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PART I ANNUAL REPORTS

1. Abstracts of Papers Published in Journals

MATHEMATICS

Structure of the Orthogonal Group $O_n(V)$ over L -Rings

H. Ishibashi

Linear Algebra Appl., **390**, 357–368 (2004)

Our purpose is to characterize the orthogonal group $O_n(V)$ on a quadratic module V of rank n with an orthogonal basis over a commutative ring R satisfying some condition which holds for the ring of rational integers \mathbf{Z} .

It will be shown that $O_n(V)$ is factorized into a semidirect product of a normal subgroup D and a subgroup S , where $D = \{\text{diagonal}(\epsilon_1, \epsilon_2, \dots, \epsilon_n) \mid \epsilon_i = \pm 1\}$ and S = a direct product of a finite number of symmetric groups. Also we determine the order of $O_n(V)$.

Further we show that any element in $O_n(V)$ is a product of three elements of order 2. Moreover, we prove that $O_n(V)$ is generated by two elements of order 2 and $2n$, respectively, also generated by three elements of order 2.

CHEMISTRY

Hyperfine Interactions in La@C_{82} Studied by W-Band Electron Paramagnetic Resonance and Electron Nuclear Double Resonance

Norbert Weiden^{*1}, Tatsuhisa Kato^{*2}, and Klaus-Peter Dinse^{*1} (*1 Chemistry Department, Darmstadt University of Technology, Petersenstrasse 20, D-64287 Darmstadt, Germany
*2 Institute for Molecular Science, Okazaki 444-8585, Japan)

J. Phys. Chem. B., **108**, 9469–9474 (2004)

The analysis of dipolar and quadrupolar lanthanum hyperfine data measured with electron spin resonance (ESR) and electron nuclear double resonance reveals that at low temperatures no significant change occurs at the internal binding site of the endohedral complex. We interpret this result as indicative of freezing of the large-scale motion of the encased ion, which is observed at room temperature. Averaging of hyperfine interactions is fast on the time scale of the ESR experiment, preventing drastic changes of dipolar and quadrupolar hyperfine interaction (hfi), providing that the equilibrium position is unchanged. The detection of hfi in disordered samples was possible by invoking orientation selection in the 94-GHz ESR spectrum. Quadrupolar hfi could be directly measured for the first time in a metallo-endohedral fullerene complex.

Chemical Reactivity and Redox Property of Sc₃@C₈₂

T. Wakahara^{*1}, A. Sakuraba^{*2}, Y. Iiduka^{*1}, M. Okamura^{*2}, T. Tsuchiya^{*1}, Y. Maeda^{*1}, T. Akasaka^{*1}, S. Okubo^{*3}, T. Kato^{*3}, K. Kobayashi^{*3}, S. Nagase^{*3}, and K. M. Kadish^{*4} (*1 Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan, *2 Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan, *3 Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, *4 Department of Chemistry, University of Houston, Houston, TX 77204-5003, USA)
Chem. Phys. Lett., **398**, 553-556 (2004)

The redox property of Sc₃@C₈₂ is investigated by using disilirane as a chemical probe. The redox potentials of Sc₃@C₈₂ in *o*-dichlorobenzene show a high reactivity attributable to its high electron-accepting and -donating ability. No EPR signal is observed at room temperature for Sc₃@C₈₂ in the presence of pyridine, indicating formation of the diamagnetic Sc₃@C₈₂ anion. The diamagnetic Sc₃@C₈₂ anion is also prepared electrochemically in 1, 2-dichlorobenzene.

Characterization of Ce@C₈₂ and Its Anion

T. Wakahara^{*1}, J. Kobayashi^{*2}, M. Yamada^{*1}, Y. Maeda^{*1}, T. Tsuchiya^{*1}, M. Okamura^{*2}, T. Akasaka^{*1}, M. Waelchli^{*3}, K. Kobayashi^{*4}, S. Nagase^{*4}, T. Kato^{*4}, M. Kako^{*5}, K. Yamamoto^{*6}, R and K. M. Kadish^{*7} (*1 Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan, *2 Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan, *3 Bruker Japan, Tsukuba, Ibaraki 305-0051, Japan, *4 Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, *5 The University of Electro-Communications, Chofu, Tokyo, 182-8585, Japan, *6 Japan Nuclear Fuel Cycle Development Institute, Tokai, Ibaraki 319-1100, Japan, *7 Department of Chemistry, University of Houston, Houston, Texas 77204-5003)
J. Am. Chem. Soc., **126**, 4883-4887 (2004)

Ce@C₈₂ is isolated by high-performance liquid chromatography (HPLC) and the cage symmetry is determined as C_{2v} by measuring the ¹³C NMR spectra of its anion. The ¹³C NMR peaks of [Ce@C₈₂]⁻ show temperature-dependent shifts ascribed to the *f* electron remaining on the Ce atom. Both Ce@C₈₂ and [Ce@C₈₂]⁻ are silent in electron paramagnetic resonance spectroscopy (EPR) because of the highly anisotropic *g* matrix as well as of the fast relaxation process originating from the orbital angular momentum of the *f* electron. This is the complementary relationship to the observation of the paramagnetic shift in ¹³C NMR. [Ce@C₈₂]⁻ has lower stability in air than [La@C₈₂]⁻.

Biscopper Complexes of meso-Aryl Substituted Hexaphyrin. Gable Structures and Varying Antiferromagnetic Coupling

Soji Shimizu^{*1}, Venkataramanarao G. Anand^{*1}, Ryuichiro Taniguchi^{*1}, Ko Furukawa^{*2}, Tatsuhisa Kato^{*2,3}, Toshihiko Yokoyama^{*2}, and Atsuhiko Osuka^{*1} (*1 Department of Chemistry, Graduate School of Science, Kyoto University, and Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, Sakyo-ku, Kyoto 606-8502, Japan, *2 Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, *3 Department of Chemistry, Josai University, Keyakidai, Sakado 350-0295, Japan) *J. Am. Chem. Soc.*, **126**, 12280-12281 (2004)

The hexaphyrins **1** and **2** can serve as an effective ligand for two copper ions with unexpected but rather common large structural changes to provide the gable biscopper complexes **3-6** that exhibit varying antiferromagnetic couplings. These are new modes of metalation of *meso*-aryl-expanded porphyrins. Relatively similar structures of **3-6** are remarkable, considering a large difference between **1** and **2** in respects of aromaticity, stable conformation, electronic demands, and the number of NH available for the metalation. Metalation of *meso*-aryl-substituted hexaphyrins and other expanded porphyrins is an attractive subject and worthy of further investigation.

A Multi-Frequency EPR Study of Metallofullerenes: Eu@C₈₂ and Eu@C₇₄

Hideto Matsuoka^{*1}, Norio Ozawa^{*2}, Takeshi Kodama^{*2}, Hiroyuki Nishikawa^{*2}, Isao Ikemoto^{*2}, Koichi Kikuchi^{*2}, Ko Furukawa^{*1}, Kazunobu Sato^{*3}, Daisuke Shiomi^{*3}, Takeji Takui^{*3}, and Tatsuhisa Kato^{*1,4} (*1 Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, *2 Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan, *3 Departments of Chemistry and Materials Science, Graduate School of Science, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585, Japan, *4 Department of Chemistry, Josai University, Keyakidai 1-1, Sakado, Saitama 350-0295, Japan) *J. Phys. Chem. B.*, **108**, 13972-13976 (2004)

In this work, the cage structure of a family of europium metallofullerenes, Eu@C₇₄ and three isomers of Eu@C₈₂, were investigated. The analogy of the electronic states of three isomers of Eu@C₈₂ with those of three isomers of Ca@C₈₂ was confirmed by UV-vis-near-IR absorption spectra. The symmetries C_s, C₂, and C_{2v} were assigned for three isomers of Eu@C₈₂ by comparing each corresponding isomer of Ca@C₈₂. The D_{3h} cage structure of Eu@C₇₄, which is expected only for the C₇₄ from the isolated pentagon rule, was also confirmed by comparing its photoabsorption spectrum with that of Ca@C₇₄. Multifrequency electron spin resonance (ESR) spectroscopy was employed to determine the zero-field splitting (ZFS) parameters of the metallofullerenes, which are closely related to the surrounding cage structures. The experimental X- and W-band ESR spectra were completely

reproduced by computer simulations based on a spin Hamiltonian considering the ZFS terms up to fourth order. The introduction of the fourth-order ZFS terms into the Hamiltonian resulted in a precise determination of the second-order ZFS terms. A nonvanishing rhombicity parameter E of $\text{Eu}@C_{74}$ demonstrated the reduction of the symmetry from D_{3h} to C_{2v} due to the positioning of Eu^{2+} ion at the off-center of C_{74} cage. Moreover, in this work, the semiphenomenological superposition-exchange model (SPEM) was invoked to examine a relationship between the molecular structures and ZFS parameters. All of the experimental ZFS parameters were satisfactorily reproduced in terms of the SPEM, leading to confirmation of the molecular symmetries. The semiphenomenological analysis also enabled us to select the most appropriate cage for $\text{Eu}@C_{82}$ with C_2 symmetry from among three possible isomers.

Isolation and Characterization of a Carbene Derivative of $\text{La}@C_{82}$

Y. Maeda^{*1}, Y. Matsunaga^{*2}, T. Wakahara^{*2}, S. Takahashi^{*3}, T. Tsuchiya^{*2}, M. O. Ishitsuka^{*2}, T. Hasegawa^{*1}, T. Akasaka^{*2}, M. T. H. Liu^{*4}, K. Kokura^{*5}, E. Horn^{*5}, K. Yoza^{*6}, T. kato^{*7}, S. Okubo^{*7}, K. Kobayashi^{*7}, S. Nagase^{*7}, and K. Yamamoto^{*8} (*1 Department of Chemistry, Tokyo Gakugei University, Tokyo 184-8501, Japan, *2 Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Ibaraki 305-8577, Japan, *3 Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan, *4 Department of Chemistry, University of Prince Edward Island, Prince Edward Island C1A4P3, Canada, *5 Department of Chemistry, Rikkyo University, Tokyo 171-8501, Japan, *6 Bruker AXS K. K., Yokohama, Kanagawa 221-0022, Japan, *7 Institute for Molecular Science, Okazaki 444-8585, Japan, *8 Japan Nuclear Fuel Cycle Development Institute, Tokai, Ibaraki 319-1100, Japan)

J. Am. Chem. Soc., **126**, 6858-6859 (2004)

Endohedral metallofullerenes encapsulate one or more metal atoms inside a hollow fullerene cage. The fullerene has attracted special attention because it engenders new spherical molecules with unique electronic properties and structures that are unexpected for empty fullerenes. The recent successful isolation and purification of endohedral metallofullerenes have encouraged the investigation of their physical and chemical properties. It would be of interest to understand how the chemical reactivity and selectivity of empty fullerenes change upon endohedral metal doping and how the electronic properties of endohedral metallofullerenes change upon reduction, oxidation, and chemical functionalization. Our earlier report indicated that the high reactivity of endohedral metallofullerenes may be ascribed to their electronic properties. The ESR spectra measured during the reaction reveal the formation of several regioisomers with different La isotopic splittings. In contrast, the regiospecific addition reaction of $\text{La}@C_{82}$ with 2-adamantane-2, 3-[3H]-diazirine (**1**) affords the first single isomer which has been successfully isolated. We now present the first instance of an isolation and crystallographic characterization of a paramagnetic endohedral monometallofullerene derivative from the

selective La@C₈₂ reaction.

A Bindschedler's Green-Based Arylamine: Its Polycations with High-Spin Multiplicity

Akihiro Ito^{*1}, Haruhiro Ino^{*1}, Yuki Matsui^{*1}, Yasukazu Hirao^{*1}, Kazuyoshi Tanaka^{*1}, Katsuichi Kanemoto^{*2}, and Tatsuhisa Kato^{*2} (*1 Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan and CREST, Japan Science and Technology Agency (JST), Japan, *2 Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan)

J. Phys. Chem. A, **108**, 5715–5720 (2004)

Intramolecular high-spin correlation in a series of the successively generated polycationic species of Bindschedler's green-based arylamine, *N*, *N*, *N'*, *N'*, *N''*, *N''*-hexakis [4-(dimethylamino)phenyl]-1, 3, 5-benzenetriamine (**1**), has been investigated by continuous wave (CW) and pulsed ESR spectroscopy. Cyclic voltammetry shows multiredox behavior of **1** that can be reversibly oxidized from monocation to hexacation. Depending on the quantity of the added oxidant, the characteristic ESR spectra are observed for polycations of **1** in frozen solution. Unequivocal determination of the spin state at each oxidation stage of **1** is given by a pulsed EPR technique, that is, electron spin transient nutation spectroscopy.

Fullerenols Revisited as Stable Radical Anions

Lars O. Husebo^{*1}, Balaji Sitharaman^{*1}, Ko Furukawa^{*2}, Tatsuhisa Kato^{*2,3}, and Lon J. Wilson^{*1} (*1 Department of Chemistry and Center for Nanoscale Science and Technology, MS-60, Rice University, Houston, Texas 77251-1892, *2 Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan, *3 Faculty of Science, Josai University, Keyakidai 1-1, Sakado 350-0295, Japan)

J. Am. Chem. Soc., **126**, 12055–12064 (2004)

The first exhaustive purification and characterization of the much-studied, “fullerenols”, prepared by reaction of C₆₀ in toluene with an oxygenated, aqueous NaOH solution using tetrabutylammonium hydroxide as a phase transfer catalyst, has been performed. The resulting fullereneol is not simply polyhydroxylated C₆₀ but rather is a structurally and electronically complex C₆₀ radical anion with a molecular formula of Na⁺[C₆₀O_x(OH)_y]ⁿ⁻ (where *n* = 2–3, *x* = 7–9, and *y* = 12–15) for three different, but identical, preparations. Surprisingly, Na⁺-fullereneol is paramagnetic, exhibiting *iB* values in aqueous solution of 1.9–2.1 B. M. at 0.5 T and 300 K and R₁ proton relaxivities of 0.55–0.77 mM⁻¹s⁻¹ at 20 MHz and 40 °C, values both slightly higher than those expected for a pure S=1/2 spin system. EPR studies (ESE-FS and 2D nutation) of frozen aqueous solutions at 1.5 and 5.0 K establish that Na⁺-fullereneol is mainly S=1/2 with a minor, but significant, component of S=1. Thus, this is the first report to characterize these widely studied, water-soluble fullereneols

as stable radical anions. The stability of the $S=1/2$ Na^+ -fullerenol radical is likely due to a highly derivatized C_{60} surface that protects a cyclopentadienyl radical center on the fullerene.

Study on Optimization of Molecular Structure using Hamiltonian Algorithm

K. Ohtawara^{*1}, H. Teramae (*1 ATR Adaptive Communication Research Laboratories), *Chem. Phys. Lett.*, **390**, 84–88 (2004)

We apply the Hamiltonian Algorithm combined with *ab initio* molecular orbital calculation to the optimization of molecular structure. The 6000 iterative calculations at Hartree-Fock 6-31G** levels shows that the **H**CN structure can be obtained even starting from the *optimized* structure of the **H**NC molecule, which cannot be achieved by conventional optimization methods, such as the Newton-Raphson method. The initial kinetic energies of less than 0.05 hartree and greater than 0.5 hartree fail in the optimization. The incorporation of a mixing term in the momentum space can accelerate the optimization.

Development of an *Ab Initio* MO-MD Program Based on Fragment MO Method-An Attempt to Analyze the Fluctuation of Protein

T. Ishimoto^{*1}, H. Tokiwa^{*2}, H. Teramae, U. Nagashima^{*1} (*1 National Institute of Advanced Industrial Science and Technology, *2 Department of Chemistry, Rikkyo University), *Chem. Phys. Lett.*, **387**, 460–465 (2004)

In order to analyze the fluctuation of proteins, which plays an important role for folding structure and stability, an *ab initio* MO-MD program (FMO-HA) based on the fragment MO method has been developed and examined its efficiency in comparison with conventional RHF MO-MD. FMO gives the same potential of dissociation energy between fragments as well as RHF. FMO-HA and RHF MO-MD calculations show similar trajectories and geometrical changes. Furthermore, FMO-HA simulation enables us to elucidate the interaction energy between fragments accompanying with the dynamics. FMO-HA method is an efficient tool to determine the driving force of fluctuation of proteins.

Biological Activity of Barbados Cherry (Acerola fruits, Fruit of *Malpighia Emarginata* DC) Extracts and Fractions

N. Motohashi^{*1}, H. Wakabayashi, T. Kurihara, H. Fukushima, T. Yamada, M. Kawase^{*2}, Y. Sohara^{*2}, S. Tani^{*2}, Y. Shirataki^{*2}, H. Sakagami^{*3}, K. Satoh^{*4}, H. Nakashima^{*5}, A. Molnár^{*6}, G. Spengler^{*6}, N. Gyémánt^{*6}, K. Ugocsai^{*6} and J. Molnár^{*6} (*1 Meiji Pharmaceutical University, *2 Faculty of Pharmaceutical Sciences, Josai University, *3 Department of Endodontics, Meikai University School of Dentistry, *4 School of Medicine, Showa University, *5 Department of Microbiology, St. Marianna University, *6 Institute of Microbiology,

Albert Szent-Györgyi Medical University)
Phytotherapy Res., **18**, 212–223 (2004)

Fractionation of barbados cherry (acerola fruit, a fruit of *Malpighia emarginata* DC.) extracts were performed by organic solvent extractions and column chromatographies, using two extraction methods. Higher cytotoxic activity was concentrated in fractions A4 and A6 (acetone extract), and H3 and HE3 (hexane extract). These four fractions showed higher cytotoxic activity against tumor cell lines such as human oral squamous cell carcinoma (HSC-2) and human submandibular gland carcinoma (HSG), when compared with that against normal cells such as human periodontal ligament fibroblasts (HPLF) and human gingival fibroblasts (HGF). HE2 (hexane extract), AE2 (ethyl acetate extract), AE3, AE4, AE5, A8, A9 and A10 showed some relatively higher anti-bacterial activity on the Gram-positive *Staphylococcus epidermidis* ATCC1228 but were ineffective on the representative Gram-negative species *E. Coli* and *Ps. aeruginosa*. The fractions were inactive against *Helicobacter pylori*, two representative *Candida* species, and human immunodeficiency virus (HIV). H3, H4 and HE3, which displayed higher tumor-specific cytotoxicity also showed higher multidrug resistance (MDR) reversal activity, than (\pm)-verapamil as positive control. ESR spectroscopy shows that the radical-mediated oxidation is not involved in the induction of tumor-specific cytotoxic activity. The tumor specific cytotoxic activity and MDR reversal activity of barbados cherry may suggest its possible application for cancer therapy.

Inhibition of LPS-stimulated NO Production in Mouse Macrophage-like Cells by Tropolones

Keiko Yokoyama, Kana Hashiba, Hidetsugu Wakabayashi, Ken Hashimoto*¹, Kazue Satoh*², Teruo Kurihara, Noboru Motohashi and Hiroshi Sakagami*¹ (*1 Department of Endodontics, Meikai University School of Dentistry, *2 Analysis Center, School of Pharmaceutical Sciences, Showa University, *3 Meiji Pharmaceutical University)
Anticancer Res., **24**, 3917–3922 (2004)

We investigated the effect of 27 tropolones on nitric oxide (NO) production by mouse macrophage-like Raw 264.7 cells. All of these compounds failed to stimulate the Raw 264.7 cells to produce detectable amounts of NO, but inhibited NO production by lipopolysaccharide (LPS)-activated Raw 264.7 cells to various extents. Generally, the ability of tropolones to inhibit LPS-stimulated NO production was inversely related to their cytotoxic activity. Western blot and RT-PCR analyses demonstrated that the most active compound, 2,4-dibromo-7-methoxytropolone (**1**), significantly reduced both the intracellular concentration of *i*NOS protein and the expression of *i*NOS *m*RNA. ESR spectroscopy showed that compound **1** did not produce radicals under alkaline condition, nor scavenged NO, produced by NOC-7. These data suggested that the inhibitory effect of compound **1** on NO production might be generated via the inhibition of *i*NOS expression, rather than a radical-mediated mechanism.

Inhibition of LPS-stimulated NO Production in Mouse Macrophage-like Cells by Azulenes

Kana Hashiba, Keiko Yokoyama, Hidetsugu Wakabayashi, Ken Hashimoto*¹, Kazue Satoh*², Teruo Kurihara, Noboru Motohashi and Hiroshi Sakagami*³ (*1 Department of Endodontics, Meikai University School of Dentistry, *2 Analysis Center, School of Pharmaceutical Sciences, Showa University, *3 Meiji Pharmaceutical University)
Anticancer Res., **24**, 3939–3944 (2004)

We investigated the effect of twenty seven azulene son nitric oxide (NO) production by mouse macrophage-like Raw 264.7 cells. No azulene derivative alone induced NO production by they Raw 264.7 cells, but inhibited lipopolysaccharide (LPS)-stimulated NO production to various extents. The ability of azulenes to inhibit NO generation by activated macrophages was generally increased when their cytotoxic activity declined. Western blot and RT-PCR analyses demonstrated that the most potent compound, 1,3-difluoroazulene (**1**), slightly inhibited the expression of inducible NO synthase (*i*NOS), but only at extremely high concentrations. ESR spectroscopy showed that compound **1** did not produce radical under alkaline condition, nor scavenged O₂⁻ (generated by HX-XOD reaction) or NO (generated by NOC-7). These data suggest that inhibitory effect of compound **1** may be produced via a mechanism other than *i*NOS induction and a radical-mediated mechanism.

Relationship between Electronic Structure and Cytotoxic Activity of Dopamine and 3-Benzazepine Derivatives

Teruo Kurihara, Tomoya Yamada, Ayako Yamamoto, Masami Kawase*¹, Noboru Motohashi*², Hiroshi Sakagami*³, and Joseph Molnar*⁴, (*1 Faculty of Pharmaceutical Sciences, Josai University, *2 Meiji Pharmaceutical University, *3 Meikai University School of Dentistry, *4 Faculty of Medicine, Institute of Microbiology, Albert Szent-Gyorgyi Medical University)
In vivo, **18**, 443–448 (2004)

QSAR of Dopamine and 3-benzazepine derivatives is discussed, using theoretically calculated results. In order to clearly divide dopamines and 3-benzazepines into a strongly active and a weakly active group, the CC₅₀, two different dipole moments ($\mu_{\text{ESP-G}}$ and $\mu_{\text{ESP-W}}$) and heat of formation (ΔH_f) of dopamines [**1–13**] and 3-benzazepine derivatives [**14–23**] were separately calculated in two states of gas-phase and water-solution by the COSMO/PM3 method. It was found that ten derivatives [**1–3**, **9**, **12–13** and **20–23**] (CC₅₀: 0.056 to 2.5 mM) showed the strongest cytotoxic activity with small ΔH_f values, whereas thirteen derivatives [**4–8**, **10–11**, **14–19**] (CC₅₀: > 3.6 mM) showed the weakest cytotoxic activity with large ΔH_f values.

Analysis of Vibrational-Rotational Spectra with Optimal Fitting Parameters for Born-Oppenheimer Corrections to Dunham's Y_{ij} : An Application to Spectral Data of HCl

Hirromichi Uehara, Kouji Horiai, and Kazufumi Akiyama

Bull. Chem. Soc. Jpn., **77**, 1821–1827 (2004)

Analytic expressions for Born-Oppenheimer corrections to Dunham's Y_{ij} with optimal fitting parameters, *i.e.*, determinable clusters of expansion coefficients, are applied in analysis of data of reported vibrational-rotational and rotational transitions of HCl. In this method of analysis the choices of a set of fitting parameters and also a corresponding set of Y_{ij} that connects the fitting parameters with the term values are unique. A layered structure for empirical parameters Δ_{ij} is revealed. All spectral lines of four isotopomers of HCl are simultaneously fitted to a single set of molecular constants well within the experimental errors. The approach thus provides a better fit of smaller standard deviations with fewer number of adjustable parameters than from other methods of analysis. The determined values for the coefficients of adiabatic effects s_1^H and s_1^{Cl} reveal the wobble-stretch term to be unimportant in the adiabatic correction for HCl.

A Non-Born-Oppenheimer Effective Hamiltonian for the Analysis of Vibrational-Rotational and Rotational Spectra of Diatomic Molecules

Hirromichi Uehara

Bull. Chem. Soc. Jpn., **77**, 2189–2191 (2004)

A non-Born-Oppenheimer effective Hamiltonian for diatomic molecules with optimal fitting parameters, *i.e.*, determinable clusters of expansion coefficients of Born-Oppenheimer corrections, has been derived. The effective Hamiltonian has formally the same form as Dunham's Hamiltonian, except for additional corrections for successive ξ^i terms of a series expansion of the rotational parameter $B(\xi)$, extending the determinacy of the optimal parameters, $\Delta_B^{a,b}$, $\Delta_\omega^{a,b}$, $\Delta_{aiq}^{a,b}$, $r_{iq}^{a,b}$, in general for $i = 1, 2, 3, \dots$ if spectra of isotopomers of atoms A and B are analyzed simultaneously. The effective Hamiltonian provides a clear-cut understanding of determinable correction parameters; *e.g.*, in Dunham-type potential fits to spectral transitions for the single isotopomer optimal parameters δr_{iq} ($i = 1, 2, \dots$) for corrections of series expansion terms of $B(\xi)$ should explicitly be included. The physical significance of the optimal parameters as well as of conventional molecular parameters, B_e , $-D_e$, H_e , ω_e , and $-\alpha_e$, etc., is described.

Physicochemical and Crystallographic Characterization of Mefenamic Acid Complexes with Alkanolamines

Liang Fang^{*1}, Sachiko Numajiri^{*1}, Daisuke Kobayashi^{*1}, Hideo Ueda^{*1}, Koji Nakayama^{*1}, Hiroshi Miyamae, and Yasunori Morimoto^{*1,2}, (*1 Faculty of Pharmaceutical Science, *2

Research Institute of TTS Technology)

J. Pharmaceutical Sciences, **93** (1), 144–154 (2004)

The preparation of mefenamic acids (MH) — alkanolamine (propanol-, diethanol- and triethanol-amine) complexes was attempted to increase the transdermal flux of MH. DSC, FT-IR and X-ray crystallographic studies demonstrated that MH and each alkanolamine formed an ion pair complex. The series of amine complexes had a lower melting point and higher solubility in water compared with pure MH.

Charge-Transfer Complexes $[[Pt(en)_2][PtX_2(en)_2]_3][\{(MX_5)X_3\}_2] \cdot 12H_2O$: Quasi-One-Dimensional Halogen-Bridged Pt^{II} - Pt^{IV} Mixed-Valence Compounds with Magnetic Counteranions

M. Yamashita*¹, D. Kawakami*¹, S. Matsunaga*¹, Y. Nakayama*¹, M. Sasaki*¹, S. Takaishi*¹, F. Iwahori*¹, H. Miyasaka*¹, K. Sugiura*¹, Y. Wada*², H. Miyamae, H. Matsuzaki*³, H. Okamoto*³, H. Tanaka*⁴, K. Marumoto*⁴, and S. Kuroda*⁴, (*1 Tokyō Metropolitan University, *2 National Institute for Material Science, *3 The University of Tokyo, *4 Nagoya University)

Angew. Chem. Int. Ed., **43**, 4763–4767 (2004)

Quasi-one-dimensional halogen-bridged mixed-valence compound of the title one have been synthesized and characterized. X-ray structural determination shows that the existence of the magnetic $MnCl_5$ counterions rather than the ClO_4^- compound makes the oxidation state of much closer to Pt^{III} . TGA study from 20 to 100°C with weight loss of ca. 8% which can be attributed to loss of water molecules is good agreement with the desorption of 12 water molecule per molecular unit. Temperature dependent X-ray powder diffraction pattern was measured and confirmed that the structure is sustained even in the absence of the water molecules. Temperature-dependent ESR measurements shows the variety of the spin species in the counterions ($M = Mn^{2+}, Fe^{2+}, Co^{2+}$; $X = Cl^-, Br^-$).

Mechanochemical Syntheses of Complexes through Solid-Solid Reactions of Divalent Transition Metal Salts (Ni (II) or Cu (II)) with Dimethylglyoxime

Goro Hihara, Masahiro Satoh, Takayuki Uchida, Fumihiro Ohtsuki, and Hiroshi Miyamae
Solid State Ionics, **172**, 221–223 (2004)

Solvent-free solid-solid reactions of dimethylglyoxime (H_2dmg) with nickel (II) salts or copper (II) acetate were conducted mechanochemically. Three types of complexes, $[Ni(Hdmg)_2]$, $[Ni(H_2dmg)_2]X_2$ [$X = Cl$ and NO_3], and $CuCH_3COO(Hdmg)$, were identified by powder X-ray diffractometry and elemental analysis. $[Ni(Hdmg)_2]$ was obtained for nickel salts of a weak acid and $[Ni(H_2dmg)_2]X_2$, for those of a strong acid. The progress of some of the solid-solid reactions was followed by the measurement of weight

change of the reaction mixture, suggesting that mechanical energy was utilized as a driving force for the reactions.

Infrared Spectroscopy of $(^{12}\text{C}^{18}\text{O}_2)_2$ and Isotope Effect on the Vibrationally Averaged Structure of $(\text{CO}_2)_2$

Toichi Konno, Yasushi Ozaki

Chem. Phys. Lett., **394**, 198–202 (2004)

The high-resolution infrared spectrum of $(^{12}\text{C}^{18}\text{O}_2)_2$ has been observed in the ν_3 band (2314cm^{-1}) region of $^{12}\text{C}^{18}\text{O}_2$ with diode laser absorption spectroscopy of pulsed molecular beam. The vibrational band origin of $(^{12}\text{C}^{18}\text{O}_2)_2$ corresponding to the ν_3 mode of $^{12}\text{C}^{18}\text{O}_2$ shows a blue shift of $1.62362(19)\text{cm}^{-1}$ with respect to that of $^{12}\text{C}^{18}\text{O}_2$. The geometrical parameters of the slipped parallel ground-state structure are $R_{\text{cc}} = 3.5947(11)\text{\AA}$ and $\theta_{\text{cco}} = 57.97(7)^\circ$. By calculating vibrational wavefunctions on *ab initio* potentials for four intermolecular degrees of freedom, the isotope effect on R_{cc} is found to arise mainly from in-plane tilting.

Thermal Behavior of Fowl Feather Keratin

K. Takahashi*, H. Yamamoto*, Y. Yokote, and M. Hattori* (*1 Department of Applied Biological Science, Faculty of Agriculture, Tokyo University of Agriculture and Technology, Tokyo 183-8509, Japan)

Biosci. Biotechnol. Biochem. **68**, 1875–1881 (2004)

Differential scanning calorimetry (DSC) was applied to elucidate the thermal behavior of fowl feather keratins (barbs, rachis, and calamus) with different morphological features. The DSC curves exhibited a clear and relatively large endothermic peak at about 110–160 °C in the wet condition. A considerable decrease in transition temperature with urea and its helical structure content estimated by Fourier transform infrared spectroscopy (FT-IR), and the disappearance of one of the diffraction peaks with heating at 160 °C for 30min, indicated that DSC could be used to evaluate the thermal behavior of keratin. Barbs showed a lower denaturation temperature than rachis and calamus. The pulverized I samples showed a slightly higher denaturation temperature than the native samples. In the dry condition, thermal transition occurred in a markedly higher temperature region close to 170–200 °C. It is hence concluded that fowl feather keratins have very high thermal stability, and that the elimination of water brings about even greater thermal stability.

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Nilpotent Endomorphisms and Semiinvolutions

H. Ishibashi

Proceedings of the Seventh Symposium on Algebra, Languages and Computation, 29–31 (2004)

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宮前 博

丸善株式会社, 179–180 (2004)

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丸善株式会社, 810–826 (2004)

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EARTH SCIENCE

関東山地三頭山地域の四万十帯ホルンフェルスの化学組成 — EPMA 線分析法による接触変成岩の研究 —

加賀美英雄, 谷口英嗣* (*駒沢大学高等学校)

城西大学研究年報 (自然科学編), 28, 27-56 (2004)

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Factorization of Nilpotent Endomorphisms

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Masayuki Yamasaki

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Toshiko Ogiwara

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Asymptotic Behavior of Solutions to Reaction-diffusion Equations with Periodic Nonlinearity

Toshiko Ogiwara

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山北奈美*, 今城尚志*, 土屋莊次, Anthony L. Merer** (*日本女子大理, **UBC, Canada)
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IR-UV double resonance spectroscopy of ungerade vibrational level structure of acetylene in the electronically excited state

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窒素内包フラーレンの光化学

松永洋一郎*¹, 若原孝次*¹, 前田 優*², 加固昌寛*³, 赤阪 健*¹, 加藤立久*⁴, Yoong-Kee Choe*⁴, 小林 郁*⁴, 永瀬 茂*⁴, Houjin Huang*⁵, 阿多誠文*⁵ (*¹ 筑波大学大学院, *² 学芸大学, *³ 電気通信大学, *⁴ 分子科学研究所, *⁵ SONY 株式会社)

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La@C₈₂ のLa 核四重極子の ESR 法による観測

加藤立久*¹, 大窪清吾*¹, Nobert Weiden*², Klaus-Peter Dinse*² (*¹ 分子科学研究所, *² Darmstadt Univ. of Technology)

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NMR による M@C₈₂ の構造解析

土屋敬広*¹, 若原孝次*¹, 前田 優*², 赤阪 健*¹, 小林 郁*³, 永瀬 茂*³, 加藤立久*^{3,4}, Karl M.

Kadish*⁵ (*1 筑波大学大学院, *2 学芸大学, *3 分子科学研究所, *4 城西大学, *5 University of Houston)

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La@C₈₂ とシクロペンタジエンの反応

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Sc₃@C₈₂ の電子的特性と反応性

飯塚裕子*¹, 桜庭明央*², 若原孝次*¹, 前田 優*³, 赤阪 健*¹, 加藤立久*⁴, 小林 郁*⁴, 永瀬 茂*⁴, (*1 筑波大学大学院, *2 新潟大学大学院, *3 学芸大学, *4 分子科学研究所)

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宮前 博, 金子美樹, 日原五郎

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Satoshi Tachiyashiki*¹, Tatuoki Morooka, Hiromasa Kowata*¹, Kazuteru Shinozaki*², Hiroshi Miyamae and Goro Hihara (*1 Laboratory of Bio-Inorganic Chemistry, Kagawa Nutrition University, *2 Division of Inorganic Photochemistry, Graduate School of Integrated Science)

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高次元アルゴリズムに基づくオリゴペプチドの構造解析Ⅲ

家入寛子*¹, 常盤広明*¹, 長嶋雲兵*², 寺前裕之 (*1 立教大理, *2 産総研グリッド研究センター) 日本コンピューター化学会 2004 春期年会 (東京), 2004 年 5 月

FMO-HA 法を用いたオリゴペプチドの相互作用ダイナミクス

石元孝佳*¹, 常盤広明*², 寺前裕之, 長嶋雲兵*¹ (*¹ 産総研グリッド研究センター, *² 立教大理)
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N. Motohashi*¹, H. Wakabayashi, T. Kurihara, H. Fukushima, T. Yamada, M. Kawase*²,
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Molnar*⁶ (*¹ Meiji Pharmaceutical University, *² Faculty of Pharmaceutical Sciences, Josai
University, *³ Department of Endodontics, Meikai University School of Dentistry, *⁴
School of Medicine, Showa University, *⁵ Department of Microbiology, St. Marianna Uni-
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EARTH SCIENCE

関東山地三頭山ホルンフェルスの変成鉱物モードと変成流体相の研究

加賀美英雄, 谷口英嗣* (* 駒沢大学高等学校)

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