Table IV. Chemical Bonding Topology of V_3Si and Related A-15 Superconductors Such As Nb_3Ge and Nb_3Sn

bond type	per V_6Si_2 cube			
	no. of such bonds	no. of electrons required	no. of V orbitals required	no. of Si orbitals required
2-center V–V bonds in chains (Figure 2)	6	12	12	0
4-center V_3Si bonds in V_3Si tetrahedral cavities	8	16	24	8
3-center V_3 bonds in one V_3 face of each diamond pair	6	12	18	0
tot. electrons and orbitals required for one V_6Si_2 cube		40	54	8

chemical bonding topology outlined in Table IV, implying that $V_6Si_2{}^{2-}$ is the closed-shell electronic configuration for this chemical bonding topology. This model for the chemical bonding in the A-15 superconductors V_3Si and its analogues Nb_3Ge and Nb_3Sn thus has the following features associated with superconductivity: (A) a porous conducting skeleton of which straight chains of V–V edge-localized bonds (Figure 6) are an important component; (B) holes in the valence band since $V_6Si_2{}^{2-}$ rather than V_6Si_2 is the closed-shell electronic configuration.

Superconductivity and Metal Valence Electrons

The structures of bulk metals may be constructed from building blocks of metal octahedra. The chemical bonding within a single isolated metal octahedron is most commonly globally delocalized with a single six-center core bond (e.g., $Rh_6(CO)_{16}$) although examples of face-localized metal octahedra with three-center bonds in each of the eight faces (e.g., $Nb_6X_{12}L_6{}^{2+}$) and edge-localized metal octahedra with two-center bonds along each of the 12 edges (e.g., $Mo_6X_8L_6{}^{4+}$) are also known.[39] Infinite fusion of metal octahedra in one, two, and three dimensions leads to metal cluster chains (e.g., Gd_2Cl_3), metal cluster sheets (e.g., $ZrCl$), and bulk metals, respectively. The skeletal electron and orbital counts in the infinite one-dimensional chains of the Gd_2Cl_3 type and the infinite two-dimensional sheets of the $ZrCl$ type suggest six-center core bonds in each octahedral cavity and multicenter bonds in the two tetrahedral cavities for each octahedral cavity.[39] Such an electron and orbital analysis can be extended to bulk metals as infinite arrays of fused octahedra in all three dimensions with two tetrahedral cavities for each octahedral cavity. Since each metal atom in such bulk metals is shared by six octahedral cavities and since an octahedral cavity is formed by six metal atoms, the number of valence electrons for each octahedral cavity is equal to the number of valence electrons of the metal. Formation of one multicenter bond each in each octahedral cavity and in the two tetrahedral cavities for each octahedral cavity requires six electrons per octahedral cavity corresponding to a group 6 metal atom with six valence electrons such as chromium, molybdenum,

or tungsten. Such a bonding topology for these metals is fully dense and is very unfavorable for the mobile electron pairs required for superconductivity in accord with the very low T_c's (<0.1 K) observed for pure chromium, molybdenum, and tungsten.[40,41] The "pseudo-closed-shell" electron configurations for chromium, molybdenum, and tungsten can also be related to other physical properties of these metals, including heats of atomization[42] and properties connected with the "transition-metal divide" of Stone.[43]

Now consider the group 5 metals vanadium, niobium, and tantalum, which have much higher T_c's than the group 6 metals considered above. The above bonding model leaves only a single electron rather than an electron pair for one of the three multi-center bonds associated with a given octahedral cavity (including two tetrahedral cavities for a given octahedral cavity). These single electrons can interact to form the Cooper pairs required for superconductivity accounting for the much higher T_c's of group 5 metals relative to the group 6 metals and the local maximum in the T_c versus Z_{av} curve at $Z_{av} = 4.8$ for transition-metal alloys.[40,41] Similarly, for the group 7 metals technetium and rhenium, the above bonding model leaves an extra electron after providing electron pairs for each of the three multicenter bonds associated with a given octahedral cavity. Pairing of these extra electrons can lead to the Cooper pairs required for superconductivity thereby accounting for the much higher T_c's of group 7 metals relative to the group 6 metals and the local maximum in the T_c versus Z_{av} curve at $Z_{av} = 7$ for transition-metal alloys. The smaller local maximum in the T_c versus Z_{av} curve at $Z_{av} = 3.3$ may have a similar origin based on pairing of the single electron remaining from each metal atom after an electron pair is provided for each six-center core bond in the centes of the octahedral cavities with no multicenter bonds in the tetrahedral cavities.

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Notes

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Spin Crossover and Light-Induced Excited-Spin-State Trapping in Bis(thiocyanato)bis(2,2′-bi-2-thiazoline)iron(II) and Bis(selenocyanato)bis(2,2′-bi-2-thiazoline)iron(II)

D. C. Figg and R. H. Herber*

The iron(II) complexes $Fe(bt)_2(NCS)_2$ (I) and $Fe(bt)_2(NCSe)_2$ (II), where bt = 2,2′-bi-2-thiazoline, have been shown to undergo a thermally driven high-spin (HS, $S = 2$) to low-spin (LS, $S = 0$) transition in the solid state.[1] Several techniques, including

^{57}Fe Mössbauer spectroscopy, powder X-ray diffraction,[2] magnetic susceptibility,[1,3] calorimetry,[4] single-crystal X-ray diffraction, and EPR spectroscopy,[5] have been utilized to study the spin-crossover transition of the isothiocyanate complex in some detail. The spin-crossover transition of the isoselenocyanate complex has been studied by using magnetic susceptibility,[1] ^{57}Fe Mössbauer spec-

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Table I. Summary of Data

	$\nu(CN)$, cm^{-1} (T, K)			T_1,[a] K	HS$_{tr}$ $\Rightarrow$ LS barrier-crossing temp,[b] K
compd	HS form	LS form	HS$_{tr}$ form		
Fe(bt)$_2$(NCS)$_2$	2079 (s), 2069 (301)	2134, 2119 (84)	2087, 2075 (6)	185.4	52.5
Fe(bt)$_2$(NCSe)$_2$	2079 (s), 2071 (302.5)	2129, 2117 (79)	2087, 2079 (6)	219.4	55
		2131, 2118 (6.5)			

[a] T_1 estimated from SQUID data (warming). [b] Estimated from the point of inflection of the trapped HS to LS conversion curve (see Figure 3).

troscopy, and powder X-ray diffraction.[6] Both complexes exhibit an abrupt transition, with hysteresis, on warming or cooling through T_1 (the temperature at which the HS and LS forms are present in equal amounts). Using ^{57}Fe Mössbauer, single-crystal optical absorption, and magnetic susceptibility techniques, Gütlich et al.[7-10] have observed the conversion of the LS form of a number of Fe^{2+} spin-crossover compounds to a "trapped" HS (HS$_{tr}$) form when the sample—held at temperatures below $\sim$50 K—is irradiated with light of the appropriate frequency. This process has been referred to as light-induced excited-spin-state trapping (LIESST). In detailed studies of a number of compounds reported to exhibit LIESST, the trapped HS form is observed to be stable indefinitely at temperatures below $\sim$50 K. On subsequent warming, this HS$_{tr}$ form is converted back to the LS form.

As previously demonstrated,[11,12] variable-temperature Fourier transform infrared (VTFTIR) spectroscopy can conveniently be used to follow the thermally driven spin-crossover transition, as well as the LIESST phenomenon, in such complexes. In the present study VTFTIR spectroscopy has been used to demonstrate the LIESST phenomenon at low temperatures in Fe(bt)$_2$(NCS)$_2$ and Fe(bt)$_2$(NCSe)$_2$.

Experimental Section

(a) Preparation of the Complexes. Samples of Fe(bt)$_2$(NCS)$_2$ and Fe(bt)$_2$(NCSe)$_2$ were prepared by using literature methods[1] and were characterized by elemental analysis, FTIR spectroscopy, and SQUID magnetic susceptibility measurements.

(b) Infrared Studies. Changes in the CN stretching modes of the NCS or NCSe ligand were used as previously described[11,12] to follow the thermal conversion between the HS and LS forms, as well as the details of the LIESST process. All VTFTIR and LIESST measurements were carried out on neat samples dispersed in Kel-F mulls, to minimize effects due to crushing and pelletizing.[3,11] All techniques and instrumentation used were as described previously[11-13] except for the following changes. As shown earlier,[11,12] the internal 0.5-mW He/Ne laser of the FTIR spectrometer is capable of optically converting some compounds at $\sim$6 K to the HS$_{tr}$ form. In previous studies a blue filter was placed between the sample and the internal He/Ne laser to control irradiation of the sample by 632-nm light without interfering with the IR measurements. In the present study, effects due to internal He/Ne laser illumination of the sample were minimized by placing an absolute filter between the sample and the internal He/Ne laser when the sample was cooled and when spectral scans were not being taken. In addition to the internal 0.5-mW He/Ne laser and an external white light source previously used for sample irradiation at low temperature, a more intense (0.8-mW nominal output), external He/Ne laser was also utilized in these studies.

Results and Discussion

(a) Variable-Temperature FTIR Spectroscopy. Changes in the intensities of the CN stretching modes of the pseudohalide ligands of Fe(bt)$_2$(NCS)$_2$ and Fe(bt)$_2$(NCSe)$_2$ serve as a convenient way to follow the conversions between the HS and LS forms.[14] The

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(14) The transition through T_1 followed with VTFTIR spectroscopy appears to be more gradual and to occur at a lower temperature than when followed with magnetic susceptibility data. Further investigation into this effect is currently underway. Characterization of T_1 values of our samples is best obtained by using magnetic susceptibility data.
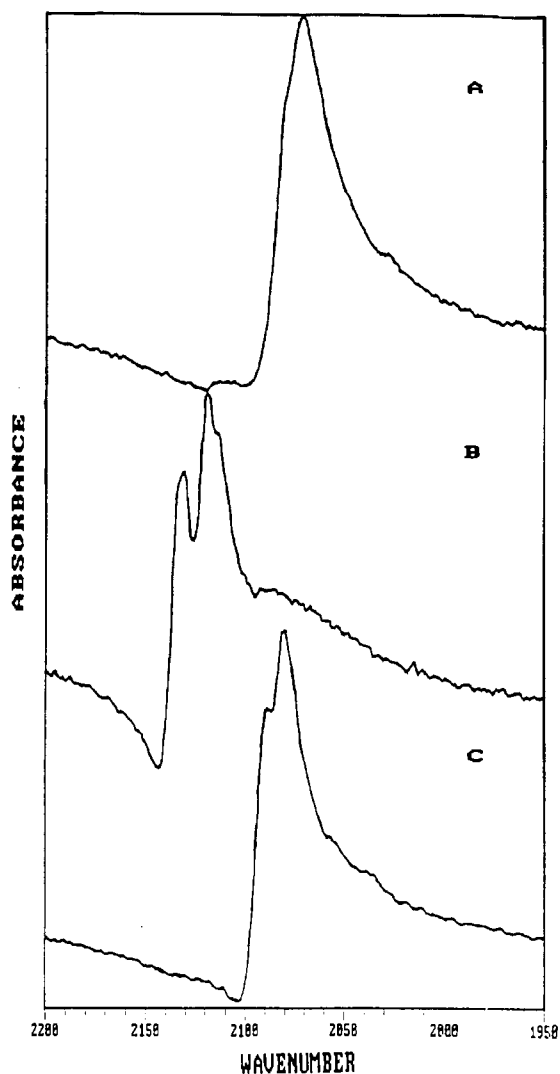
Figure 1. Portion of the infrared absorbance spectra (2200–1950 cm^{-1}) of Fe(bt)$_2$(NCSe)$_2$ showing the CN stretching modes of (A) the HS form at 302.5 K, (B) the LS form at 6.5 K, and (C) the HS$_{tr}$ form at 6 K after 1280 s of white light irradiation.

$\nu(CN)$ mode at room temperature of both complexes appears as a very strong, broad (fwhm $\sim$ 40 cm^{-1}) band at $\sim$2070 cm^{-1} with a weak shoulder at higher frequencies. The CN stretching mode region of both I and II are quite similar, and a typical room-temperature spectrum for II dispersed in Kel-F is shown in Figure 1A. The weak feature at $\sim$2028 cm^{-1} is the ^{13}C component of the CN stretching fundamental. At T_1, $\nu(CN)$ of both the HS and LS forms of I can be resolved as doublets, corresponding to the asymmetric and symmetric stretching modes, both of which are infrared active in consonance with the crystal structure,[5] which shows the NCS ligands to be N-bonded, and occupying cis positions in the coordination sphere. The spectrum of II at T_1 shows both the HS and LS $\nu(CN)$ modes as a single band with a weak shoulder at higher frequencies. Considering the fact that T_1 for II is $\sim$34 deg higher than T_1 for I, it seems likely that II at this temperature is subject to sufficient thermal broadening of the absorption band under the conditions of this study to prevent resolution of the $\nu(CN)$ modes into symmetric and asymmetric

Table II. ν(CN) Data Showing Evidence for More Than One LS or HS Form[a]

compd	form	T, K	conditions	ν(CN), cm^{-1}
Fe(bt)$_2$(NCS)$_2$	LS	28.5	after 390 s, white light irrad.	2135, 2129, 2119, 2114
Fe(bt)$_2$(NCS)$_2$	LS	177.5	warming through T_1	2131, 2118, 2110
Fe(bt)$_2$(NCS)$_2$	HS	115.5	HS starting to grow in on warming	2084, 2080, 2073, 2070
Fe(bt)$_2$(NCSe)$_2$	LS	48	warming after white light irradn	2133 (s), 2130, 2119, 2110

[a] See text.

components. When the sample is cooled to 80 K, the CN stretching region spectrum confirms that II is fully converted to the LS form (as shown in Figure 1B) while I evidences the presence of a small amount of residual HS form, which remains down to 6 K. The spectra of both complexes at 6 K are very similar to their spectra at 80 K, with both complexes displaying a doublet for the LS CN stretching modes at both temperatures. Data for the band positions of selected IR modes, as well as a number of related parameters, are summarized in Table I.

In both complexes the CN stretching region shows evidence of two coexisting phases in unequal amounts. At some intermediate temperatures, where only partial conversion of the HS form to the LS form (or vica versa) has occurred, it is possible to observe four (instead of the usual two; i.e. the symmetric and asymmetric modes) IR bands in the CN stretching region of the HS or LS forms. As an example, when a small amount of the HS form of I is present at $T < T_1$, four HS CN stretching bands are clearly observed at 2084, 2080, 2073, and 2070 cm^{-1}. As more LS form converts to the HS form on subsequent warming through T_1, the HS CN stretching bands grow more intense and the two HS doublets coalesce into a single doublet. When only a small amount of the LS form is left, on further heating, three LS ν(CN) bands are observed at 2130, 2118, and 2110 cm^{-1}. From a more detailed study it became apparent that the fourth band is very close to the 2130-cm^{-1} band and could be observed in a restricted temperature regime as a small shoulder at higher frequencies. Table II gives values of the positions of the four bands associated with the HS or LS forms of I and II under different conditions. In a previous investigation[2] König and co-workers have suggested the existence of two phases of the thiocyanate complex based on Mössbauer studies. Careful examination of warming curves obtained both from the temperature dependence of the IR-active ν(CN) modes and from SQUID magnetic susceptibility data obtained through T_1 does not afford clear evidence of two separate transitions for the two coexisting phases. The LS to HS conversion on sample warming follows the usual sigmoid behavior, but the temperature dependence of the relative spin-state population appears to be more gradual at $T < T_1$ than in the regime where $T > T_1$.[1,3] This observation may be related to the existence of more than one crossover transition occurring at nearly the same temperature.

(b) Optical-Pumping Experiments. As mentioned above, three different light sources were used for irradiating the samples at 6 K in order to optically pump the stable LS form to the HS$_{tr}$ form. The internal Ne/He laser to the FTIR spectrometer caused optical pumping of both I and II, but due to the low quantum flux, the conversion is very slow ($\sim$3–4% conversion to the HS$_{tr}$ form in 20 min for both complexes) and was followed for only a short length of time. The rate of pumping of both complexes at 6 K with an external, more intense, He/Ne laser was observed to be much more efficient. Less than 6000 s of irradiation time was required to convert either complex to its equilibrium state, which consisted of approximately 72% HS$_{tr}$ form for I and approximately 71% HS$_{tr}$ for II. White light irradiation from a tungsten-filament lamp was effective in converting both I and II completely from the LS to the HS$_{tr}$ form within a time of $\sim$1280 s. Figure 1C shows the ν(CN) bands of the trapped HS form of II at 6 K. The ν(CN) bands of the HS$_{tr}$ form are blue-shifted $\sim$8 cm^{-1} from that of the ν(CN) bands of the HS form at 300 K for both I and II, a thermal shift which is slightly larger than those that have been reported earlier.[11]

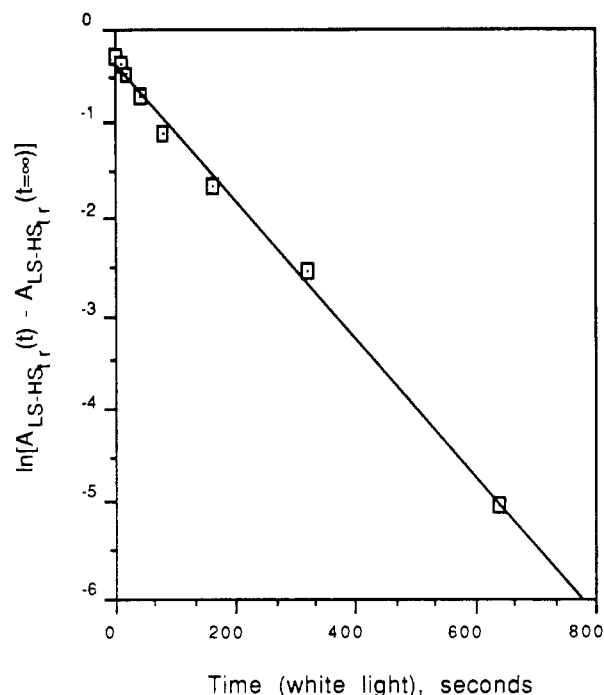As has been noted earlier for Fe(2,2'-bipyridine)$_2$(NCS)$_2$,[11] inter alia, the conversion of the thermodynamically stable LS form at

Figure 2. Semilogarithmic plot of the conversion of the LS to trapped HS form of Fe(bt)$_2$(NCS)$_2$ at 6 K as a function of time. $A_{LS-HS_{tr}}(t)$ = the difference between the absorbance of the LS ν(CN) and the HS$_{tr}$ ν(CN) at time t.

$\sim$6 K to the HS$_{tr}$ form in I and II, at constant incident light flux, obeys first-order kinetics. A typical semilogarithemic plot of this LIESST process is shown in Figure 2. The linearity of this plot suggests that the rate of the LIESST process depends only on the amount of LS form remaining, and does not involve the formation of nucleation centers, domains, or other cooperative (i.e. domain wall) effects. Using doping experiments of another iron(II) spin-crossover complex, Hauser has also concluded the LIESST process to be a noncooperative process.[15]

In order to confirm that the optically converted HS form at 6 K was indeed trapped, the following experiments were carried out. After white light irradiation had completely pumped the sample, the irradiation was stopped, the absolute filter was placed between the sample and the internal He/Ne laser source, and the sample was maintained at 6 K in the dark. After 60 and 120 min, respectively, for I and II both samples were observed to be still completely in the HS$_{tr}$ form. A similar stability of the HS$_{tr}$ form for [Fe(ptz)$_6$](BF$_4$)$_2$, where ptz = 1-propyltetrazole, has been reported by Gütlich.[7] Optically converting I from the stable LS form to the HS$_{tr}$ form with white light at $6 < T < 43$ K resulted in full conversion with the same pumping rate as at 6 K. At these temperatures, too, the samples were still completely in the HS$_{tr}$ form after being held in the dark for 60 min. This suggests that quantum-mechanical tunneling from the HS$_{tr}$ form to the LS form does not occur to any significant extent at these low temperatures. To examine the influence of unconverted LS form on the rate of the HS$_{tr}$ to LS form conversion, I was only partially converted to the HS$_{tr}$ form at 6 K with white light to give matrices containing 33% and 66% trapped HS, respectively. Each sample was then held in the dark at 6 K. After 1 h the amount of HS$_{tr}$ present

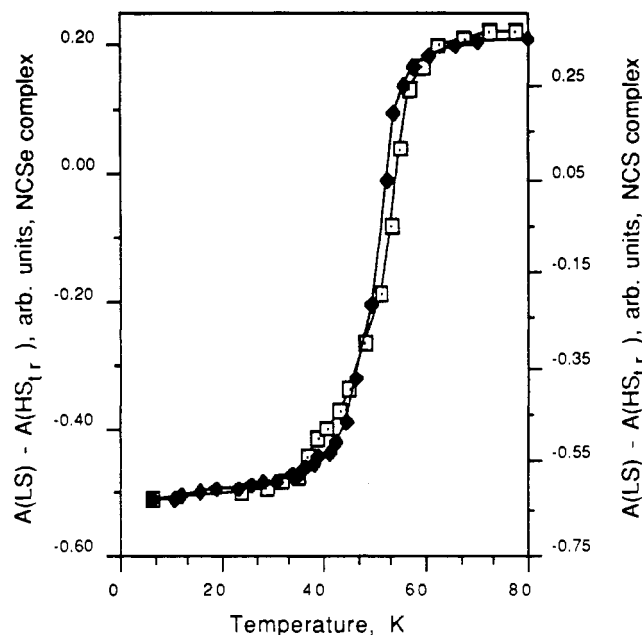(15) Hauser, A. *Chem. Phys. Lett.* **1986**, *124*, 543.

Figure 3. Reconversion of the trapped HS form of $Fe(bt)_2(NCS)_2$ (◆) and $Fe(bt)_2(NCSe)_2$ (□) to the LS form on sample warming as monitored by the absorbance of the CN stretching frequencies for the two spin states.

remained unchanged, i.e. 33% and 66%, respectively. This indicates that the amount of the LS form present in the matrix at 6 K does not lead to spontaneous conversion of the HS_{tr} form, which appears to be stable for times long compared to the time scale of the experiment.

After a sample has been converted to the HS_{tr} form at 6 K and then warmed, there is a temperature at which the HS_{tr} form has enough thermal energy to cross the barrier and convert to the more stable LS form. As the above experiment indicates, $HS_{tr} \Rightarrow$ LS tunneling at low temperatures is not a major mechanism of HS_{tr} $\Rightarrow$ LS conversion in compounds I and II, and therefore classical barrier crossing is likely to be the major mechanism by which the HS_{tr} form converts to the LS form at higher temperatures. To obtain qualitative information about the temperature at which this classical barrier crossing occurs, samples that had been completely converted to the HS_{tr} form at 6 K were warmed at a rate of ~ 0.25 K min^{-1} to a new temperature, held at that temperature until the FTIR scans were completed, and then warmed to a higher temperature, and the process was repeated. The resulting warming curves for I and II are summarized in Figure 3. The warming curve for I appears symmetric and shows the usual sigmoid behavior with an inflection point at ~ 52.5 K. The warming curve for II is less symmetric and evidences a more complex behavior in the range $37 < T < 43$ K, presumably due to the presence of two crossover phases as has been discussed above. Figure 4 is a portion of the IR spectrum in the $\nu(CN)$ region of II at 48 K during the thermal conversion from the HS_{tr} to the LS form. This spectrum shows four $\nu(CN)$ bands in the LS region. The temperature at the major inflection point in the trapped HS to LS thermal conversion plot for II is approximately 55 K, 2 deg higher than the corresponding value for I.

To elucidate further the behavior of the HS_{tr} form in the vicinity of the barrier-crossing temperature, a sample of I was held at temperatures in the range $45 < T < 67.5$ K, optically pumped to maximum LS $\Rightarrow$ HS_{tr} conversion, and then (with the excitation source turned off) followed as a function of time. As expected, the $HS_{tr} \Rightarrow$ LS relaxation rate was found to be temperature dependent, progressing at higher rates as the experimental temperature is raised. Within the measurement time of each run (up to 150 min), none of the conversions reached a true equilibrium value, but at temperatures well above the inflection point (52.5 K) of Figure 3, nearly complete conversion to the LS form was observed. At 67.5 K nearly complete conversion was obtained within 35 min. This behavior is indicative of classical potential
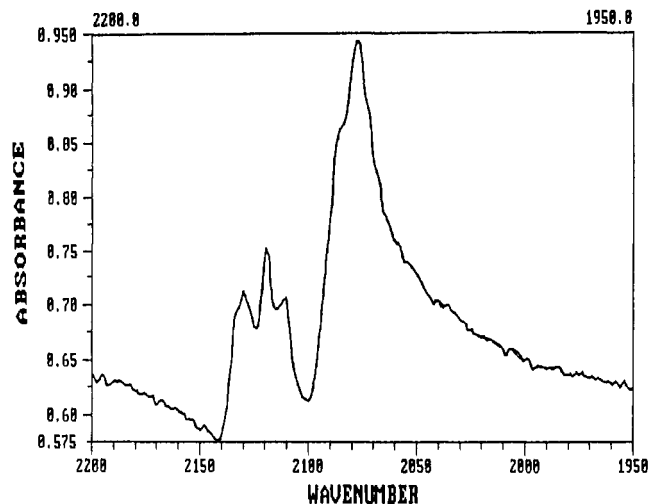

Figure 4. Infrared absorbance spectrum of $Fe(bt)_2(NCSe)_2$ showing three LS CN stretching bands at 2130, 2119, and 2110 cm^{-1} in addition to the unresolved HS absorbance at ~ 2075 cm^{-1}. The 2130-cm^{-1} band has an additional small shoulder at 2133 cm^{-1}. The spectrum was obtained at 48 K during the trapped HS to LS conversion on sample warming.

barrier crossing from a thermally excited state that is populated according to the usual Blotzmann distribution. Depletion of the excited state by intersystem crossing—presumably via a state in the ^3T manifold—is offset by thermal excitation from energy levels from which direct intersystem crossing is energetically forbidden (e.g. the HS_{tr} ground state).

Since the experimental procedure used to generate the data summarized in Figure 3 reflects, in part, this classical Boltzmann distribution, the inflection point in the warming curve can only be taken as a lower limit to the characteristic barrier-crossing temperature. An Arrhenius plot of the temperature-dependent $HS_{tr} \Rightarrow$ LS relaxation rates described above deviates from a straight line, presumably because of cooperative effects,[16] and therefore the activation energy of this process could not be determined accurately. Nonetheless, the details of the warming curve data summarized in Figure 3 can serve as a qualitative measure of the energetics of the barrier-crossing process and thus help to further characterize the LIESST phenomenon in these complexes.

In summary, the use of FTIR spectroscopic methods at low temperatures on $Fe(bt)_2(NCS)_2$ and $Fe(bt)_2(NCSe)_2$ has demonstrated that both compounds undergo the LIESST phenomenon in a well-behaved manner. Both complexes at 6 K convert completely into the trapped HS form, which then is stable for periods in excess of hours. Careful cooling and warming experiments of the thermally driven HS–LS transition have shown the persistence of absorption bands ($\nu(CN)$) associated with the minority phase discussed above, over a larger temperature range than that associated with the thermal behavior of the majority bands. This more sluggish temperature dependence of the crossover phenomenon for the minority phase is also observed in the LIESST experiments. It is not possible from the available data to extract a reliable value of T_1 or of the classical barrier-crossing temperature for the minority constituent, the dominant spectral response being due to the majority component, but some estimates can be made. The Mössbauer data reported by König[2] for the T_1 transition region of I suggest a lower T_1 value for the minority phase than for the majority phase. Further LIESST studies of related compounds are currently under way.

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