

CURIOSITIES OF THE ELECTRON DYNAMICS OF SPIN-CROSSOVER SOLIDS

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I. Introduction

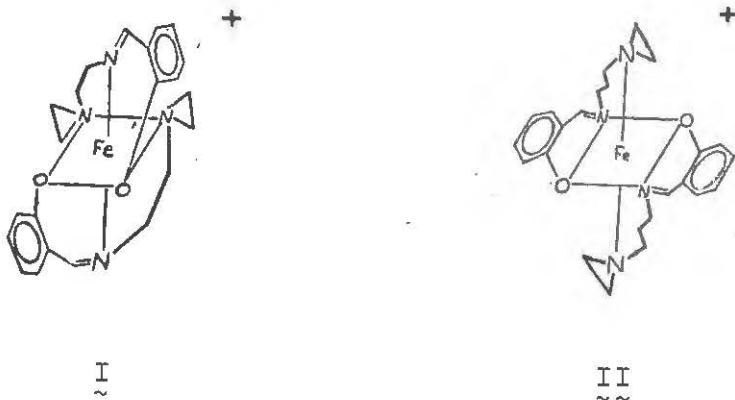
Spin-crossover complexes possess two nearly degenerate electronic states of different spin multiplicity. The aim of most investigators has been to assess ligand-field strength and substituent effects on the position of the resulting high-spin ("HS") \rightleftharpoons low-spin ("LS") "spin equilibrium." In the course of these studies, conducted over fifty years' time [1], many "curiosities" have perplexed chemists: incomplete transitions; abrupt transitions; remarkable influence of solvation or lattice counter ion [2], dependence on sample preparation; effects of grinding and doping solids [3a,c]. Non-linear plots of $\log K$ vs. $1/T$ and observations of thermal hysteresis demonstrate that kinetic influences can be as important as thermodynamic factors. In recent years efforts have intensified to explain these curiosities in terms of the theories of cooperative phase transitions, such as nucleation and growth [3], various domain models [4], or in the context of electron-phonon interactions (vibronic coupling) [5].

In spite of their non-equilibrium properties, spin-crossover coordination complexes can potentially provide valuable information about the fundamental aspects of electron transfer ("ET") processes; the "spin-flipping" phenomenon corresponds to transfer of electron(s) between thermally populated t_{2g} and e_g (*) d-orbitals with concomitant dimensional changes within the metal ion coordination sphere. For a number of spin-crossover complexes in fluid solutions near room temperature, intramolecular ET rate constants in the range $\sim 10^6 - 10^9 \text{ s}^{-1}$ have been measured directly by ultrasonic or temperature-jump techniques [6]. However, for solids no direct methods are available and one must estimate the rates by spectroscopic techniques. Almost all known spin-crossover solids observed by any such technique show discrete HS and LS resonances at all temperatures (rates considerably slower than $\sim 10^7 \text{ s}^{-1}$); the most notable exceptions are the highly covalent ferric (tris)dithiocarbamates [7], which exhibit a single population-weighted average Mössbauer quadrupole doublet at all temperatures (rates faster than $\sim 10^8 \text{ s}^{-1}$). The intent of the current investigation is to examine over a broad temperature range the electron dynamics of spin-crossover solids for which the spin-flipping occurs at an intermediate rate. An attempt is made to characterize the relationship between this intramolecular rate process and the cooperative spin-crossover phase transition.

II. Characterization of New Ferric Schiff Base Complexes

The present studies focus upon the new N_4O_2 ferric complexes of the Schiff bases derived from salicylaldehyde and N-(aminoalkyl)-aziridines. Microcrystalline solids are prepared by Schiff base formation in a methanolic solution containing either $FeCl_3 \cdot 6H_2O$ / excess $NaClO_4 \cdot H_2O$ or $Fe(ClO_4)_2 \cdot 6H_2O$. The perchlorate salts of

these bis(tridentate) complexes are identified as $[\text{FeE}]\text{ClO}_4$ and $[\text{FeP}]\text{ClO}_4$, respectively, for the cases of two-carbon ("E" = ethylene) and three-carbon ("P" = propylene) bridges between the imine and tertiary amine nitrogen donors. The existence of $[\text{FeE}]^+$ and $[\text{FeP}]^+$



as meridonal (cis-oxygen, I) and centrosymmetric facial (all trans, II) geometric isomers, respectively, may be inferred from pronounced differences in the LS g-tensors and quadrupole splittings and from the results of x-ray crystallographic studies of Schiff base complexes of structurally similar tridentate [8a] and hexadentate ligands [8b].

Both $[\text{FeE}]\text{ClO}_4$ and $[\text{FeP}]\text{ClO}_4$ exhibit spin-crossover behavior in the solid state, as demonstrated by their variable-temperature magnetic moments and EPR and Mössbauer spectroscopies. $[\text{FeE}]\text{ClO}_4$ is a "high-plateauing" compound that varies from totally HS at room temperature to ~80% HS at 4.2 K; discrete LS and HS Mössbauer doublets are observed, with only the relative areas changing significantly with temperature. The magnetic data for $[\text{FeP}]\text{ClO}_4$ reveals a gradual but complete transition from ~55% HS to entirely LS over the range 300-4.2 K; a single average quadrupole doublet is seen over this entire temperature range, characterizing $[\text{FeP}]\text{ClO}_4$ as the first N_4O_2 complex shown to have an ET rate constant greater than $\sim 10^8 \text{ s}^{-1}$ [9]. Furthermore, the variable-temperature Mössbauer spectra for $[\text{FeP}]\text{ClO}_4$ exhibit (1) a very pronounced variation in the average ΔE_Q value (2.4 mm/s at 4.2 K; 1.1 mm/s at 300 K), and (2) a maximum in linewidths at ~240 K. The latter observation is interpreted as a possible clue that the spin-flipping rate is just barely faster than the characteristic Mössbauer frequency [10].

III. Properties of "Perturbed" Samples of $[\text{FeP}]\text{ClO}_4$

Preliminary Mössbauer experiments [11] for a sample of natural isotopic composition had intimated previously that, among all spin-crossover materials, $[\text{FeP}]\text{ClO}_4$ uniquely undergoes the spin state interconversion at an intermediate rate, giving rise to line broadening and subsequent coalescence of LS and HS doublets as the temperature is increased over the range of 90-293 K. It

appeared possible to extract ET rate constants from each Mössbauer spectrum by least-squares fitting to a suitable LS \rightleftharpoons HS cross-relaxation model. The Arrhenius plots resulting from such analyses of the early Mössbauer spectra gave hints of an ET mechanism involving quantum-mechanical tunneling, as proposed quite recently in a theoretical paper by Jortner and co-workers [12]. However, the poor counting statistics offered by [FeP]ClO₄ samples of natural isotopic composition greatly limits the reliability of the Mössbauer kinetic parameters; such was the motivation for preparing ⁵⁷Fe-enriched [FeP]ClO₄.

In an attempt to understand the reasons for the disturbing contradiction between the Mössbauer results of our earlier investigation and those described in Section II, several "perturbed" samples, all originating from the same ⁵⁷Fe-enriched material characterized by "fast" ($\geq 10^8$ s⁻¹) ET rates over the entire range 4.2-310 K, have been prepared:

1. A dichloromethane-solvated compound obtained by recrystallization of a portion of the "unperturbed" [⁵⁷FeP]ClO₄ from a 3:1 CH₂Cl₂/C₆H₁₂ mixture.
2. A sample resulting from vacuum desiccation of the solvate at 56°C.
3. A hand-ground (by mortar and pestle) portion of the visibly microcrystalline unperturbed complex.
4. The products of two successive recrystallizations from CH₂Cl₂/C₆H₁₂ of the hand-ground material.
5. The microcrystalline members of an isomorphous series of cobalt-doped complexes, [(Fe_xCo_{1-x})P]ClO₄.
6. An iron-deficient, amorphous film isolated from a CH₂Cl₂/C₆H₁₂ solution made from the evaporated filtrate of the mother liquor.

These "perturbed" materials have been characterized by their infrared, EPR and Mössbauer spectra and by their magnetic moments and x-ray powder diffraction patterns. It is apparent that for all except the highly crystalline CH₂Cl₂ solvate, the mean rate of intramolecular electron transfer is considerably slower than that for unperturbed [FeP]ClO₄. These results are in keeping with the already well-established extreme sensitivity of spin-crossover complexes to their solid state environs. It is postulated that electron-phonon interactions, lattice defects or strain cause deviations from equilibrium behavior not only for a crystallite undergoing a static HS \leftrightarrow LS phase transition, but also for individual molecules undergoing a quasi-dynamic HS \rightleftharpoons LS inter-conversion.

References

1. Recent reviews: (a) Gütlich, P. Struct. Bonding, (Berlin) 1981, 44, 83.
 (b) Martin, R. H.; White, A. H. Transition Metal Chem., 1968, 4, 113.
 (c) Federer, W. D. University of Illinois Inorganic Seminar Abstracts, 1978, pp. 12-14.
2. Malliaris, A.; Papaefthimiou, V. Inorg. Chem., 1982, 21, 770.
3. (a) Haddad, M. S.; Federer, W. D.; Lynch, M. W.; Hendrickson, D. J. J. Am. Chem. Soc. 1980, 102, 1468.
 (b) Op. cit., Inorg. Chem. 1981, 20, 123.
 (c) Ibid., p. 131.
4. Sorai, M.; Seki, S. J. Phys. Chem. Solids 1974, 35, 555.
5. (a) Sasaki, N.; Kambara, T. J. Chem. Phys. 1981, 74, 3472.
 (b) Kambara, T. Ibid., p. 4557.
 (c) Kambara, T. Ibid. 1979, 70, 4199.
6. (a) Dose, E. V.; Hoselton, M. A.; Sutin, N.; Tweedle, M. F.; Wilson, L. J. J. Am. Chem. Soc. 1978, 100, 1141, and references therein.
 (b) Binstead, R. A.; Beattie, J. K.; Dose, E. V.; Tweedle, M. F.; Wilson, L. J. J. Am. Chem. Soc. 1978, 100, 5609, and references therein.
7. Rickards, R.; Johnson, C. E.; Hill, H. A. O. J. Chem. Phys. 1968, 48, 5231.
8. (a) Sim, P. G.; Sinn, E.; Petty, R. H.; Merrill, C. L.; Wilson, L. J. Inorg. Chem. 1981, 20, 1213.
 (b) Butcher, R. J.; Pouriam, M.; Thanyasiri, T.; Aviles, R. J.; Sinn, E. Abstracts 183rd ACS National Meeting, 1982, Div. Inorg. Chem. No. 24.
9. [FeP]ClO₄ is also the first reported spin-crossover N₄O₂ complex in which the nitrogen donors are separated by three carbon atoms rather than two.
10. The Mössbauer spectra described in this section for [FeP]ClO₄ were recorded using an ⁵⁷Fe-enriched sample.
11. (a) Federer, W. D.; Haddad, M. S.; Lynch, M. W.; Hendrickson, D. 179th ACS National Meeting, 1980, ACS Abstract No. 74.

(b) Haddad, M. S.; Federer, W. D.; Lynch, M. W.; Hendrickson, D. N. (IUPAC) Coord. Chem., Vol. 21, J. P. Laurent, Ed., Pergamon Press: Oxford, 1981, p. 75.

12. Buhks, E.; Navon, G.; Bixon, M.; Jortner, J. J. Am. Chem. Soc. 1981, 102, 2918.
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