The Symmetry of Gaseous Dibenzenechromium[1a]

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Abstract: The gas-phase infrared spectrum of dibenzenechromium was observed in the range 400–4000 cm^{-1} and is consistent with D_{6h} symmetry.

The molecular structure of dibenzenechromium, $Cr(C_6H_6)_2$, has repeatedly been discussed in the literature,[2] and repeatedly the results were contradictory. So far, no experimental results have been reported to decide the main issue in question: the symmetry of the ring ligands.

X-Ray studies have been published which claimed[3] and some which denied[4–6] the necessity of assuming a symmetry for the C_6H_6 ligand in $Cr(C_6H_6)_2$ which is lower (D_{3d}) than that of the free molecule (D_{6h}). Unfortunately the X-ray results so far available are not unequivocal since orientational disorder in the crystal cannot be ruled out as a cause of the (apparent) D_{6h} symmetry.[6]

A gas-phase electron diffraction study[7] produced a similar result. D_{6h} molecular symmetry was found to explain the electron diffraction pattern in a satisfying manner. A distortion of the ligands, however, with a C–C bond distance difference of ≤ 0.02 Å could not be rejected.

The vibrational spectrum of solid $Cr(C_6H_6)_2$ was first interpreted as evidence for,[8] later against,[9] and then again for[2,10] a distortion of the ligands. A tentative assignment of all strong bands of the solution spectrum[11] could be made on the basis of sixfold symmetry. In view of this it appeared not unreasonable to assume that the lower symmetry solid-state spectrum was caused by crystal rather than by intramolecular forces. Fritz and Fischer[2,10] denied this possibility and claimed a distortion for C_6H_6 in crystalline $Cr(C_6H_6)_2$ which is not caused only by crystal forces.[2] This claim was based mainly on the assumption that the crystal factor and site groups of the molecule are not important for the spectra of the ligands as shown by results found for $V(C_6H_6)_2$. A direct study of $Cr(C_6H_6)_2$ in different crystal surroundings, however, shows that the influence of the crystal field on the ligand spectrum cannot be completely rejected. Thus the KBr pellet spectrum[12] is noticeably different from the low-temperature thin film spectrum[13] with regard to the number as well as the exact positions and intensities of the observed frequencies. In his paper Snyder[13] mentioned that changes in the solid state were apparent in his spectra, and he proved that such alterations were not caused by different recording temperatures. We found[11] similar differences between the spectra of $Cr(C_6H_6)_2$ in a KBr disk and that of a pure $Cr(C_6H_6)_2$ pellet. It cannot be excluded that these differences are caused by the influence of the crystal field.

The quoted results, therefore, seemed to us to be conflicting. Furthermore, what is generally of interest in qualitative structural studies is the symmetry of the molecule in the least disturbing surroundings, the gaseous phase. The vapor-phase ir spectrum of $Cr(C_6H_6)_2$ is only partly known because of experimental difficulties.[2,12] In view of its importance for the problem at hand, this spectrum has been measured from 400 to 4000 cm^{-1}.

A Beckman IR-9 spectrometer, modified to accept a 1-m long, stainless steel gas diffusion barrier cell described previously,[14] was used to record spectra at nominal temperatures of 25–255°. The central portion of the cell was heated by a Kanthal wound mullite tube furnace with power supplied by a Thermac proportional temperature controller (R.I. Inc., Minneapolis, Minn.). A thermocouple located at the center of the furnace and adjacent to the sample boat was used for temperature measurement. The dibenzenechromium was placed in an alumina boat in the center of the hot zone. The whole system was evacuated before filling with argon which was used as a diffusion barrier and which flowed slowly through the cell. The temperature remained constant (±1°) during any given scan.

A benzene spectrum was observed at 150°. Snyder[13] and Fritz[12] also report benzene in their spectra. The intensity of benzene in the present spectra decreased with time due to transport by the argon flow. The presence of these bands caused no uncertainty in the present results. At 185°, bands at 450 and 480 cm^{-1} appeared and indicated unequivocally the presence of

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the complex. Spectra were measured at ~20° intervals between 185 and 255° with optimum conditions occurring at 215°. The spectrum is shown in Figure 1. Frequencies are given in Table I together with the classifications following Fritz, *et al.*[12] Also shown is the observed benzene spectrum. There is only one observed overlap region for the ligand and free benzene spectra at 3070–3100 cm^{-1}. This overlap could be readily verified from the time and temperature dependence of the spectra.

Table I. Infrared Frequencies (cm^{-1}) and Assignments for Solid and Gaseous Dibenzenechromium

Vapor frequency	Frequency no.[a]	Classification[a]	Solid frequency[a]
450 vs[b]	23	A_{2u}	459
480 vs	25	E_{1u}	490
650 675 m, C_6H_6[c] 680			
780 m	11 s	A_{2u}	794
830 vw			833[d]
860[e] w	10[d] as	E_{1u}	866
970[e] m	1 as	A_{2u}	971
	18 s	E_{1u}	999
1030 1040 w, C_6H_6 1050			
1250 vvw	11 as + 25	E_{1u}	1251
1420 vw	19 s	E_{1u}	1426
1480 m, br, C_6H_6			
1750 w	19 s + 24	A_{2u}	1757
1810 w, C_6H_6			
1950 w, C_6H_6			
3070–3100[f] vs	2 as, 20 s	A_{2u}, E_{1u}	3037

[a] Fritz, *et al.*[12] [b] s = strong, m = medium, w = weak, v = very, br = broad, C_6H_6 = free benzene. [c] Benzene was present as a decomposition product. [d] See text. Not as assumed by Fritz, *et al.*[12] [e] Shoulders indicating the presence of P and R branches. [f] $Cr(C_6H_6)_2$ and free C_6H_6 bands overlap.

There is some uncertainty concerning the assignment of $\omega_{10as}(E_{1u})$. This mode is generated from the 846-cm^{-1} free benzene frequency. As a nonplanar C–H bending mode it should be expected in the complex above rather than below 846 cm^{-1}. Thus, ω_{11s}, being of the same type, is shifted from 671 to 780 cm^{-1} in free and complexed benzene, respectively. A similar behavior of such modes has been reported for five-membered ring complexes.[11,13] The band at 833 cm^{-1} was assigned[12] previously to ω_{10as}. It now seems more likely that it is a combination ($2 \times 332 + 152^2 = 816$ or $2 \times 332 + 171^2 = 835$) and that ω_{10as} be reassigned to the 860-cm^{-1} band. For the results of this study this ambiguity is of no importance. As is seen from Table I, all recorded frequencies can be explained by a sixfold molecular symmetry of $Cr(C_6H_6)_2$. All D_{6h} modes have been observed which were to be expected in the inspected 400–4000-cm^{-1} region, with the exception of $\omega_{18s}(E_{1u})$. So, of the nine infrared-active frequencies to be expected for D_{6h} $Cr(C_6H_6)_2$ in the mentioned region, eight have been found. By no means can the 19 D_{3d} $Cr(C_6H_6)_2$ infrared-active frequencies be assigned.

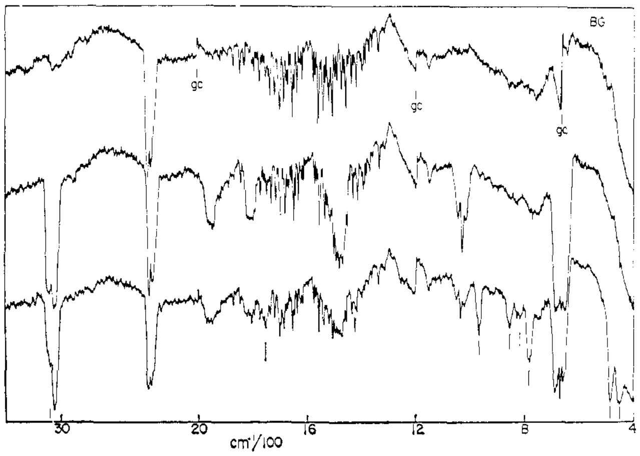

Figure 1. Background spectrum at 25° (top), free benzene vapor at 175° (middle), and gaseous $Cr(C_6H_6)_2$ at 215° as indicated by pips (bottom). Grating changes are indicated by gc at 670, 1200, and 2000 cm^{-1}. These are single-beam spectra.

In view of the facts given above, it is difficult to infer a threefold symmetry for benzene in $Cr(C_6H_6)_2$ from the recorded vapor-phase ir spectrum. The additional frequencies found in the ir spectrum of solid $Cr(C_6H_6)_2$ therefore are likely due to the influence of the crystal field.

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