

Molecular Design Laboratory

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1. Current Research and Principal Research Interests

The interests of my research stand on "Coordination chemistry of transition metals". The actual projects focus on "Investigation of the novel properties of the first transition metal complexes toward functional materials using pyridine and sulfur as the composite units of the ligand."

Cluster Complexes. The aggregation of Complex units provides novel relationship between structure, property and reactivity. The use of suitable building unit to construct the aggregate enables us to explore novel featuring of M•••M interactions. One of the useful ligand for this purpose is 2-pyridinethiolate. This ligand can coordinate to metal ion through monodentate, chelate, bridging, or multidentate fashion. The resulting multi-nuclear complexes possess reasonable short Metal-Metal interaction suitable to produce novel property.

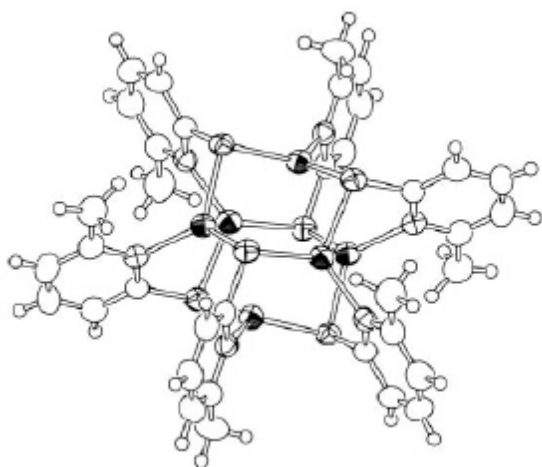


Figure 1. Structure of $[\text{Cu}(4\text{m-pyt})]_6$

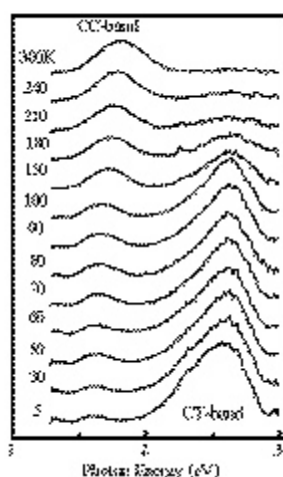


Figure 2. Luminescent thermochromism of $[\text{Cu}(4\text{m-pyt})]_6$

The resulting complex, $[\text{Cu}(6\text{m-pyt})]_6$ (6m-pyt: 6-methyl-2-pyridinethiolato), exhibits luminescent thermo-chromism that emit red light at ambient temperature from cluster centered excited state and emit blue light at low temperature from ligand π^* state. Pyridinethiol is also a

good candidate to construct novel M-M state like Pt(III)-Co(II), and Pd(III)-Pd(III) states which are hardly accessed under usual condition.

Novel functional ligands for elucidating valuable properties. The combination of pyridines and sulfurs in a ligand produces the special circumstances for first transition metals with particular structure-property relationship. The strong interaction of p orbital of S atoms with $p\pi$ orbital of pyridines affords electronic diversity to the ligand. The resulting complexes of first transition metals would present catalytic activities alternative to the noble metal catalyst. Under this principle, we have prepared the first example of transition metal complexes with macrocyclic pyridines, thiacalix[n]pyridines, as a ligand. Especially, thiacalix[3]pyridine (Py_3S_3) stabilizes Cu(I) in certain extent, and the resulting complex has remarkable affinity to olefins and CO molecules. We have now examined the catalytic activity of this complex. The complex also present interesting photochemical behavior with relatively strong luminescent. The unprecedented coordination of the ligand to a particular metal ion presents the novel feature for the complexes. No previous research predicts the presence of the stable copper(II) complex with Cu(II)-C(sp^3) bond. We have designed and made an C3 symmetrical ligand of tris(pyridyl-2-thio)methane that can coordinate via tetradentate fashion with liberation of the proton at the central carbon atom. The analogous ligand of bis(pyridylthio)methane was found during the course of our previous research. Using tris(pyridyl-2-thio)methane, we have synthesized the first example of Cu(II)-C(sp^3) bond. Contrary to the Py_3S_3 , tris(pyridyl-2-thio)methane stabilizes the divalent and trivalent oxidation state of copper complex. It is possible to elucidate the rational reason for these properties as the significant mixing of sulfur p orbital with pyridine $p\pi$ orbital. Now we are examining to arrange these system suitable for further application for catalyst, photophysical devices, and others.

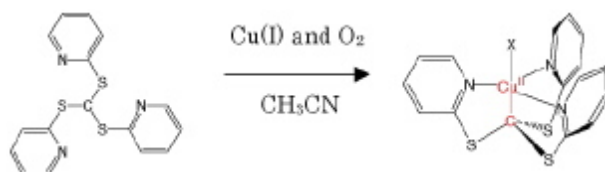


Figure 3. Reaction of tris(pyridyl-2-thio)methane with Cu(I)

2. Selected Publications

1. "A complete series of copper(II) halide complexes ($X = F, Cl, Br, I$) with a novel $Cu^{II}-C(sp^3)$ bond " R. Miyamoto, R. Santo, T. Matsushita, T. Nishioka, A. Ichimura, Y. Teki and I. Kinoshita, *Dalton Trans.* , **2005**, 3179-3186.
2. "A two-dimensional clathrate hydrate sandwiched by planar arrays of a copper complex." R. Miyamoto, R. T. Hamazawa, M. Hirotsu, T. Nishioka, I. Kinoshita, L. J. Wright, *Chem. Commun.*, **2005**, 4047-4049.
3. "Selective oxygenation of amphiphilic thiacalix[3]pyridine Rh(I) diene complexes in both water and organic solvents.." T. Nishioka, Y. Onishi, K. Nakajo, J. Guo-Xin, R. Tanaka, I. Kinoshita, *J. Chem. Soc., Dalton Trans.*, **2005**, 2130-2137.
4. "Catalytically Active Catalytically Active μ -oxodiiron(IV) Oxidants from Iron(III) and Dioxygen." A. Ghosh, F. Tiago de Oliveira, T. Yano, T. Nishioka, E. S. Beach, I. Kinoshita, E. Mu'nck, A. D. Ryabov, C. P. Horwitz, and T. J. Collins, *J. Am Chem. Soc.*, **2005**, 127, 2505-2513.

5. "Luminescence processes of hexanuclear methylpyridinethiolato-copper(I) crystals." Xie, H. Y.; Tougezaka, M; Oishi, S; Kinoshita, I; Kanemoto, K; Akai, I; Karasawa, T., *J. Luminescence*, **2004**, *108*, 91-95.
6. "Activation of C-Cl and C-H bonds by ligated S⁻²(2-) ions: Conversion of organic chlorides into organosulfur compounds in cis-[(IrCp*)₂(μ-CH₂)₂(μ-S₂R)](+)." T. S. Lobana, K. Isobe, H. Kitayama, T. Nishioka, I. Kinoshita, *Angew. Chem. Int.-ed.*, **43**, 213-215 (2004).
7. "Pyridine-2-sulfonates as Versatile Ligands for the Synthesis of Novel Coordinative and Hydrogen-Bonded Supramolecules." T. S. Lobana, I. Kinoshita, K. Kimura, T. Nishioka, D. Shiomi, K. Isobe, *Eur. J. Inorg. Chem.*, **2004**, 356-367.
8. "Design and Synthesis of Copper Complexes of Novel Ligands based on the Pyridinethiol Group", I. Kinoshita, L. J. Wright, S. Kubo, K. Kimura, A. Akata, T. Yano, R. Miyamoto, T. Nishioka, K. Isobe, *J. Chem. SOC., Dalton Trans.*, **2003**, Special issue for Dalton Discussion 5.
9. "Laser Photolysis Studies on CuI Complexes of Thia-calix[3]pyridine. Phosphorescence from the Intramolecular Charge-Transfer Excited State" I. Kinoshita, A. Hamazawa, T. Nishioka, H. Adachi, H. Suzuki, Y. Miyazaki, A. Tsuboyoma, S. Okada, M. Hoshino, *Chem. Phys. Lett.*, **2003**, *371*, 451-457.
10. "Thia-calix[n]pyridines, Synthesis and Coordination to Cu(I,II) ions with both N and S Donor Atoms" R. Tanaka, T. Yano, T. Nishioka K. Nakajo, B. K. Breedlove; K. Kimura, I. Kinoshita, K. Isobe, *Chem. Commun.*, **2002**, 1686-1687.

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在 職 中 の 複合先端研究機構 (平成22年4月 ~ 平成27年3月)
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