

The Solid State Ferric Spin-Crossover Transition:
Spectroscopic, Magnetic, and Structural Investigations

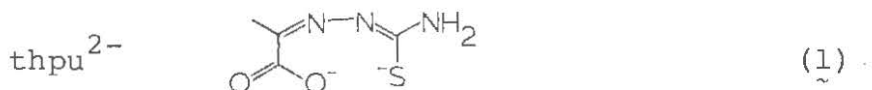
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Although most first-row transition metal complexes possess either pure low-spin or high-spin electronic ground states, complexes which show evidence for the thermal population of both spin states are not unknown [1]. These so-called spin-crossover complexes are typically identified by their temperature-dependent magnetic and spectroscopic properties that reflect the changes in the relative populations of the two spin-states. The role of spin-state interconversions in a number of biochemical, oxidation-reduction, and photochemical processes has led to interest in spin-crossover complexes [2]. The research to be reported here has been motivated by two general questions: (1) What factors influence the rates of intramolecular spin-state interconversions? (2) What factors affect the bulk thermodynamics of the solid state spin-crossover transformation? With these questions in mind, three new solid state ferric spin-crossover systems have been synthesized and physically characterized.

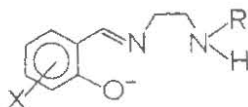
Ferric complexes of pyruvic acid thiosemicarbazone (1) have been known for some time to possess spin-crossover properties [3]. As indicated by variable temperature magnetic susceptibility,



electron paramagnetic resonance, and ^{57}Fe Mössbauer examinations, the new ferric complex $[\text{Fe}(\text{Hthpu})(\text{thpu})]$ exhibits a thermally discontinuous spin-state transformation at ca. 230 K. The observation of thermal hysteresis ($T_C(\uparrow) = 235 \text{ K}$, $T_C(\downarrow) = 225 \text{ K}$) identifies the thermodynamic first-order nature of the transition. Distinct and narrow Mössbauer linewidths are evident for both the high- and low-spin electronic states. Two conclusions can be drawn from these observations: (1) the spin-state interconversion rates are slower than $\sim 10^9 \text{ s}^{-1}$, (2) short intermolecular Fe-Fe distances are leading to rapid electron spin relaxation times. The chemical inequivalence of the Hthpu^- and thpu^{2-} ligands has been verified by the single-crystal X-ray structure of $[\text{Cr}(\text{Hthpu})(\text{thpu})] \cdot \text{H}_2\text{O}$. Not surprisingly, the chromium complexes are tightly bound in the lattice by a three-dimensional network of hydrogen bonds. Although crystals of the ferric complex were unobtainable, it is likely that similar hydrogen bonding interactions are responsible for the cooperative (i.e., discontinuous) nature of the spin-state transition.

The complex $[\text{Fe}(3\text{-OEtSalBzen})_2]\text{BPh}_4 \cdot \text{CH}_3\text{CN}(3\text{-OEtSalBzen}^- (2))$ exhibits a very gradual thermal spin-crossover transformation. As seen for similar complexes [4], the observation of distinct high- and low-spin EPR signals suggests that the rate of intramolecular spin-state interconversion is less than $\sim 10^{10} \text{ s}^{-1}$.

3-OEtSalBzen⁻
 x = 3-ethoxy

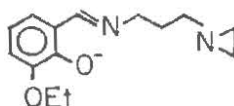


(2)

Despite the use of 43% ⁵⁷Fe-enriched samples, it is difficult to identify distinct high- and low-spin Mössbauer absorptions due to the very broad linewidths. It is reasonable that the benzyl ligand substituent and the large BPh₄⁻ counterions give rise to well separated ferric centers and long spin-spin relaxation times. Consequently, sharp EPR signals are seen, as are magnetically broadened Mössbauer signals.

A number of recent reports [5-8] have shown that ferric complexes with N₄O₂ ligand atom donor sets can interconvert spin-states rapidly relative to the Mössbauer spectroscopic time scale. Following the work of Federer, the spin-crossover compound [Fe(3-OEtSalAPA)₂]-ClO₄·C₆H₆(3-OEtSalAPA⁻ (3)) has been synthesized and studied in detail. Magnetic and spectroscopic examinations reveal a thermally

3-OEtSalAPA⁻



(3)

gradual and complete spin-crossover transformation. Mössbauer spectroscopy of a 95% ⁵⁷Fe-enriched sample shows a single, temperature-dependent quadrupole split doublet; the rate of intramolecular spin-state interconversion is more rapid than $\sim 10^8 \text{ s}^{-1}$. Electron paramagnetic resonance studies reveal a spin-state interconversion rate less than $\sim 10^{10} \text{ s}^{-1}$. Variable temperature (300-13 K) single crystal X-ray diffraction experiments were performed by C. E. Strouse and coworkers at U.C.L.A. These experiments indicate that in addition to the gradual spin-crossover transformation, there is also a first-order (i.e., discontinuous) order-disorder phase transition at ca. 175 K. Although this discontinuous transition does not apparently influence the thermodynamics of the spin-crossover transformation, it is possible that rapid disorder of perchlorate counterions and benzene solvate molecules is coupled to the rapid intramolecular spin-state interconversions.

References

1. Gütlich, P. Struct. Bonding (Berlin) 1981, 41, 83.
2. Scheidt, W. R.; Reed, C. A. Chem. Rev. 1981, 81, 543.
3. Zelentsov, V. V.; Ablov, A. V.; Turta, K. I.; Stuken, R. A.; Gerbeleu, N. V.; Ivanov, E. V.; Bogdanov, A. P.; Barba, N. A.; Bodyu, V. G. Russ. J. Inorg. Chem. 1972, 17, 1000.
4. Haddad, M. S.; Lynch, M. W.; Federer, W. D.; Hendrickson, D. N. Inorg. Chem. 1981, 20, 123.

5. Ohshio, H.; Maeda, Y.; Takashima, Y. Inorg. Chem. 1983, 22, 2684.
6. Maeda, Y.; Tsutsumi, N.; Takashima, Y. Inorg. Chem. 1984, 23, 2440.
7. Federer, W. D.; Hendrickson, D. N. Inorg. Chem. 1984, 23, 3861.
8. Federer, W. D.; Hendrickson, D. N. Inorg. Chem. 1984, 23, 3870.