as the pK_a of the conjugated acid of the base increases. This trend may hold for the 1:1 adduct series although not enough points are available to confirm it. Furthermore, type A and B bases give different straight lines with the type B line shifted to a lower position on the ordinate scale. The difference between these two slopes may indicate the magnitude of π contribution to the basicity (hence the lowering of $\nu(O_2)$). Similar results have been obtained for the 1:2 adducts of Co(J-en).[12]

According to the spin-pairing model of the Co–O_2 bond,[13] the amount of negative charge on the O_2 depends upon the nature of the in-plane (chelating) and axial (base) ligands. In fact, our studies indicate that the $\nu(O_2)$ of Co(chelate)(B)O_2 complexes can vary over a wide range from 1278 (Co(TPP)O_2) to 1003 cm^{-1} (Co(acacen)(*n*-BuNH_2)O_2). This range is much wider than that previously defined[2] and is contrary to the statement[13] that "the values of $\nu(O_2)$ are relatively insensitive to the metal, the ligand field strength, and the strength of dioxygen binding". However, the latter conclusion is based in part on tentative $\nu(O_2)$ assignments which we have now shown to be in error. Clearly, more data must be obtained before a general statement can be made regarding the sensitivity of $\nu(O_2)$ to the metal and the ligand field strength. This is particularly true for the O_2 adducts of metalloporphyrins since thus far very limited data are available on their $\nu(O_2)$.

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Registry No. Co(acacen)O_2, 56295-08-0; Co(acacen)(py)O_2, 42742-62-1; Co(acacen)(1-MeIm)O_2, 80186-61-4; Co(acacen)(benzylamine)O_2, 80186-62-5; Co(acacen)(*n*-BuNH_2)O_2, 80186-63-6; [Co(acacen)(CNpy)]$_2O_2$, 80186-64-7; [Co(acacen)(aniline)]$_2O_2$, 80186-65-8; [Co(acacen)(py)]$_2O_2$, 80186-66-9; [Co(acacen)(1-MeIm)]$_2O_2$, 80186-67-0; [Co(acacen)(benzylamine)]$_2O_2$, 80186-68-1; [Co(acacen)(*n*-BuNH_2)]$_2O_2$, 80186-69-2; Co(acacen), 36802-26-3.

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[12] Nakamoto, K.; Nonaka, Y.; Ishiguro, T.; Urban, M. W.; Suzuki, M.; Kozuka, M.; Nishida, Y.; Kida, S., submitted to *J. Am. Chem. Soc.*

[13] Drago, R. S.; Corden, B. B. *Acc. Chem. Res.* **1980**, *13*, 353 and references therein.

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Spectroscopy at Very High Pressures. 36. An Infrared Study of Spin-State Equilibria in Some Iron(II) Complexes

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The complexes *cis*-[Fe(*o*-phen)$_2X_2$] (X = I, NCS, NCSe, and N_3) have been studied under hydrostatic pressures of up to 40 kbar in a diamond-anvil cell. The spectra of these, and of the related complexes [M(*o*-phen)$_3$]$^{n+}$, are interpreted by deriving the skeletal modes from those of the free-ligand translations and rotations. The spectrum of the iodide is consistent with the presence of a mixture of high-spin and low-spin isomers in roughly equal proportions at 30 kbar, but the azido complex appears to be almost entirely converted to low-spin at this pressure. The new data for the thiocyanato and isocyanato complexes indicate that the spin-state transitions occur near 8 and 6 kbar, respectively, lower than previous estimates based upon samples under shear stress, and are quite sharp.

Introduction

The spin configurations of certain transition-metal complexes can be affected by change of temperature and/or pressure.[2,3] Among the best known examples are the materials *cis*-[Fe(*o*-phen)$_2X_2$], where X is an anionic ligand.[4] The behavior under pressure of members of this series has been followed by using Mössbauer, optical,[5] and far-IR spectroscopies.[6] Changes in IR absorption associated with passing through the high- to low-spin transition on cooling have also been reported.[7,8]

We have examined the far-IR absorption spectra of the compounds with X = I, NCS, NCSe, and N_3 under high pressure in a diamond-anvil cell (dac). The iodide and azide complexes have not been studied previously by high-pressure IR spectroscopy. They have proved to be valuable in reaching an understanding of the spectra of the whole series. We have repeated Ferraro and Takemoto's work[6] on the NCS and NCSe complexes using hydrostatic pressure conditions (i.e., with a gasket between the two diamonds); in their work the dac was used without a gasket, and the samples were therefore subjected to a large shear stress. Further, we wished to find whether the IR results substantiated the rather curious spin-equilibria vs. pressure data of Fisher and Drickamer,[5] which suggest that increase of pressure first brings about partial conversion of high-spin material to low-spin and that with further pressure increase there is partial reversion to high-spin behavior.

Experimental Section

The compounds were prepared by standard methods. The dac and the technique for high-pressure far-IR spectroscopy have been described elsewhere.[9] Samples were contained within molybdenum gaskets initially 0.1 mm thick with a central hole of 0.4-mm diameter. The pressure-transmitting liquid within the gasket hole was Nujol: this does not interfere in the far-IR but it freezes under pressure at about 13 kbar. At higher pressures an increasingly large shear component is thus applied to the samples but this is very small compared with that developed in the sample in a nongasketed dac.

The pressure-transmitting fluid contained the sample to be studied, plus a small chip of ruby, which acted as the pressure calibrant.[10,11] The ruby R lines were followed by using a Raman spectrometer. Far-IR spectra were obtained by using a Beckman-RIIC FS-620 Fourier spectrometer. As the energy transmitted through a hole 0.4

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[1] (a) University of Leicester. (b) University of Missouri—Rolla.

[2] Ferraro, J. R. *Coord. Chem. Rev.* **1979**, *29*, 1.

[3] Ferraro, J. R.; Long, G. J. *Acc. Chem. Res.* **1975**, *8*, 171.

[4] König, E.; Madeja, K. *Inorg. Chem.* **1967**, *6*, 48.

[5] Fisher, D. C.; Drickamer, H. G. *J. Chem. Phys.* **1971**, *54*, 4825.

[6] Ferraro, J. R.; Takemoto, J. H. *Appl. Spectrosc.* **1974**, *28*, 66.

[7] Takemoto, J. H.; Hutchinson, B. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 769.

[8] Takemoto, J. H.; Hutchinson, B. *Inorg. Chem.* **1973**, *12*, 705.

[9] Adams, D. M.; Payne, S. J.; Martin, K. *Appl. Spectrosc.* **1973**, *27*, 377.

[10] Piermarini, G. J.; Block, S.; Barnett, J. D.; Forman, R. A. *J. Appl. Phys.* **1975**, *16*, 2774.

[11] Adams, D. M.; Appleby, R.; Sharma, S. K. *J. Phys. E* **1976**, *9*, 1140.

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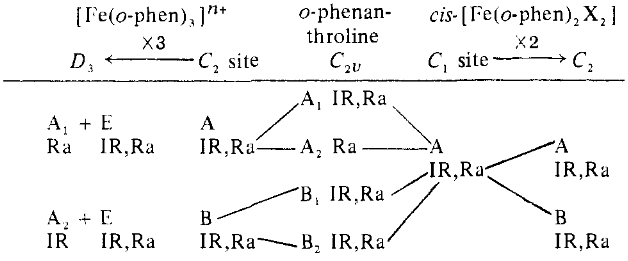
Table I. Correlations and Selection Rules for *o*-Phenanthroline Complexes



mm in diameter is very low, spectra below 100 cm^{-1} are regarded as unreliable. The present work is therefore restricted to the 100–400-cm^{-1} region, the upper bound being set by the beam-splitter characteristics of the instrument.

Results and Discussion

Assignment. The vibrational spectra of these materials are extremely complex. Indeed, the structures even of the more symmetrical tris(phenanthroline) complexes have been described[12] as "too complicated to allow rigorous vibrational analysis". Valuable insight has resulted nevertheless from the use of metal isotopes, revealing bands in both tris(phenanthroline)[12,13] and Fe(*o*-phen)$_2$X$_2$ compounds[7] that may be attributed to M–N bond stretching, but more detailed assignments do not exist.

In order to interpret the high-pressure data we first give an outline assignment for the tris(phenanthroline) materials. Having shown that the model used accords with observations, we then consider the spin-equilibrium data.

Since *o*-phenanthroline is a particularly rigid ligand, we base our analysis of the spectra of its complexes on a model in which the skeletal modes are taken to arise from symmetry-adapted combinations of the translations and rotations permitted to each free-ligand molecule. From the correlation shown in the left-hand side of Table I we obtain for a D_3 tris(*o*-phenanthroline) complex

$$\Gamma(\text{skeletal}) = 2\ A_1 + 3\ A_2 + 5\ E$$

Hence the far-IR spectrum should contain 8 bands (3 A_2 + 5 E) due to skeletal modes. Of these, ν(Fe–N) accounts for A_2 + 2 E, and there is a further ν(Fe–N) mode of A_1 symmetry, which is inactive in the IR spectrum. The far-IR spectrum is completed by addition of low-frequency internal modes of *o*-phenanthroline itself. From a recent, very detailed, vibrational analysis of this ligand[14,15] we see that from 200 to 400 cm^{-1} there are no modes, either active or inactive; there are three in the 212–258-cm^{-1} region and two more at 106 and 142 cm^{-1}. The published far-IR spectrum of *o*-phenanthroline for the region above 100 cm^{-1} shows bands at 242 m, 259 s, 411 s, and 432 w cm^{-1}.[12]

For [Fe(*o*-phen)$_3$]$^{2+}$ salts, ν(Fe–N) has been located by the metal isotope method[12] at 359 and 374 cm^{-1} (i.e., two of the three allowed modes), but [Ni(*o*-phen)$_3$]$^{2+}$ shows the correct number of ν(Ni–N) bands, at 243, 260, and 300 cm^{-1}. In the region above 150 cm^{-1} three different salts of [Fe(*o*-phen)$_3$]$^{2+}$ exhibit the same number of far-IR bands:[12] all must therefore arise from the cation. Below 400 cm^{-1}, each complex shows the 10 absorption bands listed in Table II, in close accord with the above theory. Thus, we first identify the strong band(s) near 296 cm^{-1} with the pure ligand modes originally at 242, 259 cm^{-1}. As will appear below, this strong feature remains prominent in all the *cis*-[Fe(*o*-phen)$_2$X$_2$] compounds, in both high- and low-spin forms and throughout all published spectra of the tris(*o*-phenanthroline) complexes, showing little frequency variation.

Table II. Assignments of IR bands (cm^{-1}) for [Fe(*o*-phen)$_3$]$^{2+}$ in the 150–400-cm^{-1} Interval

o-phen[a]	[Fe(*o*-phen)$_3$]$^{2+\,a,b}$	ref 12	this work
	375 359	ν(Fe–N)	ν(Fe–N)
259 242	296 288	ligand B	ν_{21}, A_1; ν_{59}, B_2 of *o*-phen
	245 235	ligand C	*o*-phen wag
	214 211	δ(NFeN)	δ(NFeN)/*o*-phen wag
	191 176	ligand D	*o*-phen torsions

[a] Reference 12. [b] For BF_4^- salt.

There remain six further low-frequency bands, whereas only five are expected. Two explanations may be advanced. Either the additional band may be due to crystal-site splitting of one of the E modes (the most probable reason) or it may be ν_{59}, B_2 of *o*-phenanthroline, in which case it is one of the pair of bands in the 240–250-cm^{-1} region. In support of the first explanation we note that [Fe(*o*-phen)$_3$](ClO$_4$)$_3$·H$_2$O crystallizes in the monoclinic group $A_2/a = C_{2h}^6$ with all molecules on general sites,[16] thus providing a mechanism for lifting degeneracies in D_3.

We note particularly that more bands[12] are found in [Fe(*o*-phen)$_3$](BF$_4$)$_2$, and in the wrong spectral regions, than can be accounted for on the basis of inactive (in C_{2v}) free-ligand modes made active in the complex. Hence the published description of several of the low-frequency modes as ligand B, C, etc. (since followed by others[17]) is erroneous. Our model applies equally well to tris(bipyridyl) complexes and, indeed, to any other containing reasonably rigid ligands. Thus, the basic features of the [M(bpy)$_3$]$^{n+}$ spectra[12] also are accounted for.

The theory used above is for a single isolated complex ion. In a crystal the site field will in general relax selection rules and may lift degeneracies: this was the explanation used above for the presence of an additional band in the [Fe(*o*-phen)$_3$]$^{2+}$ spectra. However, these effects will not affect the *cis*-[Fe(*o*-phen)$_2$X$_2$] compounds as their molecular symmetry (C_2) is already so low that no additional bands can arise in the solid-state spectra from site effects. There are no crystal structure determinations of the compounds we have used, but one of the three polymorphs of [Fe(bpy)$_2$(NCS)$_2$] crystallizes in the orthorhombic space group D_{2h}^{14} with $Z = 4$, each molecule being on a C_2 site.[18] In the absence of other structural data, we assume a similar crystal structure for the [Fe(*o*-phen)$_2$X$_2$] compounds. If, as assumed, the molecular and the site symmetries are the same, the spectrum of the cation is not affected; there will be coupling between the molecules according to the scheme:

$$\begin{array}{ll} C_2\ \text{site} \xrightarrow{\times 4} D_{2h}^{14} & \\ \text{A} & A_g + B_{1g} + A_u + B_{1u} \\ \text{B} & B_{2g} + B_{3g} + B_{2u} + B_{3u} \end{array}$$

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[12] Hutchinson, B.; Takemoto, J.; Nakamoto, K. *J. Am. Chem. Soc.* **1970**, *92*, 3335.

[13] Saito, Y.; Takemoto, J.; Hutchinson, B.; Nakamoto, K. *Inorg. Chem.* **1972**, *11*, 2003.

[14] Altmann, W.; Perkampus, H. H. *Spectrochim. Acta, Part A* **1979**, *35A*, 253.

[15] Altmann, W.; Kleindienst, H.; Perkampus, H. H. *Spectrochim. Acta, Part A* **1979**, *35A*, 259.

[16] Baker, J.; Engelhardt, L. M.; Figgis, B. N.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 530.

[17] Wilde, R. E.; Srinivasan, T. K. K. *J. Inorg. Nucl. Chem.* **1974**, *36*, 323.

[18] König, E.; Watson, K. J. *Chem. Phys. Lett.* **1970**, *6*, 457. König, E.; Madeja, K.; Watson, K. J. *J. Am. Chem. Soc.* **1968**, *90*, 1146.

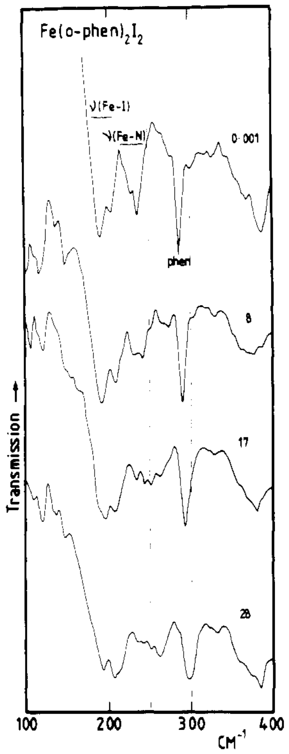

Figure 1. Far-IR spectra of *cis*-[Fe(*o*-phen)$_2$I$_2$] at various pressures (kbar).

Since only B_{nu} modes (n = 1–3) are IR active, it follows that molecular A modes will always appear as single bands (B_{1u}) but that B modes may appear as correlation doublets (B_{2u} + B_{3u}). In molecular crystals such as these, correlation coupling is usually small and is only seen clearly at low temperature and high resolution, conditions not met in this work. We conclude that C_2 selection rules are a good basis for interpretation of the *cis*-[Fe(*o*-phen)$_2$X$_2$] spectra.

For a complex *cis*-[Fe(*o*-phen)$_2$X$_2$] from which the X ligands have been removed, the skeletal vibrations are 5 A + 4 B. ν(Fe–N) accounts for 2 A + 2 B of these. In addition, when X is a monatomic anion, there exist the modes

ν(Fe-X): A + B   δ(FeX$_2$): A
FeX$_2$ rock: B   FeX$_2$ wag: B
FeX$_2$ twist: A

where the descriptions are, of course, very approximate. Thus, their low-frequency spectra should show 6 A + 5 B skeletal modes in addition to ν(Fe–N) and ligand internal modes.

Before considering the high-pressure results, we note the following assignments for ν(Fe–N) obtained by the metal isotope method for *cis*-[Fe(*o*-phen)$_2$X$_2$] (cm^{-1}).

	X = NCS[7]		X = NCSe[8]	
	low spin	high spin	low spin	high spin
ν(Fe-NCE)	532.6 528.5	252.0	530.5 527.0	228.0
ν(Fe-N(phen))	379.0 371.0	220.0	366.0 360.0	218.0

The high spin–low spin transition induced by cooling the thiocyanato complex to 100 K is accompanied by a decrease in the Fe–NCS bond of 0.08 Å and in the Fe–N(phen) bonds of 0.12 and 0.16 Å.[18]

[Fe(*o*-phen)$_2$I$_2$]. For this compound, as for the X = NCS and NCSe analogues, ν(Fe–N) is expected near 225 cm^{-1}. ν(Fe–I) is unlikely to be >200 cm^{-1}; it is at 185, 195 cm^{-1} in *cis*-[Fe^{II}(CO)$_4$I$_2$].[19] Any conversion to the low-spin form is expected to raise both ν(Fe–N) and ν(Fe–I). Fisher and Drickamer reported[5] that at 40 kbar, there is 17% conversion to low spin for X = Cl and 30% for X = Br. No such data are available for X = I but perhaps 50% low spin may be expected, with correspondingly less at lower pressures. The spectra of Figure 1 are thus of mixtures of the two forms.

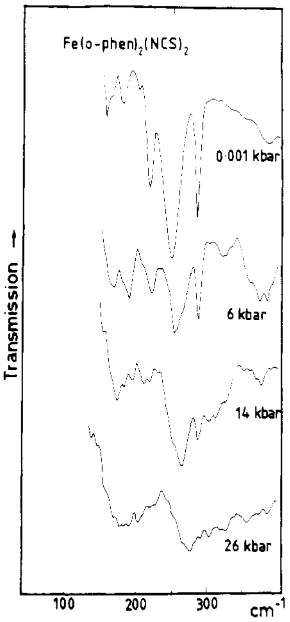

Figure 2. Far-IR spectra of *cis*-[Fe(*o*-phen)$_2$(NCS)$_2$] at various pressures (kbar).

With increase of pressure there is a steady decrease in intensity of a group of bands (ν(Fe–N)) initially near 230 cm^{-1}: they have not entirely disappeared by 28 kbar (see Table III). Concurrently, the strong bands between 150 and 200 cm^{-1} attributed to ν(Fe–I) show new contributions on their high-frequency side, consistent with a change to low-spin behavior. Further progressive changes are exhibited in the 250–280-cm^{-1} range, chiefly growth in intensity of bands >250 cm^{-1}. Strengthening ν(Fe–N) on changing to low-spin implies that the various skeletal modes associated with *o*-phenanthroline will also be raised: there appears to be a loss of intensity around 150 cm^{-1} concurrent with the gain near 250 cm^{-1}, suggesting that some of the 3 A + 2 B deformations are involved.

These results are consistent with change to low-spin behavior increasing with applied pressure; unfortunately, runs above 30 kbar were unsuccessful due to decreasing size of the gasket aperture.

[Fe(*o*-phen)$_2$(NCS)$_2$]. The ambient-pressure spectrum, Figure 2, compares well with those of Takemoto and Hutchinson,[8] both at ambient temperature and at 100 K. The clearest indicators of the spin isomers present are the bands due to ν(Fe–N(phen)), which are at 217 cm^{-1} (high spin) and near 370 cm^{-1} (low spin).

On pressurization of the sample, the 217-cm^{-1} band both shifts to 222 cm^{-1} (at 6 kbar) and begins to lose intensity. Absorption appears at 372 cm^{-1}. Characteristic changes also take place in the 150–200-cm^{-1} region: in particular, a sharp feature appears at 190 cm^{-1} at 6 kbar; indeed, superimposition of the 100 K and ambient-temperature spectra in this region fairly closely reproduces the pattern of absorption at 6 kbar.

By 14 kbar the characteristic features of the high-spin material have effectively disappeared, and with further in-

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(19) Clark, R. J. H.; Crosse, B. C. *Chem. Ind.* (*London*) **1969**, 1593.

(20) Sabatini, A.; Bertini, I. *Inorg. Chem.* **1965**, *4*, 959.

(21) Hellner, E.; Ahsbahs, H.; Dehnicke, G.; Dehnicke, K. *Naturwissenschaften* **1974**, *61*, 502.

(22) Clark, R. J. H.; Williams, C. S. *Spectrochim. Acta* **1966**, *22*, 1081.

Table III. Infrared Spectral Results at Various Pressures and Temperatures[a]

compd	pressure, kbar	spectral bands, cm^{-1}															
Fe(*o*-phen)$_2$I$_2$	0.001		190 s	204 m	227 w	236 m				274 w	285 s						
	8		190.5 s	207 m	230.5 wm	240 wm		~250.5 sh	262.5 w	274.5 w	208.5 s		353 w				
	17	187 sh	194 s	208 s	233 m	243 m		251 m	262 m	274 sh	293 s		355 w				
	28	187 sh	195 s	209 s	234 w	243 m		252 m	264 s		298 s		357 w				
Fe(*o*-phen)$_2$(NCS)$_2$ [b]	0.001[c]	~152 sh	164 s	~184 sh	194 s	213 sh		230 vs	~242 sh	~262 sh	268 w	298 m	~310 sh	367 sh		376 m	
	0.001	156 m	~164 sh	179 m	202 w	217 s		~235 sh	248 vs		283 s						
	6	167 m	~182 sh	190 m	~207 sh	222 m		~240 sh	255 vs	~266 sh	286 s		322 wm	~357 sh		372 s	383 s
	14	173 m	183 w	194 wm	210 wm	218 wm		~240 sh	~252 sh	265 vs	286 s	301 m	311 w	~325 sh	350 w	367 w	375 wm
Fe(*o*-phen)$_2$(NCSe)$_2$	0.001		179 m			~220 sh		229 vs	~239 sh		284 s						
	9	~161 sh	174 s	190 s		210 m		232 m	248 s	264 sh	~285 sh	293 s	321 w	360 s			
	22	~163 sh	174 s	184 s	205 sh	216 m		233 m	260 s	~272 sh		302 s	~330 vw	360 s			
Fe(*o*-phen)$_2$(N$_3$)$_2$	0.001[c]	135 m	151.5 w	161 s	174 sh	184 s		203 s	235.5 s		245 m		272 vs	288 s		324.5 vs	
	10	135 m	150 w	160 m	~173 sh	183 s		202 m	230 m		~250 sh		269 vs	286 s		324 vs	
	13	141 m	153 w	166 m		185 s		206 m	233 m		~250 sh		272 vs	286.5 s		326 vs	
	17	136 w	~150 sh	~172 sh	~177 sh	184 s	~193 sh	204 m	232 m		252 w	262 w	~275 sh	288 s	309 w	332 m	368 m
	41	~146 sh	~164 sh	174 s		184 s		206 m	235 m	243 m	264 w	272 w		293 s	313 m		372 m

[a] Data obtained at room temperature except as noted. [b] The signal-to-noise ratio of the 26-kbar spectrum makes measurements of peaks of little value. [c] Data obtained at ca. 100 K.

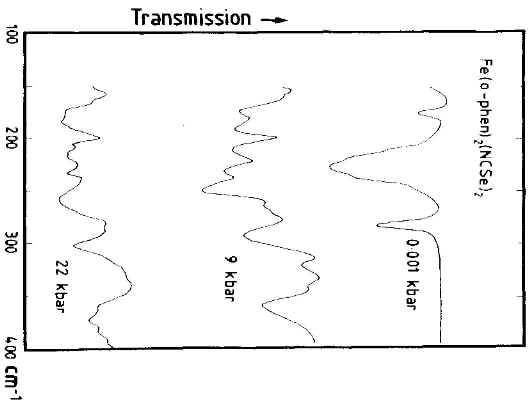

Figure 3. Far-IR spectra of *cis*-[Fe(*o*-phen)$_2$(NCSe)$_2$] at various pressures (kbar).

crements of pressure up to 26 kbar (at which point closure of the gasket hole precluded further experiments) only minor shifts and no major changes in absorption pattern are observed. We conclude that under hydrostatic conditions the transformation, which begins at 6 kbar and apparently is complete at 14 kbar, occurs near 8 kbar. This is much lower than the value of 18 kbar estimated under sheer-stress conditions.[6] The rather sharp nature of this spin-state change accords with the thermal behavior of this solid, which magnetic data show to have a $^5T_2$ ground state above 174 K and $^1A_1$ below that temperature.[4]

[Fe(*o*-phen)$_2$(NCSe)$_2$]. According to the Mössbauer evidence of Fisher and Drickamer,[5] this compound is converted rapidly from high to low spin with increase of pressure, becoming fully transformed by about 12 kbar. Ferraro and Takemoto report that the transition to low spin is sluggish and takes place in the range 8–10 kbar at 353 K in an ungasketed dac (far-IR observations),[6] but no spectra were reproduced. Takemoto and Hutchinson[8] have, however, obtained the low-spin form at ambient pressure by cooling at 100 K. Our ambient-pressure spectrum, Figure 3, is in close agreement with their room-temperature spectrum, and the major features of the low-spin phase that we have prepared at elevated pressures at room temperature also accord, with some shifts in frequency, with their 100 K results.

Under the hydrostatic conditions used in our work, progressive conversion to the low-spin form occurred with increase of pressure (see Figure 3). By 9 kbar the differences from the ambient spectrum were so pronounced as to indicate that the material had transformed. The spectra from 12 to 33 kbar likewise represent fully transformed material suffering the usual progressive changes with pressure. As with the thiocyanate complex, the conclusion is that the high- to low-spin transition occurs cleanly and quite sharply under hydrostatic conditions, and at lower pressures than are estimated under the shear-stress conditions inherent in the earlier experimental procedures.[5,6]

The low-spin material at 9 kbar shows ν(Fe–N(phen)) at 360 cm^{-1}, with the ~220 (sh) and 229 cm^{-1} bands of high-spin [Fe(*o*-phen)$_2$(NCSe)$_2$] absent. The phenanthroline band originally at 284 cm^{-1} is replaced by a new one at 293 cm^{-1}: the 9-cm^{-1} shift implies that this is a new band rather than the initial one, which in other materials in this series is not very pressure sensitive. We note that a further 13-kbar pressure is required to move the new band up by a further 9 cm^{-1}.

Comparison of the 9- and 22-kbar spectra with that of [Fe(*o*-phen)$_3$]$^{2+}$, Table II, shows remarkable similarity, sup-

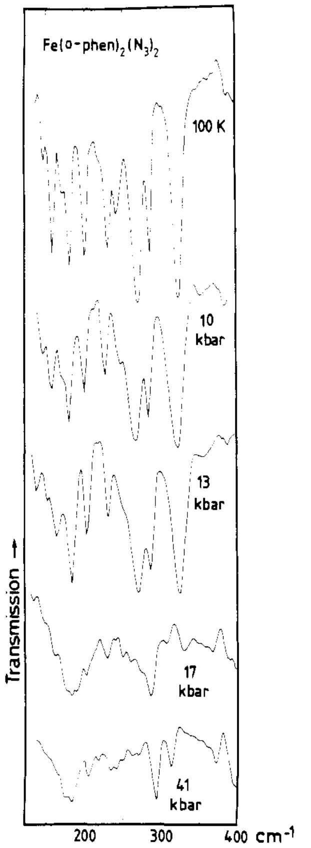

Figure 4. Far-IR spectra of *cis*-[Fe(*o*-phen)$_2$(N$_3$)$_2$] at various pressures (kbar).

porting the essential correctness of the interpretation outlined in the Introduction.

[Fe(*o*-phen)$_2$(N$_3$)$_2$]. Comparison of the ambient-pressure spectra at 100 K and room temperature shows that transformation to the low-spin form is not induced by cooling (Figure 4). However, by 17 kbar major changes have occurred at ambient temperature, consistent with transformation of at least 75% of the sample to low spin, although residual high-spin material is still present as indicated, for example, by the fairly weak band at 332 cm^{-1}, which is the remnant of the intense 324-cm^{-1} mode. Thereafter, the residual high-spin material is lost and appears to be entirely absent at 41 kbar. This conflicts with Fisher and Drickamer's Mössbauer results,[5] which indicate that at 40 kbar the sample consists of only about 70% of the low-spin isomer. It is highly unlikely that we could have missed 30% of high-spin material in view of the ease with which the intense 324-cm^{-1} band can be followed.

We consider that the difference between our conclusions arises because the type of high-pressure cell used by Fisher and Drickamer (in which solid boron with a trace of lithium hydride is used as the pressure-transmitting medium) applies far from hydrostatic pressures.[23] Hence, the sample consists of molecules not only experiencing a variety of pressures but also being subjected to a shear stress: it may be that a shear stress is less effective in bringing about this spin transformation. This calls into question details of the Mössbauer work: a reinvestigation using a gasketed dac would be valuable.

Assignments for ν(Fe–N) for the X = NCS and NCSe compounds imply that ν(Fe–N(phen)) for the high-spin azido complex is to be identified with the 230-cm^{-1} band and that ν(Fe–N$_3$) is at 272 cm^{-1}. We note that these bands suffer a dramatic decrease in intensity due to the spin-state change, as does the 324-cm^{-1} band, which may also be associated with ν(Fe–N$_3$); as with other members of the series, the new ν(Fe–N(phen)) appears near 370 cm^{-1} and then rises with pressure, while the low-spin ν(Fe–N$_3$) is presumed to be >500 cm^{-1}. We again note the similarity of the spectra of the low-spin material to that of [Fe(*o*-phen)$_3$]$^{2+}$.

Conclusions

Under hydrostatic conditions the spin-state transitions in these compounds appear to take place fairly sharply with rise of pressure, with the possible exception of the iodide. The transition pressures estimated are lower than those obtained in experiments in which a substantial shear stress is also present.

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Registry No. *cis*-[Fe(*o*-phen)$_2$I$_2$], 79951-62-5; *cis*-[Fe(*o*-phen)$_2$(NCS)$_2$], 15319-93-4; *cis*-[Fe(*o*-phen)$_2$(NCSe)$_2$], 53447-28-2; *cis*-[Fe(*o*-phen)$_2$(N$_3$)$_2$], 53649-51-7; [Fe(*o*-phen)$_3$](BF$_4$)$_2$, 21780-78-9.

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(23) Debrunner, P.; Vaughan, R. W.; Champion, A. R.; Cohen, J.; Moyzis, J.; Drickamer, H. G. *Rev. Sci. Instrum.* **1966**, *37*, 1310.