RESEARCH ACTIVITIES VII
Coordination Chemistry Laboratories

Prof. Hiroyuki Matsusaka (Osaka Prefecture Univ.), Assoc. Prof. Keiji Ueno (Gunma Univ.) took the position of Laboratory of Coordination Bond from April 2003. Prof. Nobuhiro Tokito (Kyoto University) and Assoc. Prof. Kiyotaka Onizuka (Osaka University) finished their term as Adjunct Prof. of the Coordination Bond in March 2003. Their effort during their term is gratefully appreciated. Prof. Masahito Yamashita (Tokyo Metropolitan Univ.) and Prof. Naoto Chatani (Osaka Univ.) continue the position of the Laboratory of Synthetic Coordination Chemistry.

VII-A Nano-Sciences of Advanced Metal Complexes

Recently, nano-sciences or nano-technologies have been attracting much attention because they show very interesting physical properties based on the non-linearity and quantum effect. There are two methods to obtain the nano-size materials, that is, “top-down” and “bottom-up.” The top-down method such as laser abrasion has a limitation to make particles with the size less than 100 nm. On the other hand, the bottom-up method is promising to control the nano-size since the chemical reactions are available. However, the researches based on the bottom-up methods are rare and such methods have not been accomplished so far. There are three types of the target materials such as inorganic compounds, organic compounds, and metal complexes. The inorganic compounds easily take three-dimensional bulk structures. The organic compounds easily take 0- and 1-dimesional bulk materials. Therefore, neither inorganic nor organic compounds are suitable for the nano-sciences. On the other hand, the metal complexes easily take nano-size clusters where they are surrounded with the organic ligands. Therefore, the nano-sciences of the advanced metal complexes are most promising. As for the non-linearity, we focus on the gigantic third-order optical non-linearity. As for the quantum effect, we focus on the single-molecule magnets, nano-wire molecule-magnets, and nano-network molecule-magnets.

VII-A-1 Out-of-Plane Dimers of Mn(III) Quadridentate Schiff-Base Complexes with Saltmen^{2-} and Naphtmen^{2-} Ligands: Structure Analysis and Ferromagnetic Exchange

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[*J. Chem. Soc., Dalton Trans.* **7**, 1528–1534 (2002)]

Six Mn(III) quadridentate Schiff base compounds with N,N’-(1,1,2,2-tetramethylethylene)bis(salicylideneiminato) dianion (saltmen^{2-}) and N,N’-(1,1,2,2-tetramethylethylene)bis(naphthylideneiminato) dianion (naphtmen^{2-}) were prepared and structurally characterized: [Mn(saltmen)(H_2O)]ClO_4 (1), [Mn(naphtmen)(H_2O)]ClO_4 (2), [Mn(saltmen)(NCS)] (3), [Mn(naphtmen)(NCS)] (4), [Mn(saltmen)(Cl)] (5) and [Mn(naphtmen)(Cl)] (6). Among them, 1 and 2 form phenolate-bridged out-of-plane dimers with Mn-Ophenolate bond distances of 2.434(2) and 2.662(3) Å, respectively. X-ray diffraction analyses show that compounds 3, 4 and 6 can also be considered as out-of-plane dimers in spite of long Mn-Ophenolate interacting distances (3.441(2) Å for 3, 3.758(3) Å for 4 and 3.505(5) Å for 6). In contrast with the above compounds, 5 is a discrete Mn(III) mononuclear complex with a square-pyramidal geometry. In the dimer series (compounds 1–4 and 6), the out-of-plane intermolecular distance varies dramatically according to equatorial ligands, saltmen^{2-} or naphtmen^{2-}, and axial ligands, H_2O, NCS^- and Cl^-. The relation between substitution of the ligands and structural parameters of the dimeric molecules are discussed. Magnetic susceptibility studies reveal interesting intra-dimer ferromagnetic interactions between Mn(III) ions. These new $S = 4$ building blocks open new possibilities in the design of magnetic molecule-based materials.

VII-A-2 Electron Spin Resonance Studies of Co(tbp)·C_{60} Single Crystal

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[*J. Phys.: Condens. Matter* **14**, 3993–4000 (2002)]

ESR measurements were made on a newly synthesized cocrystallite of C_{60} with the Co^{II} complex of 5, 10, 15, 20-tetrakis[3, 5-(di-tert-butyl)-phenyl]porphyrin (tbp) single crystal to study the strong intermolecular interactions which are suggested by x-ray structural analyses. A single anisotropic ESR absorption line is observed. At room temperature with the principal g-values ($g_\perp = 2.423$ and $g_\parallel = 2.005$), which are typical values for the low-spin Co^{II} ions ($S = 1/2$). The antiferromagnetic superexchange interaction between Co^{II}

ions *via* C_{60} is confirmed from the observation of the finite Weiss temperature, which is further supported by the absence of the hyperfine splitting due to ^{59}Co (I = 7/2) nuclei. As the temperature is lowered, the $g_{\perp}$-value decreases monotonically suggesting an increase of the crystal-field splitting energy. This result is consistent with the fact that the intermolecular distance between Co^{II} and C_{60} becomes shorter as the temperature decreases. The peak-to-peak ESR linewidths ΔHpp along both principal axes increase with temperature due to the shorter spin-lattice relaxation time.

VII-A-3 Structure, Magnetic and Electronic Properties of Charge Transfer Complex Containing Hexacyanoferrate Chain and BEDT-TTF Column

NAKATA, Kazuya[1]; YOSHINO, Yuko[1]; HARA, Hatsune[1]; MANABE, Toshio[1]; ISHII, Tomohiko[1]; MIYASAKA, Hitoshi[1]; YAMASHITA, Masahiro[2]; MATSUZAKA, Hiroyuki[1]; KATADA, Motomi[1]
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[*Mol. Cryst. Liq. Cryst.* **380**, 117–122 (2002)]

A novel charge transfer complex containing of hexacyanoferrate ($Fe(CN)_6$) unit, which has been exhibited variety of magnetic topics in prussian blue systems, was synthesized. X-ray analysis of the single crystal obtained by electrolysis of BEDT-TTF (ET) and hexacyanoferrate suggests that this complex contains 1-dimensional magnetic hexacyanoferrate chain perpendicular to the conducting ET column. This significant structure implies that significant properties can be expected caused by the interaction between the spin momentum on *d*-electrons and a conducting π-electrons influenced vertically by the applied magnetic field. From the electronical conducting measurement, it is suggested that is a semiconductor, with the activation energy and the conductivity at room temperature to be 0.113 eV and 0.46 S/cm, respectively. Detailed x-ray analysis suggests that the occupancies of Fe and C elements in the 1-dimensional hexacyanoferrate chain are 0.5, that of N element is 1.0.

VII-A-4 Creations of Solitons and Polarons in MX-Chain Compounds, $\{[Pt(en)_2][PtX_2(en)_2]\}_3(CuX_4)_4$ (X = Cl and Br)

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([1]Tokyo Metropolitan Univ. and PRESTO(JST); [2]IMS and Tokyo Metropolitan Univ.; [3]Nagoya Univ.; [4]Kumamoto Univ.; [5]Rigaku Co.)

[*Mol. Cryst. Liq. Cryst.* **376**, 7–12 (2002)]

The creations of solitons and polarons in the $\{[Pt(en)_2][PtX_2(en)_2]\}_3(CuX_4)_4$ (X = Cl and Br) which consist of the double linear chain structures of the main one-dimensional halogen-bridged Pt(II)-Pt(IV) mixed-valence units and one-dimensional counteranions of trigonal bipyramidal Cu(I) ions, have been investigated by the absorption spectra, photoinduced absorption spectra, and ESR spectra. The ESR signals of the Pt(III) and Cu(II) species, which were introduced during the synthetic process, are observed in the compound. The relative intensities of *d-d* transitions and ESR spectra of Cu(II) species in counteranions are consistent with each other in the Cl-bridged compounds obtained by pH control. The photoinduced absorption of the Cl-bridged compound is observed in the mid-gap region, which is attributable to the soliton. The doping effect by Br_2 was investigated for the Br-bridged compound. The relative intensities of *d-d* transition and ESR spectra in Cu(II) increase with increasing exposure time. However, the electrical conductivities do not increase. Therefore, the induced Pt(III) species are attributable to neutral solitons.

VII-A-5 Syntheses and Physical Properties of Complexes of Fullerene with Magnetic Metal Porphyrins

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[*Mol. Cryst. Liq. Cryst.* **376**, 13–18 (2002)]

Crystals containing C_{60} and M(OEP) (M^{2+} = Pd, Cu, Ag; OEP^{2-} = octaethylporphinato) were synthesized. Crystal structures were determined for $Cu(OEP)\cdot C_{60}\cdot 2C_6H_6$, $Ag(OEP)\cdot C_{60}\cdot 2C_6H_6$ and $Pd(OEP)\cdot C_{60}\cdot 1.5C_6H_6$. From the x-ray analysis of the cocrystallites, the porphyrin molecules still retain their planar structures without deforming to the fit to the curved surface of the fullerene.

VII-A-6 Crystal and Electronic Structures of Quasi-One-Dimensional Halogen-Bridged Binuclear Platinum Complexes, $\{(C_nH_{2n+1})_2NH_2\}_4[Pt_2(pop)_4I]$ (n = 2–6)

TAKIZAWA, Kouichi[1]; ISHII, Tomohiko[1]; MIYASAKA, Hitoshi[1]; MATSUZAKA, Hiroyuki[1]; YAMASHITA, Masahiro[2]; KAWASHIMA, Takuya[3]; MATSUZAKI, Hiroyuki[4]; KISHIDA, Hideo[4]; OKAMOTO, Hiroshi[4]
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[*Mol. Cryst. Liq. Cryst.* **376**, 159–164 (2002)]

The crystal structures of $\{(C_nH_{2n+1})_2NH_2\}_4[Pt_2(pop)_4I]$ (pop = $O(PO_2H)_2^{2-}$, n = 2–6) were determined. Judging from the results of the x-ray structural analyses and Raman spectra, 1-dimensional electronic structures of these compounds are considered to be $\cdots Pt^{2+}–Pt^{3+}–X\cdots Pt^{2+}–Pt^{3+}–X\cdots$ charge-polarized states.

VII-A-7 Physical Properties of Quasi-One-Dimensional Mixed-Metal and Mixed-Halogen Complexes, $Ni_{1-x}Pd_x(chxn)_2Cl_yBr_{1-y}Y_2$

MANABE, Toshio[1]; YOKOYAMA, Kohei[1]; ISHII, Tomohiko[1]; MIYASAKA, Hitoshi[1]; MATSUZAKA, Hiroyuki[1]; YAMASHITA, Masahiro[2]; KAWASHIMA, Takuya[3]; MATSUZAKI, Hiroyuki[4]; KISHIDA, Hideo[4]; OKAMOTO, Hiroshi[4]; MARUMOTO, Kazuhiro[3]; TANAKA, Hisaaki[3]; ITOH, Hiroshi[3]; KURODA, Shin-ichi[3]
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[*Mol. Cryst. Liq. Cryst.* **376**, 165–170 (2002)]

Single crystals of quasi-one-dimensional Ni-Pd mixed-metal MX-chain compounds, $Ni_{1-x}Pd_x(chxn)_2Br_3$, and mixed-halogen MX-chain compounds, $Ni(chxn)_2Cl_yBr_{1-y}(NO_3)_2$ were obtained by electrochemical oxidation methods. To investigate the electronic states of these compounds, the optical conducting spectra were measured. The electronic states of the Ni compounds can be controlled by forming the mixed-metal or mixed-halogen systems.

VII-A-8 Magnetic/Conducting Hybrid Compound Composed of 1-D Chain $[Mn^{II}_2Cl_5(EtOH)]_\infty^-$ and BEDT-TTF Stacking Layer

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[*J. Solid State Chem.* **168**, 418–426 (2002)]

An assembled compound $(BEDT\text{-}TTF)_2[Mn_2Cl_5(EtOH)]$ (1) consisting of two structural lattices of Mn(II)-Cl 1-dimensional (1-D) chains and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) stacking layers was synthesized by electrochemical method. Compound 1 crystallized in triclinic space group with a = 13.1628(5), b = 20.3985(9), c = 7.4966(3) Å, α = 98.3498(8), β =104.980(1), γ = 74.602(2)°, and Z = 2. The 1-dimensional chains and the stacking layers are aligned along the c-axis of the unit cell. The 1-dimensional chain is described as $[Mn_2Cl_5(EtOH)]_\infty^-$ in which two Mn(II) ions and four Cl^- ions form a ladder-like chain with Kagome (cuboidal) sublattices, and the remaining Cl^- ion and an EtOH molecule cap the edge-positioned Mn(II) ions of the chains. The BEDT-TTF molecules are packed between the Mn-Cl chains (ac-plane), the intermolecules S···S contacts of which are approximately found in the range 3.440(2)–3.599(2) Å. The packing feature of BEDT-TTF molecule is very similar to that of $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$ (TCE = 1,1,2-trichloroethane). Regarding the electronic state of each BEDT-TTF molecule, Raman spectroscopic analysis and ESR study revealed half-valence BEDT-TTF molecules (charge delocalization) in 1. Magnetic measurements clearly demonstrated that the paramagnetic spins on the 1-dimensional chain $[Mn_2Cl_5(EtOH)]_\infty^-$ arrange antiferromagnetically in the low-temperature region. Additionally, 1 exhibits metallic conduction in the temperature range 2.0–300 K (σ = 21 S cm^{-1} at 300 K and 1719 S cm^{-1} at 2.0 K), due to the contribution of the stacked BEDT-TTFs. Consequently, these peculiarities that correspond to antiferromagnetic/metallic conduction demonstrate the bifunctionality of 1.

VII-A-9 Structure and Electrochemistry of the Bridging-Ligand Mono-Substituted Diruthenium Compound, $[Ru_2(II,III)(O_2CCH_3)_3(admpym)(Cl)(MeOH)]$ (Hadmpym = 2-amino-4,6-dimethylpyrimidine)

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[*Inorg. Chim. Acta* **332**, 210–215 (2002)]

The ligand substitution reaction of $Ru_2(O_2CCH_3)_4Cl$ with 2-amino-4,6-dimethylpyrimidine (Hadmpym) under gentle refluxing conditions in MeOH gave a bridging-ligand mono-substituted compound, $[Ru_2(O_2CCH_3)_3(admpym)(Cl)(MeOH)]$ (**1**). **1** Crystallized in monoclinic space group $P2_1/n$ with a = 8.3074(8), b = 12.3722(8) Å, c = 18.913(1) Å, β =95.559(3)°, V = 1934.8(3) Å^3, and Z = 4. Temperature dependence of the magnetic susceptibility of 1 revealed it to be in a spin ground state S = 3/2 arising from the electronic configuration of $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$. Compound 1 undergoes three metal-centered redox reactions in electrochem.: $E_{1/2}$ (ox) = +0.72 V (Ia/Ic < 1, ΔEp = 0.17 V); $E_{1/2}$ (1,red) = –0.65 V (Ia/Ic ≈ 1, ΔEp = 0.10 V); and $E_{1/2}$ (2,red) = –1.80 V (Ia/Ic.mchlt.1, ΔEp = 0.16 V). Then, the redox species produced by electrolysis were characterized by spectroscopic studies.

VII-A-10 Electrical Conduction of Halogen-Bridged Metal Complexes $Ni_{1-x}Pd_x(chxn)_2Br_3$

ITO, Hiroshi[1]; SUNATA, Makoto[1]; KURODA, Shin-ichi[1]; MANABE, Toshio[2]; YAMASHITA, Masahiro[3]
([1]Nagoya Univ.; [2]Tokyo Metropolitan Univ.; [3]IMS and Tokyo Metropolitan Univ.)

[*Mol. Cryst. Liq. Cryst.* **379**, 285–290 (2002)]

The resistance and thermopower of the quasi-one-dimensional halogen-bridged metal complexes $Ni_{1-x}Pd_x(chxn)_2Br_3$ were studied. Pressure dependence of the resistance indicates the crossover from SDW state to CDW state at x = 0.84–0.95. For almost all x region, thermopower is negative. For x < 0.5, thermopower is independent of temperature, while it is semiconducting for x > 0.6.

VII-A-11 Reactions of Mn(III) Quadridentate Schiff Base Compounds with TCNQ Anion to Form Unusual TCNQ Derivatives by Alcoholysis

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[*Mol. Cryst. Liq. Cryst.* **379**, 197–204 (2002)]

The reactions of Mn(III) quadridentate Schiff base compounds, [Mn(saltmen)(H_2O)]ClO_4 (1; saltmen^{2-} = N,N'-(1,1,2,2-tetramethylethylene)bis(salicylideneiminato)) and [Mn(naphtmen)(H_2O)]ClO_4 (2; naphtmen^{2-} = N,N'-(1,1,2,2-tetramethylethylene)bis-(naphthylideneiminato)), with LiTCNQ gave three types of compounds depending on reaction conditions: [Mn(saltmen)(H_2O)](TCNQ) (3), [Mn(saltmen)-(MeOH)(TCNQ-OMe)] (4, TCNQ-OMe$^-$ = p-(α,α-dicyano-α-methoxytolyl)dicyanomethanide), and [Mn(naphtmen)(MeOH)(TCNQA-OMe)] (5, TCNQA-OMe$^-$ = p-(α-cyano-α-methoxy-a-methylamidotolyl)$^-$ dicyanomethanide). Compounds 3·MeOH and 5 were characterized by x-ray crystallography. Compounds 3 and 4 were prepared under anaerobic and aerobic conditions, respectively, in MeOH/H_2O. Compound 5 was synthesized under aerobic conditions analogous to 4. For 4 and 5, unusual additional reactions on the anionic TCNQ molecule occurred to form (TCNQ-OMe)$^-$ for 4 and (TCNQA-OMe)$^-$ for 5. Ferromagnetic and antiferromagnetic interactions in the prepared compounds were investigated.

VII-A-12 Out-of-Plane Dimer Structures and Magnetic Properties of Mn(III) Quadridentate Schiff Base Compounds with N,N'-(1,1,2,2-tetramethylethylene)bis(5-chlorosalicylideneiminato)

MIYASAKA, Hitoshi[1]; MIZUSHIMA, Kaori[1]; FURUKAWA, Sachie[1]; SUGIURA, Ken-ichi[1]; ISHII, Tomohiko[1]; YAMASHITA, Masahiro[2]
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[*Mol. Cryst. Liq. Cryst.* **379**, 171–178 (2002)]

Three Mn(III) quadridentate Schiff base compounds with N,N'-(1,1,2,2-tetramethylethylene)bis(5-chlorosalicylideneiminato) (5-Clsaltmen^{2-}) were prepared and characterized: [Mn_2(5-Clsaltmen)$_2$(H_2O)$_2$](ClO_4)$_2$ (1), [Mn_2(5-Clsaltmen)$_2$(5-Clsal)$_2$] (2, 5-Clsal = phenol-bonded 5-chlorosalicylaldehyde), and [NEt_4]$_2$[Mn_2(5-Clsaltmen)$_2$(MeOH)$_2$][Fe(CN)$_6$]ClO_4·2MeOH (3). All compounds contain Mn(III) out-of-plane dimer units. The magnetic measurements revealed intra-dimer ferromagnetic exchange interaction between Mn(III) ions via phenolate O, producing a $S = 4$ spin ground state. The structures of 2 and 3 were determined by x-ray crystallography.

VII-A-13 Synthesis, Structure and Magnetic Properties of the Antiferromagnetic Hexamanganese Cluster [Mn_6(μ_4-O)$_2$($O_2CC_6HF_4$)$_{10}$(HO_2CCH_3)$_4$]·(C_7H_8)

NAKATA, Kazuya[1]; MIYASAKA, Hitoshi[1]; ISHII, Tomohiko[1]; YAMASHITA, Masahiro[2]; AWAGA, Kunio[3]
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[*Mol. Cryst. Liq. Cryst.* **379**, 211–216 (2002)]

A hexanuclear Mn^{II}-Mn^{III}-cluster, [Mn_6(O)$_2$-($O_2CC_6HF_4$)$_{10}$(HO_2CCH_3)$_4$]·(C_7H_8) (1), was synthesized by a typical acetate-substitution reaction of the known Mn_{12}-cluster, [Mn_{12}(O)$_{12}$(O_2CCH_3)$_{16}$(H_2O)$_4$]·2CH_3CO_2H·4H_2O in the presence of an excess of 2,3,5,6-tetrafluorobenzoic acid. Each unpaired spin on Mn(II) and Mn(III) ions is promoted as to be antiferromagnetically cancelled to produce an $S = 0$ ground state.

VII-A-14 Evidence for Single-Chain Magnet Behavior in a Mn^{III}-Ni^{II} Chain Designed with High Spin Magnetic Units: A Route to High Temperature Metastable Magnets

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([1]Cent. Recherche Paul Pascal; [2]Tokyo Metropolitan Univ.; [3]IMS and Tokyo Metropolitan Univ.)

[*J. Am. Chem. Soc.* **124**, 12837–12844 (2002)]

The authors herein present the synthesis, crystal structure, and magnetic properties of a new heterometallic chain of Mn^{III} and Ni^{II} ions, [Mn_2-(saltmen)$_2$Ni(pao)$_2$(py)$_2$](ClO_4)$_2$ (1) (saltmen^{2-} = N,N'-(1,1,2,2-tetramethylethylene)bis(salicylideneiminate) and pao$^-$ = pyridine-2-aldoximate). The crystal structure of 1 was studied by x-ray crystallography analysis: compound 1 crystallized in monoclinic, space group $C2/c$ with $a = 21.140(3)$, $b = 15.975(1)$, $c = 18.6212(4)$ Å, $\beta = 98.0586(4)°$, and $Z = 4$. This compound consists of two fragments, the out-of-plane dimer [Mn_2-(saltmen)$_2$]$^{2+}$ as a coordination acceptor building block and the neutral mononuclear unit [Ni(pao)$_2$(py)$_2$] as a coordination donor building block, forming an alternating chain having the repeating unit [–Mn–(O)$_2$–Mn–ON–Ni–NO–]$_n$. In the crystal structure, each chain is well separated with a minimum intermetallic distance between Mn and Ni ions of 10.39 Å and with the absence of interchain π overlaps between organic ligands. These features ensure a good magnetic isolation of the chains. The *d.c.* and *a.c.* magnetic measurements were performed on both the polycrystalline sample and the aligned single crystals of 1. Above 30 K, the magnetic susceptibility of this 1-dimensional compound was successfully described in a mean field approximation as an assembly of trimers (Mn···Ni···Mn) with a Ni^{II}···Mn^{III} antiferromagnetic interaction ($J = -21$ K) connected through a ferromagnetic Mn^{III}···Mn^{III} interaction (J'). However, the mean field theory fails to describe the magnetic behavior < 30 K emphasizing the

1-dimensional magnetic character of the title compound. Between 5 and 15 K, the susceptibility in the chain direction was fitted to a 1-dimensional Ising model leading to the same value of *J'*. Hysteresis loops are observed < 3.5 K, indicating a magnet-type behavior. In the same range of temperature, combined *a.c.* and *d.c.* measurements show a slow relaxation of the magnetization. This result indicates a metastable state without magnetic long-range order. This material is the 1st experimental design of a heterometallic chain with S_T = 3 magnetic units showing a single-chain magnet behavior predicted in 1963 by R. J. Glauber for an Ising 1-dimensional system. This work opens new perspectives for 1-dimensional systems to obtain high temperature metastable magnets by combining high spin magnetic units, strong inter-unit interactions, and uniaxial anisotropy.

VII-A-15 Tuning of Spin Density Wave Strengths in Quasi-One-Dimensional Mixed-Halogen-Bridged Ni(III) Complexes with Strong-Electron Correlation, $[\mathrm{Ni^{III}(chxn)_2Cl_{1-\mathit{x}}Br_{\mathit{x}}](NO_3)_2}$

MANABE, Toshio[1]; YOKOYAMA, Kohei[1]; FURUKAWA, Sachie[1]; KACHI-TERAJIMA, Chihiro[1]; NAKATA, Kazuya[1]; IWAHORI, Fumiyasu[1]; MIYASAKA, Hitoshi[1]; SUGIURA, Ken-ichi[1]; YAMASHITA, Masahiro[2]; KISHIDA, Hideo[3]; OKAMOTO, Hiroshi[3]
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[*Inorg. Chem.* **41**, 4993–4995 (2002)]

This communication describes the syntheses of the quasi-one-dimensional mixed-halogen-bridged $\mathrm{Ni^{III}}$ complexes with strong electron correlation $[\mathrm{Ni(chxn)_2Cl_{1-\mathit{x}}Br_{\mathit{x}}](NO_3)_2}$ and the tuning of the spin density wave strengths of these compounds. If the Cl 3*p* and Br 4*p* make one band in the compounds, we should observe a single peak in the electronic spectra. As a result, we should observe the single peak from 1.45 to 2.00 eV depending on the mixing ratios of Cl and Br ions. Therefore, the Cl 3*p* and Br 4*p* make one band. Then, we have succeeded in tuning the spin density wave strengths of the $\mathrm{Ni^{III}}$ complexes with the strong electron correlation by mixing the bridging halogen ions successively.

VII-A-16 Syntheses and Physical Properties of New Charge-Transfer Salts Consisting of a Conducting BEDT-TTF Column and Magnetic 1D or 2D Fe(III) Networks

KANEHAMA, Ryo[1]; YOSHINO, Yuko[1]; ISHII, Tomohiko[1]; MANABE, Toshio[1]; HARA, Hatsune[1]; MIYASAKA, Hitoshi[1]; MATSUZAKA, Hiroyuki[1]; YAMASHITA, Masahiro[2]; KATADA, Motomi[1]; NISHIKAWA, Hiroyuki[1]; IKEMOTO, Isao[1]
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[*Synth. Met.* **133-134**, 553–554 (2003)]

Two new molecular-based charge-transfer salts of bis(ethylenedithio)tetrathiafulvalene were prepared, that is $\mathrm{(BEDT\text{-}TTF)_3Fe(CN)_6 \cdot 4H_2O}$ and $\mathrm{(BEDT\text{-}TTF)_4Fe(C_2O_4)_3K \cdot PhCl}$. Their crystal structures and physical properties were studied. Their structures consist of conducting columns of BEDT-TTF and magnetic 1-dimensional or 2-dimensional networks containing Fe(III) ions connected by cyano- or oxalate-bridges. The *d*-π interactions are discussed.

VII-A-17 Novel Optical and Magnetic Bistability and Photoinduced Transition in a One-Dimensional Halogen-Bridged Binuclear Pt Complex

MATSUZAKI, Hiroyuki[1]; MATSUOKA, Takashi[1]; KISHIDA, Hideo[1]; TAKIZAWA, Kouichi[2]; MIYASAKA, Hitoshi[2]; SUGIURA, Ken-ichi[2]; YAMASHITA, Masahiro[3]; OKAMOTO, Hiroshi[1]
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[*Phys. Rev. Lett.* **90**, 046401 (4 pages) (2003)]

In I-bridged binuclear Pt compounds, $\mathrm{R_4[Pt_2(pop)_4I]}n\mathrm{H_2O}$ and $\mathrm{R'_2[Pt_2(pop)_4I]}n\mathrm{H_2O}$ (pop = $\mathrm{P_2O_5H_2{}^{2-}}$), electronic structures on the PtPtI chains were controlled between a diamagnetic charge-density-wave (CDW) state and a paramagnetic charge-polarization (CP) state by modification of the counterions (R, R') located between chains. In the R = $\mathrm{Et_2NH_2{}^+}$ compound, a pressure-induced CP to CDW transition with a drastic color change is identified. This transition is accompanied by a large hysteresis loop within which photoinduced transition between CDW and CP can be driven by selecting the excitation photon energy.

VII-A-18 Unprecedented Soliton Formation Mechanism in Quasi-One-Dimensional Chloro-Bridged $\mathrm{Pt^{II}\text{-}Pt^{IV}}$ Mixed-Valence Compound, $\mathrm{\{[Pt(en)_2][PtCl_2(en)_2]\}_3(CuCl_4)_4 \cdot 12H_2O}$

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[*Chem. Lett.* **32**, 278–279 (2003)]

A new type of complex consisting of double liner-chain structure $\mathrm{\{[Pt(en)_2][PtCl_2(en)_2]\}_3(CuCl_4)_4 \cdot 12H_2O}$ was synthesized. High concentration (*ca.* 200 times larger than the literature) of neutral soliton ($\mathrm{Pt^{III}}$ component) formation was found. This unprecedented soliton formation mechanism will be discussed.

VII-A-19 A Series of Ni(II) Pyridyloximato (pao$^-$) Compounds [Ni(pao)$_2$(L)$_2$] (L = Unidentate Ligand): As a Coordination Donor Building Block in the Assembly with Mn(III) Salen Analogues

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[*Synth. Met.* **137**, 1245–1246 (2003)]

A series of mononuclear Ni(II) compounds [Ni(pao)$_2$(L)$_2$] (pao$^-$ = 2-pyridyloximate, L = pyridine (1), 4-picoline (2), 4-ethylpyridine (3), 4-tert-butylpyridine (4), and N-methylimidazole (5)) were synthesized and characterized. The structures of 1–3 were determined by X-ray crystallography and revealed that all compounds have the same structural motif with trans coordination fashion for the identical ligands. For magnetic data, the best-fitting to an S = 1 ground state with the zero-field splitting effect found to have the zero-field splitting parameter |D| of 3 as approximate 4 K in this series. These compounds are good coordination donor building blocks for assembly with Mn(III) salen analogs as coordination acceptor building blocks to form 1-D magnetic chains.

VII-A-20 Pressure Effects on an S = 1 Haldane Compound Ni(C$_5$H$_{14}$N$_2$)$_2$N$_3$(PF$_6$)

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[*J. Phys. Soc. Jpn.* **72**, 399–404 (2003)]

The pressure effects on an S = 1 Haldane compound Ni(C$_5$H$_{14}$N$_2$)$_2$N$_3$(PF$_6$) (NDMAP) were studied through the magnetic susceptibility (χ) measurements using single crystal samples and the powder x-ray structural analysis experiment under pressure up to 11.5 kbar. The crystal-axis dependence of χ was analyzed with the results of quantum Monte Carlo simulation. Probably both the intrachain interaction (J) and single-ion anisotropy (D) are enhanced by pressure: J = 31.5 K (P = 0 kbar) → 90.0 K (10.0 kbar) and D/J = 0.3 (P = 0 kbar) → 0.4 (9.5 kbar). As for J, there is the linear increase against pressure as dJ/dP = 2.0 K/kbar in the pressure region below P = 8.0 kbar, at around which dJ/dP rapidly changes to dJ/dP = 2.1 × 101 K/kbar. The ratio of D/J changes within 0.3–0.4, and probably D as well as J drastically change at around P = 8.0 kbar. Also, at P = 9.5 kbar, the development of paramagnetic moment on the easy plane is detected, and it is assumed that the interchain interaction may be also enhanced under pressure. The structural analysis shows that the interchain shrinkage is larger than the intrachain one. However, a result concerning the rapid changes of J and D at around P = 8.0 kbar was not observed, and the authors suppose that the changes of bond-angles such as –N–Ni–N– and –N–N–N– as well as interatomic shrinkage probably change under pressure. The authors assume that those bond-angles of NDMAP at around P = 9.0 kbar (J .simeq. 70 K) may become close to those of Ni(C$_5$H$_{14}$N$_2$)$_2$N$_3$(ClO$_4$) (NDMAZ), where the value of J is 71.0 K.

VII-A-21 Platinum(II) Complex with S = 1/2 Organic Radical Ligand

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[*Synth. Met.* **135-136**, 355–356 (2003)]

A platinum(II) complex with organic radical ligand p-NNpy (= 2-(4'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) is synthesized. X-ray crystallographic analysis revealed that it has a square-planer four-coordinate anionic structure with formula of [Pt(p-NNpy)Cl$_3$]$^-$. Paramagnetic behavior which corresponds to S = 1/2 was observed with weak intermolecular antiferromagnetic interaction in the temperature range of 2–300 K. The structure, magnetic property and spectroscopic data will be reported.

VII-A-22 Tuning of Spin Density Wave Strength of Ni(III) Complexes with Strong Electron-Correlation

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[*Synth. Met.* **135-136**, 257–258 (2003)]

We have succeeded in synthesizing the Ni^{III} complexes doped by Co^{III} ions, [Ni$_{1-x}$Co$_x$(chxn)$_2$Br]Br$_2$ (x = 0, 0.044, 0.098, 0.118) by using an electrochemical oxidation method. The reflectance spectrum of [Ni$_{1-x}$Co$_x$(chxn)$_2$Br]Br$_2$ shows intense charge transfer bands about 0.5 eV, which are lower than that of [Ni(chxn)$_2$Br]Br$_2$. (1.3 eV).

VII-A-23 New Charge-Transfer Salts (ET)$_8$(Mn^{II}Br$_4$)$_2$(DCE)$_2$ and (ET)$_3$Mn^{II}Br$_4$: Preparations, Structures and Physical Properties (ET = BEDT-TTF, DCE = 1,2-Dichloroethane)

KANEHAMA, Ryo[1]; MIYASAKA, Hitoshi[1];

SUGIURA, Ken-ichi[1]; YAMASHITA, Masahiro[2]; ITOH, Hiroshi[3]; KURODA, Shin-ichi[3]; KISHIDA, Hideo[4]; OKAMOTO, Hiroshi[4]
([1]Tokyo Metropolitan Univ.; [2]IMS and Tokyo Metropolitan Univ.; [3]Nagoya Univ.; [4]Univ. Tokyo)

[*Synth. Met.* **135-136**, 633–634 (2003)]

New charge-transfer salts $(ET)_8(MnBr_4)_2(DCE)_2$ **1** and $(ET)_3MnBr_4$ **2** have been synthesized electrochemically and characterized. In both compounds, the magnetic $MnBr_4^{2-}$ anions exist between the conducting ET-layers. The shortest intermolecular $Mn\cdots Mn$ distances are 7.28 and 10.12 Å, respectively, which are too far to magnetically interact directly. But magnetic susceptibility measurements demonstrated that the antiferromagnetic interactions was observed at low temperature. This aniferromagnetic interactions between Mn ions may be operative *via* the π-electrons of conducting layers, that are so-called *d*-π interactions. The crystal structures and physical properties of these compounds are reported.

VII-A-24 Gigantic Third-Order Optical Nonlinearity in One-Dimensional Mott Insulators

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[*Synth. Met.* **135-136**, 315–316 (2003)]

Third-order optical nonlinearity has been studied in one-dimensional Mott- insulators, Sr_2CuO_3, Ca_2CuO_3, and halogen-bridged Ni compounds $[Ni(chxn)_2X]Y_2$ (X = Br, Cl; Y = Br, Cl, NO_3), by electroreflectance (ER) spectroscopy. In $\chi(3)(-\omega;0,0,\omega)$ (ER) is evaluated to be $\chi(3) \approx 10^{-8}$ to 10^{-5} esu, which is significantly larger than those of conjugated polymers, $10^{-10} \approx 10^{-8}$ esu. An analysis of the ER spectral shape reveals that the strong enhancement of nonlinear optical response originates from the large transition dipole moments between nearly degenerate odd and even states.

VII-A-25 Structure and Magnetic Properties of the Two-Dimensional Ferrimagnet $(NEt_4)[\{Mn(salen)\}_2Fe(CN)_6]$: Investigation of Magnetic Anisotropy on a Single Crystal

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[*Inorg. Chem.* **42**, 3509–3515 (2003)]

The title compound, $(NEt_4)[\{Mn(salen)\}_2Fe(CN)_6]$ (1), was synthesized *via* a 1:1 reaction of $[Mn(salen)(H_2O)]ClO_4$ with $(NEt_4)_3[Fe(CN)_6]$ in a MeOH/EtOH medium ($NEt_4^+ = Et_4N^+$ cation, $salen^{2-}$ = N,N'-ethylenebis(salicylidene)iminate). The two-dimensional layered structure of 1 was revealed by x-ray crystallographic analysis: 1 crystallizes in monoclinic space group $P2_1/c$ with a = 12.3660(8), b = 15.311(1), c = 12.918(1) Å, β = 110.971(4)°, Z = 2 and is isostructural to the previously synthesized compound, $(NEt_4)[\{Mn(5\text{-}Clsalen)\}_2Fe(CN)_6]$ (5-$Clsalen^{2-}$ = N,N'-ethylenebis(5-chlorosalicylidene)iminate). The Mn ion is surrounded by an equatorial salen quadridentate ligand and two axial N atoms from the $[Fe(CN)_6]^{3-}$ unit, the four Fe-CN groups of which coordinate to the Mn ions of $[Mn(salen)]^+$ units, forming a two-dimensional network having $[-Mn-NC-Fe-CN-]_4$ cyclic repeating units. The network is spread over the *bc*-plane of the unit cell, and the layers are stacked along the *a*-axis. The countercation NEt_4^+ is located between the layers. Compound 1 is a ferrimagnet with T_c = 7.7 K and exhibits hysteresis with a remnant magnetization of 13.44 $cm^3\ mol^{-1}$ at zero field and a coercivity of 1000 Oe when the powder sample was measured at 1.9 K. Magnetic measurements of a direction-arranged single crystal were also carried out. The orientation of the crystallographic axes of a selected single crystal was determined by x-ray analysis, and magnetization was measured when an external field was applied in the *a**, *b*, and *c* directions. The magnetization in the *a** direction increased more easily than those in the *b* and *c* directions below the critical temperature. No hysteresis was observed only for the measurement in the *a** direction, indicating the presence of strong structural anisotropy with potential anisotropy on Mn(III) ions.

VII-A-26 LESR Studies of Long-Lived Photogenerated Spins in the MX-Chain Complex, $Pd(chxn)_2Br_3$

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[*Synth. Met.* **135-136**, 317–318 (2003)]

Light-induced ESR (LESR) measurements have been applied on the halogen-bridged metal complex (MX-chain), $Pd(chxn)_2Br_3$, to study the dynamics of the photogenerated spin such as neutral soliton and polaron. The time evolution of the LESR intensity is interpleted in terms of the pair-creation and recombination model of photo-generated spins which are separated by the finite potential barriers on the chain. The LESR intensity showed the same excitation power dependence with the one in the Pt-Cl compound.

VII-A-27 Heterometallic Hexanuclear Cluster with an $S = 8$ Spin Ground State: $Mn^{II}\{Mn^{II}(hfac)_2\}_3\{Ni^{II}(pao)_3\}_2$ ($hfac^-$ = Hexafluoroacetylacetonate, pao^- = Pyridine-2-aldoximate)

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[*Inorg. Chem.* **42**, 4501–4503 (2003)]

The heterometallic $Mn^{II}_4Ni^{II}_2$ title compound has been synthesized and characterized by X-ray crystallography. The compound consists of a Ni–Mn–Ni linear moiety, $[\{Ni\text{-}(\mu\text{-}NO)_3\}_2\text{-}Mn]$, linked by oximate bridges and three Mn(II) hfac terminal units attached by oximate oxygens in a di-μ-oxo fashion, forming a novel heterometallic cluster: $Mn\{Mn(hfac)_2\}_3\{Ni(pao)_3\}_2$ (1). Magnetic measurements reveal the antiferromagnetic nature of the oximate pathway between Mn(II) and Ni(II) metal ions, which imposes an unusual high-spin ground state (S = 8) for 1.