新規シアノ架橋複核金属錯体の設計・開発およびそのロタキサンの合成

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Design and development of new cyano-bridged metal complexes and syntheses of its rotaxane

Research Project

Project/Area Number

07640741

Research Category

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Allocation Type

Single-year Grants

Section

一般

Research Field

Inorganic chemistry

Research Institution

Kanazawa University

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Keywords

Cyano-bridged metal complex / f-d mixed dinuclear complex / Solvatochromism / Cis-trans isomerization

Research Abstract

(1) Mixed copper (II) chelates of the type [Cu (trop/hino) (diamine)] ClO_4 were prepared with a tropolonato or hinokitiolato ligand (trop/hino) and N,N-dimethyl, N,N'-dimethyl, N,N,N'-trimethyl or N,N,N', N'-tetramethyl-ethylenediamine. These chelates were generally similar to the corresponding beta-diketonato chelates, in particular with respect to their characteristic solvatochromism, i.e., the shifts of their d-d bands to the red with

increasing DN (donor number) of the solvent.
(2) Eleven mixed-ligand chelates of Ni (II) containing a molecule of N,N-di-, N,N,N'-tri-, or N,N,N', N'-tetramethyl-ethylenediamine, and a tropolone (trop) or hinokitiolate (hino) ligand, were prepared, and their electronic spectra in solid state and in various organic solvents were studied. Most systems studied were green, containing octahedral chelate species [Ni (trop/hino) (diamine) (H_2O/Solvent)_2]^+ or [Ni (NO_3) (trop/hino) (diamine)], but some were red, containing square planar [Ni (trop/hino) (dia mine)]^+, an equilibrium between the octahedral and square planar species was sometimes observed in solutions. Strong spectral resemblances with the corresponding diamine-beta-diketonate chelates of Ni (II) were observed.
(3) The solid-phase thermal reactions of trans-diaquabis (diamine) nickel (II) complexes (trans- [Ni (diamine)_2 (H_2O)_2] X_2) were investigated by means of TG/DTA and DSC,and high-temperature electronic spectrometry, where the diamine is an optically active diamine such as (1S,2S) -1,2-diphenyl-1,2-ethanediamine, (1R,2R) -1,2-cyclo-hexanediamine, or (S) -4-methyl-1,2-pentanediamine, and X is Cl^-, Br^-, or NO_3^-. Several complexes were peculiarly transformed into cis- [NiX_2 (diamine)_2] upon thermal deaquation-anation, and then isomerized to trans- [NiX_2(dimaine)_2] upon further heating. The results were in contrast to the reactions of the complexes with the coresponding racemic diamines which underwent a simple deaquation-anation, retaining an original trans configuration. The differences must come from a slight difference in the conformation of diamine ligands between trans- [Ni (R-diamine) (S-diamine) (H_2O)_2]X_2 which is obtained for the rac-diamines and trans- [Ni (R- or S-diamine)_2 (H_2O)_2]X_2 which is obtained for the optically active diamines.▲ Less

Research Products (8 results)

All | Other

All | Publications (8 results)

[Publications] 井原 良訓: "Solvatochromic Mixed-ligand Copper(II)Chelates with N-or N,N'-Methylated Ethylenediamines and Tropolonato or Hinokitiolato Ligands" Polyhedron. 15. 3643-3646 (1996)

[Publications] 井原 良訓: "Solid-phase Thermal Cis-to-trans Isomerization of the Nickel (II) Complexes Containing 1-Benzyl-1,2-ethanediamine" Thermochim.Acta. 302. 211-214 (1997)

[Publications] 井原 良訓: "Cis-trans Isomerism among the Octahedral Diaquabis (optically activeC-substituted ethylenediamine) nickel(II) Complexes and Their Thermal Reaction Products" Bull.Chem.Soc.Jpn. 70. 3025-3029 (1997)

[Publications] 井原 良訓: "Preparation and Spectral Studyof Mixed-ligand Nickel (II) Chelates Containing N-or N,N'-Methylated Ethylenediamines and Tropolonate or Hinokitiolate Ligands" Polyhedron. (in press). (1998)

[Publications] Y.Ihara, M.Yoshizakiya, R.Yoshiyama and K.Sone: "Solvatochromic mixed-ligand copper (II) chelates with N- or N,N'-methylated ethylenediamines and tropolonato or hinokitiolato ligands" Polyhedron. 15 (20). 3643-3646 (1996)

[Publications] Y.Ihara and R.Nakamura: "Solid-phase thermal cis-to-trans isomerization of the mickel (II) complexes containing 1-benzyl-1,2-ethanediamine" Thermochim.Acta. 302. 211-214 (1997)

[Publications] Y.Ihara, T.Sakino, E.Ishikawa and T.Koyata: "Cis-trans isomerism among the octahedral diaquabis (optically active C-substituted ethylenediamine) nickel (II) complexes. An explanation for a variety in colors and stereochemistry of Lifschitz complexes" Bull.Chem.Soc.Jpn.70 (12). 3925-3029 (1997)

[Publications] Y.Ihara, K.Teranishi, N.Hirose and K.Sone: "Preparation and spectral study of mixed-ligand nickel (II) chelates containing N- or N,N'-methylated ethylenediamines and tropolonate or hinokitiolate ligands" Polyhedron. (in press).

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