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Cooperativity in Thermally Induced Intersystem Crossing in Solids: $Fe(phen)_2(NCR)_2$, R = BH_3, BPh_3, S, Se

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Variable-temperature magnetic moment data for $Fe(phen)_2X_2$, X = NCS^-, $NCSe^-$, and $NCBH_3^-$, have been analyzed for cooperativity contributions to singlet/quintet intersystem crossing. To account for the curve shape characteristics of the magnetic data, use is made of a simple, generalized thermodynamic formulation of intermolecular and domain interactions, including lattice continuity terms. This formalism is applied to the $Fe(phen)_2X_2$ series with the findings that the differential quintet:singlet and quintet:quintet intermolecular interaction (Gibbs) energies, Γ_c, span a narrow range, while the transition cooperativities, $\Gamma_c/2RT_c$, markedly vary; the latter reflect the importance of the singlet/quintet electronic energy gap and differential Q:Q, S:S interaction energies to T_c and to the sharpness of the transition.

Introduction

Among Fe(II) complexes, some of which are known to undergo thermally induced singlet/quintet intersystem crossing in solution and as solids,[1] the series of general formula *cis*-$Fe(phen)_2X_2$ is of special interest because the series members are closely related in molecular symmetry but vary widely in electronic ground state and in intersystem crossing characteristics. The subseries with X = $NCBH_3^-$, $NCBPh_3^-$, NCS^-, and $NCSe^-$ is highly isostructural at the molecular level, but the members differ greatly with respect to the conditions required to induce solid-state intersystem crossing,[2-4] the nature of which is defined in part by the temperature at which there are equal numbers of singlet and quintet sites and in part by the sharpness of the phase transition at this temperature.

It is the purpose of this report to formulate a flexible, thermodynamic description of solid-state intersystem crossing in a format that allows identification of intermolecular interaction and lattice continuity effects, to apply this model to data for the subseries, and to examine the relative importance of intermolecular interactions and singlet/quintet energy gap on the cooperative nature of the transition.

Data Fitting

Figure 1 contains the observed and calculated relation of μ and T for each of the $Fe(phen)_2(NCE)_2$ complexes, E = S, Se, and BH_3 (the member E = BPh_3 is diamagnetic to above 450 K[3]). The data for E = S, Se are taken from the work of Madeja and König,[4] while that for E = BH_3 comes from our laboratories.[2] Table I gives the values obtained for μ_S, μ_Q, ΔH, ΔS, and the intermolecular interaction parameters Γ_H, Γ_S; Table II lists parameters derived from those in Table I.

The parameter values given in Table I were obtained by means of Chandler's STEPIT algorithm[5] to search for a self-consistent fit of the Slichter/Drickamer[6] phenomenological expression (1) to the $\mu(T)$ data. This expression was implemented by conversion of μ(obsd) to f_Q (the fraction of quintet molecules in the sample) using adjustable, temperature-independent values of μ_Q and μ_S. K was calculated as f_Q/f_S. It was necessary to permit Γ, the nonlinear Gibbs energy parameter, to be temperature dependent via (2).

$$-\Delta G - \Gamma(1 - 2f_Q) = RT \ln K \qquad (1)$$

$$\Gamma = \Gamma_H - T\Gamma_S \qquad (2)$$

Table I. Thermodynamic Parameters[a]

compd	μ_S	μ_Q	ΔH	ΔS	Γ_H	Γ_S	residual
S	0.65	5.20	2.08	12.08	984.8	0.77	0.089
Se	0.84	5.10	2.73	11.66	583.0	−1.74	0.065
BH_3	1.07	5.56	4.45	12.35	105.8	−1.773	0.059

[a] μ is μ_{eff}. ΔH is in kilocalorie units. ΔS, Γ_H, and Γ_S are in calorie units.

Table II. Derived Parameters[a]

compd	Γ_c	T_c	C
S	0.85	172	1.25
Se	0.99	234	1.06
BH_3	0.74	360	0.52

[a] Γ_c is in kilocalorie units. T_c is in Kelvin units.

Minimization of the residual

$$(1/N)\sum_i[(\mu_i(\text{obsd})^2 - \mu_i(\text{calcd})^2)/\mu_i(\text{obsd})^2]^2$$

thus reduces to finding a best fit of ΔH, ΔS, Γ_H, and Γ_S to (1) for the best μ_S, μ_Q pair.

The transition temperature, T_c, is the temperature at which $K = 1$ and is given by eq 3.

$$T_c = \Delta H/\Delta S \qquad (3)$$

Fitting eq 1 to the data for the abrupt-transition cases of S and Se is not a trivial exercise. The transcendental nature of (1) prohibits derivation of an analytical function for minimization of the residual. A self-consistent solution must be sought. Another difficulty centers on the sensitivity of (1) to even small errors in the data in the transition region. Data errors in this region also tend to broaden the bottom of the well in the residual hyperspace. Furthermore, the nature of (1) is to be continuous through the transition region, so that it cannot be expected to apply through an abrupt-transition region (see the further comments on this point in the Discussion); it was thus necessary to exclude points along the sharp rises for S and Se for the purpose of fitting (1) to the data. The S-shaped portions of the calculated curves in the abrupt region for S and Se (Figure 1) were plotted in the spirit of full disclosure, to emphasize to the reader the existence of this situation.

When the fitting was performed, μ_S and μ_Q were allowed free range, subject to upper and lower limits, respectively, of the lowest and highest of the observed μ values for each

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(1) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293. Gütlich, P. *Struct. Bonding* (*Berlin*) **1981**, *44*, 83.

(2) Edwards, M. P.; Hoff, C. D.; Curnutte, B.; Eck, J. S.; Purcell, K. F. *Inorg. Chem.*, preceding paper in this issue.

(3) Purcell, K. F.; Zapata, J. P. *J. Chem. Soc., Chem. Commun.* **1978**, 497. Bartholomew, C., unpublished data.

(4) König, E.; Madeja, K. *Inorg. Chem.* **1967**, *6*, 48.

(5) Chandler, J. C. "STEPIT", available from Quantum Chemistry Program Exchange, Indiana University (*QCPE* **1965**, *No. 66*).

(6) Slichter, C. P.; Drickamer, H. G. *J. Chem. Phys.* **1972**, *56*, 2142.

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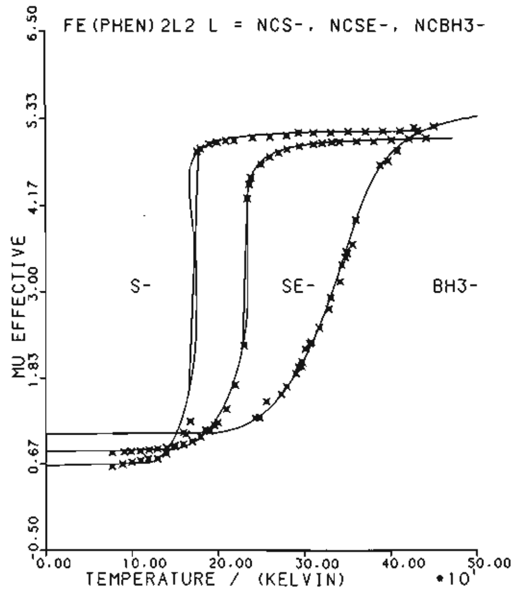

Figure 1. Experimental and calculated temperature dependence of μ_{eff} for Fe(phen)$_2$(NCE)$_2$, where E = S, Se, BH$_3$.

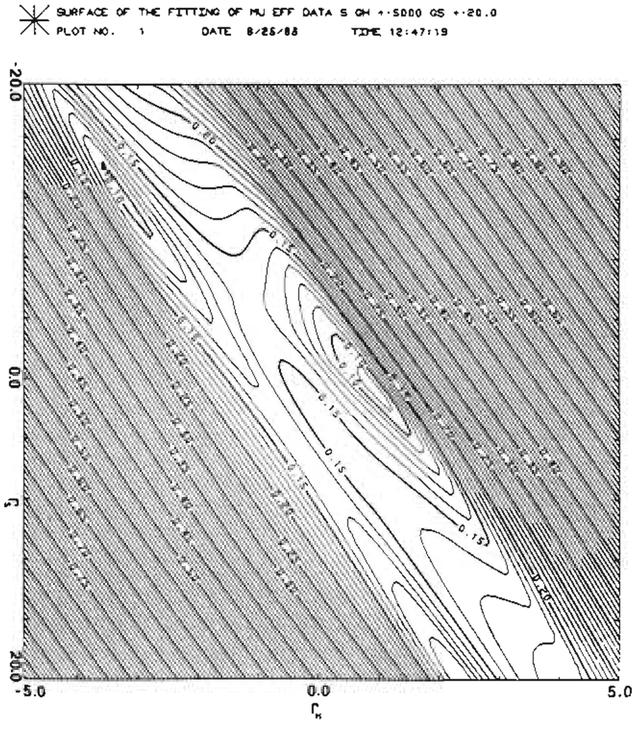

Figure 2. Residual contour map from the fitting of μ_{eff} for Fe(phen)$_2$(NCS)$_2$ by eq 1. The two variables are Γ_H (GH) and Γ_S (GS). Γ_H is in kcal/mol, and Γ_S is in eu.

compound; the other parameters were unrestricted in range. A multitude of starting values for the fit parameters and of convergence tightness and a variety of search control parameters were investigated for their effects on the final fit parameters. The results in Table I derive from the minimization of the residual until the variation in each parameter passed below 0.01% of the parameter. It was also useful to visually examine superimposed plots of calculated and observed $\mu(T)$ curves to arrive at the results in Table I.

To better understand the nature of the minimization process, contour maps of the residual surface were generated from the parameters in Table I. For each pair of variables the other four parameters were held fixed. Figure 2 contains the residual map for the Γ_H and Γ_S pair, as a sample of these surfaces. There is but one global minimum on each surface; local minima are also evident, but the search procedure could be controlled to successfully avoid them. To prove that the local minima were unsatisfactory, we were able to control the search process to force convergence at the local minima. Not only were the residuals larger than found for the global minimum but also superposition of calculated and observed $\mu(T)$ curves quickly convinced us of the unacceptibility of associated parameter sets. An additional value of such maps is that they give one an appreciation of the flatness of the global well.

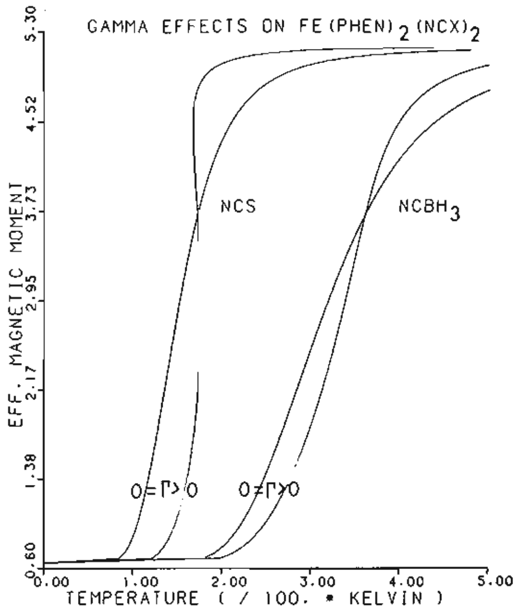

Figure 3. Calculation for the effect of temperature and Γ_c on the intersystem crossing. The value used for $\Gamma > 0$ is Γ_c of the S complex; the ΔH and ΔS values for both S and BH$_3$ complexes are used, respectively, for the low- and high-temperature curve pairs.

To establish the effects of Γ and T_c on the appearance of the μ vs. T curve, we show in Figure 3 curves computed as follows. With $\Gamma = 0$, the remaining four parameters (ΔH, ΔS, μ_S, μ_Q) for E = S produced one curve and a second is plotted with ΔH, ΔS changed to the E = BH$_3$ values. A second curve for each compound was generated by setting $\Gamma = \Gamma_c$ for the E = S values. These results illustrate how both low T_c and positive Γ enhance the suddenness of the transition and how increasing T_c moderates the role of Γ, making it necessary to separately account for these contributions to the transition sharpness. The effects of Γ and T_c are apparent in analytical form from (1), where it is seen that $\Gamma > 0$ suppresses K for $T < T_c$ and enhances K for $T > T_c$ and that the effect of increased T_c is to reduce the influence of Γ.

Models for Intermolecular Interactions and Lattice Continuity Effects

We wish to develop a general molecular level basis for (1) using concepts of intermolecular interaction energies and entropies, domain formation, and physical interruption of lattice uniformity. To maintain generality, the formulation is kept phenomenological in that it is not formulated a priori in terms of quantum-mechanical principles.

The most general formulation of the Gibbs energy for a sample of N_S singlet-state and N_Q quintet-state molecules is simply

$$G = G_{free} + G_{mix} + G_{inter} \qquad (4)$$

where G_{free} is the sample Gibbs energy associated with isolated molecule behavior and can be written

$$G_{free} = N_S g_S + N_Q g_Q \qquad (5)$$

in which g_i is the Gibbs energy/molecule. G_{mix} is the Gibbs energy (entropy) derived from maximization of ensemble probability

$$G_{\text{mix}} = kT \ln [N_Q^{N_Q} N_S^{N_S}/N^N] \qquad (6)$$

The term G_{inter} carries into the formulation all effects associated with cooperativity, lattice continuity, and domain formation and may be written

$$G_{\text{inter}} = I_{SS}g_{SS} + I_{QQ}g_{QQ} + I_{QS}g_{QS} \qquad (7)$$

where I_{ij} counts the number of ij molecular pairs and g_{ij} is the Gibbs energy of interaction for a molecular pair in intermolecular "contact" and, in a "first principles" treatment, it would be implicitly assumed that the g_{ij} values may be dependent upon I_{ij} through N_Q. Equilibrium for the ensemble is assumed to correspond to minimization of G with respect to N_Q:

$$\mathrm{d}G_{\text{free}}/\mathrm{d}N_Q = g_Q - g_S = \Delta g_{\text{free}} \qquad (8)$$

$$\mathrm{d}G_{\text{mix}}/\mathrm{d}N_Q = kT \ln K \qquad (9)$$

$$\mathrm{d}G_{\text{inter}}/\mathrm{d}N_Q = \sum_{ij}(I'_{ij}g_{ij} + I_{ij}g'_{ij}) \qquad (10)$$

with $I'_{ij} = \mathrm{d}I_{ij}/\mathrm{d}N_q$. It follows then that

$$kT \ln K + \Delta g_{\text{free}} + \mathrm{d}G_{\text{inter}}/\mathrm{d}N_Q = 0$$

and

$$RT \ln K = -\Delta G_{\text{free}} - \sum_{ij}[I'_{ij}G_{ij} + I_{ij}G'_{ij}] \qquad (11)$$

where (8)–(10) have been scaled by Avogadro's number.

Uncooperative Case. In the absence of intermolecular contacts $G_{ij} = 0$

$$RT \ln K = -\Delta G_{\text{free}} = -\Delta H_{\text{free}} + T(\Delta S_{\text{free}}) \qquad (12)$$

and

$$T_c = \Delta H_{\text{free}}/\Delta S_{\text{free}} \qquad (13)$$

and $R \ln K$ is linear in $1/T$. This is the situation for solution systems but does not generally apply to solids.

Cooperative Case. To develop an analytical form for G_{inter} one needs expressions for I_{ij} and G_{ij}. We will ignore the I dependence of G_{ij} (this prohibits the *prediction* of domain formation but not the incorporation of the domain concept into the general scheme). To obtain an expression for I_{ij}, we turn to statistical determination of the number of like- and unlike-pair contacts in the solid. Since the molecular packing of the molecules is unknown, we assume the molecules are arranged in chains of alternating Λ and Δ enantiomers, with "charge transfer contacts" between phenanthroline rings. This is the packing pattern for $\text{Fe(phen)}_3\text{I}_2\cdot\text{H}_2\text{O}$.[7] Further, we will ignore interchain interaction energies.

Assuming a temperature-independent molecular chain of length $\lambda = n_S + n_Q$ molecules, we select any of the $\lambda - 2$ nonterminal sites. The molecule at this site is of type i (i = S or Q). The probability (p_{ii}) for the same type molecule at an adjacent site is $2(n_i - 1)/(\lambda - 1)$, while that (p_{ij}) for an unlike molecule is $2n_j/(\lambda - 1)$. The probabilities (p_i) that the first molecule is of type S and Q, respectively, are n_S/λ and n_Q/λ.[8] Recognizing that there are $\lambda - 1$ possible "first" sites, that each pair should only be counted once, and that there are $\lambda - 1$ pairs possible, the following number of interchain contacts are derived:

$$p_S p_{SS} = n_S(n_S - 1)/\lambda \qquad p_Q p_{QQ} = n_Q(n_Q - 1)/\lambda$$
$$p_S p_{SQ} + p_Q p_{QS} = 2n_S n_Q/\lambda$$

The sum of pair contacts is $\lambda - 1$, as required. Considering the entire sample of L chains, the total number of SS, QQ, and SQ contact pairs is

$$I_{SS} = N_S(N_S - L)/N \qquad I_{QQ} = N_Q(N_Q - L)/N$$
$$I_{SQ} = 2N_S N_Q/N$$

where, as before, N_S and N_Q are the total numbers of singlet and quintet molecules in the N-molecule sample and there are $N - L$ intermolecular contacts. Minimization of I_{ij} with respect to N_Q yields

$$\sum_{ij} I'_{ij}G_{ij} = \Gamma'(1 - 2f_Q) - \Delta G_{QQ}(1/\lambda - 2f_Q) \qquad (14)$$

where $\Gamma' = 2\Delta G_{QS}$ and $\Delta G_{ij} = G_{ij} - G_{SS}$. Substitution in (11) gives the final results

$$RT \ln K = -\Delta G_{\text{free}} - \Gamma'(1 - 2f_Q) + \Delta G_{QQ}(1/\lambda - 2f_Q)$$

which can be arranged as

$$RT \ln K = -\Delta G_{\text{free}} - F(\Delta G_{QQ}) - \Gamma(1 - 2f_Q) \qquad (15)$$

$$\Gamma = 2\Delta G_{QS} - \Delta G_{QQ} \qquad 0 \leq F = (1 - 1/\lambda) \leq 1$$

and

$$T_c = [\Delta H_{\text{free}} + F(\Delta H_{QQ})]/[\Delta S_{\text{free}} + F(\Delta S_{QQ})] \qquad (16)$$

These general expressions show that the physical continuity of the lattice (λ) influences both the shape of the μ vs. T curve ($\ln K$) and T_c, so convincingly established by Hendrickson's group[9] for a series of Fe(III) compounds. Furthermore, sample-dependent curve shape and T_c require a significant distinction between Q:Q and S:S interactions, the magnitude of which in turn determines the range of λ over which lattice continuity effects will be observed. (15) is of the same form as the Slichter/Drickamer expression (1) used to fit the data.

Domain Case. A direct extension of the above formulation to the case of domain formation is possible with analogous results. Here we suppose the sample to consist of chains of domains, where λ becomes the chain length and n is the (fixed) number of molecules in a domain. There are now two contributions to G_{inter} to consider: intra- and interdomain interactions. The numbers of interdomain contacts are

$$I_{ii}^{\text{inter}} = d_i(d_i - 1)L/\lambda = D_i(D_i - L)/D$$

$$I_{ij}^{\text{inter}} = 2d_i d_j L/\lambda = 2D_i D_j/D$$

where $d_{i(j)}$ = the number of i (j) type domains in a chain, $D_{i(j)}$ is the number of i (j) type domains in the sample of D total domains, and L is the number of chains. For the intradomain contacts

$$I_{ii}^{\text{intra}} = (n - 1)D_i$$

Note that a distinction must be made between g_{ij} values within and between domains because the electric and/or magnetic fields at the domain boundaries are necessarily quite different from those responsible for intermolecular interaction within a domain; the ΔG^D terms below arise from the interdomain g_{ij}. Minimization of the Gibbs energy with respect to the number of Q domains (D_Q) gives (taking care to note that G_{mix} is defined by domains)

$$RT \ln K = -n(\Delta G_{\text{free}}) - (n - 1)\Delta G_{QQ} - 2\sigma(\Delta G_{QS}{}^D)(1 - 2f_Q) + \sigma(\Delta G_{QQ}{}^D)(1/\lambda - 2f_Q)$$

or

$$RT \ln K = -n(\Delta G_{\text{free}}) - (n - 1)\Delta G_{QQ} - \sigma F(\Delta G_{QQ}{}^D) - \Gamma(1 - 2f_Q) \qquad (17)$$

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(7) Johansson, L.; Molund, M.; Oskarsson, A. *Inorg. Chim. Acta* **1978**, *31*, 117.

(8) These forms for the p_i values ignore "end effects", which is valid as long as $\lambda >> 1$. The more traditional way to ignore "end effects" is to assume rings (closed chains) of λ molecules, for which case the p_i values are rigorous; in this case, $\lambda - 1$ replaces λ in the $p_i p_{ij}$ formulas and the sum over pair contacts becomes λ.

(9) Haddad, M. S.; Federer, W. D.; Lynch, M. W.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1980**, *102*, 1468; *Inorg. Chem.* **1981**, *20*, 123, 131.

Table III. Summary of Parameter Interpretations and Relations

$$RT \ln K = -\Delta H + T\Delta S + \Gamma_H(1 - 2f_Q) - T\Gamma_S(1 - 2f_Q)$$
$$T_c = \Delta H/\Delta S$$

parameter	model			
	isolated domains	contact domains	coop	uncoop
ΔH	$n(\Delta H_{free}) + (n-1)\Delta H_{QQ}$	$n(\Delta H_{free}) + (n-1)\Delta H_{QQ} + \sigma F(\Delta H_{QQ}{}^D)$	$\Delta H_{free} + F(\Delta H_{QQ})$	ΔH_{free}
ΔS	$n(\Delta S_{free}) + (n-1)\Delta S_{QQ}$	$n(\Delta S_{free}) + (n-1)\Delta S_{QQ} + \sigma F(\Delta S_{QQ}{}^D)$	$\Delta S_{free} + F(\Delta S_{QQ})$	ΔS_{free}
Γ_H	0	$\sigma[2(\Delta H_{QS}{}^D) - \Delta H_{QQ}{}^D]$	$[2(\Delta H_{QS}) - \Delta H_{QQ}]$	0
Γ_S	0	$\sigma[2(\Delta S_{QS}{}^D) - \Delta S_{QQ}{}^D]$	$[2(\Delta S_{QS}) - \Delta S_{QQ}]$	0

$$\xleftarrow[\lambda = 1,\, \sigma = 0]{\qquad} \quad \xrightarrow[n = 1,\, \sigma = 1]{\qquad} \quad \xrightarrow[\lambda = 1,\, \Delta G_{ij} = 0]{\qquad}$$

where $\Gamma = \sigma(2\Delta G_{QS}{}^D - \Delta G_{QQ}{}^D)$ and $F = (1 - 1/\lambda)$ and σ counts the number of interdomain pair contacts at the domain interface. For T_c

$$T_c = \frac{\Delta H_{free} + [(n-1)/n]\Delta H_{QQ} + [\sigma F/n]\Delta H_{QQ}{}^D}{\Delta S_{free} + [(n-1)/n]\Delta S_{QQ} + [\sigma F/n]\Delta S_{QQ}{}^D} \tag{18}$$

Expression 17 is also of the form (1), and (17) and (18) correctly reduce to those of (15) and (16) when n goes to unity (one molecule per domain). Also note that curve shape and T_c can be sensitive to λ; when $\lambda = 1$ (isolated domains), the domain contact energies do not affect either T_c (because $F = 0$) or $\ln K$ (because $\sigma = 0$).

Interrelation of Models. Since the domain case expressions for $\ln K$ (eq 17) and T_c (eq 18) reduce to the corresponding expressions for the cooperative and uncooperative cases with appropriate n, σ, λ values, it is possible to write all of them in the form (1). This is convenient for data-fitting purposes, but it is also unfortunate in the sense that to distinguish between cases requires additional information for interpretation of ΔG and Γ. Specifically

$$RT \ln K = -\Delta H + T(\Delta S) - (\Gamma_H - T\Gamma_S)(1 - 2f_Q) \tag{19}$$

$$T_c = \Delta H/\Delta S \tag{20}$$

The interpretations of each of the four thermodynamic terms for domain, cooperative, and uncooperative cases are outlined in Table III.

Of considerable interest is the sharpness of the transition, which can be measured in terms of the temperature dependence of $\ln K$ or f_Q at T_c. Differentiation of $\ln K$ with respect to $1/T$ leads to an expression for the rate of change with reciprocal temperature of f_Q

$$\frac{df_Q}{d(1/T)} = \frac{[(-\Delta H - \Gamma_H(1 - 2f_Q))f_Qf_S]}{R[1 - 2\Gamma f_Qf_S/RT]} \tag{21}$$

which is negative at all temperatures not equal to T_c. Slichter and Drickamer have noted that at T_c two situations may occur, depending on whether f_Q is a continuous or discontinuous function of T. For the continuous case, and at T_c, it is required that Γ_c is less than or greater than $2RT_c$, depending on whether the numerator of (21) is less than or greater than 0. Discontinuous $\ln K$ behavior at T_c results from nonadherence of Γ to the appropriate inequality. For example, with the numerator of (21) <0, abrupt transitions are expected when $\Gamma/2RT_c \geq 1$.

As a summary of the implications of the contents of Table III for $\ln K(1/T)$ and T_c, we give the following comments as useful:

(i) Both domain and cooperative cases exhibit nonlinear $R \ln K(1/T)$ behavior, through the f_Q terms, as long as $\Gamma^{(D)} \neq 0$.

(ii) Chain-length effects arise through ΔH and ΔS.

(iii) $\ln K$ is chain length dependent as long as $\Delta G_{QQ}{}^{(D)} \neq 0$. This inverse dependence on λ is such that shorter chains favor the quintet molecules when $\Delta G_{QQ}{}^{(D)} > 0$ and disfavor them when $\Delta G_{QQ}{}^{(D)} < 0$. These biases are temperature dependent and accommodate Hendrickson's results at low and high temperatures when $\Delta H_{QQ}{}^{(D)}$ and $\Delta S_{QQ}{}^{(D)}$ are both >0. The crossover in bias occurs at a temperature given by $\Delta H_{QQ}{}^{(D)}/\Delta S_{QQ}{}^{(D)}$ and of unknown relation to T_c.

(iv) T_c differs from its "free molecule" value through nonzero $\Delta G_{QQ}{}^{(D)}$ terms and can show a chain-length dependence. This dependence has the effect of shifting T_c from its free-molecule value to the temperature at which $\Delta G_{free} = -[(n - 1)/n]\Delta G_{QQ} - (\sigma F/n)\Delta G_{QQ}{}^D$ (domain case) $= -F(\Delta G_{QQ})$ (cooperative case). The sensitivity of T_c to λ is complex:

$$\frac{dT_c}{d\lambda} = \frac{\Delta H_{QQ} - T(\Delta S_{QQ})}{\lambda^2[\Delta S_{free} + F(\Delta S_{QQ})]}$$

(v) The question as to the conditions for experimental observation of the chain length-dependent terms in (15) and (17) derive from

$$F \doteq (1/\sigma)|\sigma(2R_{QS}{}^{(D)} - 1)(1 - 2f_Q) + nR_{free} + (n - 1)R_{QQ}{}^{(D)}|$$

where $R_{free} = \Delta G_{free}/\Delta G_{QQ}{}^{(D)}$ and

$$R_{QS}{}^{(D)} = \Delta G_{QS}{}^{(D)}/\Delta G_{QQ}{}^{(D)} \qquad R_{QQ}{}^{(D)} = \Delta G_{QQ}/\Delta G_{QQ}{}^{(D)}$$

Two temperature regions are to be distinguished: At T_c

$$F \doteq (n/\sigma)|R_{free} + ((n - 1)/n)R_{QQ}{}^D| \quad \text{(domain)}$$
$$\doteq |R_{free}| \quad \text{(cooperative)}$$

For both domain and cooperative cases these conditions reduce to $F \doteq F$ and are always met! Far from T_c ($f_Q = 0, 1$)

$$F \doteq (n/\sigma)|R_{free} \pm (\sigma/n)(2R_{QS}{}^D - 1) + ((n - 1)/n)R_{QQ}{}^D| \quad \text{(domain)}$$
$$\doteq |R_{free} \pm (2R_{QS} - 1)| \quad \text{(cooperative)}$$

These last conditions are likely to be met when ΔG_{free} is small, and in particular when the singlet/quintet energy gap is small.

(vi) Regarding the shape of $\ln K(1/T)$ we observe the following. For the uncooperative case, $\lambda = 1$ and $(f_Q')_{T_c} = -\Delta H_{free}/4R$ (the normal free-molecule result). For the cooperative and domain continuous cases, a chain length dependence for $(f_Q')_{T_c}$ appears through ΔH; the dependence is inverse in λ and serves to decrease $|(f_Q')_{T_c}|$ when $\Delta H_{QQ}{}^{(D)} > 0$. This result, like that in (iii), agrees with Hendrickson's findings.

(vii) When f_Q' is defined in the transition region, and only under certain limits, (21) permits a connection to be established between the domain size and Γ. With $\lambda = 1$ or ΔH_{QQ} and $\Delta H_{ij}{}^D$ very small (very weak domain-forming forces; $\Gamma^D = 0$), $(f_Q')_{T_c}$ for the domain case takes the value $-n(\Delta H_{free})/4R$. Equating the expressions for $(f_Q')_{T_c}$ for the cooperative and domain cases produces the result

$$n_c = (1 - \Gamma_c/2RT_c)^{-1}$$

This interconnection between physical models, proposed earlier by Gütlich,[10] is thus seen to be applicable only in the limit of feeble domain formation and is not generally valid. Specifically, it cannot be applied with physical significance to solids exhibiting discontinuous behavior ($\Gamma_c/2RT_c > 1$), for which n_c becomes <0.

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(10) Gütlich, P.; Koppen, H.; Link, R.; Steinhauser, H. G. *J. Chem. Phys.* **1979**, *70*, 3977.

Discussion

The findings of Figure 3 regarding the complementary roles of Γ and T_c have special meaning in the context of eq 21. The factor $\Gamma_c/2RT_c$ is a logical choice for the indicator of cooperativity in singlet/quintet transitions. For the $Fe(phen)_2(NCE)_2$ series this cooperativity factor, *C*, decreases in the order S (1.25) > Se (1.06) > BH_3 (0.52), and the discontinuous behaviors of the S and Se compounds correctly appear through $C > 1$. In the weak domain limit, *C* for the BH_3 compound corresponds to a "domain size" of about two molecules; the *C* factors for the S and Se compounds (both >1) preclude determination of n_c from the magnetic data. Invoking the equivalent of the isolated-domain limit ($\lambda = 1$) at T_c, Sorai and Seki[11] extracted from their heat capacity data n_c values of 95 and 77 for the S and Se molecules, respectively.

Consideration of the inversion symmetry properties about $f_Q = {}^1/_2$ at $T = T_c$ of the left- and right-hand sides of the transcendental equation (19) (see Figure 9 and the accompanying discussion in ref 6) allows one to examine properties of the three roots of f_Q which arise when $T = T_c$ in abrupt-transition cases ($C > 1$). In addition to $f_Q = {}^1/_2$ (which corresponds to a Gibbs energy maximum), there are two symmetrically disposed, isoenergetic Gibbs minima, at f_{Ql} and f_{Qh}, for example, which satisfy $f_{Qh} = 1 - f_{Ql}$. $\Delta f_Q = f_{Qh} - f_{Ql}$ obeys the relation

$$C = \frac{1}{2(\Delta f_Q)} \ln \frac{1 + \Delta f_Q}{1 - \Delta f_Q}$$

which in the limit of $\Delta f_Q \rightarrow 0$ correctly reproduces the inequality $C \geq 1$ for discontinuous transitions. This relation is of interest because it allows calculation of Δf_Q for the S and Se compounds: 0.8 and 0.2, respectively.

Regarding Γ_c, the differential intermolecular interaction energies fall in the order Se > S > BH_3. The Se, S order is interesting in that it is reminiscent of the effects of heavy atoms on organic–metal intermolecular interactions. While a rigorous relationship is not apparent at this time, the connection between Γ_c and solid-state conductivity will be interesting to explore.

The values of ΔH and ΔS for the S and Se compounds are in good agreement with the values (2.06, 11.7 and 2.77, 12.2) extracted by Sorai and Seki, suggesting the heat capacity maximum is insensitive to Γ_c. From Table III, the values of ΔH are not, strictly speaking, to be taken as values of ΔH_{free}, even in the isolated domain limit. Clearly, with $\Delta H_{free} > 0$ and $\Delta H/n_c$ about 0.03 kcal/mol for the S and Se molecules, their Q:Q interaction is more exothermic than their S:S interaction and the singlet/quintet energy gaps are comparable to the differential Q:Q and S:S intermolecular interaction energies. The ΔH value for the BH_3 compound indicates that its quintet/singlet energy gap is larger, and/or that the differential Q:Q, S:S interaction energy correction is smaller than for its analogues. The latter could be due to smaller *F* or smaller ΔH_{QQ}. We have no estimate of *F*, but there is independent evidence that the energy gap is larger[12] and that the ligands are not rigidly constrained by intermolecular forces in the transition region.[2,13]

That the ΔS values for all three compounds are at least 2 times larger than expected on the basis of electronic state degeneracy factors alone clearly reflects significant changes in both intra- and intermolecular contributions to the vibrational partition functions. This has been discussed by Sorai and Seki, as well as others.

The Γ_H and Γ_S values suggest less attractive, more constrained S:Q than Q:Q interactions. For a cooperative class system the Γ_H terms are compatible with a view of reduced S:Q intercomplex ligand "charge transfer" interactions or simply increased steric congestion due to the radial expansion associated with a quintet molecule relative to its singlet structure ($\Delta H_{QS} > 0$). An additional contribution to $\Gamma_H > 0$ may be that of an attractive magnetic interaction between quintet molecules ($\Delta H_{QQ} < 0$). Interestingly, Γ_H is lower for the BH_3 compound than for its analogues, a result that is also consistent with less rigid lattice forces (see the end of the ΔH paragraph above).

Similarly, the Γ_S terms are of critical importance to the fitting of the experimental line shapes. When weighted by *T*, they can significantly reinforce the Γ_H contributions to the cooperativity (for BH_3, in fact, $-T_c\Gamma_S > \Gamma_H$). The negative values of these parameters could arise from either or both of nearest-neighbor S:Q steric constraint ($\Delta S_{QS} < 0$) and reduced lattice vibrational frequencies for the quintet lattices ($\Delta S_{QQ} > 0$). The sign of Γ_S for *S* requires reversal of these signs.

Returning to the cooperativity factors *C*, we note (Table II) that the variation in *C* for these three compounds reflects less the variation in Γ_c than in T_c, which itself derives from the variation in ΔH. Thus, for this series of compounds, it is the variation in ΔH that determines the variation in *C*, and not some pronounced variation in Γ. In view of the molecular structure similarity of the three compounds and the small differential interaction energies in general, it is perhaps more reasonable to view the low *C* of the BH_3 compound as due to a larger quintet/singlet gap than to a marked change in ΔH_{QQ}. In this vein, our recent characterization[2] of the BH_3 compound as a species that undergoes dynamic intersystem crossing in the transition region is a result not primarily due to weak intermolecular forces but is a consequence of the high transition temperature associated with a "large" singlet/quintet energy gap. An even larger gap is presumably the reason for the lack of an intersystem crossing transition for the BPh_3 analogue in the solid state[3] (the molecular packing for this compound may differ significantly from that of its analogues, reducing the intermolecular interaction energies[14]). Now that this emphasis has been given to the role of ΔH in the transition sharpness, it is important that the role of ΔS of the transition should not be understated. Were ΔS due to electronic degeneracy factors only ($\Delta S = 5$ eu), none of the compounds would exhibit an abrupt transition!

We have saved mentioning until last a point of some interest. This concerns the expected sign of Γ_H for the domain case. The formation of finite domains of singlet and quintet sites within the lattice depends on the existence within and at the domain boundaries of electromagnetic fields which confer on internal and adjacent molecules the same and opposite "states", respectively. It thus seems necessary that $\Delta H_{QS}{}^D$ be negative; perhaps naively, $\Delta H_{QQ}{}^D$ is expected to be positive, and therefore $\Gamma_H{}^D < 0$. This is not the sign found for the S and Se compounds, which are reported to be domain cases. We tentatively conclude that the S and Se compounds do not form as lattices containing both singlet and quintet domains in contact; rather, the crystallites may individually define "domains" of pure singlet or pure quintet molecules. Note, however, that such "isolated domains" are expected to have $\Gamma_H = \Gamma_S = 0$. We are continuing our study of this aspect of

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(14) In ref 3 it is noted that the intersystem crossing for the BPh_3 complex is rapid below room temperature in CH_2Cl_2 solution. We presume at this time that the marked difference in solid and solution behavior is due to solvent interactions with the donor N atoms. For an example of *donor* solvent hydrogen bonding to ligand NH groups, to *increase* ligand basicity, see: Sinn, E.; Sim, G.; Dose, E. V.; Tweedle, M. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3375. Katz, B. A.; Strouse, C. E. *Ibid.* **1979**, *101*, 6214.

the intersystem crossing in solids to explore the relationship of Γ in (1) to the distribution of individual crystallite (or domain) size.[15]

Summary

A treatment of the thermodynamics of the intersystem crossing from the postulation of intermolecular enthalpies and entropies of interaction provides a basis for the definition of a cooperativity factor, $C = \Gamma_c/2RT_c$, and for the effects of lattice continuity (1) on transition completeness, (2) on T_c, and (3) on the sharpness of the intersystem crossing transition. The visually immediate diagnostics of "cooperativity", curve shape and position, are very sensitive functions of ΔH, ΔS, and Γ, and it is through the former that lattice continuity effects operate. The analytical expressions of these effects have yet to be subjected to quantitative experimental test but are of the correct qualitative form.

By investigating in detail the thermally induced intersystem crossing transitions in the $Fe(phen)_2(NCE)_2$ series with E = S, Se, BH_3, we have determined that comparable intermolecular interactions and lattice phonon contributions to the transitions are exhibited by all three compounds. The pronounced differences in cooperativities appear to be determined by the singlet/quintet energy gaps. For the BH_3 member, indications are that the intersystem crossing is effected on an individual molecule basis, in sharp contrast to the case for its S and Se analogues.

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Registry No. *cis*-$Fe(phen)_2(NCBH_3)_2$, 62561-27-7; *cis*-$Fe(phen)_2(NCBPh_3)_2$, 68581-81-7; *cis*-$Fe(phen)_2(NCS)_2$, 15319-93-4; *cis*-$Fe(phen)_2(NCSe)_2$, 53447-28-2.

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Core Photoelectron Emission Study of Binary and Ternary Indium Chlorides. Metal Binding Energy as a Function of Oxidation State and Other Parameters

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Binding energies for indium d and chlorine p core and valence levels are reported for $InCl_n$ (n = 1, 1.5, 1.8, 2, 3), $Cs_3In_2Cl_9$, PCl_4InCl_4, $Rb_2LiInCl_6$, $Cs_2InInCl_6$, and InY_2Cl_7. Data secured by using a C 1s calibrant from either the mounting tape or admixed graphite are consistent for the reduced phases but show variations of 1.5 eV in In 3d binding energy for $InCl_3$ and a 1.1-eV range among the indium(III) compounds mounted on tape. The spectra contain no evidence for the presence of mixed oxidation states, in spite of an apparent 2–3-eV increase in In binding energy within the binary chlorides. Differential charging of insulating phases with respect to tape or graphite standards (e.g., $InCl_3$ and $Cs_3In_2Cl_9$) together with unpredictable variations of the fundamental Fermi level reference appear responsible for most of the observed shifts and probably affect many other data in the literature. Some inferred Fermi level changes correlate well with differences in valence-band spectra, color, coordination number, and distances about indium(I), e.g., for InCl vs. InY_2Cl_7. The internally referenced binding energy In $3d_{5/2}$ – Cl $2p_{3/2}$ is essentially invariant (±0.3 eV) for all compounds studied, and similar results are obtained with published data for indium and antimony halides. This invariancy with oxidation state and the contrasting increases in metal binding energies in simple transition-metal systems appear to reflect the effect of both radius and Fermi level changes. In particular, a significantly greater decrease in metal radius on oxidation in some posttransition $d^{10}s^2/d^{10}$ systems is probably important in counteracting the expected increase in binding energy in most cases. Some instances of negative binding energy shifts on oxidation of s^1 or s^2 metals are also considered.

Introduction

The utility of core photoelectron spectroscopy[3–5] with X-ray excitation (XPS) in the characterization of inorganic compounds shows a marked dependence on both the state of the material and the nature of the element examined. The light and small non-metals with sizable ranges of oxidation states and inductive (polarization) effects in their compounds exhibit therewith relatively large chemical shifts. Furthermore, binding energies in individual compounds can often be measured particularly well in the gas phase where intermolecular effects are absent and referencing to the vacuum level is straightforward. Shifts in measured binding energies of core electrons then reflect changes in valence orbital and charge distributions, and significant correlations with other parameters or theory may be possible. Electronic relaxation elsewhere in the molecule in response to the creation of the core hole, reducing the ionization energy below that for the vertical process, may not be an important factor in many comparisons although it is still apt to be significant in an absolute sense.

On the other hand, metal ions are characteristically larger, and their core binding energies generally shift more slowly with charge or oxidation state. Moreover, the study of metal compounds often requires that the measurements be made on solids, and then additional factors must be recognized. The

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