

# 行政院國家科學委員會專題研究計畫 期中進度報告

## 錯合物中過渡金屬離子之電子組態研究(1/3)

計畫類別：個別型計畫

計畫編號：NSC92-2113-M-002-040-

執行期間：92年08月01日至93年07月31日

執行單位：國立臺灣大學化學系暨研究所

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報告類型：精簡報告

報告附件：出席國際會議研究心得報告及發表論文

處理方式：本計畫可公開查詢

中 華 民 國 93 年 5 月 28 日

- In the Ni related complexes coordinated with noninnocent ligands, two series of complexes were synthesized and characterized by X-ray diffraction and X-ray absorption spectroscopy. In the dithiolene complexes, the Complex  $[\text{Ni}(\text{S}_2\text{C}_2\text{Me}_2)_2]^{0, -1, -2}$ ,  $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]^{0, -1}$  and  $[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{-1, -2}$  were synthesized and the Ni  $L_{\text{III,II}}$ -edge spectra were displayed in the Figure 1. The results indicated that the formal oxidation state of Ni atom increases with the increasing of  $n$  value, where  $n$  is the charge of  $[\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2]^n$  ( $n = 0, -1, -2$ ). For other complexes: *trans*- $[\text{Ni}(-\text{SC}_6\text{H}_4\text{-}o\text{-NH-})_2]^-$ , *trans*- $[\text{Ni}(-\text{SeC}_6\text{H}_4\text{-}o\text{-NH-})_2]^-$  and *cis*- $[\text{Ni}(-\text{TeC}_6\text{H}_4\text{-}o\text{-NH-})_2]^-$ , the results indicate that: (i) Based on the topological analysis, the variation in S, Se and Te atom of ligand does not change the bonding characters of Ni-N and the N-C bonds. However, the covalence of X-C and Ni-X (X=S, Se, Te) bonds decrease in the order, S ~ Se > Te. The covalent character in these complexes is therefore in the order of Ni-N > Ni-S ~ Ni-Se > Ni-Te. (ii) The anisotropy in g-values of these complexes from EPR measurement as well as the magnetic measurement is consistent with the spin located at either the Ni site or one of the ligand site, i.e. L-Ni(III)-L or L-Ni(II)-L\* with probable (1/2, 0) or (1/2, 1/2) for (total S, sum S of L) as the ground state. The spin exchange between Ni and L could be accomplished through Ni-L  $\pi$  bond, namely  $p_z$ - $d_{xz}$  molecular orbitals as realized by DFT calculation.
- In the nitrosyl complex, based on the NEXAFS of N K-edge, XANES of Fe K-edge and  $L_{\text{III,II}}$ -edge spectra, as well as the topological analysis of electron densities obtained from experiment and quantum chemical calculation, the  $[(\text{NO})_2\text{FeS}_5][\text{PPN}]$  compound can be described as the  $\{\text{Fe}(\text{NO})_2\}^9$  with Fe(I) (d7) bonded to two NO radical. This result implies that the biomimetic compound  $[(\text{NO})_2\text{FeS}_5][\text{PPN}]$  has the same character as those of low molecular mass of DNICs which could store and transport the  $\text{NO}\bullet$ .
- The powder experiment carried on SPring-8 BL12B2 does not work out as smooth as predicted. For the moment, the powder end station is still under commission. The studied on  $\text{KNiF}_3$  at room temperature shows that: electron density based on MEM/Rietveld analysis does provide reasonable results which are the same as those from multipole refinement of single crystal data and theoretical calculation.
- In the spin crossover related complexes, the *trans*- $[\text{Fe}(\text{tzpy})_2(\text{NCS})_2]$  (tzpy = 3-(2-pyridyl)[1,2,3]triazolo[1,5-a]pyridine; X = S(**1**), Se(**2**)) has been synthesized and structurally characterized as shown in Figure 2. Complex **1** crystallizes in a monoclinic cell ( $P2_1/c$ ) and **2** in a triclinic one ( $P\bar{1}$ ).  $\text{Fe}^{\text{II}}$  atoms in both compounds are at inversion centers in the distorted octahedral environment and are both coordinated by two equatorial tzpy ligands and two axial  $\text{NCS}^-$  anions. The temperature dependent magnetic susceptibility measurement of complex **1** (Figure

3) shows that it is at high spin state ( $S = 2$ ) at room temperature and is at low spin state ( $S = 0$ ) below 75K. The  $T_{1/2}$  of 140K is slight higher than that of the solvent contained complex, *trans*-[Fe(tzpy)<sub>2</sub>(NCS)<sub>2</sub>]·H<sub>2</sub>O ( $T_{1/2} = 118$ K). Light-induced excited spin state trapping (LIESST) effect was confirmed by Fe K-edge and L-edge x-ray absorption spectroscopy at 30 K using green light laser irradiation (532 nm). The excited-state structural investigation will be performed soon.

Another Fe spin crossover complex with btr ligands (Fe(btr)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> (**3**); btr = 4,4'-bis-1,2,4-triazole) has also been studied. Two unique Fe sites were found in complex **3** from the structural analysis. Evolution of the electronic configuration of complex **3** was investigated by soft X-ray absorption spectroscopy. A two-step spin transition is observed in the Fe L<sub>III,II</sub>-edge spectra (Figure 5) as well as the magnetic susceptibility measurement (Figure 3). One Fe site undergoes an abrupt spin transition while the other one remains at HS (high spin) state from 95K to 197K. Further heating the sample causes the other Fe site to undergo a gradual spin transition which is consistent with the SQUID result.

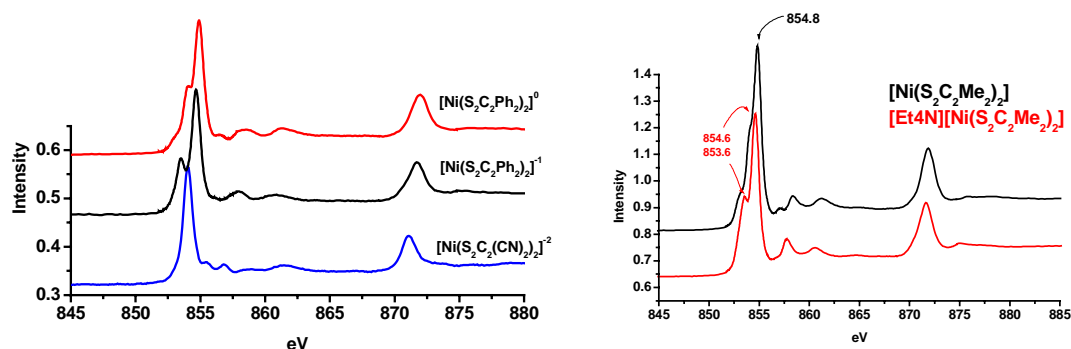


Fig. 1 The L-edge spectra of  $[\text{Ni}(\text{S}_2\text{C}_2\text{Ph}_2)_2]^{0, -1}$ ,  $[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{-2}$  and  $[\text{Ni}(\text{S}_2\text{C}_2\text{Me}_2)_2]^{0, -1}$



Fig. 2 The ORTEP diagrams of *trans*-[Fe(tzpy)<sub>2</sub>(NCX)<sub>2</sub>] (X = S(left), Se(right)) with atomic numbering scheme with 30% thermal ellipsoids

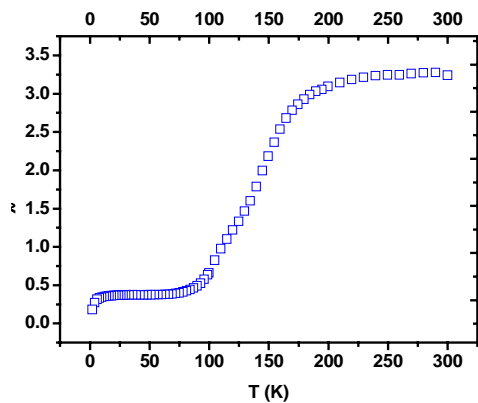


Fig. 3 Susceptibility measurement of **2**

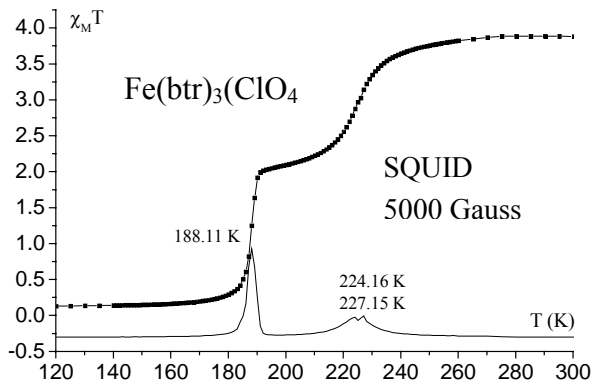


Fig. 4 Susceptibility measurement of **3**

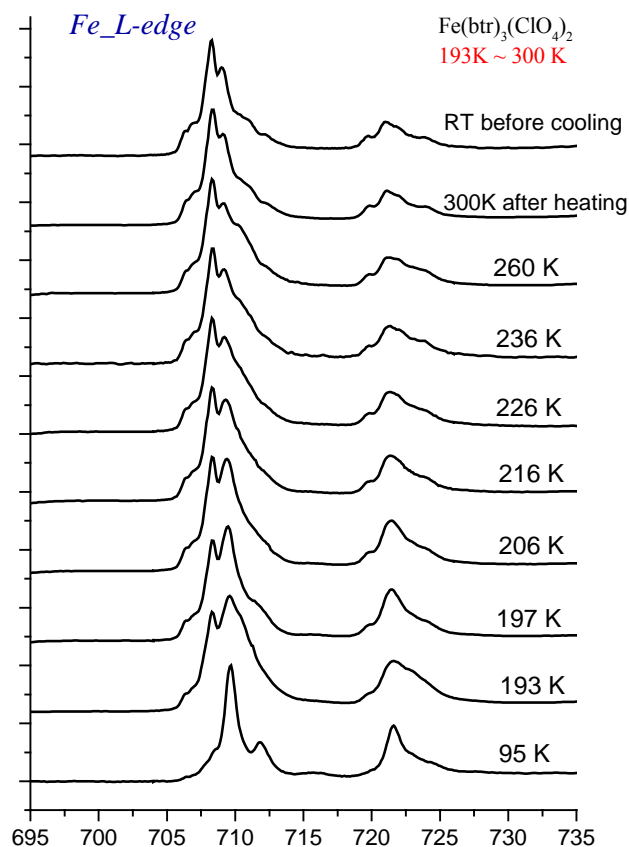
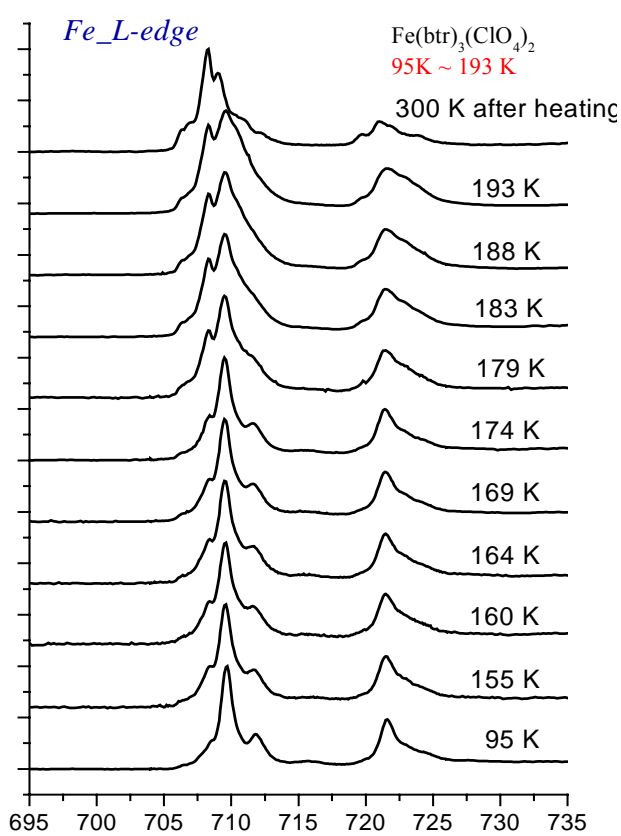


Fig. 5 Fe L-edge spectra of **3**