneously or exclusively in a high yield, either by one-pot or stepwise manner, from its starting materials: 2-formylpyridine, 2-methyl-1*H*-4-imidazolecarbaldehyde and hydrazine, was fruitless. Instead, a mixture of symmetrical bis(pyridyl)- and bis(2-methyl-1*H*-imidazolyl) azines as well as the asymmetrical one (HL-Me) were obtained. However, in the presence of iron(II) salt, as reported by Sunatsuki Y. *et al.*, *2014* [1], a highly selective iron(II) complex with the unsymmetric ligand (HL-Me) was obtained in a yield of 79%. This unexpected formation of the unsymmetrical azine complex of iron(II) has aroused our next interest, worth investigating using other metal(II) ions.

In this work, we synthesized the corresponding nickel(II) complex, (**Fig. 1**) of HL-Me by a one-pot reaction of $NiCl_2$•$6H_2O$, 2-methyl-1*H*-4-imidazolecarbaldehyde, 2-pyridinecarbaldehyde and hydrazine monohydrate with NH_4PF_6 (in a 1: 2: 2: 2: 2 molar ratio) in methanol. The complex exclusively formed the unsymmetrical azine ligand with nickel(II) in high yield (83%), with coordination by pyridine-N, imidazole-N and one azine-N atom to the nickel(II) center. The detailed X-ray structure analysis revealed that, there are H-bonding interactions between imidazole-N-H and F atom of the counter (PF_6^-) ion.

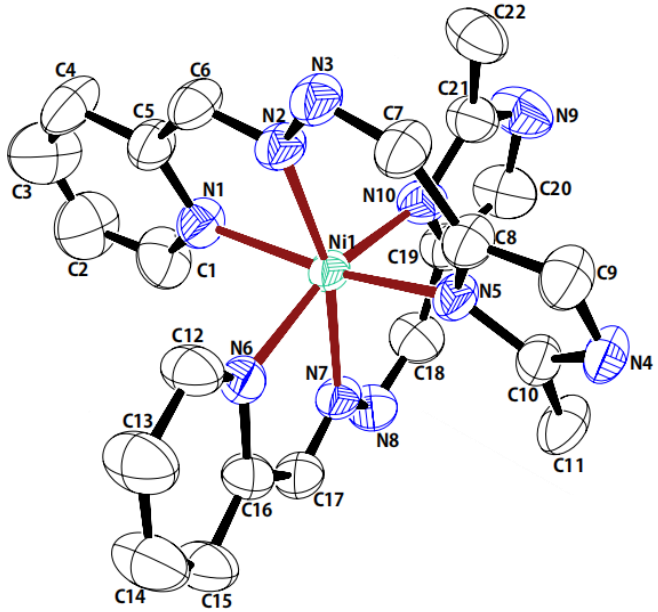

Fig.1 ORTEP drawing of the cation in $[Ni(HL\text{-}Me)_2](PF_6)_2$ with the atom numbering scheme (thermal ellipsoids drawn at 50% probability). Hydrogen atoms were omitted for clarity.

[1] Sunatsuki Y. *et al.*, *Cryst. Growth & Des.* 2014, *14*, 3692