

第35回・理学部化学科コロキウムの御案内

Linert 博士をお迎えし、第35回化学科コロキウムを開催いたします。
多数のご来場をお待ちしております。

日時：2004年1月22日（木曜日） 15：00～

場所：国際交流会館・中会議室

Part-I

Tomokura MADANBASHI, Doctoral Candidate (YAMASHITA Group)

Magnetic Properties of self-assembled Mn(III)salen Complexes with Organic Radicals.

Yusuke NAKASHIMA, Doctoral Candidate (KAMIGATA Group)

Optical Resolution and Stereochemistry of Seleninic Acids.

Kazuya NAKATA, Doctoral Candidate (YAMASHITA Group)

Magnetic Properties of Multi-Dimensional Assembly Based on Single-Molecule Magnets.

Part-II

W. Linert

Institute of Applied Synthetic Chemistry, TU-Vienna, Austria

Isokinetic and Isolequilibrium Relationships in Spin Crossover Systems

Isokinetic and Isoequilibrium Relationships in Spin Crossover Systems

W. Linert

Institut of Applied Synthetic Chemistry, TU-Vienna, Getreidemarkt 9/163-AC, 1060- Vienna, Austria

A thorough statistical mechanical analysis of sources of variations and correlations in ΔE^0 and ΔS^0 of spin crossover equilibrium in the solid state is given. Attention has been brought to possible contributions of vibrations and rotations towards the entropy of reactions. In the ideal approximation the isoequilibrium relationship (IER) can be observed due to variations in the intermediate-frequency vibrational modes (θ_{vib} lying within experimental range of temperatures). Such IER are characterised by high or infinite T_{iso} . Cases of isoequilibrium temperatures lying within the experimental range or below cannot be explained in the approximation of an ideal crystal. These (and actually all known) types of IER are explained by invoking non-ideality within the models of double and triple molecular interactions. Stochastic model of chemical kinetics applied to a isokinetic relationship (IKR) in spin crossover explains cases of IKR characterised by positive T_{iso} . Negative T_{iso} can arise from concerted variations in parameters separately determining activation energy and entropy. IKR and IER are versatile tools in detecting reactions, which follow the same mechanisms.

Figure 0

Linertf000.tif

Figure 1: Iso-equilibrium investigations show an intersection point for all $[\text{Fe}(\text{ntz})_6](\text{BF}_4)_2$ with $n = 1, 2, 4-8, 12, 16$ which indicate one mechanism for all their spin transitions. The $[\text{Fe}(\text{3tz})_6](\text{BF}_4)_2$ do not intersect, because of its extreme good cooperative effects.