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Contribution from the Department of Chemistry,
Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

VTFTIR and Light-Induced Excited Spin State Trapping in $\mathrm{Fe(2,2'\text{-}bpy)_2(SCN)_2}$ and Related Spin-Crossover Compounds

Rolfe H. Herber

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The spin-crossover behavior of a number of ferrous complexes has been studied by using variable-temperature Fourier transform infrared spectroscopy by following the characteristic absorptions of the CN stretching mode of the SCN ligand of such complexes. The observed value of T_1, the thermally driven HS → LS transition in samples mulled in Kel-F grease, is in good agreement with data extracted from specific heat or magnetic susceptibility data. The gradual HS → LS transition in $\mathrm{Fe(2,2'\text{-}bpy)(SCN)_2}$ is shown to be both qualitatively and quantitatively different from the sudden spin transition in $\mathrm{Fe(2,2'\text{-}bpy)_2(SCN)_2}$. The phenomenon of light-induced excited spin state trapping (LIESST) has been demonstrated in a number of Fe(II) complexes. The transition temperature, T_2, at which the (trapped) HS spin state is reconverted to the LS configuration has been determined, and a correlation between T_1 and T_2 for compounds undergoing a first-order crystallographic phase transition between the two spin states is suggested.

The phenomenon of spin-crossover in compounds of the first transition series with d^4 to d^7 electron configurations is a well-studied phenomenon and has been thoroughly reviewed in the literature.[1,2] In particular, a number of Fe(II) complexes have been examined in great detail by Konig et al.[3] and by Gutlich and his co-workers,[4-6] using magnetic susceptibility, heat capacity, crystallographic, and ^{57}Fe Mössbauer spectroscopic techniques. It was in connection with a Mössbauer study of $\mathrm{[Fe(ptze_6](BF_4)_2}$ that Gutlich et al.[7,8] observed the conversion of the low-spin (LS) form of this complex at temperatures below ~50 K to a "trapped" high-spin (HS) form, on irradiation of the sample with white light. This conversion has been termed[8] "light-induced excited spin state trapping" (LIESST), and can be monitored—albeit somewhat laboriously—by ^{57}Fe Mössbauer spectroscopic techniques. The trapped HS form is stable indefinitely at temperatures below ~50 K but is reconverted to the LS form (the stable form at low temperature) when the sample is warmed to ~80 K.

In a recent detailed study[9] of the variable-temperature Fourier transform infrared (VTFTIR) spectra of the spin-crossover compound $\mathrm{Fe(phen)_2(SCN)_2}$, it was possible to show that VTFTIR methods are particularly appropriate for the study not only of the spin-crossover phenomenon but, especially, of the LIESST phenomenon in such complexes. In the present study, variable-temperature infrared measurements have been carried out on the spin-crossover complex $\mathrm{Fe(2,2'\text{-}bpy)_2(SCN)_2}$ (I) and the related polymer $\mathrm{Fe(2,2'\text{-}bpy)(SCN)_2}$ (II) reported by Reiff et al.,[10,11] as well as on a number of related ferrous iron systems, in order to elucidate the correlation between the characteristics of the spin-crossover phenomenon and the LIESST conversion at low temperature.

Experimental Section

(a) Preparation of the Complexes. The ferrous complexes used in the present study were prepared by using literature methods and were characterized by elemental analysis and IR and Mössbauer spectroscopic techniques, as appropriate. $\mathrm{Fe(2,2'\text{-}bpy)_2(SCN)_2}$ (I) was prepared by using the method of Burstall and Nyholm[12] to yield reddish single crystals of $\mathrm{[Fe(2,2'\text{-}bpy)_3](SCN)_2}$, which, after a 20-h reflux in methylcyclohexane under inert atmosphere, gave the desired product in good yield.

The polymeric complex $\mathrm{Fe(2,2'\text{-}bpy)(SCN)_2}$ (II), described by Dockum and Reiff,[10] was generously made available by Prof. Reiff and used without further sample treatment.

$\mathrm{Fe(py)_4(SCN)_2}$ (III), first described by Grossmann and Hunseler,[13] was obtained by using the method of Spacu et al.,[14,15] which yielded only the yellow form of the complex. Anal. Found (calcd): C, 54.29 (54.05); H, 4.03 (4.13); N, 17.22 (17.21). This material, which is sensitive to air oxidation, was maintained under vacuum at room temperature until further examined by VTFTIR methods or was used in further synthetic steps (vide infra). The identification of the yellow complex as having the trans, N-bonded NCS configuration has been reported by Erickson and Sutin[14a] on the basis of systematic ^{57}Fe Mössbauer studies. These authors also concluded that the violet form, prepared by recrystallizing the yellow form from $\mathrm{CHCl_3}$, was in fact an impure sample of (III) containing traces of a ferric iron impurity.

$\mathrm{Fe(py)_2(1,10\text{-}phen)(SCN)_2}$ (IV) was obtained by adding to a pyridine solution of III, cooled to 0 °C, a stoichiometric amount of 1,10-phenanthroline dissolved in pyridine, and stirring this for 15 h at 0 °C under inert atmosphere. The resulting purple solid was separated by filtration, washed with cold pyridine, methyl alcohol, and ether, and dried at room temperature under vacuum. Anal. Found (calcd): C, 56.64 (56.43); H, 3.62 (3.55); N, 16.31 (16.53).

$\mathrm{Fe(phen)_2(SCN)_2}$ (V) was obtained by refluxing $\mathrm{[Fe(phen)_3](SCN)_2}$ in acetonitrile as discussed earlier.[9] The corresponding $\mathrm{Fe(phen)_2(SeCN)_2}$ (VI) was obtained similarly from the corresponding precursor.

(b) Infrared Studies. Initial infrared characterization of the subject compounds was effected by preparing ~0.5–1% by weight samples in KBr by using the usual pelleting techniques and examining these samples over the appropriate temperature range by using the low-temperature cell and spectrometer described previously.[9,16] As noted in the earlier study of $\mathrm{Fe(phen)_2(SCN)_2}$, the details of the HS = LS spin conversion are sensitive to the conditions of sample preparation, and in particular, the temperature of the spin crossover is strongly influenced by the pelletizing technique. Similar observations in the ^{57}Fe Mössbauer experiments of Gutlich et al. have been reported in detail.[5] In the present instance, these difficulties can be overcome by taking advantage of the fact that the characteristic change in the infrared signature of the HS and LS forms of the SCN-containing crossover compounds involves the CN stretch, which is normally found in a region of the IR spectrum (2150–2000 $\mathrm{cm^{-1}}$) that is free of interfering absorbances. Consequently, the detailed spin-crossover characteristics of the sample compounds were examined by using mulls of these materials in Kel-F grease (3 M Co.) since this dispersant is transparent in the critical spectral region. As will be evident below, this mulling procedure avoids the distortion of the crossover tem-

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Table I. Summary of Data

compound	ν_{CN} (300 K) (HS form), cm^{-1}	T_1,[a] K	T_2,[b] K	$10^2(d\nu_{CN}/dT)$, cm^{-1} K^{-1}	T interval for linear regression, K
Fe(2,2′-bpy)$_2$(SCN)$_2$ (I)	2068, 2061	208 (c)	63.2	HS: −1.8, +0.54	210–303
		210 (w)		LS: −1.8, 0	170–205
Fe(2,2′-bpy)(SCN)$_2$ (II)	2113, 2083			−2.1, −2.3	80–210
Fe(py)$_4$(SCN)$_2$ (III)	2068, 2064			−1.7	150–280
Fe(py)$_2$(phen)(SCN)$_2$ (IV)	2075, 2058	91 (inc)	~47		
Fe(phen)$_2$(SCN)$_2$ (V)	2073, 2062	176.3	55	HS: −1.28 −0.77	170–303
				LS: −0.45, −0.07	80–170
Fe(phen)$_2$(SeCN)$_2$ (VI)	2073, 2063	231.3	29	HS: −0.79	204–305
				LS: −1.35	180–200

[a] Key: (c) cooling, (w) warming, (inc) incomplete. T_1 is the estimated transition temperature for the thermally driven LS ⇌ HS transition of the unirradiated sample. (b) T_2 is the estimated transition temperature for the thermally driven trapped HS → LS transition of the irradiated sample.

perature inherent in the pelletizing process used earlier and commented on by one of the reviewers as noted.[9] In the experiments discussed below these mulled samples were sandwiched between two neat KBr pellets and clamped in the Invar sample cell discussed earlier,[16] and then examined over the appropriate temperature range.

The temperature dependence of the CN stretch band center was determined to a precision of ~0.02 cm^{-1} by fitting the intensity vs. frequency data in the well-isolated CN stretching absorption region by a second-order polynomial-fitting routine[17] (POLYCALC), making the assumpting that the absorbance vs. frequency data are reasonably well fitted by an equation of the form

$$A_{CN} = a_0 + a_1\nu + a_2\nu^2 \qquad (1)$$

The band center was calculated by setting the first derivative of this function to zero. The sample temperature was controlled by a proportional feedback heating circuit coupled to a thermocouple attached to the cold finger of the sample cell. The sample temperature was monitored, in turn, by two Au(Fe)–chromel thermocouples directly attached to the sample cell, as described earlier.

In a typical infrared spectrum, 100 interferometer scans were coadded, and ratioed to a background acquired by using a blank KBr disk in the sample compartment. After the appropriate controller change (typically 10 deg or less), sufficient time was allowed for the system to reach thermal equilibrium before acquisition of the next data point. For the LIESST experiments, two sources of sample illumination were controlled in these experiments. Earlier studies had shown that the 0.5-mW He/Ne laser (632 nm) used to generate the interference pattern in the spectrometer is capable of optically pumping LS Fe(phen)$_2$(SCN)$_2$ to the HS form at ~8 K. To monitor this effect in the present study, a blue filter, which permits passage of the IR beam through the sample but efficiently reduces the transmission of the He/Ne laser line, could be interposed in the sample beam. Removal of this blue filter under controlled conditions permitted the study of optical pumping by 632 nm radiation. White light irradiation in situ at low temperatures was effected by transmission of radiation from an external incandescent (W filament) light source through a fiber optic cable, into the sample compartment of the spectrometer. The length of time of this irradiation was controlled by the interposition of an absolute shutter between the source and the admittance end of the fiber optic cable.

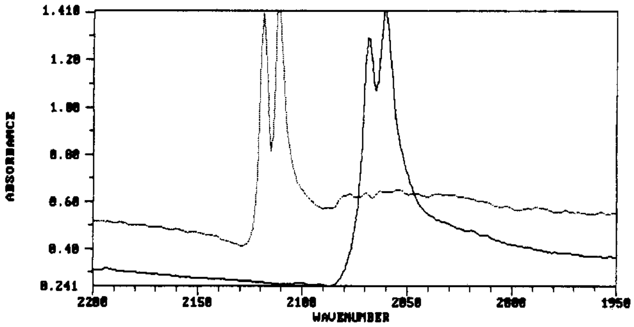

Figure 1. Portion of the infrared absorbance spectrum (2200–1950 cm^{-1}) of Fe(2,2′-bpy)$_2$(SCN)$_2$ [I] showing the C≡N stretching mode of the high-spin (HS) and low-spin (LS) forms of the complex at 300 (solid line) and 80 K (dotted line), respectively.

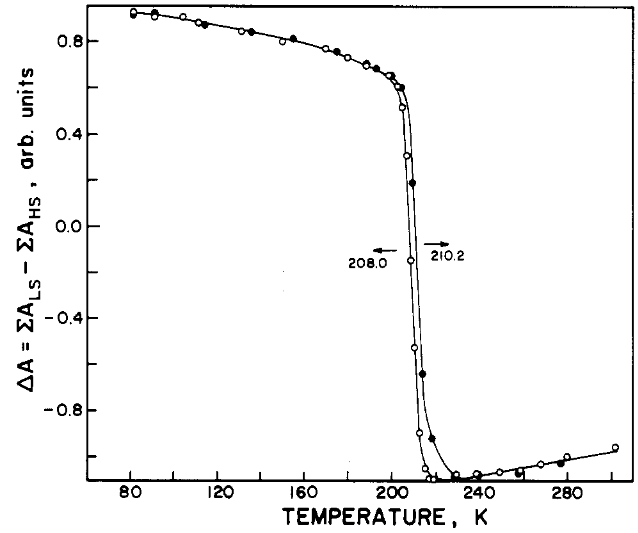

Figure 2. Temperature dependence of ΔA for I. The open circles reflect the data for the cooling portion of the cycle, and the filled circles represent the data for the warming portion. A hysteresis width of ~2 deg (characteristic of a first-order phase transition) is to be noted in these data.

Results and Discussion

(a) Fe(2,2′-bpy)$_2$(SCN)$_2$. The infrared spectrum of I has been discussed in some detail by Konig et al.,[3] who noted the significant spectral differences between the room-temperature and liquid-nitrogen-temperature forms, especially in the CN stretching mode region. In the present study, the two HS absorbances were observed at 2068 and 2061 cm^{-1}, and the coresponding LS absorptions at 2119 and 2111 cm^{-1} at 300 and 80 K, respectively. A portion of the infrared spectrum, covering the range 2200–1950 cm^{-1} is shown in Figure 1, in which the CN stretching mode of the HS and LS form of I are shown superimposed on the same wavelength scale. To follow the HS = LS conversion it is useful to determine the differences between the sum of the LS absorbances and the HS absorbances at each temperature, and this quantity is referred to as ΔA in the following discussion; that is, $\Delta A = \sum A_{LS} - \sum A_{HS}$. In the case of I, $\Delta A(T) = \{[A(2119) + A(2111)] - [A(2068) + A(2061)]\}$, and a similar convention will be employed for the other compounds discussed in the present study. A plot of ΔA for I is shown for the Kel-F mull sample in Figure 2 in which the open circles reflect the data during a cooling cycle and the filled circles represent the corresponding data for a warming cycle. Due to the usual sharpening of IR bands on sample cooling, as well as the fact that the ^{13}C component of the LS CN stretch absorption lies under one of the components of the HS absorption, the temperature at which the HS = LS conversion is half-complete does not correspond to a ΔA value of zero but is more appropriately defined by the temperature at which ΔA is the mean between the high-temperature and low-temperature limiting values. For I, this temperature is observed at 208 ± 1 K on cooling and 210 ± 1 K on warming. The apparent hysteresis of 2 deg is consistent with the first-order nature of the HS = LS transition, and the cited values are in reasonable

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(17) The author is indebted to D. Shombert for making a working version of this software available prior to release.

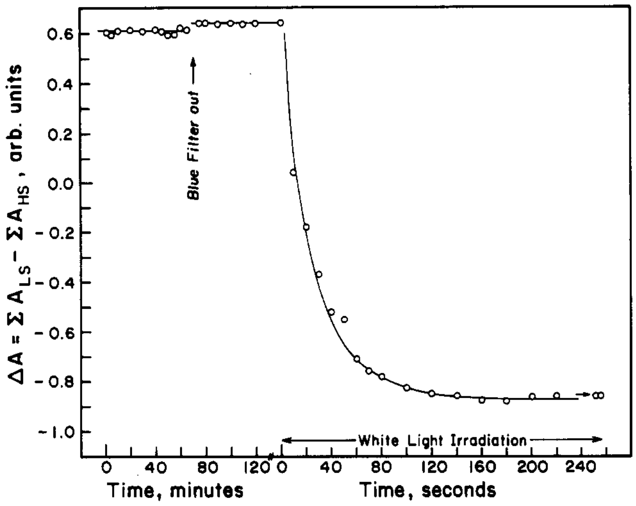

Figure 3. Stability in the dark and under 632-nm light irradiation and conversion of the LS form of I to the (trapped) HF form on white light irradiation at 8 K. Note change in absissa scale for $t > 120$ min.

agreement with those reported by Casey[18] (212–213 K), by Kulshreshtra and Iyer[19] (210.5 K on cooling, 213.5 K on warming), and Konig et al.[3] (~215 K).

The temperature dependences of the band centers are summarized in Table I, and these data show that while the 2073-cm^{-1} band (HS) shows a modest negative temperature coefficient, the 2059-cm^{-1} band (HS) and the 2121- and 2111-cm^{-1} bands (LS) are essentially insensitive to temperature change over the indicated range.

On further cooling of the sample below liquid-nitrogen temperature, the intensity of the LS absorptions at 2118 and 2111 cm^{-1} remain essentially constant to the low-temperature limit (~8 K) accessible in the present experimental arrangement. At 8 K, the intensity of the CN stretching frequency remains constant over time, both with (0.615 ± 0.018 absorbance unit) and without (0.677 ± 0.005 absorbance unit) the blue filter in place. Thus, in contrast to the observations made[9] for the spin-crossover complex $Fe(phen)_2(SCN)_2$, the 632-nm He/Ne laser line does not effect appreciable conversion of I from the LS to the trapped HS form over a period of ~120 min. The strikingly different behavior on irradiation with white light is summarized graphically in Figure 3, from which it is seen that an equilibrium value of ΔA, at which point the LS form can no longer be detected by IR means, is reached in about 140 s of illumination under the conditions of the present experiment. A semilogarithmic plot of the LS CN stretching band intensities as a function of time is shown in Figure 4, in which the quantity plotted on the ordinate is $\ln [I(t) - I(\infty)]$, where the two intensity values are calculated at time t and at "infinite" time, respectively. The linearity of this plot, which obeys a relationship of the form $\ln [I(t) - I(\infty)] = 0.3556 - 0.0359t$, with a correlation coefficient of 0.9994 for 11 data points, demonstrates that at constant light intensity, the LS to (trapped) HS conversion obeys the expected first-order kinetics.

When the sample of trapped HS 1, formed by the LIESST process at 8 K, is warmed, no change in absorption is noted until a sample temperature of approximately 50 K is reached. Above this temperature, further warming results in the rapid reconversion of the trapped HS form of I to the normal LS form, which is the dominant stable form below about 210 K, as noted above. This reconversion is shown graphically in Figure 5. The median temperature for the trapped HS to LS conversion is 63 ± 1 K.

(b) $Fe(2,2'\text{-}bpy)(SCN)_2$. The VTFTIR behavior of II, which has been described in considerable detail by Dockum and Reiff,[6,11] is very different from that described above for I. At room temperature, the absorbances observed in the CN stretching region are quite broad for the Kel-F mulled samples, and these vibrational modes are only slightly better resolved for a 0.37 w/w sample in KBr. When this sample is cooled to $T < 220$ K, two bands can be resolved that are assigned to the CN stretching mode, both on the basis of frequency and oscillator strength. On further cooling, these two bands show a temperature dependence, which is summarized in Figure 6. The data in the range $80 < T < 210$ K are reasonably well fit by a linear regression, and the quantitative data are summarized in Table I. Below liquid-nitrogen temperature, the position of the two band centers becomes temperature independent, reaching limiting (8 K) values of 2117.4 and 2088.9 cm^{-1}, respectively. In contrast to I, this sample shows no change in the two CN stretching mode band positions associated with a first-order HS = LS transition, despite the fact that the effective moment on the metal atom changes from ~5 μ_B at 300 K to 0.88 μ_B at 1.39 K, as reported in the susceptibility study of Dockum and Reiff. As will be inferred from the data summarized in Table I, the temperature dependence of the band center positions for II are typical of those associated with changes in the CN stretching mode with temperature for noncrossover compounds, and corresponds to a change of ~4.5 cm^{-1} over 200 deg, much smaller than the 40–60-cm^{-1} differences in the HS and LS band

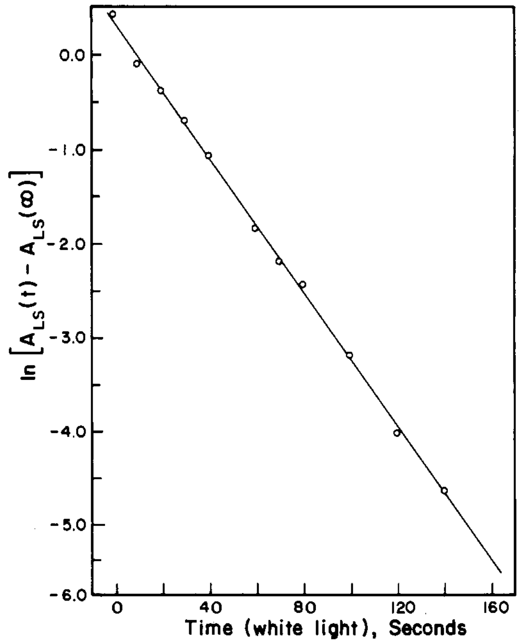

Figure 4. Semilogarithmic plot of the conversion of the LS to (trapped) HS form of I at 8 K as a function of time. The pseudo-first-order kinetics of the conversion are clearly evident from the data.

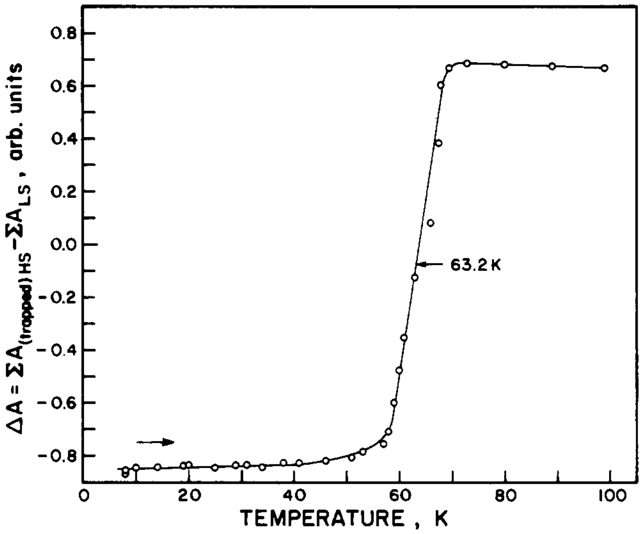

Figure 5. Reconversion of the (trapped) HS form of I to the LS form on sample annealing.

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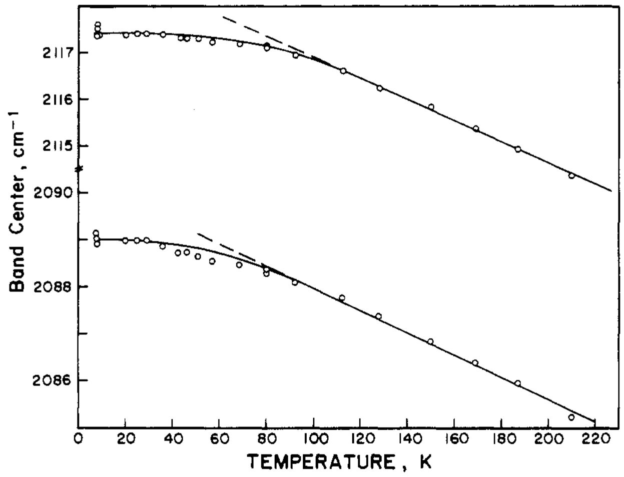

Figure 6. Temperature dependence of the CN stretching mode band position for II.

center positions observed in I, IV, V, and VI. Reiff et al.[11] have also obtained ^{57}Fe Mössbauer evidence for a distinct hyperfine interaction difference between the high- and low-temperature forms of II but note that this change occurs over a temperature range of about 70 deg (200–130 K). The present VTFTIR data strongly support the inference that the nature of the effective moment variation between the high- and low-temperature forms of this complex is both quantitatively and qualitatively different from the HS = LS crossover in complexes of the type discussed above.

Finally, it is worth noting that (not unexpectedly) white light irradiation of II at 8 K for 300 s resulted in no observable change in the IR spectrum of II over the range 4800–400 cm^{-1}.

(c) $Fe(py)_4(SCN)_2$. The tetrakis(pyridine)bis(thiocyanato)-iron(II) complex has been described as existing in two isomeric forms: a yellow form, first prepared by Grossmann and Hunseler[13] some 81 year ago, and a violet form, described by Spacu et al.[20] From dipole moments and infrared and UV–vis spectroscopic data, the latter authors[14] concluded that the violet form adopted a structure with the two SCN groups (S-bonded) occupying trans positions in the octahedral configuration. By inference, the yellow form was assumed to have the SCN groups in cis positions. In a subsequent paper, in which the compound $Fe(py)_2(phen)(SCN)_2$ (compound IV, vide infra) was obtained from III (yellow form), Spacu et al.[15] formulate the latter as having S-bonded ("rhodanit typus") pseudohalide ligands, without any further reference to their earlier work. Additionally, it is worth noting that the only difference in the IR spectra of the yellow and violet forms isolated by Spacu et al.[14] is the appearance of an additional strong band at 1200 cm^{-1} in the former in addition to the 1220-cm^{-1} absorption present in the spectra of both forms. The yellow complex (III) obtained in the present study shows a strong absorbance at 1213 cm^{-1} at 300 K (1211 cm^{-1} at 80 K), with a resolved, somewhat smaller absorbance at 1217 cm^{-1} (1216 cm^{-1}) for a sample dispersed in KBr. As noted above, the ^{57}Fe Mössbauer data of Erickson and Sutin[14a] have served to resolve the difference between the violet and yellow forms of III.

The definitive crystal structure of the yellow form has been published by Sotofte and Rasmussen,[21] who showed, in fact, that the yellow form had the two N-bonded SCN groups in trans positions. The space group was found to be $C2/c$ with $Z = 4$, and the SCN bond angle is 179.4°. Both the yellow (α) and black/violet (β) form have temperature-independent susceptibilities in the temperature range $77 < T < 296$ K, with $\mu_{\text{eff}} = 5.38$–5.52 μ_B. Clearly, neither of these two forms show crossover behavior and thus provide model compound behavior for some of the VTFTIR properties to be discussed below. In the present investigation, only the yellow form (III), characterized in the crystallographic study, has been examined in detail.

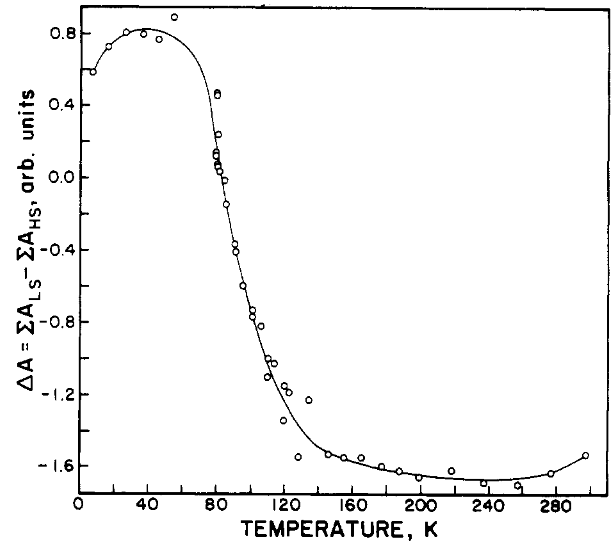

Figure 7. Temperature dependence of ΔA for IV.

The room-temperature FTIR spectrum of III shows a somewhat broadened absorption band at 2067 cm^{-1} assigned to the CN stretching mode, which evidences a small (unresolved) splitting on cooling to 80 K. The temperature dependence of the band center shows an approximately linear behavior in the range $150 < T < 280$ K, and the relevant data are included in Table I. At lower temperatures, the band center position becomes temperature independent and reaches a limiting value of ~2069 cm^{-1} at liquid-nitrogen temperature. As expected from the susceptibility data of Golding et al.[22] and of Sotofte and Rasmussen,[21] there is no evidence of spin-crossover in the IR spectra of this complex. The thiocyanate groups are N-bonded with an Fe–N distance of 2.097 Å, while the four pyridine nitrogens are at 2.241 (N_a) and 2.272 (N_b) Å. As noted above, the thiocyanate ligands are linear, but the FeNC bond angle is 155.28°, giving rise to a structure that lacks an ideal inversion center. Comparison of the IR spectra of (KBr pelleted) samples at 300 and 80 K shows no significant differences other than the CN band center shifts noted above. The ^{57}Fe Mössbauer spectra, electronic and infrared spectra, and the elucidation of bonding and crystal field parameters of this compound have been discussed in detail by Little and Long.[23]

(d) $Fe(py)_2(phen)(SCN)_2$. The magnetic behavior of $Fe(py)_2(phen)(SCN)_2$ has been discussed in detail by Spacu et al.,[15] who showed that the product of their synthetic procedure afforded a material that shows a sharp crossover transition at a temperature of 180–185 K. The LS effective moment observed by them is 2.09 μ_B at temperatures below ~150 K. The VTFTIR behavior of IV, obtained by the synthetic procedure discussed above, is summarized graphically in Figure 7. In view of the acceptable analytical data, as well as the infrared results (vide infra) obtained for this material (IV), it is unlikely that the reaction product isolated in this study is, in fact, a mixture of $Fe(py)_4(SCN)_2$ and $Fe(phen)_2(SCN)_2$, which would, of course, show the same elemental analysis as the presumed product. In this context, the infrared data observed are unexpected from the earlier results of Spacu et al.[15] The spectrum of IV mulled in Kel-F shows two well-resolved maxima in the CN stretching region, being located at 2075.7 and 2062.2 cm^{-1} at 298 K. The sum of the intensities of these two bands does not change markedly as the sample is cooled, until a temperature of ~140 K is reached. On further cooling, a sharp crossover transition behavior is observed, with a transition temperature of ~91 K. This behavior is quite different from the susceptibility results reported by Spacu et al.,[15] who reported a transition from the HS form to a form with an effective moment of ~2 μ_B at a temperature of ~180–185 K. There are

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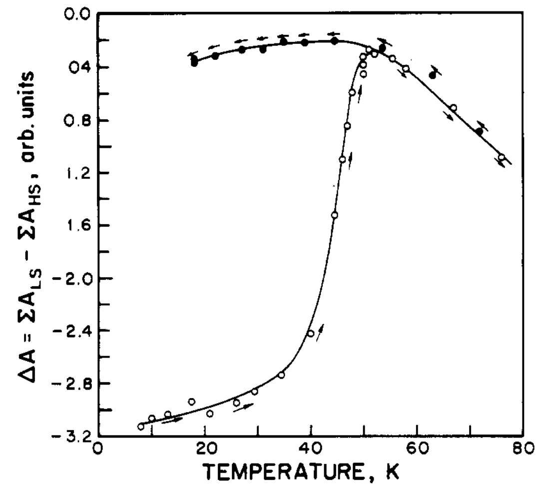

Figure 8. Infrared absorbance data showing the reconversion of the (trapped) HS form of IV on sample warming and subsequent recooling of this sample to <20 K.

two other features of the VTFTIR results obtained in the present study that require comment. In contrast to the other crossover compounds for which such results have been reported, the ΔA value below the crossover transition temperature does not reach a low-temperature limiting value, but goes through a maximum and then decreases as the temperature is further reduced. When the low-temperature limit of the present study (7 K) is reached, the ΔA value slowly changes with time, but over a period of about 1 h, the decrease is just outside the estimated error of the measurements. This apparent time-dependent change in the ΔA value is not associated with the 632-nm He/Ne laser line pumping effect noted for Fe(phen)$_2$(SCN)$_2$, since the interposition and withdrawal of the blue filter did not significantly change the rate of the change of ΔA. When a sample of IV, held at 6.5–7 K, is irradiated with white light, the appearance of two bands at 2082 and 2064 cm^{-1}, and the concomitant decrease in the intensity of the bands at 2117 and 2103 cm^{-1}, again signals the LS to (trapped) HS conversion associated with the LIESST phenomenon. Gradual warming of this irradiated sample leads to a reconversion to the LS form, with a transition temperature of ~47 K. When this "annealed" sample, raised to a temperature of 80 K, is again subjected to cooling in the absence of light, the same behavior as that noted in the original cooling process is again observed. These results are summarized graphically in Figure 8.

It is clear from the results discussed above that IV shows both the spin-crossover and LIESST phenomena associated with Fe(phen)$_2$(SCN)$_2$ and I, but at values somewhat different from those that would be inferred from the published susceptibility results. The origin of this discrepancy is not clear from the presently available experimental data.

(e) Fe(phen)$_2$(SCN)$_2$ and Fe(phen)$_2$(SeCN)$_2$. The VTFTIR behavior of V has been discussed earlier,[9] and the pertinent data are included in Table I. The only comment that needs to be made is that the discrepenacy in the crossover temperature noted for the KBr pelleted samples, which was addressed by a reviewer of the earlier study (footnote 28 in ref 9), has been eliminated by the Kel-F mulling technique discussed in the Experimental Section, above. The apparent crossover temperature, as educted from the VTFTIR data, is 174 K, in good agreement with the values of 176.29 K obtained by Sorai and Seki[24] from heat capacity data and 174 K reported by Baker and Bobonich.[25]

The VTFTIR behavior of Fe(phen)$_2$(SeCN)$_2$ (VI) is similar to that observed for V. The spin crossover is relatively sharp with a characteristic temperature of 231 K (Kel-F dispersed sample). Conversion to the LS form is essentially complete on sample cooling to liquid-nitrogen temperature. A typical optical pumping experiment at 8.5 ± 0.5 K showed that VI is not converted to the trapped HS form by He/Ne line excitation but does show the characteristic LIESST phenomenon on irradiation with white light. As noted above, this excitation follows first-order kinetics and results in the complete conversion of the LS form to the (trapped) HS form within 10 min under the conditions of the present study. As was observed for the optical pumping process in I (Figure 4) the LS → HS (trapped) conversion of VI under constant white light flux conditions follows first-order kinetics and results in the complete disappearance of the infrared signature characteristic of the LS form. Subsequent warming of the irradiated sample results in the reconversion to the LS form, with a characteristic transition temperature of ~29 K, as summarized in Figure 9. It is worth noting, however, that this (trapped) HS to LS conversion appears to be significantly more "sluggish" than has been noted in the SCN complexes. The present data are too limited to permit drawing any inferences from these results pertaining to the potential differences in behavior of the thiocyanate vs. selenocyanate spin-crossover complexes.

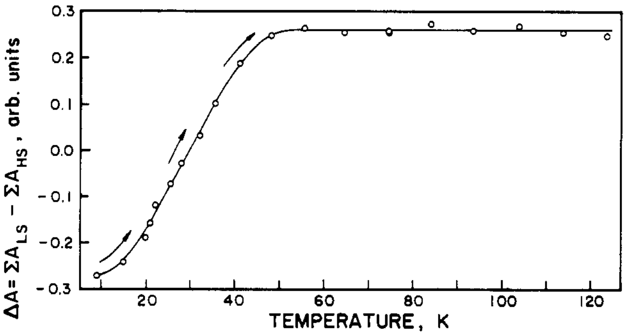

Figure 9. Reconversion of the (trapped) HS form of VI to the LS form on sample annealing.

(f) Nature of the HS ⇌ LS Transition and the Relationship between T_1 and T_2. The spin-crossover transition in Fe(II) complexes can be described in terms of a critical energy, E_c, by a relationship of the form

$$E_c = \Delta - (E_p + k_B T)$$

in which Δ is the crystal field splitting energy between the 3d electronic e_g doublet and the t_{2g} triplet levels (assuming ideal octahedral symmetry), k_B is Boltzmann's constant, T is the absolute temperature, and E_p is the electronic spin pairing energy. If E_c is < 0, $(E_p + k_B T)$ is larger than Δ, and the HS configuration will be the ground state. If $E_c > 0$, $(E_p + k_B T)$ is smaller than Δ, and the favored configuration is LS.

It is now clear from a wealth of experimental data, including that discussed above, that spin-crossover transitions can be broadly classed into two types, the "sudden", in which the crossover occurs over a relatively narrow temperature range, and the "gradual", in which the high-spin to low-spin transformation is smeared out with respect to temperature. Gutlich and his co-workers[4,5] have shown that a number of factors can influence the "suddenness" of the HS ⇌ LS transitions, including crystal quality, D for H isotopic substitution in complexes solvated with C$_2$H$_5$OH or C$_2$D$_5$OH, metal ion substitution (e.g. Zn^{2+} for Fe^{2+}), and pressure, inter alia. A qualitative explanation of some of these effects in terms of a "lattice expansion model" has been suggested.[26] In terms of the present study, however, from the crystallographic data of Mikami et al.[27] and the data cited by Gutlich,[5] it may be inferred that the "sudden" spin transition behavior is associated with a first-order phase transition between two distinct crystallographic phases and is accompanied by a hysteresis that is characteristic of such transitions. The relatively sudden change in sign of E_c may then reasonably be associated with a change in the crystal field splitting energy between the two phases, with

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$\Delta_{HS} < \Delta_{LS}$. Moreover, such a crystallographic phase transition can be inferred from the lattice dynamical behavior of spin-crossover compounds, as extracted from temperature-dependent ^{57}Fe Mössbauer experiments, as will be reported elsewhere.[28] Such lattice dynamical data are consistent with the observation that the metal–ligand bond lengths decrease in going from the HS to the LS form of Fe(II) spin-crossover complexes.

The present study affords for the first time a self-consistent data set for comparison of the characteristic temperature for HS $\rightleftharpoons$ LS conversion of Fe(II) spin-crossover complexes (T_1), and the temperature at which the (trapped) HS form—produced by visible light irradiation of the LS form at low temperatures—is reannealed to the LS form (T_2). Such a comparison can be effected for complexes I, IV, and V, the three (isothiocyanato)-iron(II) compounds examined in detail in the VTFTIR experiments discussed above. The present data suggest that a lower T_2 is associated with a lower T_1 for a given complex, suggesting that the lower thermal excitation required to "freeze-in" the LS form of a given complex is also required to "freeze-in" the (trapped) HS form produced by optical excitation of the LS form matrix. Clearly, the present data can only be considered as suggestive of such a relationship between T_1 and T_2, and further experiments to explore this behavior are currently under way.

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Contribution from the Discipline of Coordination Chemistry and Homogeneous Catalysis,
Central Salt and Marine Chemicals Research Institute, Bhavnagar 364002, India

Synthesis and Characterization of Binuclear Platinum Group Metal Complexes of Novel Hexadentate Ligands α,α′-Bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene and α,α′-Bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene

M. M. Taqui Khan* and B. Swamy[†]

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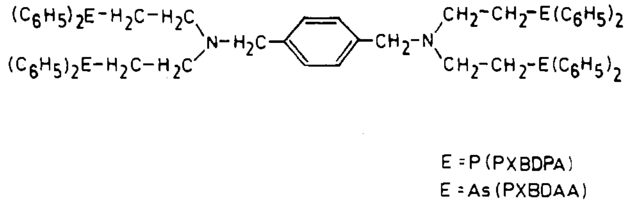
The hexadentate ligands α,α′-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene (PXBDPA) and α,α′-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene (PXBDAA) were synthesized and characterized on the basis of their ^{1}H, ^{31}P, and ^{13}C NMR spectra. Binuclear metal complexes of these ligands with Ru(II), Ru(III), Rh(I), Ir(I), Pd(II), and Pt(II) are reported. Reaction of $RuCl_2(PPh_3)_3$ with PXBDPA or PXBDAA in benzene in a 2:1 ratio gave neutral, binuclear Ru(II) complexes of the type $[Ru_2Cl_4(PPh_3)_2(L)]$ (L = PXBDPA, PXBDAA). The salt $[Ru_2Cl_2(Me_2SO)_4(PXBDPA)](PF_6)_2$ was obtained by the reaction of $RuCl_2(Me_2SO)_4$, PXBDPA, and NH_4PF_6 in an ethanol–benzene mixture. Neutral, binuclear, and octahedral complexes of the type $[Ru_2Cl_6(L)]$ (L = PXBDPA, PXBDAA) were obtained by the reaction of L with $RuCl_3(AsPh_3)_2MeOH$ in benzene. Reaction of $RuBr_3(AsPh_3)_2MeOH$ with PXBDPA or PXBDAA yielded Ru(III) complexes of the composition $[Ru_2Br_4(AsPh_3)_2(L)]Br_2$ (L = PXBDPA, PXBDAA). The reaction of $[Rh(COD)Cl]_2$ or $[Ir(COD)Cl]_2$ with PXBDPA or PXBDAA in an ethanol–benzene mixture yielded neutral, binuclear, and square-planar complexes of the type $[M_2Cl_2(L)]$ (M = Rh, Ir; L = PXBDPA, PXBDAA). Binuclear, square-planar cationic complexes of the composition $[Rh_2(S)_2(L)](PF_6)_2$ (S = PPh_3, CH_3CN; L = PXBDPA, PXBDAA) were obtained by the reaction of $[Rh(COD)Cl]_2$, L, and PPh_3 or acetonitrile in boiling ethanol. Binuclear, cationic, and square-planar complexes of Pd(II) and Pt(II) of the composition $[M_2X_2(L)]Y$ (X = Cl, Br, SCN; L = PXBDPA, PXBDAA; Y = Cl, BPh_4, PF_6) were obtained by the reaction of L with $MX_2(PhCN)_2$ (M = Pd, Pt; X = Cl, Br) in ethanol. The thiocyanato complex $[Pd_2(SCN)(PXBDPA)](BPh_4)_2$ was obtained by stirring the reaction mixture of $PdCl_2(PhCN)_2$, NH_4SCN, and PXBDPA in ethanol. All the complexes were characterized on the basis of their elemental analyses, molar conductance data, magnetic susceptibilities, infrared spectral measurements, and ^{1}H, ^{31}P, and ^{13}C NMR spectral data.

Introduction

Recently we have been interested in the synthesis and chemistry of transition-metal complexes of polydentate ligands containing mixed donor atoms like N, P, As, and O[1-5] due to their increasing importance in the field of catalysis[6] and also in the construction of bi- and polynuclear transition-metal complexes. In our earlier communications,[3,4] we have reported the synthesis and characterization of two novel terdentate ligands containing N and P or As as donor atoms, bis(2-(diphenylphosphino)ethyl)benzylamine and bis(2-(diphenylarsino)ethyl)benzylamine, and their transition-metal complexes. We have also reported[1,2,5] the platinum group metal complexes of bis(2-(diphenylphosphino)ethyl)amine, bis(2-(diphenylarsino)ethyl)amine, and (diphenylphosphino)acetic acid.

In this paper we report the synthesis of two novel potential hexadentate ligands, α,α′-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene (PXBDPA) and α,α′-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene (PXBDAA) (I), which contain N and P or As as donor atoms. These ligands contain two terdentate moieties (PNP or AsNAs) separated by a rigid *p*-xylyl bridge capable of forming binuclear complexes in which the metal ions are held apart at a sufficient distance such that the two groups of donor atoms cannot coordinate to the same metal ion. Synthesis of binuclear complexes of d^5, d^6, and d^8 metal ions of the platinum



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[†] Department of Chemistry, Kakatiya University, Warangal, India

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