Coordination polymers og Hg(II) with 2,2'- bipyrimidine

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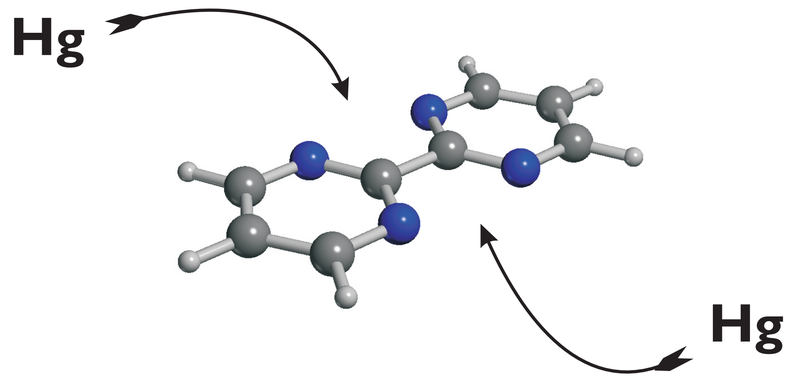
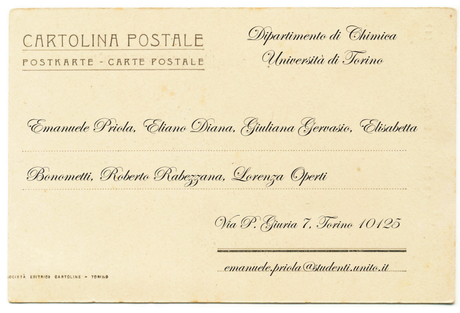
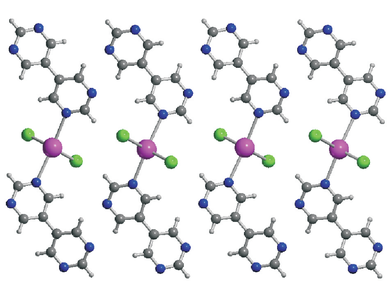
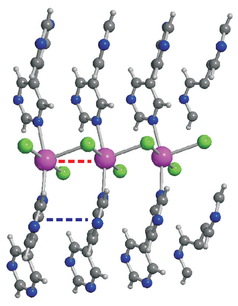




In 1983 S. Lanza reported the preparation and spectroscopic characterization of a binuclear complex of 2,2'-bipyrimidine (bpym) with $HgCl_2$ (Inorg. Chim. Acta, 1983, 75(1), 131). This work has been developed by Q. Jaradat, K. Barqawi and T.S. Akasheh in 1986 (Inorg. Chim. Acta, 1986, 116(1), 63), that prepared the omologous with bromine and iodine and did a spectroscopic and electrochemical characterization of the complexes. Recently, a renovated interest on this kind of chelating ligand has been inspired by his flexibility in the formation of coordination polymers. Jing-Yun Wu, Hung-Yu Hsu, Chun-Chieh Chan, Yuh-Sheng Wen, Chiitang Tsai, and Kuang-Lieh Lu reported a brilliant synthesis of a layered structure obtained by interaction of $HgCl_2$ and $HgBr_2$ with 5,5'-bipyrimidine (Cryst. Growth Des., 2009, 9(1), 258):

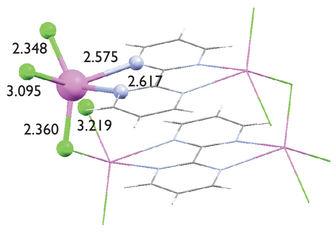




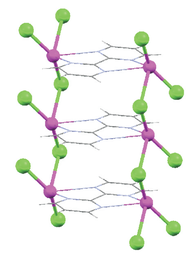
Bridging halogenide, **mercuriophilic** interaction and π-π interactions between aromatic rings have permitted to obtain a columnar structure based on a Hg-Cl-Hg coordination polymer.

Because of the interesting structural and luminescent properties usually shown by coordination polymers of d^{10} metals containing aromatic ligands, we decided to develop the study of the interactions between 2,2-bipyrimidine and HgX_2 compounds, where X=Cl^-, I^-, CN^-, SCN^-, with the purpose to obtain $Hg_2(bpym)X_4$ complexes.

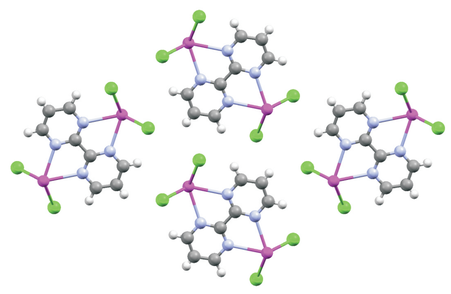
[μ-(2,2'-bipyrimidine-N1,N1':N3,N3')]tetrachlorodimercury



Esa-coordinated Hg(II) geometry derives from a distorted tetrahedron with insertion of two chlorine atoms.

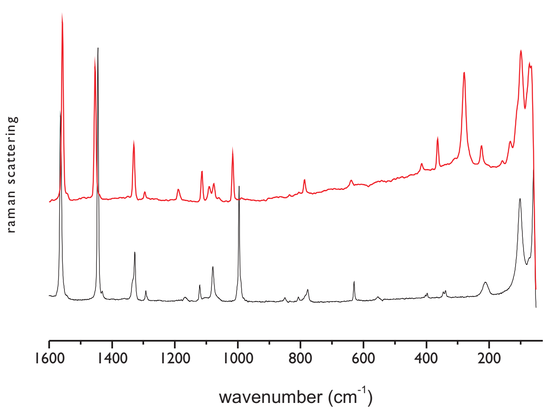


Bridgin chlorine and π-π interactions among bpym generates 1-D polymeric chains

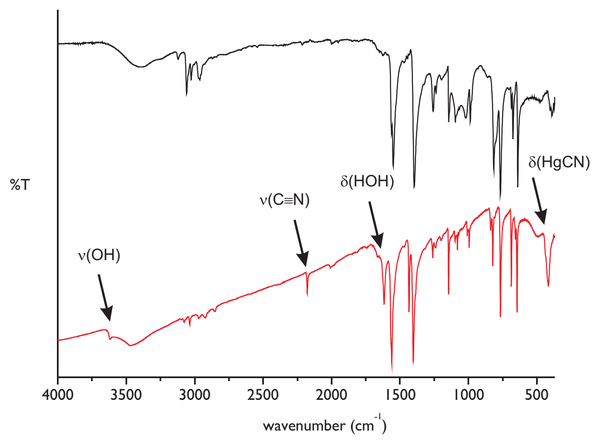


1-D chains develop along crystallographic a axis and don't interact each others

The synthesis of the complexes has been executed by refluxing an acetonitrile solution of bpym and the appropriate mercury salt, in the ratio 1:2. The clear solution obtained has been slowly evaporated and crystal suitable for XRD analysis have been obtained.

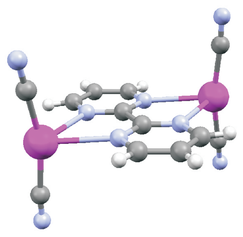


Raman spectra of $(bipym)Hg_2Cl_4$ (red) and bpym (black). It's possible to notice the effect of the coordination on the vibrational modes of bpym (the shift of ring modes in the range 1600-1400 cm^{-1} and at 1000 cm^{-1}), and the appearance of a strong mode at 280 cm^{-1}, attributable to Hg-Cl stretching.

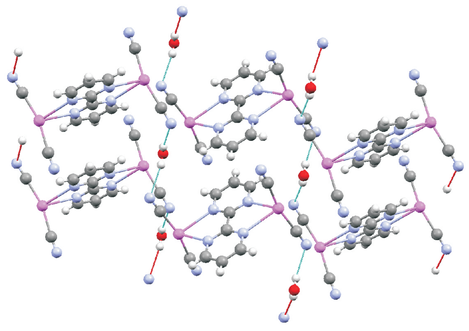


Infrared spectra of $(bipym)Hg_2(CN)_4$ (bottom) and bpym (top) with some significant assignments

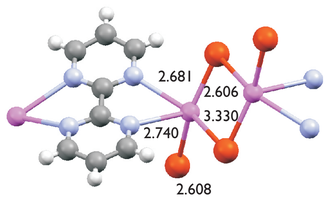
[μ-(2,2'-bipyrimidine-N1,N1':N3,N3')]tetrakis(cyano)dimercury



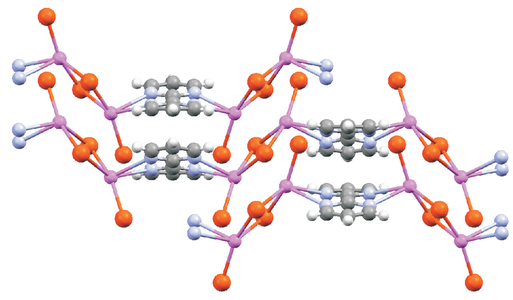
The cyanide complex is a molecular compound. Mercury has a distorted tetrahedral coordination. The stacking of bipym is staggered. A significant contribution to the crystalline packing comes from N···H hydrogen bond between cyanide ligands and the water.



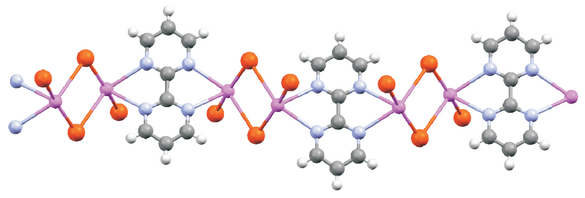
[μ-(2,2'-bipyrimidine-N1,N1':N3,N3')]tetraiododimercury



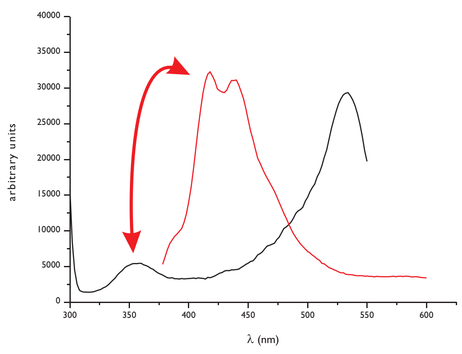
In the iodide complex, Hg(II) is coordinated to five atoms: two bpym nitrogen, two bridging iodide, one terminal iodide.



Ribbons of iodide-mercury-bpym are stacked thanks to weak π-π interaction between aromatic rings. The angle between superposed C_4N_2 rings is 15.5°

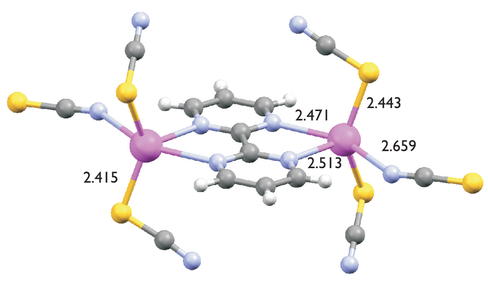


Bridging iodide generate a 1-D coordination polymer



Excitation-emission spectra of $(bipym)Hg_2(SCN)_4$ The intense emission obtained upon excitation at 350 nm is under study, in order to discriminate the contribution of ligand transition from those of the metal.

[μ-(2,2'-bipyrimidine-N1,N1':N3,N3')]tetrakis(thiocyanate)dimercury



Thiocyanate ligand generate an interesting structure: mercury is penta-coordinate to three nitrogen (two of bpym and one of SCN^-) and to two sulfur. The ambidentate nature of SCN^- permits the formation of a 3-D polymer