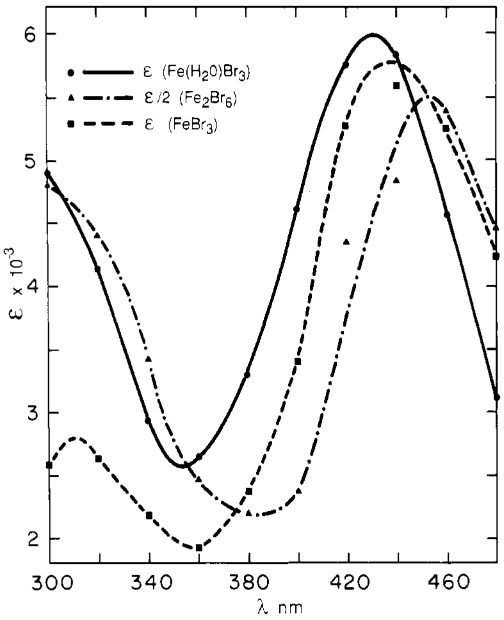

Figure 6. Derived spectra for $Fe(H_2O)Br_3(g)$, $Fe_2Br_6(g)$, and $FeBr_3(g)$, respectively, at 500 K.

300 and 480 nm for each component, the hydrate, the dimer, and the monomer (Figure 6).

Inclusion of various estimates of the temperature dependence of ϵ_{300} values for the dimer and monomer did not significantly reduce the scatter in the result for the hydrate, nor did values of the latter show a systematic trend with temperature. As seen in Figure 6, the wavelength range of the observations does not include the entire range of the overlapping absorption bands; a study of the integrated absorptivities over the observed range did not prove useful as a basis for estimating the temperature dependence of the various ϵ_{300} values.

The assigned mean value of $\epsilon_{300,h}$, 4900 M^{-1} cm^{-1}, was used with the least-squares results to calculate thermodynamic constants for the various reactions; see Table V. Previously reported constants for the corresponding reactions in the chloride system are included for comparison. A standard enthalpy of formation and a standard entropy for $Fe(H_2O)Br_3(g)$ at 500 K were derived from $\Delta H°$ and $\Delta S°$, respectively, for the assumed reaction 3 and literature values[13] for $FeBr_2(s)$, $H_2O(g)$, and $Br_2(g)$. An uncertainty of 500 M^{-1} cm^{-1} in $\epsilon_{300,h}$ introduces an uncertainty of 0.9 J K^{-1} mol^{-1} in the entropy. If $\epsilon_{300,h}$ varies significantly with temperature, a correction will be required in the derived enthalpy changes. The overall uncertainties in the derived thermodynamic properties are difficult to estimate, probably several percent.

Enthalpy and entropy changes derived for reaction 22, eq 3 − eq 2, reflect properties of the Fe–OH_2 bond for the assumed hydrate vapor molecule. Values for the chloride and the bromide

$$FeX_3(g) + H_2O(g) = Fe(H_2O)X_3(g) \qquad (22)$$

are very similar (Table V). The difference $S°(Fe(H_2O)Br_3(g)) - S°(Fe(H_2O)Cl_3(g))$, 31 J K^{-1} mol^{-1}, agrees well with that expected from the different masses of the halogen atoms.[14]

Acknowledgment. Helpful discussions with Professor D. S. Rustad are acknowledged with thanks.

Supplementary Material Available: Table II, listing temperatures, calculated contributions of hydrate, dimer, and monomer, respectively, to A_{300}, (A_{300}(obs) − A_{300}(calc)) × path length, fraction of absorbance contributed by hydrate, ln ($\epsilon_{300,h}K_3$), ln K_{4e}, C_w, and C_b, and Table III, listing observed absorbances for the various samples at 20-nm intervals, 300–480 nm (4 pages). Ordering information is given on any current masthead page.

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Vapor-Phase Infrared Spectrum of Bis(cyclopentadienyl)beryllium

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The vapor-phase infrared spectrum of bis(cyclopentadienyl)beryllium has been recorded at room temperature with a FTIR spectrometer. Although the absorption is very weak, two regions of the spectrum can be used to infer structural features of the molecule. The appearance of seven bands above 3000 cm^{-1} in the C–H stretching region excludes highly symmetric ferrocene-like structures and cyclopentadiene-like σ-bonded structures. The similarity of the spectrum in the 1100–700-cm^{-1} region to those of the molecule in condensed phases is further evidence that the slip-sandwich structure of the condensed phases persists in the vapor phase. This conclusion is opposite that reached in an earlier infrared study but is consistent with the conclusions of the most recent electron diffraction investigation.

Introduction

At least four different structures have been proposed for bis(cyclopentadienyl)beryllium ($BeCp_2$), commonly but inappropriately termed "beryllocene". These are illustrated in Figure 1. When first prepared in 1958,[1] the compound was found to be polar with quite large dipole moments of 2.46 D in benzene and 2.24 D in cyclohexane.[2] This excludes the D_{5d} structures of ferrocene and of the homologous compound magnesocene,[3] which are nonpolar. The space group of solid $BeCp_2$ was determined to be $P2_1/c$, however, with two molecules per unit cell.[4] This is isomorphous with ferrocene and means that the structure of $BeCp_2$ in the solid state must be centrosymmetric. It was therefore suggested that the compound might have different structures in the solid and solution states.

The first structural study of the compound was made by vapor-phase electron diffraction in 1964.[5] The data could not be fitted to either of the existing models, and a new model that was consistent with both the electron diffraction data and with the existing knowledge about the compound was proposed. This was the C_{5v} unsymmetrical sandwich model, with two parallel rings, as a ferrocene, but with the beryllium atom much closer to one ring than to the other (Figure 1c). This model could explain the

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0020-1669/88/1327-4269$01.50/0

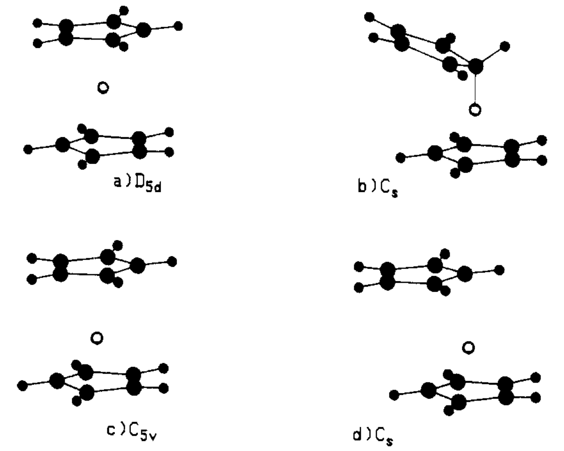

Figure 1. Proposed structures for $BeCp_2$: (a) symmetric sandwich model; (b) σ–π model; (c) unsymmetrical sandwich model; (d) slip-sandwich model. The Be atom is shown by an open circle.

polarity of the molecule and, with disorder in the crystal, the centrosymmetric structure in the solid state.

The unsymmetrical sandwich model could be considered to be an ion pair, $CpBe^+Cp^-$. This ion-pair model was used as a basis for assignment of the solid-state and solution infrared spectra of the compound.[6] The spectra in the two phases were shown to be very similar, indicating similar structures in the solid and in solution. The vapor-phase infrared spectrum was reported to show significant differences from the solid-state and solution spectra, however, and was interpreted as showing that the compound has extremely ionic bonding, $Cp^-Be^{2+}Cp^-$, in the vapor phase.[7]

The first single-crystal X-ray diffraction study was published in 1972.[8] The structure once again was found not to conform to any previously proposed models. The structure observed at low temperature in the solid state was described as a "slipped sandwich", which is similar to the proposed C_{5v} electron diffraction structure except that the less tightly bonded ring is moved by 1.2 Å in a direction parallel to the ring plane, so that the beryllium atom is perpendicularly under one carbon atom of the ring (Figure 1d). A recent redetermination of the structure by low-temperature X-ray diffraction has confirmed the slip-sandwich geometry.[9] The more precise bond lengths and angles now available limit the possible descriptions of the molecular bonding.

This structure was difficult to rationalize. The slip-sandwich structure is, however, very closely related to the σ–π structure (Figure 1b), which is much more readily rationalized. A number of theoretical studies have found the minimum energy structures to be either the symmetrical sandwich (Figure 1a) or the σ–π structure (Figure 1b).[10-16] It might be expected then that, in the absence of further effects, a slip-sandwich structure would distort further to give the σ–π structure.

The electron diffraction data were reconsidered in the light of the proposed new model for the structure from the X-ray diffraction study. The slip-sandwich structure was found to be incompatible with the data.[17] For some years, therefore, it was thought that the structure of bis(cyclopentadienyl)beryllium in the vapor phase is very different from the structure determined in the solid state. A redetermination of the vapor-phase structure was performed in 1979, using improved programs for subtracting the background atomic scattering.[18] The new electron diffraction results were found to be in good agreement with the solid-state model. It thus seems possible that the slip-sandwich structure found in the solid state persists in the vapor phase.

There remains the inconsistency of the vapor-phase infrared spectrum, which suggests a structure different from that in the condensed phases. To this end we have examined the infrared spectrum of the vapor using FTIR spectrometers.

Experimental Section

Materials. *Caution*! Beryllium compounds are very toxic by inhalation and in contact with the skin, are irritating to the respiratory system, and present the danger of very serious irreversible effects.

Bis(cyclopentadienyl)beryllium is a volatile white solid with a melting point of 59–60 °C.[1] It reacts readily with air and water. The reaction with air results in the formation of a yellow-brown tar, which inhibits further reaction if the compound is not finely divided, and a smoke, which is likely to consist chiefly of beryllium oxide. The reaction with liquid water is particularly violent, causing the water to boil and again dispersing beryllium oxide.

Thus, bis(cyclopentadienyl)beryllium must be handled in a manner appropriate for an air-sensitive compound, but with additional precautions due to the extreme toxicity of the beryllium oxide smokes formed on decomposition of the compound. Some of the common techniques for the handling of air-sensitive compounds are inappropriate for this reason. Schlenk techniques and the use of dryboxes, which involve passing a stream of nitrogen over the compound, would result in the release of small amounts of $BeCp_2$ vapor into the atmosphere and would be particularly hazardous if decomposition products including finely divided beryllium oxide were present.

The volatility of $BeCp_2$ is appreciable, with the vapor pressure being on the order of 0.2–0.3 Torr at room temperature, and therefore the compound is fairly easily transferred by sublimation within a glass vacuum line. This technique allows the compound to be completely segregated from the atmosphere at all times. Thus, vacuum-line techniques fulfill both of the requirements for handling organoberyllium compounds, by keeping the bulk compound protected from air and by keeping all trace quantities of the compound and decomposition products segregated from work areas.

Sodium cyclopentadienide was prepared by the reaction between sodium wire and cyclopentadiene in dimethoxyethane. The yield of the cream-colored product indicated that the product of this reaction was the solvated compound NaCp·DME. The dimethoxyethane had to be removed at this stage, as its volatility is low enough to make it difficult to remove from $BeCp_2$ at a later stage. This was carried out by placing a Schlenk flask containing the complex under high vacuum for about 1 day, in which time the crystals had crumbled to powder and the vapor pressure of dimethoxyethane over the compound had dropped to a negligible level.

Bis(cyclopentadienyl)beryllium was prepared by the method of Fischer and Hofmann[1] as elaborated by Beedell[19] in these laboratories. The reaction was performed under nitrogen without using Schlenk methods. Details can be found in ref 19. Typically, anhydrous beryllium chloride ($BeCl_2$, Fluka, 0.9 g, 0.011 mol) was dissolved in diethyl ether (10 mL) and the solution placed in a pressure-equalizing dropping funnel. Unsolvated sodium cyclopentadienide (2.9 g, 0.033 mol) was placed in the flask through the side neck by using Schlenk techniques, and ether (40 mL) was added. The dropping funnel was fitted to the top opening of the flask and the side neck stoppered. The solution of $BeCl_2$ was added to the flask dropwise, while the suspension was stirred. The flask was then sealed completely, and the contents were stirred for 4 h. No noticeable changes in the appearance of the mixture occurred. Ether was then removed through the side stopcock under vacuum, and the apparatus was connected to one of two U-tube traps in series on the vacuum line. All volatile substances were removed from the residue of NaCl and excess NaCp into a trap cooled with liquid nitrogen. The product was then purified by sublimation between the traps to remove impurities, chiefly cyclopentadiene, ether, and traces of dimethoxyethane and (cyclopentadienyl)beryllium chloride. The identity of the compound was checked by melting point and/or ^1H NMR.

Methods. The samples for vapor-phase infrared spectroscopy were contained in a cell constructed from the halves of a 28 mm outer diameter

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Table I. Band Positions and Assignments for the Vapor-Phase Spectrum of (Cyclopentadienyl)beryllium Chloride[a]

band position	assignt[24]	band position	assignt[24]
3050 vw	ν_1, ν_6 (A_1, E_1)	1086 w	ν_{13} (E_2)
1822 w		1007 vs	ν_8 (E_1)
1733 w		1001 vs	
1644 w		995 vs	
1619 w		939 w	ν_{14} (E_2)
1450 w	ν_7 (E_1)	913 w	
1363 vw	ν_{11} (E_2)	889 s	ν_9 (E_1)
1260 vw	ν_{12} (E_2)	882 s	
1127 m	ν_2 (A_1)	781 w	ν_3 (A_1)

[a] Explanation of symbols: s, strong; m, medium; w, weak.

O-ring joint. Viton A O-rings were used to give a vacuum seal between the glass and the potassium bromide windows. The windows were held in place by being glued to the glass with Dow Corning Silastic 738RTV sealant, which also served as a secondary vacuum seal.

The spectrum of CpBeCl was recorded with a Nicolet MX1 Fourier transform infrared spectrometer. The spectrum was corrected for bands from cyclopentadiene, which resulted from decomposition of the sample, although some very strong Q branches could not be completely subtracted. The peaks from residual carbon dioxide and water were also subtracted from the spectrum. The spectrum of bis(cyclopentadienyl)beryllium was recorded with a Digilab FTS-80 Fourier transform infrared spectrometer.

The infrared spectrum of bis(cyclopentadienyl)beryllium in the vapor phase at room temperature is extremely weak. This appears to be due to a combination of low volatility of the compound at room temperature and of low oscillator strength of the infrared absorption bands. (Cyclopentadienyl)beryllium chloride has a vapor pressure at room temperature of 1 Torr,[20] compared with about 0.1–0.2 Torr for bis(cyclopentadienyl)beryllium.[21] The strongest band in the spectrum of CpBeCl has an absorbance of 0.36 absorbance unit and that in the spectrum of $BeCp_2$ an absorbance of less than 0.02 absorbance unit. As the spectrum of $BeCp_2$ is so weak, precautions had to be taken to prevent bands from volatile impurities, particularly cyclopentadiene, obscuring the spectrum of the compound. The cell was periodically placed on the vacuum line and evacuated for about 10 min while an area of the glass wall was cooled with ice to lower the volatility of bis(cyclopentadienyl)beryllium. The peaks due to the impurities were much stronger in spectra taken a considerable time after evacuation of the cell, while those due to bis(cyclopentadienyl)beryllium varied little in intensity with time, with the variation being solely due to the equilibration of the cell temperature in the sample compartment. The cell was not heated to avoid the risk of subliming material onto slightly cooler cell windows and inadvertently recording the spectrum of the solid phase.

The data quoted are only taken from the areas of the spectrum where a number of reproducible peaks of reasonable intensity were observed. These regions were between 3200 and 3000 cm^{-1} and between 1100 and 700 cm^{-1}. Eight separate spectra were recorded with resolutions of 2 and 4 cm^{-1} and with 256–4000 scans. The peak positions in these spectra were compared. All of the reported peak positions were reproducible, and the peaks appeared in the spectrum after the impurity spectra were nulled. As the peaks commonly appeared as shoulders on a sloping base line, the exact positions for the peaks were dependent on the precise region of the spectrum over which a base line correction was applied. The positions and infrared intensities of the bands observed were compared with those reported in ref 22 and 23, as well as with the previously reported vapor-phase spectrum,[7] to establish whether the observed peaks were likely to correspond to vibrations of gaseous bis(cyclopentadienyl)beryllium.

Results

The infrared spectrum of (cyclopentadienyl)beryllium chloride in the vapor phase has previously been reported.[20] The spectrum recorded in this work is virtually identical in peak positions with that reported before, and the infrared-active fundamentals previously assigned[24] could all be located in the vapor-phase spectrum (Table I). The fundamentals assigned in Table I are numbered for a $C_5H_5Be^+$ group of C_{5v} symmetry. No attempt was made to assign the modes due to the Be–Cl group.

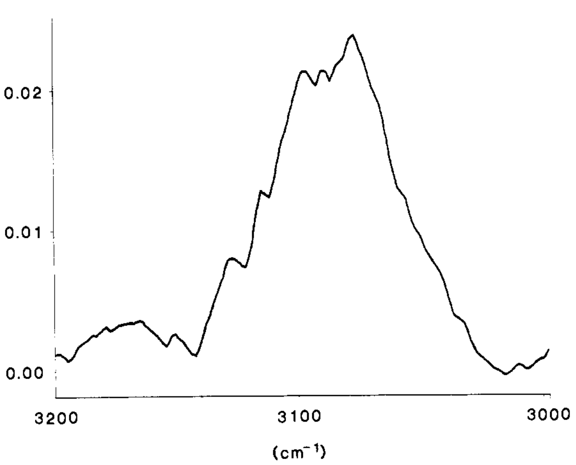

Figure 2. Vapor-phase infrared spectrum of $BeCp_2$ in the C–H stretching region.

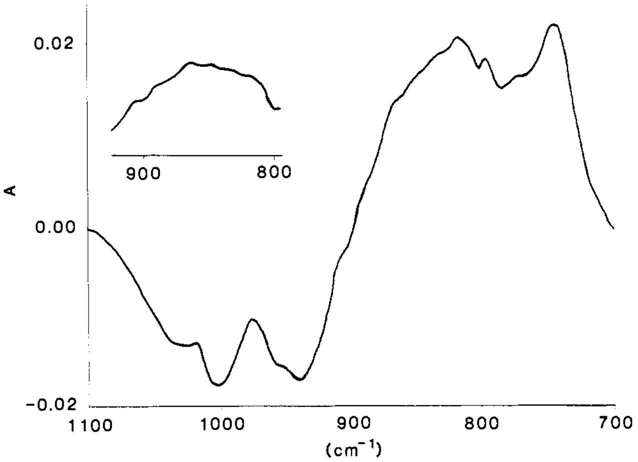

Figure 3. Vapor-phase infrared spectrum of $BeCp_2$ in the region 1100–700 cm^{-1}, with base line subtracted. The inset shows the region between 930 and 800 cm^{-1} with a different base line correction.

The spectrum of bis(cyclopentadienyl)beryllium differs in some respects from that which has been previously reported.[7] The chief reason for this is that the previous spectrum was recorded directly onto chart paper, and thus only the strongest peaks of the spectrum were observable. As discussed above, the absorbances of the vibrational bands of this compound are low in the infrared region and the volatility of the compound even at 50 °C is sufficiently low that it would be extremely difficult to detect many of the peaks. The spectrum reported here, while much weaker due to the lower temperature used (approximately 26 °C), was recorded with a Digilab 3200 Data Station and could therefore be enlarged so that very weak features could be observed. The spectrum of this compound in the vapor phase in the regions 3200–3000 and 1100–700 cm^{-1} is shown in Figures 2 and 3, respectively. The problems presented by the base line are evident in Figure 3.

The spectrum, except in the region of the C–H stretching bands, is best considered as a fingerprint for this compound. The positions of the observed bands are compared in Table II with those from the condensed-phase spectra[22,23] and also with those from the previously reported vapor-phase spectrum.[7] Bands in the regions not observed in this study are omitted. One such region is between 2900 and 1350 cm^{-1}. In the lower range of this region, the sharp peaks of the water bending vibration could not be completely cancelled and tended to obscure the spectrum excessively. In a region around 660 cm^{-1}, the strong CO_2 bending mode made the peak positions imprecise. A number of bands observed in the low-temperature Raman study, and some weak bands observed in the solution infrared study, did not have observable counterparts in this spectrum and are also omitted from Table II.

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Table II. Infrared Bands Observed for Bis(cyclopentadienyl)beryllium[a]

IR			
vapor[b]	vapor[c]	soln[d]	Raman[e]
3126			3122 s (p)
3114		3110 sh	3110 m
3098			3100 sh (p)
3089			3094 m
3082	3084 m	3080 s	3087 m
3076			3076 m
3045		3050 sh	3069 m
			3013 s
1302		1305 vw	
1263			1267 vvw
1196			
1181			
1124		1124 s	1129 vs (p)
1115		1106 w	1118 vs (p)
			1030 vw
1017		1015 s	996 w (dp)
972	969 vs	969 vs, b	
948			934 vw (dp)
909		915 sh	905 vvw
890		890 sh	883 w
866	862 vw	862 ms	869 w (dp)
850			846 w
835	828 vvw	829 m	838 w (dp)
819			
796		785 sh	789 w (p)
772	772 vw	770 ms	
745	736 vs	740 vs	736 vvw
586		590 vw	600 s (p)

[a] Explanation of symbols: s, strong; m, medium; w, weak; b, broad; p, polarized; dp, depolarized; sh, shoulder. [b] This work. [c] Reference 7. [d] Reference 23. [e] Reference 22. The band positions are from the low-temperature spectrum, while the polarizations are from the liquid spectrum.

Discussion

Although vibrational spectra have been reported for a large number of cyclopentadienyl compounds, the assignment of the spectra for compounds with symmetry lower than C_{5v} has been generally less than adequate. There are many difficulties in such assignments. Peripherally bonded cyclopentadienyl compounds generally have a local symmetry of the cyclopentadienyl ring of C_s. In this point group all vibrational modes are active in both the infrared and Raman spectra, and there are no degenerate representations. Thus, for the C_5H_5 group alone, there are 24 vibrations that may be observed in both the infrared and Raman spectra, including five separate C–H stretching modes.

C–H Stretching Vibrations. The region between 3200 and 3000 cm^{-1} encompasses all of the C–H stretching bands of this compound. Seven peaks and shoulders have been observed reproducibly in the vapor phase, corresponding to bands observed in the infrared and Raman spectra of the condensed phases. As no rotational fine structure is observable on any of the other bands of the vapor-phase spectrum, it is therefore probable that there are indeed seven individual vibrational bands observable in this region of the spectrum.

The local symmetry of the centrally bonded ring is effectively C_{5v}, so only two bands due to vibrations of this ring should be observable in the infrared spectrum in this region. Thus, for a C_{5v} overall structure for this compound in the vapor phase (Figure 1c), as proposed to explain the original electron diffraction data,[5] a maximum of four bands should appear in this region. The observation of seven bands appears to exclude this model.

A model in which the ring–metal bonding is extremely ionic was proposed to explain the small number of bands observed in the earlier vapor-phase spectrum.[7] In this model, the rings, while structurally different, both effectively have the D_{5h} symmetry of the free $C_5H_5^-$ ion. For this model, only two bands are expected in this spectral region. This model is similarly excluded.

The appearance of the C–H stretching region is quite similar in complexity to the same regions in the Raman spectra of R_2AlCp and R_2GaCp,[25] where the number of bands observed shows that these compounds have peripherally bonded cyclopentadienyl groups. The observation of such complexity in the C–H stretching region suggests that at least one of the rings in gaseous bis(cyclopentadienyl)beryllium is peripherally bonded.

The absence of bands below 3000 cm^{-1} indicates that the structure of the peripherally bonded ring is similar to the solid-state structure of this ring, rather than to the structure of cyclopentadiene.[26,27] No bands have been observed in this region below 3000 cm^{-1} in the spectra of $BeCp_2$ in the condensed phases. If the structure of this compound changed significantly toward the σ–π structure of Figure 1b upon vaporization, the bond between C(5) and H(5) would have significant carbon sp^3 character and the corresponding stretching vibration would decrease in energy toward 2900 cm^{-1}. The evidence from the C–H stretching region thus suggests that the solid-state "slip-sandwich" structure of this compound persists in the vapor phase.

Band Assignments in the 1100–700-cm^{-1} Region. It is possible to assign the bands of the centrally bonded ring by analogy with the spectra of many other centrally bonded cyclopentadienyl rings, in particular that of (cyclopentadienyl)beryllium chloride. This has been done in ref 22, with use of Raman depolarization ratios as well as position and intensity to identify analogous bands. This assignment appears reasonable, particularly for the infrared-active A_1 and E_1 modes, all of which also appear at these positions in the infrared spectrum. These infrared bands are therefore assigned herein as fundamentals of the centrally bonded ring.

The strong infrared bands at 972 and 745 cm^{-1} are proposed herein to correspond chiefly to in-plane and out-of-plane C–H bending modes, respectively, of the peripherally bonded ring and to be important evidence that the peripherally bonded ring has the same structure in the vapor phase as in the condensed phase. These modes have previously been assigned as Be–Cp stretching vibrations,[23] and therefore alternative assignments of the skeletal stretching modes are discussed below.

Be–Cp Stretching Modes. The assignment of the Be–C stretching bands varies greatly in the literature, even in the simple monomeric compounds di-*tert*-butylberyllium and dimethylberyllium (in the vapor phase). In the series of compounds CpBeX, the Be–Cp(central) stretching frequency has been assigned in the region of 310–390 cm^{-1} for compounds with X = Cp,[22] Cl,[28] and BH_4[24] but in the region of 960–1000 cm^{-1} for X = Cp, Cl, and Br in another work.[23]

The Raman depolarization ratios have particular value in this assignment. The Be–ring stretching mode has A_1 symmetry, and thus the corresponding band must be polarized. No significant polarized band is observed[22] in the spectrum of $BeCp_2$ in the region between 1055 and 598 cm^{-1}, except for one in the expected region of the A_1 out-of-plane C–H bending mode, at 795 cm^{-1}. The band at 1055 cm^{-1} is of too high an energy to be assigned to this mode. The polarized bands at 598 and 313 cm^{-1} appear to correspond to the Be–C stretching modes, with that at 313 cm^{-1} corresponding to polarized bands in the spectra of the half-sandwich compounds. This band, therefore, is assigned to the Be–Cp(central) stretching mode. There are no other modes of A_1 symmetry in compounds such as CpBeCl that can possibly appear at such low energy. This assigment indicates that the force constant for this mode is very much smaller than for the equivalent mode of ferrocene.

It remains to predict the frequency region in which the Be–C(peripherally bonded ring) stretching mode might be expected. A number of assignments of the frequency of Be–C single-bond stretching modes have been made. For the monomeric dialkyls dimethylberyllium and di-*tert*-butylberyllium, the assignments are respectively 1081 cm^{-1} (ν_{as})[29] and 545 cm^{-1} (ν_s), 458 cm^{-1} (ν_{as}).[30]

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The Be–Me stretching vibration for (cyclopentadienyl)methylberyllium was assigned to the peak at 1080 cm^{-1} [20] and the asymmetric stretch for $BeMe_2{\cdot}NMe_3$ to a peak at 790 cm^{-1}.[29] The stretching frequency for the Be–Cp bond must be very much lower than that for dimethylberyllium for several reasons. The mass of the peripherally bonded cyclopentadienyl group is much larger than that of a methyl group, and the vibrational band would therefore be lower in energy for this reason. The Be–C distance in monomeric dimethylberyllium is 1.698 Å,[31] compared with a distance of 1.826 Å for the Be′–C(5) bond in bis(cyclopentadienyl)beryllium,[9] and therefore the force constant for the stretching of the latter bond is likely to be very much lower than in $BeMe_2$.

For these reasons, it is unlikely that either of the Be–C stretching vibrations of this compound occur above about 700 cm^{-1}. On the basis of the Raman assignments above, the higher energy one of the two Be–C stretching modes (which will be significantly coupled) is tentatively assigned to the feature at 590 cm^{-1}.

Major Infrared Bands of the Peripherally Bonded Ring. The bands observed in the region 1100–700 cm^{-1} have been assigned as chiefly C–H bending modes of the two types of rings in this compound. The features at 796, 866, and 1017 cm^{-1} may be assigned as A_1 and E_1 C–H bending modes of the centrally bonded ring by comparison with the spectrum of (cyclopentadienyl)beryllium chloride. The bands in both spectra have similar frequencies, Raman depolarization ratios (where reported), and relative activities in the infrared and Raman spectra. There remain several strong infrared absorbances that have no counterparts in the spectrum of CpBeCl. The most notable of these are the bands at 972 and 745 cm^{-1}, which have the strongest infrared absorbances of all bands of this compound, although very little Raman intensity.

The spectra of a number of peripherally bonded main-group cyclopentadienyl compounds have been published. Bis(cyclopentadienyl)mercury and the (cyclopentadienyl)mercury halides show very strong bands in the region of 750 cm^{-1}, and several strong- and medium-intensity bands in the region 1000–900 cm^{-1}.[32] Similarly (cyclopentadienyl)trimethyltin has a very strong absorbance assigned to the cyclopentadienyl ring at 735 cm^{-1} and a very strong band at 973 cm^{-1},[25] and the cyclopentadienyl dialkyl compounds of aluminum and gallium have very strong infrared absorbances around 750 cm^{-1} and a number of strong bands around 950–1000 cm^{-1}.[33] The corresponding Raman bands, particularly for the vibration at about 750 cm^{-1}, have very little intensity for the tin, gallium, and aluminum compounds. A similar relationship of the infrared and Raman band intensities for these bands has been noted for the beryllium compound. In the spectra of two peripherally bonded compounds with less polar bonding between the ring and the metal atom, cyclopentadiene and (cyclopentadienyl)germane, there are also several bands in the 1000–900-cm^{-1} region, while the band at around 750 cm^{-1} appears to lose intensity and shift to higher energy, to 781 cm^{-1} in the germanium compound[34] and to 807 cm^{-1} in cyclopentadiene.[25]

The structure of the cyclopentadienyl ring changes significantly with changes in the polarity of the bond between C(5) and the metal atom.[35] The normal coordinate corresponding to the band at 807 cm^{-1} in cyclopentadiene is complex, including a significant amount of a ring bending mode, and the position of this band might therefore be expected to be sensitive to the degree of delocalization of the cyclopentadienyl ring. The major contributions to these bands are likely to be in-plane C–H bending (for the bands at 1000–900 cm^{-1}) and out-of-plane C–H bending (for the band at 745 cm^{-1}).

Vapor-Phase Structure of Bis(cyclopentadienyl)beryllium. The strong bands observed in the condensed-phase infrared spectra at around 740 and 970 cm^{-1} may therefore be considered to be diagnostic of the presence of a peripherally bonded ring, as similar bands are found in the same regions of the infrared spectra of many compounds related to bis(cyclopentadienyl)beryllium. These bands dominated the previously published vapor-phase infrared spectrum and were observed in the present study. This strongly suggests that the vapor-phase structure of the compound includes a peripherally bonded ring. The similarities of intensity and position of the bands assigned to the peripherally bonded ring in the infrared spectra of this compound in the solid, solution, and vapor phases indicate that the structure of this ring does not differ significantly among the different states. Vibrations corresponding to the centrally bonded ring are also present. Consequently, in this region the vapor-phase spectrum in comparison with the spectra of this compound in the condensed phases is a fingerprint which indicates that the structure of the compound does not differ among the various states.

The C–H stretching region also gives information on the vapor-phase structure of this compound. The complexity of this region, in which seven bands were observed, is inconsistent with the high-symmetry D_{5h} and C_{5v} models for this compound (Figure 1a,c). Seven bands due to C–H stretching vibrations are expected on the basis of the σ–π and slip-sandwich structural models. If the structure of this compound in the vapor phase were similar to the σ–π model of Figure 1b, one of the bands would be expected to occur at much lower energy, around 2900 cm^{-1}, and this has not been observed. The observation of seven bands between 3100 and 3000 cm^{-1} therefore indicates that the structure of bis(cyclopentadienyl)beryllium in the vapor phase is effectively identical with that observed in the solid state in the X-ray diffraction studies. A rationalization of this structure type is presented elsewhere.[35]

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