

Fig. 1. Metal-ligand skeletal region for  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  under varying conditions of temperature and pressure.

$\text{N}_3^-$ ,  $\text{NCO}^-$ ,  $\text{OAc}^-$ ,  $\text{HCOO}^-$ ) or low spin states ( $X = \text{CN}^-$ ,  $\text{CNO}^-$ ,  $\text{NO}_2^-$ ) or can exhibit the phenomenon of magnetic spin crossover.<sup>1-3</sup> A recent study of the effect of pressure on the Mössbauer spectra for this type of complex indicates that high pressure is capable of partial conversion of the high spin state to the low spin state.<sup>4</sup> However, there is still some disagreement concerning the interpretation of the Mössbauer data in systems which are in spin state equilibrium, as evidenced by some recent work on  $\text{Fe}(\text{III})$  complexes with *N,N*-dialkyldithiocarbamates.<sup>5</sup> High pressure studies have also been made on these  $\text{Fe}(\text{III})$  dithio chelates.<sup>6,7</sup> The results of these investigations on the solution electronic spectra indicate that the spin state is again pressure-sensitive.

In this paper we have undertaken a study of the effects of pressure on the low frequency spectra of  $\text{Fe}(\text{phen})_2(\text{NCS})_2$ ,  $\text{Fe}(\text{phen})_2(\text{NCSe})_2$ , and  $\text{Fe}(\text{bipy})_2(\text{NCS})_2$ . Recent investigations on the far infrared spectra of these complexes show that the spectra are temperature-dependent.<sup>8,9</sup> The room temperature (high spin state) spectra are markedly different from the spectra at  $\sim 100^\circ\text{K}$  (low spin state). The effect of increasing pressure on the low frequency spectra shows a partial high spin to low spin conversion. However, it is not possible to convert completely to low spin using pressure alone. For all systems studied, the pressure effects are reversible.

We have examined the skeletal region for three iron complexes at high pressures to 24 kbar at  $100^\circ\text{K}$ , room temperature, and  $353^\circ\text{K}$ . Figs. 1 and 2 record a comparison of spectra for  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  and  $\text{Fe}(\text{bipy})_2(\text{NCS})_2$ . From an examination of Fig. 1 it may be observed that at  $\sim 10$  kbar new bands appear at 299 and  $251\text{ cm}^{-1}$  indicative of some conversion to the low spin form. At about  $\sim 18$  kbar the spectrum continues to demonstrate a mixture of high spin and low spin forms. At this pressure two weak bands appear at  $380\text{ cm}^{-1}$ , which have been assigned as the Fe-N(phen) stretching modes.<sup>8,9</sup> Fig. 2 illustrates similar features for  $\text{Fe}(\text{bipy})_2(\text{NCS})_2$ . Complete conversion with pressure to low spin does not occur. However, the mixtures

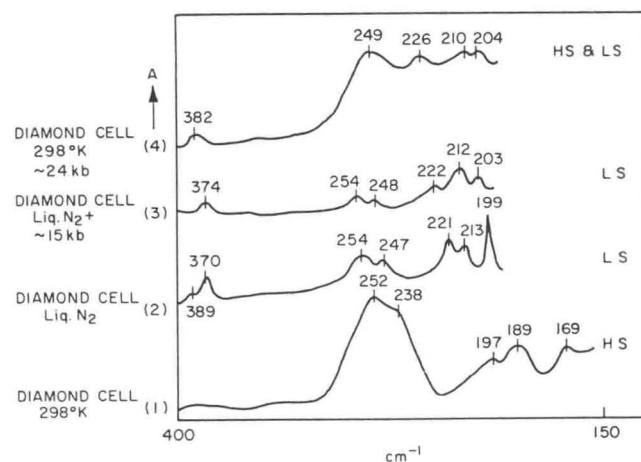


Fig. 2. Metal-ligand skeletal region for  $\text{Fe}(\text{bipy})_2(\text{NCS})_2$  under varying conditions of temperature and pressure.

of high spin and low spin forms, maintained at high pressure, can be converted to the low spin form by cooling to  $100^\circ\text{K}$ . Heating the mixture to  $353^\circ\text{K}$  causes conversion to the high spin form, although the conversion may be somewhat sluggish, as some weak absorptions attributed to the low spin form still persist. Similar results were obtained with  $\text{Fe}(\text{phen})_2(\text{NCSe})_2$ . Figs. 3 to 5 summarize the data. These pressure data parallel the results observed from temperature effects alone. The actual crossover temperatures for  $\text{Fe}(\text{phen})_2(\text{NCS})_2$ ,  $\text{Fe}(\text{phen})_2(\text{NCSe})_2$ , and  $\text{Fe}(\text{bipy})_2(\text{NCS})_2$  are 174, 232, and  $215^\circ\text{K}$ , respectively.<sup>2, 3</sup> Thus, for this group of compounds,  $\text{Fe}(\text{phen})_2(\text{NCSe})_2$  exhibits the highest crossover temperature, and evidence for the high spin to low spin conversion can be seen at the lowest pressure.

Drickamer, using the Mössbauer technique for  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  and  $\text{Fe}(\text{phen})_2(\text{NCSe})_2$ , showed that only partial conversion to low spin was possible with pressure.<sup>4</sup> Thus, our low frequency data confirm the Mössbauer results. It is also interesting to note that Drickamer reports that it is possible to achieve a partial spin state conversion of  $\text{Fe}(\text{phen})_2\text{X}_2$  ( $X = \text{Cl}^-$ ,  $\text{Br}^-$ ,

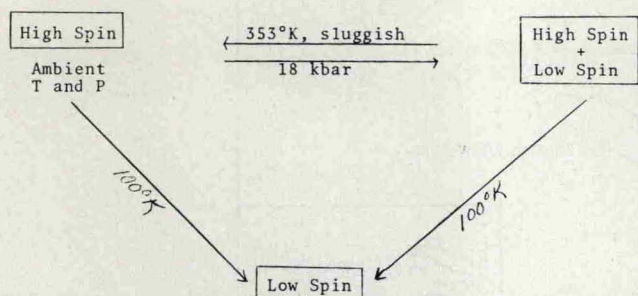


FIG. 3. Pressure-temperature relationships of  $\text{Fe}(\text{phen})_2(\text{NCS})_2$ .

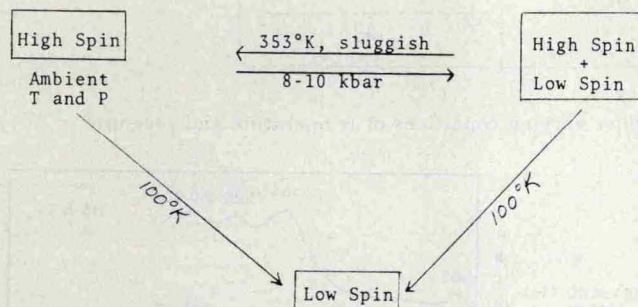


FIG. 4. Pressure-temperature relationships of  $\text{Fe}(\text{phen})_2(\text{NCSe})_2$ .

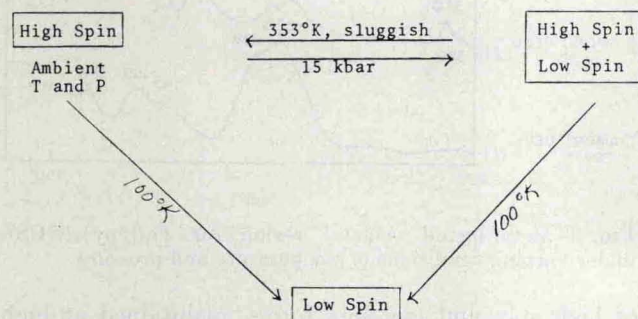


FIG. 5. Pressure-temperature relationships of  $\text{Fe}(\text{bipy})_2(\text{NCS})_2$ .

$\text{N}_3^-$ , and  $\text{NCO}^-$ ) at high pressures. No anomalous magnetic behavior for these complexes is reported over the temperature range 77 to 440°K (at 1 atm pressure).<sup>1</sup> Our preliminary results on  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  and  $\text{Fe}(\text{phen})_2(\text{NCSe})_2$  indicate that it may be possible to completely convert the above  $\text{Fe}(\text{phen})_2\text{X}_2$  series to the low spin state using a combination of pressure and temperature.

The results of the low temperature conversion to low spin for these compounds were explained in terms of strengthening of the Fe-N(phen or bipy) and FeN(NCS and NCSe) bonds due to the back-donation of the  $t_2$  electrons of the metal to the  $\pi^*$  orbitals of the organic ligand and NCS or NCSe.<sup>8</sup> This mechanism may also be operative at the outset of pressure application, but with increasing pressure, the back-donation of the metal is reduced by the accessibility of  $\pi$  electrons from the ligand to the ligand  $\pi^*$  orbitals.<sup>4</sup>

The experiments were conducted in a diamond-anvil

cell using a 6X beam condenser and a Perkin-Elmer model 301 far infrared spectrophotometer. Details of the technique are described elsewhere.<sup>10</sup> For the low temperature studies a special anvil cell containing an entry and exit port and a cooling element surrounding the diamonds was used. This allowed the entry of helium which was previously cooled in a liquid nitrogen trap. We estimate the variation in temperature to be  $\pm 5^\circ\text{K}$  at 100°K. For the heated experiments we used a cell which contained a heating element surrounding the diamonds. The higher temperatures were measured with a standard chromel-alumel thermocouple. We estimate that the variation at 353°K was  $\pm 1^\circ\text{K}$ .

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## Application of Carbon Rod Atomizer for the Analysis of Mercury in Air

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The analysis of air for traces of poisonous metals usually involves passing large volumes of air through filters or absorbing solutions followed by extensive manipulation before actual analysis. In order to simplify these analyses, several workers have reported upon the measurement of airborne particulates filtered onto spectroscopic electrodes.<sup>1-4</sup> Woodriff and Lech<sup>3</sup> draw air through porous graphite cups which then are inserted into a graphite furnace atomizer. Analysis of lead particulates at levels present in the atmosphere can be accomplished on only 50 cc of air. Amos and co-workers<sup>4</sup> have described application of the carbon rod atomizer to the analysis of lead in air. An essentially standard