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# Molecular Design and Synthesis of Ferro- and Ferri-Magnetic Inorganic Polymers and Complexes with Tetrathiolate Ligands

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# MOLECULAR DESIGN AND SYNTHESIS OF FERRO- AND FERRIMAGNETIC INORGANIC POLYMERS AND COMPLEXES WITH TETRATHIOLATE LIGANDS

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Abstract The orbital-symmetry rules for superexchange couplings of unpaired electrons via ligands were applied to one-dimensional (1D) polymers composed of heteropoly transition-metal tetrathiolates (poly(M1TM2), T: tetrathiolate). The polymers composed of the Cu(II)-Fe(III)(LS) and Ni(II)(HS)-Fe(III)(LS) units are predicted to be ferromagnetic within 1D chains, whereas several polymers such as the Co(II)(HS)-Cu(II) alternating one are considered to be ferrimagnetic. Ferromagnetic metals, dense Kondo and spin-mediated superconductors composed of trinuclear M2TM1TM2 complexes (M1=Ni) are also designed on the basis of the theoretical results. According to these guiding principles, we have performed the synthesis of ferro- and ferrimagnetic polymers composed of heteropoly transition-metal tetrathiolates (poly(M1TM2), T: tetrathiolate). The magnetic measurements of the solids were also carried out and the observed intrachain effective exchange integrals are summarized.

## INTRODUCTION

About ten years ago, Hirsch and Scalapino pointed out a strong-coupling mechanism of high-Tc superconductivity expected for weakly coupled double valence fluctuating molecules.[1,2] Their quantum Monte Carlo simulations suggested an important role of superconducting fluctuations at temperatures of order of antiferromagnetic effective exchange integrals ($J_{ab}$). After the discovery of the high Tc superconductivity in copper oxide systems,[3] several synergistic effects were expected for the conduction electrons (or holes) plus spin systems, which were generated by electron or hole doping into anti-(or ferro) magnetic insulators. The superconducting transition temperatures (Tc) of several transition metal oxides were estimated on the basis of the spin fluctuation model coupled with the $J_{ab}$ values calculated by ab initio UHF MO method.[4] Many theoretical models involving electron-phonon and electron-exciton couplings were also presented to explain the high Tc superconductivity specific to the copper oxides. However, its

mechanism has not been settled yet. Therefore, strongly or intermediately electron-correlated systems have received continuous interest in relation to both magnetism and (super)conductivity.[5]

Recently, several types of ferromagnetic compounds were synthesized and their magnetic properties were throughly investigated.[6-8] Here, we first design new types of ferromagnetic or ferrimagnetic polymers composed of heteropoly transition-metal tetrathiolates; (poly(M1TM2), T: tetrathiolates) on the basis of the orbital-symmetry rules for superexchange couplings of unpaired electrons via anionic lingands, which have been derived from previous ab initio calculations of the binuclear complex $(HS)_2M1TM2(SH)_2$.[9] Spin-fluctuations also play important roles in spin-mediated exotic materials. Then theoretical results are utilized for molecular design of ferromagnetic metals, dense Kondo and spin-mediated superconductors composed of the segregated columns of trinuclear complexes $(L)_2M2TM1TM2(L)_2$ (L=proper ligand).[10] The isologous analogy among these inorganic systems and TTF derivatives with radical groups is clearly shown on the basis of the Anderson-type Hamiltonian.

According to these theoretical guiding principles, our experimental approach to achieve molecular ferromagnet and other exotic magnetic materials has been to impose ferro (or antiferro)-magnetic superexchange interactions between nearest neighbor hereto metal centers in alternating arrayed manner. In order to rearize the heterometallic systems, tetrathiolate was selected because of its very desirable combination of structural features. In fact the transition metal centers with large spin multiplicities would be coordinated in close proximity, enhancing one-dimensional ferro- or antiferro-magnetic interactions. This ligand is unsaturated and therefore has a fairly polarizable molecular orbitals. In square planar complex it should provide good $d\pi$-$p\pi$ orbital interaction,[11,12] which has received current interest in relation to development of new magnetic conductors and superconductors.

## DESIGN OF FERRO(FERRI)MAGNETIC POLYMERS

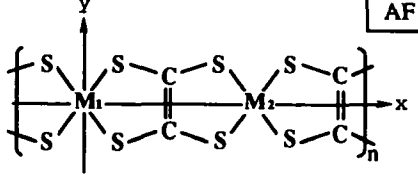
Previous ab initio calculations[9] of the binuclear complexes (M1TM2) indicated that the superexchange interaction ($J_{ab}$) between the transition metal ions M1 and M2 via tetrathiolate ligand is generally expressed by

$$J_{ab} = \Sigma \{ K_{ab} - C (S_{ab})^2 \}, \quad (1)$$

where $K_{ab}$ and $S_{ab}$ are the Coulombic exchange integral and orbital overlap, respectively. The magnetic orbitals **a** on M1 and **b** on M2 are significantly delocalized over the tetrathiolate ligand (T). Then the orbital overlap ($S_{ab}$) becomes large when the

TABLE I. Spin alignment rules for poly metal tetrathiolates.

| $M_2$ \ $M_1$ | Co(II) LS | Co(II) HS | Co(III) LS | Co(III) IS | Co(III) HS | Fe(II) LS | Fe(II) IS | Fe(II) HS | Fe(III) LS | Fe(III) IS | Fe(III) HS | Ni(II) LS | Ni(II) HS | Ni(III) LS | Ni(III) HS | Cu(II) | Cu(III) LS | Cu(III) HS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Co(II) LS ↓↑↑ ↓ \| | AF | FERI | P | FERI | FERI | P | FERI | FERI | F | FERI | FERI | P | FERI | AF | FERI | F | P | FERI |
| Co(II) HS ↓↑↑ ↓ ↓ | | AF | P | FERI | FERI | P | FERI | FERI | FERI | FERI | FERI | P | FERI | FERI | AF | FERI | P | FERI |
| Co(III) LS ↓↑↑ \| \| | | | DM | P | P | DM | P | P | P | P | P | DM | P | P | P | P | DM | P |
| Co(III) IS ↓↑↑ ↓ \| | | | | AF | FERI | P | AF | FERI | FERI | FERI | FERI | P | FERI | FERI | FERI | F | P | FERI |
| Co(III) HS ↓↑↑ ↓ ↓ | | | | | AF | P | FERI | FERI | FERI | FERI | FERI | P | FERI | FERI | FERI | FERI | P | FERI |
| Fe(II) LS ↓↑↑ \| \| | | | | | | DM | P | P | P | P | P | DM | P | P | P | P | DM | P |
| Fe(II) IS ↓↑↑ ↓ \| | | | | | | | AF | FERI | FERI | AF | FERI | P | FERI | FERI | FERI | F | P | FERI |
| Fe(II) HS ↓↑↑ ↓ ↓ | | | | | | | | AF | FERI | AF | FERI | P | FERI | FERI | FERI | FERI | P | FERI |
| Fe(III) LS ↓↑↑ \| \| | | | | | | | | | AF | FERI | FERI | P | F | F | FERI | F | P | F |
| Fe(III) IS ↓↑↑ ↓ \| | | | | | | | | | | AF | FERI | P | FERI | FERI | AF | F | P | FERI |
| Fe(III) HS ↓↑↑ ↓ ↓ | | | | | | | | | | | AF | P | FERI | FERI | FERI | FERI | P | FERI |
| Ni(II) LS ↓↑↑ ↓ \| | | | | | | | | | | | | DM | P | P | P | P | DM | P |
| Ni(II) HS ↓↑↑ ↓ ↓ | | | | | | | | | | | | | AF | FERI | FERI | FERI | P | FERI |
| Ni(III) LS ↓↑↑ ↓ \| | | | | | | | | | | | | | | AF | FERI | F | P | FERI |
| Ni(III) HS ↓↑↑ ↓ ↓ | | | | | | | | | | | | | | | AF | FERI | P | FERI |
| Cu(II) ↓↑↑ ↓ ↓ | | | | | | | | | | | | | | | | AF | P | FERI |
| Cu(III) LS ↓↑↑ ↓ \| | | | | | | | | | | | | | | | | | DM | P |
| Cu(III) HS ↓↑↑ ↓ ↓ | | | | | | | | | | | | | | | | | | AF |




F : ferromagnetic
FERI : ferrimagnetic
AF : antiferromagnetic
P : paramagnetic
DM : diamagnetic

$d_{xy}$
$d_{x^2-y^2}$
$d_{z^2}$
$d_{yz}$, $d_{xz}$

orbitals **a** and **b** have the same symmetry, and $J_{ab}$ becomes negative (antiferromagnetic) since the second term in Equation (1) overcomes the first term. On the other hand, the $J_{ab}$-values are positive (ferromagnetic) in other orbital-orthogonal cases ($S_{ab}$=0). Table I shows the signs of the $J_{ab}$-values for the M1TM2 pairs based on the orbital symmetry rules and ab initio calculations.[9] From Table I, ferromagnetic spin couplings are feasible for several Cu(II)-M2 and Ni(II)-M2 pairs, whereas antiferromagnetic spin couplings are concluded for many other cases. Therefore, the alternating polymers composed of these units may become the ferromagnetic and ferrimagnetic one-dimensional polymers as illustrated in Table I.

## DESIGN OF FERROMAGNETIC METALS, DENSE KONDO AND SPIN-MEDIATED SUPERCONDUCTORS

The $Ni(dmit)_2$ plus TTF (or $N(Me)_4$) systems (2:1 complexes) exhibit the superconductivity at a low temperature under the high pressure. The trinuclear complexes M2TNiTM2 have the $Ni(dmit)_2$ skeleton coupled with spins on M2 (for example, Fe(III), etc). Therefore, cooperative effects between conduction electrons and spins are expected theoretically. Previously, we examined their organic analogs R-TTF(BEDT-TTF)-R (R = organic radicals) in relation to possibilities of organic ferro(ferri) magnetic metals, dense Kondo systems and spin-mediated superconductors composed of these units. The same synthetic strategies are feasible for segragated columns composed of the trinuclear complexes as shown in Figure 1, since both systems are described by the Anderson Hamiltonian:

$$H = \Sigma\ \varepsilon_K\, \sigma_{ks}^*\, \sigma_{ks} + \Sigma\ (\, V_K\, \sigma_{ks}^*\, R_{ks} + \Sigma\ V_K\, R_{ks}^*\, \sigma_{ks}\,) + \Sigma\ \varepsilon_d\, R_{ks}^*\, R_{ks} + U\, R_{ks}^*\, R_{ks}\, R_{ks}^*\, R_{ks}\,, \qquad (2)$$

where $\sigma_{ks}^*$ and $R_{ks}^*$ denote, respectively, the creation operators of conduction and localized electrons, and V is the coupling constant between them.

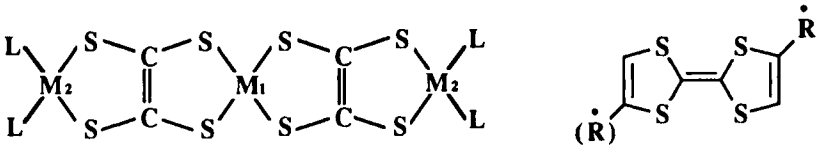



FIGURE 1. Trinuclear complexes with Ni(dimt) and isoelectronic TTF derivatives

## SYNTHESIS

According the guiding princples discussed above, we performed the experimental efforts to synthesize the ferromagnetic polymers in past several years. Here, the experimental details are summarized. First, heteropoly metal tetrathiolates (poly (M1TM2), T:tetrathiolate) were synthesized as shown in Figure 2. In case of poly(Cu(II)TCo(II)), to 2.0 g of the copper thio bis-chelate were added 11.2 ml of 1 molar sodium metoxide in methanol and a solution of 0.66 g of $CoCl_2 \cdot 6H_2O$ in 35 ml of methanol. The mixture was refluxed for 5 hours, and the resulting solids were filtered and rinsed with methanol, deionized water, again with methanol, toluene, and with ether. Then they were dried under vacuum. The product (1.83 g) was a finely powdered, dark-brown solid. Although the infrared spectrum is inconclusive as to whether the product consists of hetero metal centers in alternating arrayed manner or not, both the elemental analysis and scanning electron micrograph show that the ratio of copper to cobalt is almost 1 to 1. Other trnasition metal-tetrathiolate systems were synthesized and are characterized in the same manner.

The electronic and spin state of metal centers in poly metal tetrathiolates were examined based on ESCA and Mössbauer spectra. The results are shown in Table II. These results show that the metals were most probably oxidized to higher oxidation states, in exactly the same way as in the case of cobalt and iron.

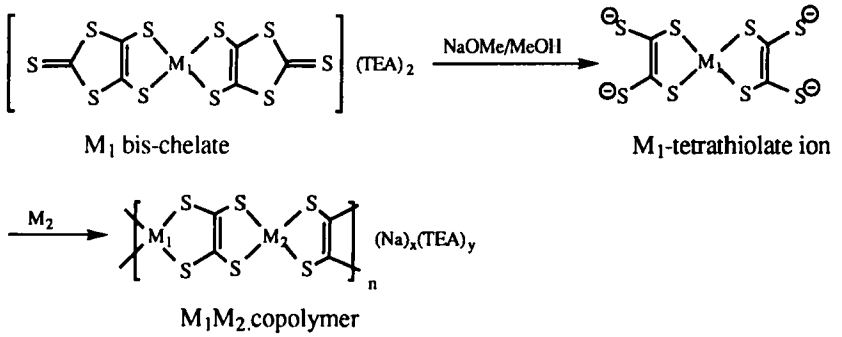



FIGURE 2. Synthetic scheme for heteropoly transition metal tetrathiolate polymers

## MAGNETIC MEASUREMENT AND DISCUSSION

In Table III, we summarized Curie-Weiss parameters and Curie-Weiss temperatures of hetero poly metal tetrathiolates (poly (M1TM2), T:tetrathiolate). Both Curie-Weiss parameters and Curie-Weiss temperatures were estimated by extrapolation of the

TABLE II. Valency numbers for poly metal tetrathiolates analyzed by the Mössbauer and ESCA spectroscopy

| metal combination | analysis results on the basis of Mössbauer spectra and ESCA |
|---|---|
| Co(II)/Cu(II) | mixture of Co(II)/Cu(II) and Co(III)/Cu(II). Co(II) is high spin state |
| Co(II)/Fe(II) | actually Co(II)/Fe(III), Fe(II) is oxidized to Fe(III). Co(II) is high spin state. |
| Ni(II)/Co(II) | actually Ni(II)/Co(II), Ni(II) is oxidized to Ni(III) and low spin state. |
| Fe(II)/Fe(III) | actually Fe(III)/Fe(III), Fe(II) is oxidized to Fe(III). |
| Fe(II)/Cr(III) | actually Fe(III)/Cr(II), Fe(II) is oxidized to Fe(III). |
| Co(II)/Fe(II) | actually Co(II)/Fe(III), Co(II) is high spin state. Fe(II) is oxidized to Fe(III) and low spin state. |
| Cu(II)/Fe(II) | actually Cu(II)/Fe(III), Fe(II) is oxidized to Fe(III) and low spin state. |
| Ni(II)/Fe(II) | actually Ni(II)/Fe(III), Ni(II) is high spin state. Fe(II) is oxidized to Fe(III) and low spin state. |
| Ni(II)/Fe(III) | actually Ni(II)/Fe(III) |
| Ni(II)/Cu(II) | actually Ni(II)/Cu(II) |

Curie-Weiss plot is given by Equation (3). The detailed experimental results will be published elsewhere.[13]

$$1/\chi = (1/C)(T - \theta) \qquad (3)$$

The calculations on effective exchange integrals of tetramethyllead dimers indicate that these magnetic properties of heliotrope metal systems are consistent with the predictions based on the symmetry rules.[7] In fact, alternating polymers with the Cu(II)-Fe(III)(low-spin; LS) and Ni(II)(high-spin; HS) units were found to be ferromagnetic from the magnetic measurements .[4] On the other hand, the experiments elucidated that the polymers with the Co(II)(HS)-Cu(II), Co(II)(HS)-Fe(III)(LS) and Ni(III)(LS)-Co(II)(HS) units are antiferromagntic, which supports the preceding theoretical prediction and calculations.[2]

Unfortunately, we could not obtain X-ray diffraction data for these inorganic polymers. Figure 3 shows that the M1M2 alternating ordered heteropolymetallic chains, where M1=Fe(III), M2=Cu(II), Ni(II), exhibit one-dimensional ferromagnet-like

TABLE III. Curie-Weiss parameters and Curie-Weiss temperatures of hetero poly metal tetrathiolates (poly (M1TM2), T:tetrathiolate)

| | Cr(III) | Fe(III) | Co(II) | Ni(II) | Ni(III) | Cu(II) |
|---|---|---|---|---|---|---|
| Cr(III) | 14 | 12 | | 8 | | |
| | -45 | -63 | | -33 | | |
| Fe(III) | | 8 | 23 | 47 | | 13 |
| | | -74 | +100 | +100 | | +100 |
| Co(II) | | | 17 | | 10 | 7 |
| | | | -25 | | -15 | -10 |
| Ni(II) | | | | 16 | | 2 |
| | | | | -20 | | -10 |
| Cu(II) | | | | | | 1 |
| | | | | | | -29 |

(upper row: Curie-Weiss parameter ($x10^6$))
(lower row: Curie-Weiss temperature(K))

behaviors in the low temperatures, which arise from ferromagnetic intrachain interactions. However, upon cooling further to lower temperature, magnetic susceptibility decreases. The magnetic behavior in this range is prdiminatingly attributed to an interchain antiferromagnetic interaction based on the structure shown in Figure 3.

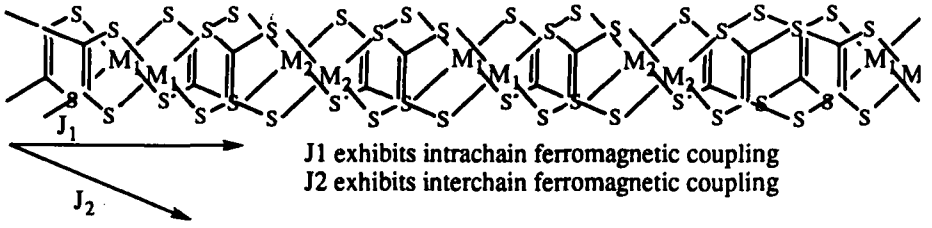



FIGURE 3. Possible interchain stacks derived from the experimental data

It is concluded that the control of the interchain interactions is essential for further developments of the inorganic polymer sytems under investigation.

## ACKNOWLEDGMENT

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