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Structural and spectroscopic study of the asymmetric 2-(2'-pyridyl)-1,8-naphthyridine ligand with closed-shell metals

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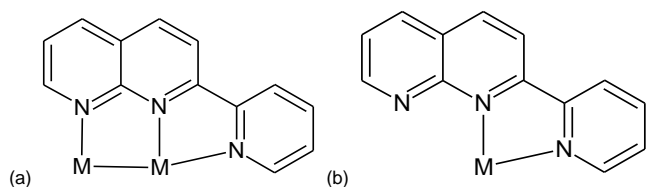
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Abstract: Herein, we report the synthesis and characterization of a series of complexes of the asymmetric ligand 2-(2'-pyridyl)-1,8-naphthyridine (pyNP, **1**) with different closed-shell metals. For the first time ligand pyNP has been structurally and vibrationally characterized. The geometry of the pyNP ligand, with 3 N donor sites, can favor metalphilic interaction in complexes, so we performed a study on its coordination chemistry with different metals (Ag(I), Hg(II) and Pb(II)). Twelve new complexes, namely [Ag₂(pyNP)₂(NO₃)₂] (**2**), [Hg(pyNP)X₂](X=Cl(**3**), Br(**4**), I(**5**), CN(**6**), SCN(**7**, **8**)), [Pb(pyNP)₂(NO₃)₂] (**9**), [Pb(pyNP)(NO₃)₂] (**10**), [Cu(pyNP)Cl₂(H₂O)] (**11**), [Cu(pyNP)₂(H₂O)][Hg₂(CN)₄Cl₂]·H₂O (**12**) and [Cu(pyNP)(H₂O)₂(μ-CN)Hg₂(CN)₃Cl₂]·H₂O (**13**), have been synthesized and characterized by single crystal X-Ray diffraction, Raman, FTIR and electronic spectroscopies. Structure of complex **2** shows a supported argentophilic interaction, and is the first structure in which pyNP bonds two previously unbounded metal centers.

Keywords: naphthyridine • d¹⁰ metals • coordination complexes • luminescence • metalphilic interactions

Introduction

Molecular and polymeric complexes of transition metals with *N*-heterocyclic polyaromatic Schiff base ligands have been widely studied because of their stability in different conditions, and their luminescence, electrochemical and catalytic properties.^[1] Naphthyridines consist of a group of diazanaphthalenes with one nitrogen in each ring but none at the bridgehead position. Among the six possible isomers, the 1,8-naphthyridine(NP) and its derivatives have shown the most interesting properties. They exhibit biological activity: nalidixic acid (1-ethyl-7-methyl-4-oxo-1,8-naphthyridine-3-carboxylic acid) was the first NP approved as an antibacterial drug.^[2] This molecule is active against gram-negative and gram-positive bacteria. It prevents the DNA repetition in prokaryotes by exclusion of several bacteriophages,^[3] and his derivatives have led to a new set of powerful antibiotics, alone and in the form of silver complexes.^[4, 5, 6] Some oxadiazole and triazole derivatives have shown recently a very strong HIV-1 integrase inhibitor activity.^[7, 8] 1,8-Naphthyridin-BF₂ complexes are known to be fluorescent dyes with high chemical stability, high fluorescence quantum yields, high extinction coefficients and sharp fluorescence peaks.^[9,10] Starting from 1970, NP has been regularly used as a ligand in the field of coordination chemistry.^[11] A great number of mononuclear molecular complexes of transition metals and lanthanide has been reported.^[4] In these compounds NP can act as unidentate or bidentate chelating ligand. The small distance between N atoms promotes the formation of four-member chelate rings that allow high coordination for the metals involved. The *syn* disposition of two N lone pairs of NP favours the formation of binuclear systems by means of a bridging coordination.^[2] The pliability of NP bite allows it to bridge a range of preformed dimetallic cores, like the singly bonded dirhodium(II)^[12] or the quadruply bonded dimolybdenum(II)^[13] systems, and to stabilize mixed valence complexes.^[14] The formation of weakly interacting dimetallic cores, such as Cu(I)···Cu(I)^[15] and Ag(I)···Ag(I)^[16], bridged by supported metalphilic interactions, has also been reported, while the only reported Au(I) complex doesn't show this behavior.^[17] Incorporation of coordinating substituent in position 2 and 7 (like pyridyl and dicarboxylate) favours the formation of polydentate, cavity-shaped molecules. Symmetric 2,7-bis(2'-pyridyl)-1,8-naphthyridine (bpNP) can act as bridging and chelating ligands, and the "double chelation" specular chelation strongly stabilizes dimetallic cores, like in complexes of the type [M₂(μ-bpNP)(μ-O₂CMe)₂] (M=Rh, Ru)^[18] in which the bpNP ligand occupies the axial position, *trans* to the metal-metal bond. Asymmetric substituted derivatives of NP can be interesting systems. Among them, one of the less studied is 2-(2'-pyridyl)-1,8-naphthyridine(pyNP, **1**) which, in addition to the *syn* N atom of the naphthyridinyl rings, has a pyridyl substituent. This molecule doesn't have a strong dipole (calculated 4.56 D) or hydrogen donor groups.



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