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TABLE II. Absorbances of CO_2, CH_4, and NH_3 as a function of temperature of the cylinder.

Day	CO_2			CH_4			NH_3		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
1	0.006	0.480	0.054			0.017			
2	0.031	0.566	0.106			0.043			
3	0.058	0.542			0.046	0.478			
4	0.042	0.511	0.666		0.084	0.568			
7	0.208	0.388	0.434		0.059	0.454		0.087	
8	0.034	0.335	0.541		0.079	0.301		0.092	
9	0.301	0.335	0.752		0.086		0.088	0.094	0.072
10	0.024	0.306	0.467		0.086	0.073	0.088	0.094	
11	0.029	0.244	0.681		0.066	0.078	0.090		
14	0.024	0.139	0.102		0.045	0.051		0.028	
15		0.097	0.069		0.038	0.042			
16		0.105	0.058		0.048	0.063			
17		0.103			0.052				
18		0.098			0.036				
21		0.174			0.059				

composition gases was studied when the controlled sanitary landfill was maintained 30, 40, and 50°C and the soil layers were saturated with water but not to the point of becoming muddy, i.e., wet soil layers. The nature of these gases was also studied at 30°C using dry soil layers in the cylinder.

The decomposition gases from the cylinders containing wet soil layers were the same at 30, 40, and 50°C. That is, the infrared spectra indicated the presence of H_2O, CO_2, NH_3, and CH_4 at all temperatures (Table I). However, the rates at which the gases evolved were temperature-dependent. The gases were identified by comparison with a catalog of infrared spectra of various gases.[4] Analysis for ammonia gas was not reported in previous analytical studies of the gases from sanitary landfills.[1-3]

The absorbances of CO_2, CH_4, and NH_3 gases were measured at different times with the cylinder maintained at 30, at 40, and at 50°C. The results of these studies are shown in Table II. Methane gas is not indicated in Table II for the cylinder at 30°C. At this temperature, CH_4 was not observed until the 70th day.

The decomposition gases from a cylinder containing dry soil layers and maintained at 30°C were also analyzed by infrared spectroscopy over a period of time. The major change in the gases due to the use of dry soil instead of wet soil is that N_2O is observed in the infrared spectra of the gases recorded between the 17th and 24th days of decomposition. The presence of N_2O is indicated by an absorption band located near 2220 cm^{-1} of the spectrum.[4] Further, no ammonia gas was observed. The presence of CH_4 was not observed until after the 70th day.

The results of this study indicate that infrared spectroscopy can be a useful analytical tool in the analysis of the decomposition gases of sanitary landfills. The presence of NH_3 gas or N_2O gas, depending on the condition of the soil, would be difficult to ascertain quickly by other conventional means and with such simple sampling procedures. Further, simultaneous qualitative and quantitative analysis may be performed on a sample. The availability of commercial portable gas analyzers permits on-site analyses for the decomposition gases of sanitary landfills.

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Fourier Transform Infrared Determination of Parts per Billion of Oxygen in Silicon

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Previous work on oxygen in silicon resulted in producing an infrared calibration curve based on gas fusion analysis[1]. This calibration curve was also compared with an activation analysis method.[2] The normal spectrometric technique employs a double beam grating spectrophotometer and a 1-cm polished silicon sample and reference slices.[3] The silicon lattice band at 1100 cm^{-1} overlaps the silicon-oxygen vibration band at 1107 cm^{-1}. Thus, to measure the baseline accurately it is necessary to have an oxygen-free silicon in the reference beam. The lattice band is ratioed out of the spectra, and only the oxygen-silicon vibration band appears. Using 1-cm thick sample and reference slices a limit of

detection of 50 ppb atomic is obtained. The 1-cm thickness used is the maximum possible; the lattice absorption band absorbs sufficient energy for greater thickness to degrade the signal-to-noise ratio. The poor signal-to-noise ratio for thicker samples results in meaningless results when a spectral scan is run.

Since the oxygen content of many gas float-zoned crystals ranges between 300 ppb atomic and an undetectable 50 ppb atomic, it has become necessary to improve the lower limit of detection. Low temperature infrared spectroscopy with the grating spectrophotometer will give an improvement in detection limit.[4] The factor of 5 or 10 improvement is paid for by increased run time and special sawing of crystals to fit the cryostat. Large scale measurement of crystals is thus not desirable under these conditions.

The recent advances in Fourier Transform Spectrophotometry presents us with a simple solution to the measurement problem. With an instrument of this design we have achieved a substantial improvement in detection limit without adding extra costs for sample preparation and instrument time.

Fig. 1 is the spectrum of an oxygen-containing silicon slug, 2 cm in thickness, computer-ratioed against a reference 2-cm thick oxygen-free silicon slug as obtained on a Digilab FTS-14. The Digilab FTS-14 was used in the STORE/RATIO single beam mode.[5] Both sample and reference spectra were measured by coadding 500 scans using a spectral resolution of 16 cm⁻¹ with a triangular apodization function and 4 cm⁻¹ with a boxcar apodization function. The triangular apodization function further decreases the spectral resolution to about 20 cm⁻¹, but with an improved signal-to-noise ratio. The trade-off in resolution for increased signal-to-noise ratio presents no problem here because of the relatively large half-band width (32 cm⁻¹) of the asymmetric Si-O stretching vibration at 1107 cm⁻¹. A small uncertainty in absolute transmission amounting to less than $\pm 0.4\%$ ($\pm 1.1\%$ absorbance) was noted in going from a boxcar to triangular apodization function at 16 cm⁻¹ resolution. This should not alter the results reported here since all measurements are referred to a reference run under identical conditions.

The computer scale expanded trace of the Si-O band shows the peak height of the band at 0.999 %T and the baseline at 1.023 %T. This calculates as 122 ppb atomic oxygen compared with the value 124 ppb atomic oxygen obtained from a low temperature scan on a Beckman IR-12. The signal-to-noise ratio in Fig. 1 is estimated as ~30/1. If the lower limit of detectability is assumed to be twice the noise level, then one would conclude that for a 2-cm thick slug, the lower limit of detectability for oxygen is about 8 ppb atomic. This figure, 8 ppb atomic oxygen, is in the same range as the estimated lower limit of detectability for oxygen using low temperature techniques with a grating spectrophotometer. However, there are time-saving features associated with the FTS-14 analysis. The crystals do not have to be specially cut to fit into a cryostat. The total run time is approximately 10 min per sample. The system was found stable enough so that the same reference (run time 10 min) could be used over a period of several hours.

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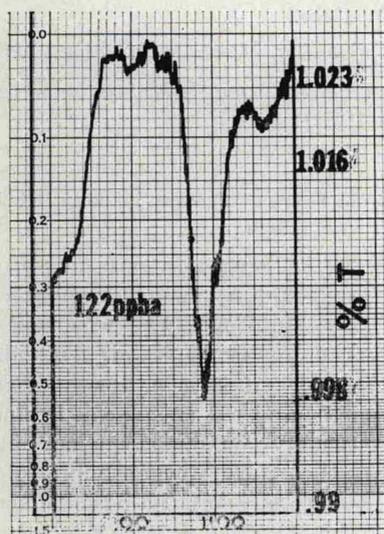FIG. 1. Scale-expanded spectrum of 122 ppba 0 in silicon computer ratioed against an oxygen-free silicon slug run at 4 cm⁻¹ resolution.

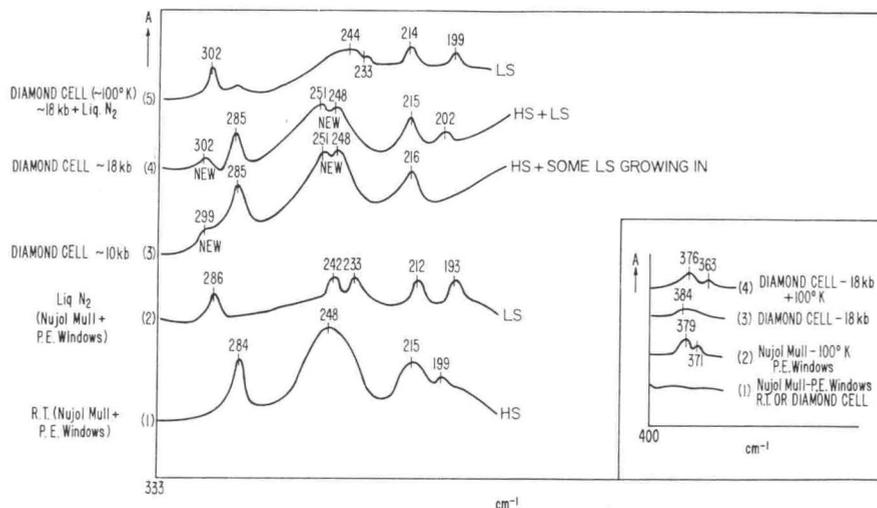# Pressure-Temperature Relationships for Fe(II) Complexes of 1,10-Phenanthroline and 2,2′-Bipyridine*

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The complexes of the type Fe(phen)$_2$X$_2$ and Fe(bipy)$_2$X$_2$ (phen = 1,10-phenanthroline, bipy = 2,2′-bipyridine) exist in high spin states (X = Cl⁻, Br⁻,

FIG. 1. Metal-ligand skeletal region for Fe(phen)$_2$(NCS)$_2$ under varying conditions of temperature and pressure.

N$_3^-$, NCO$^-$, OAc$^-$, HCOO$^-$) or low spin states (X = CN$^-$, CNO$^-$, NO$_2^-$) or can exhibit the phenomenon of magnetic spin crossover.[1-3] 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.[4] 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 Fe(III) complexes with N,N-dialkyldithiocarbamates.[5] High pressure studies have also been made on these Fe(III) dithio chelates.[6,7] 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 Fe(phen)$_2$(NCS)$_2$, Fe(phen)$_2$(NCSe)$_2$, and Fe(bipy)$_2$-(NCS)$_2$. Recent investigations on the far infrared spectra of these complexes show that the spectra are temperature-dependent.[8,9] The room temperature (high spin state) spectra are markedly different from the spectra at $\sim 100°$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°K, room temperature, and 353°K. Figs. 1 and 2 record a comparison of spectra for Fe(phen)$_2$(NCS)$_2$ and Fe(bipy)$_2$-(NCS)$_2$. From an examination of Fig. 1 it may be observed that at ~ 10 kbar new bands appear at 299 and 251 cm^{-1} indicative of some conversion to the low spin form. At about ~ 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 cm^{-1}, which have been assigned as the Fe-N(phen) stretching modes.[8,9] Fig. 2 illustrates similar features for Fe(bipy)$_2$(NCS)$_2$. Complete conversion with pressure to low spin does not occur. However, the mixtures
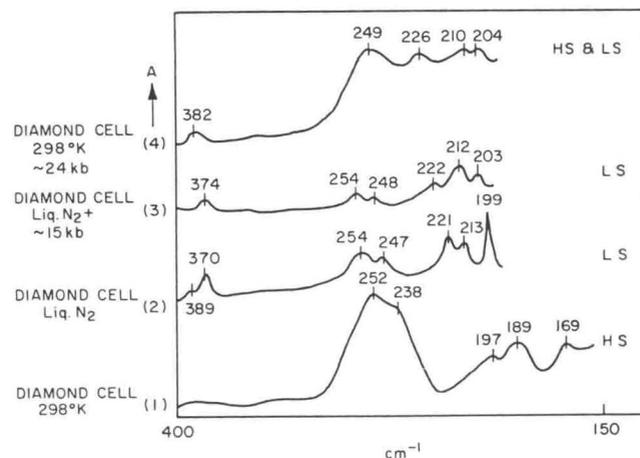

FIG. 2. Metal-ligand skeletal region for Fe(bipy)$_2$(NCS)$_2$ under varying conditions of temperature and pressure.

of high spin and low spin forms, maintained at high pressure, can be converted to the low spin form by cooling to 100°K. Heating the mixture to 353°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 Fe(phen)$_2$(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 Fe(phen)$_2$-(NCS)$_2$, Fe(phen)$_2$(NCSe)$_2$, and Fe(bipy)$_2$(NCS)$_2$ are 174, 232, and 215°K, respectively.[2,3] Thus, for this group of compounds, Fe(phen)$_2$(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 Fe(phen)$_2$(NCS)$_2$ and Fe(phen)$_2$(NCSe)$_2$, showed that only partial conversion to low spin was possible with pressure.[4] 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 Fe(phen)$_2$X$_2$ (X = Cl$^-$, Br$^-$,
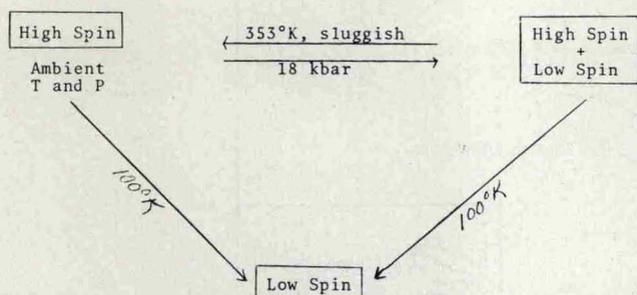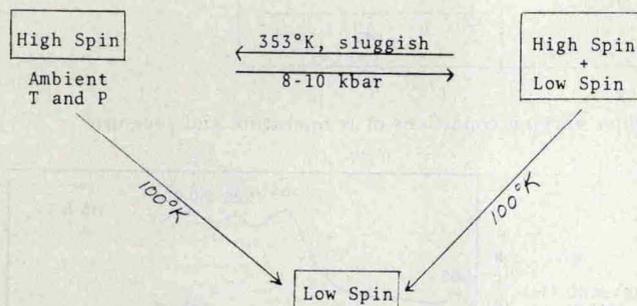
FIG. 3. Pressure-temperature relationships of Fe(phen)$_2$-(NCS)$_2$.

FIG. 4. Pressure-temperature relationships of Fe(phen)$_2$-(NCSe)$_2$.
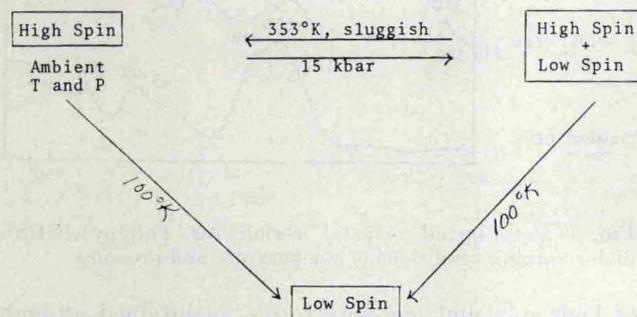

FIG. 5. Pressure-temperature relationships of Fe(bipy)$_2$-(NCS)$_2$.

N$_3^-$, and 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).[1] Our preliminary results on Fe(phen)$_2$(NCS)$_2$ and Fe(phen)$_2$(NCSe)$_2$ indicate that it may be possible to completely convert the above Fe(phen)$_2$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 π^* orbitals of the organic ligand and NCS or NCSe.[8] 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 π electrons from the ligand to the ligand π^* orbitals.[4]

The experiments were conducted in a diamond-anvil

cell using a 6× beam condenser and a Perkin-Elmer model 301 far infrared spectrophotometer. Details of the technique are described elsewhere.[10] 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 ±5°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 ±1°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.[1-4] Woodriff and Lech[3] 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[4] have described application of the carbon rod atomizer to the analysis of lead in air. An essentially standard