

MS36-P25

Structures and physical properties of some derivatives of 2,2';6',2''-terpyridine chelating Fe/Co metal complexes

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The multi-functional metal complex with magnetic, luminescence, or conductivity properties is one of the directions to design new modern materials. Spin crossover (SCO) compound is one kind of these complexes due to its potential applications to sensors, information storage, cantilever and so on. In this work, we modify terpyridine to 4'-(2-Furyl)-2,2';6',2''-terpyridine (ftpy) and 1-methyl-1H-Pyrrol-2-yl-2,2';6',2''-terpyridine (mtpy), and successfully obtained metal complexes $M(II)L_2(BF_4)_2$ ($M = Fe(II), Co(II)$; $L = ftpy, mtpy$). In these metal complexes, $Co(II)(ftpy)_2(BF_4)_2 \cdot 1.5H_2O$ (complex **1**) exhibits SCO behavior from high spin (HS) state with $\mu_{eff} = 4.10$ B.M. at 350K to low spin (LS) state with $\mu_{eff} = 2.14$ B.M. at 100K, but $Co(mtpy)_2(BF_4)_2$ (complex **2**) only displays HS state. The other Fe(II) complexes both exhibit diamagnetism. To resolve how structure variation leads to the SCO phenomenon so that we can realize why complex **1** exhibits SCO character, the temperature dependent powder x-ray diffraction (PXRD) measurements are carried out at TPS09A beamline and the high resolution PXRD data are analyzed by Rietveld refinement to obtain detailed structural information. The results indicate that the crystal structures are still in triclinic system from 90K (LS) to 350K (HS) with averaged Co-N distance varied from 2.02(3) Å to 2.10(1) Å. Taking insight into crystal packing structure, one H₂O is located at ~ 2.41 Å away from one of furan in complex **1**, but no solvent molecule in complex **2**. This short distance may indicate intermolecular interaction plays a critical role in tuning SCO phenomenon. In addition, the temperature dependent of x-ray absorption spectroscopy (XAS) is applied to study the electronic structures of complex **1**. Moreover, the UV absorption and photoluminescence characters of ftpy and mtpy are also discussed in this study.

Keywords: PXRD, XAS, spin crossover

MS36-P26

Unexpected long-lived photogenerated High-Spin phase investigated by X-ray diffraction

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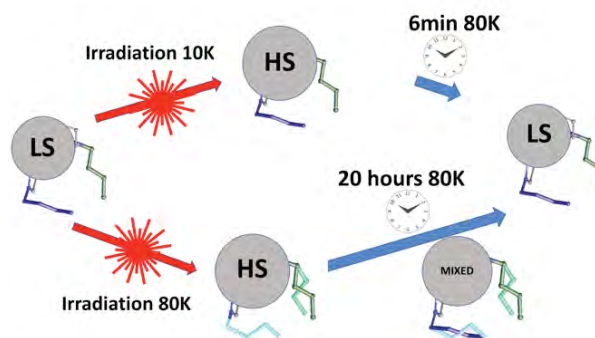
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Spin crossover compounds are interesting photoswitchable materials, with possible applications in sensing or memory devices. At low temperature the Low-Spin state can be excited into the photoexcited High-Spin state through the Light-Induced Excited Spin-State Trapping (LIESST) effect. The relaxation time is however usually short at higher temperatures.

The spin-crossover compound $[Fe(n-Bu-im)_3(tren)](PF_6)_2$ ¹ shows an unusual long relaxation time at 80K of 20 hours after Light-Induced Excited Spin-State Trapping when irradiated at 80 K. This is more than 40 times longer than the 80K relaxation time when irradiated at 10 K. To explain this unusual behavior single crystal structures were determined after irradiation at low temperature and at 80K. The structures of the two excited High-Spin states differ in the configuration of the side alkyl chains of the compound. Using synchrotron radiation, the long relaxation at 80K could be monitored by single-crystal X-ray diffraction. We showed that the rearrangements of the alkyl chains, which undergo order-disorder transitions, are responsible for the unexpected long relaxation time.

These results highlight the importance of structural studies to better understand and control the LIESST photoexcited states. Multimetastability can be exploited to tune the properties of the system.



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MS36-P27

Halogen bonding, actinide contraction and coordination modes of ligands in uranyl, neptunyl and plutonyl trichloroacetates with ammonium cations

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Uranyl, neptunyl and plutonyl ions usually form series of isostructural compounds. This fact is very favorable for investigation of the relationship between composition, structure and properties, since it is possible to obtain series of compounds with single varying parameter, for example, the actinide atom, the ligand or the counterion.

In order to obtain new series of U, Np, Pu compounds, we attempted to use trichloroacetate ions as ligands. As a result, single crystals of isostructural compounds $(\text{NH}_4)_4\text{AnO}_2(\text{tca})_6(\text{Htca})(\text{H}_2\text{O})_3$ (where An is U, Np or Pu and tca is a trichloroacetate ion) were grown and studied using X-ray diffraction analysis. These compounds are of great importance for studying actinide contraction as well as halogen bonding. For example, it has recently been shown that bonds involving halogen atoms can serve as synthons in the formation of supramolecular architectures as well as chemical bonds in the presence of secondary metal atoms in uranyl carboxylate complexes [1]. Halogen bonds in the title crystal structures were analyzed using the method of molecular Voronoi-Dirichlet polyhedra. Actinide contraction in the row of hexavalent U, Np and Pu atoms is discussed on the example of all available series of isostructural compounds.

Aspects of theoretical crystal chemistry are also discussed in the current project. With an increase in the number of structurally studied coordination compounds, it becomes necessary to systematize them in order to facilitate the search for analogous structures, their comparison and identification of common trends in coordination chemistry. One of the methods of description and systematization of complex compounds is the use of crystal-chemical formulae (CCF) [2]. With the help of CCF it is possible to describe any mono- and polynuclear, as well as homo- and heteroligand complexes. CCF's are concise and can be recorded and used automatically by computer algorithms. However, the discussion of halogen-substituted organic ligands in the title compounds required an additional improvement of the recording of CCF and of coordination modes of ligands. In the course of this project, we analyzed coordination modes of trichloroacetate ions in all compounds from CSD [3], what is of great importance for crystal structure prediction and crystal design.

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Keywords: halogen bonding, actinide contraction, coordination modes