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THE CRYSTAL STRUCTURE OF CYCLOPENTADIENYLBERYLLIUM CHLORIDE

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Summary

The crystal structure of CpBeCl has been determined by X-ray diffraction. This shows that the molecule has the same structure in the solid state as in the gas phase. No significant intermolecular interactions were observed although such interactions had been expected on the basis of previously obtained mass spectral data.

The structure of cyclopentadienylberyllium chloride has been investigated by means of electron diffraction [1], infrared and Raman spectroscopy [2,3]. These studies indicate the presence of monomeric molecules in the gas phase and in solution, but little is known about the structure in the solid and liquid phase. The presence of associated molecules could not be excluded on the basis of the mass spectrum, which shows ions corresponding to dimeric and trimeric species [4] *. The assignment of the Be–Cl stretch in the vibrational spectrum is also ambiguous [4]. In order to resolve the question of the interaction between the CpBeCl molecules in the solid state, we undertook an X-ray diffraction study.

Experimental procedure

Cyclopentadienylberyllium chloride was prepared from a solution of freshly sublimed $BeCl_2$ in ether, which was added dropwise to an equimolar solution of

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* Such a spectrum was only obtained when the sample was introduced into the ion source by a direct inlet system [4].

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CpNa in ether; after 3 h stirring the ether was removed and the residue was cooled in an ice bath. The product was sublimed three times, the first portion of the sublimate being rejected each time. Colourless crystals suitable for the X-ray study were obtained by sublimation. Because of its extreme air and water sensitivity, a crystal of the compound was mounted in a glass capillary tube under argon.

Structure determination

Reflections were collected on an Enraf–Nonius CAD-4 diffractometer using Mo-K_α graphite monochromated X-radiation. Intensities were measured by a coupled θ–2θ scan technique with scan speeds varying from 1.3–5.0° min^{-1} depending on the standard deviation to intensity ratio of a preliminary 5.0° min^{-1} scan. The intensity of a reflection and its standard deviation were calculated from INT − 2(BGL + BGR) and $[\text{INT} + 4(\text{BGL} + \text{BGR})]^{0.5}$, respectively, where INT, BGL and BGR are the peak intensity, the left and right backgrounds, and the time spent measuring the background was half that taken to measure the peak. A Zr filter was placed in front of the detector if the peak count was greater than 50000 counts sec^{-1}. The intensities of three monitor reflections remeasured after every 90 minutes of X-ray exposure showed no significant variation during the course of data collection.

Intensities were corrected for Lorentz and polarisation effects and averaged to give a total of 521 independent observed reflections $[I \geqslant 2.0\sigma(I)]$. Pertinent crystal data are given in Table 3; the cell parameters were obtained by a least-squares fit to the θ values of 75 automatically centred reflections ($9 < \theta < 23°$). No correction for X-ray absorption was applied $[\mu(\text{Mo-}K_\alpha) < 10\ \text{cm}^{-1}]$.

The structure was solved by Patterson (Cl) and Fourier methods (C and Be). Refinement of the structure with isotropic thermal parameters for all atoms gave $R = 0.137$. The five hydrogen atoms were located at this stage by a difference Fourier synthesis and their positional and isotropic thermal parameters were included in the final refinement cycles. Refinement of the structure was by full-matrix least-squares where the quantity being minimised was $\Sigma w(F_o - k|F_c|)^2$ with $w = 1/\sigma^2(F_o)$. All non-hydrogen atoms (Cl, C and Be) were allowed anisotropic thermal

TABLE 1

FINAL ATOMIC COORDINATES WITH STANDARD DEVIATIONS (×10000)

Atom	x	y	z
Cl	1749(1)	1124(1)	1235(1)
Be	278(3)	1041(5)	3127(5)
C(1)	−83(4)	1039(5)	5948(4)
C(2)	−519(3)	−184(4)	5028(5)
C(3)	−1441(3)	137(5)	3474(5)
C(4)	−1604(4)	1569(5)	3407(6)
C(5)	−745(4)	2152(5)	4961(7)
H(1)	553(35)	1114(47)	6887(60)
H(2)	−272(26)	−1113(39)	5262(42)
H(3)	−1720(46)	−567(52)	2532(74)
H(4)	−1908(53)	1984(59)	2320(87)
H(5)	−668(32)	2985(55)	5075(54)

motion during the refinement. Refinement converged at $R = 0.032$, $R_w = 0.029$ (Goodness of fit 1.76). In the final refinement cycle the mean shift to error ratio was 0.005 and a subsequent difference Fourier synthesis was essentially featureless except for several peaks (0.13 eA^{-3}) in the vicinity of the chlorine atom. Neutral atom scattering factors for all non-hydrogen atoms were those of Cromer and Waber [5] while those for hydrogen were taken from Stewart, Davidson and Simpson [6]. The real and imaginary components of the anomalous scattering factor for Cl ($\Delta f' = 0.132$; $\Delta f'' = 0.159$) were included in the structure factor calculation. Refinement of the enantiomorphic structure led to no significant improvement in the

TABLE 2

DISTANCES (Å) AND ANGLES (°)

(a) Interatomic distances			
Be–Cl	1.869(3)	C(1)–C(2)	1.378(6)
Be–C(1)	1.870(5)	C(2)–C(3)	1.376(5)
Be–C(2)	1.867(5)	C(3)–C(4)	1.377(7)
Be–C(3)	1.868(5)	C(5)–C(5)	1.416(6)
Be–C(4)	1.875(5)	C(5)–C(1)	1.393(6)
Be–C(5)	1.873(6)	C–H_{mean}	0.88(6)
Be–C_e [a]	1.451(5)		
(b) Angles			
Cl–Be–C(1)	141.9(2)	C(5)–C(1)–C(2)	108.0(3)
Cl–Be–C(2)	140.4(3)	C(1)–C(2)–C(3)	108.9(4)
Cl–Be–C(3)	139.4(2)	C(2)–C(3)–C(4)	108.5(4)
Cl–Be–C(4)	140.5(2)	C(3)–C(4)–C(5)	107.6(4)
Cl–Be–C(5)	142.0(3)	C(4)–C(5)–C(1)	107.0(4)
Cl–Be–C_e [a]	178.4(3)		
(c) Intermolecular distances < 3.2 Å			
C(1)...H(1) [b]	3.05(4)	C(2)...H(3) [c]	3.18(5)

[a] C_e is a point at the centre of the C_5-ring. [b] Refers to the symmetry operation: $[x, y, z-1]$. [c] Refers to the symmetry operation: $[-1/2-x, -y, 1/2+z]$.

TABLE 3

CRYSTAL DATA FOR η^5-CYCLOPENTADIENYLBERYLLIUM CHLORIDE

C_5H_5BeCl	$M = 109.6$ a.m.u.
a 9.539(2) Å	Crystal system, orthorhombic
b 9.549(2) Å	Space group $P2_12_12_1$
c 6.513(1) Å	$F(000) = 224$
$Z = 4$	V 593.2 $Å^3$
D_c 1.23 g cm^{-3}	T 20°C
Monochromated(graphite) Mo-K_α X-radiation: λ 0.71069 Å	
Reflections measured: 1537	
$[\pm h,k,l]$ in the range $2.0 < \theta < 27.0°$	$\sin\theta/\lambda_{max}$ 0.65 $Å^{-1}$
μ 5.03 cm^{-1}	$\theta - 2\theta$ scan technique (96 steps)
$\sigma(F_o) = [\sigma(I)^2_{Poisson} + (Ik)^2]^{0.5}/2F$, $k = 0.02$	
Number of observed reflections (N_o): 521,	
$I \geq 2.0\sigma(I)$	Horizontal detector aperture:
$R = 0.032$	$4.0 + 1.0 \tan\theta$ mm
$R_w = 0.029$, $w = 1/\sigma^2(F_o)$	Vertical aperture: 4.0 mm
Number of variables (N_v): 84	(ω)scan range: $0.7 + 0.14 \tan\theta^0$
Goodness of fit, $[\Sigma w(F_o - \lvert F_c \rvert)^2/(N_o - N_v)]^{1/2} = 1.76$	

weighted R-value and so it was not possible to determine the true absolute configuration of the crystal. Final positional parameters are listed in Table 1. Thermal parameters and observed and calculated structure factors have been deposited with the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, (F.R.G.) and may be obtained on request on submission of the deposition number CSD 51095, the names of the authors and a full literature citation for this paper.

Discussion

The results of the X-ray analysis are summarised in Tables 1 and 2 and Figs. 1 and 2. They show that in the crystalline state cyclopentadienylberyllium chloride consists of discrete monomeric molecules separated by distances greater than the sum of the Van der Waals radii of the relevant atoms. This appears to be no significant change in the geometry of the molecule on crystallisation. The arrangement of the molecules in the unit cell is shown in Fig. 2. Intermolecular distances less than 3.2 Å are given in Table 2 and only involve bonds to hydrogen. The shortest intermolecular Be ··· Cl distance is 4.052(3) Å, and is between molecules related by a 2-fold screw axis directed along c. The corresponding Cl...Cl contact 4.156(1) Å is substantially longer than the sum of the Van der Waals radii for chlorine (3.6 Å) [7]. The absence of association may be attributed to the ability of the cyclopentadienyl ligand to satisfy the electronic requirements of the metal.

The results rule out the possibility, suggested by the mass spectrum, that CpBeCl is associated in solid state [4]. The probable explanation of MS results is that during very fast evaporation of the sample, crystalline aggregates vaporize out of the solid and into the ion beam before they are able to separate into discrete molecules.

Within the limit of experimental error the molecules possess a C_{5v}-axis of symmetry which passes through the centroid of the C_5-ring (C_e), the beryllium atom and the chlorine atom. Distances along this axis are Be–Cl 1.869(3) Å and Be–C_e 1.451(5) Å. The beryllium–chlorine bond is shorter than that in the tetracoordinated $Cl_2Be(NCMe)_2$ (1.98 Å [8]). The latter value corresponds to the sum of the covalent

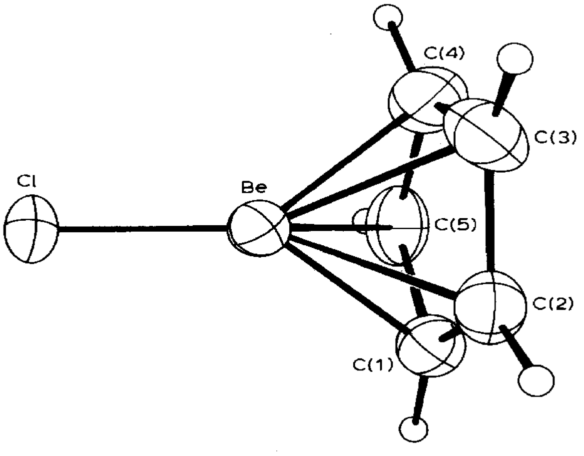

Fig. 1. The molecular structure of η^5-cyclopentadienylberyllium chloride showing the arbitrary atomic numbering system.

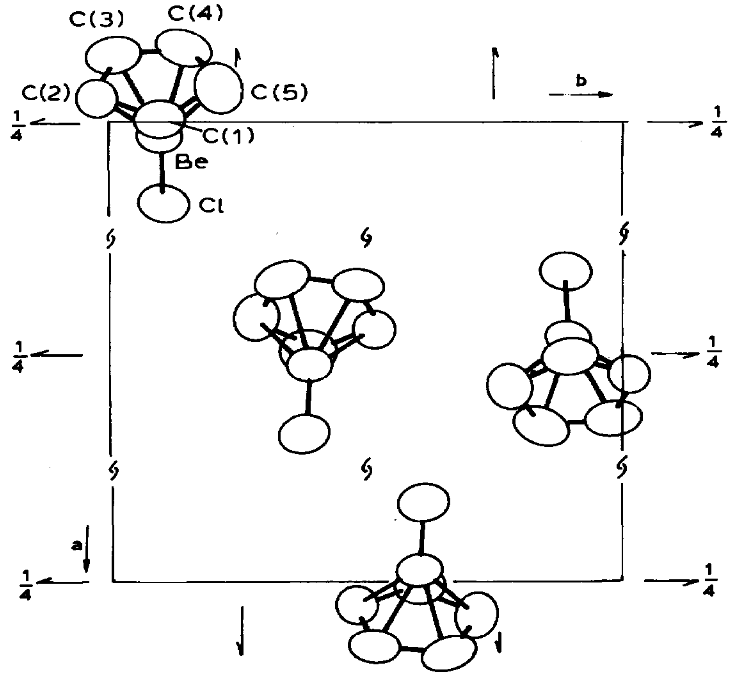

Fig. 2. The orthorhombic unit cell of cyclopentadienylberyllium chloride looking down *c* towards the origin. Hydrogen atoms have been omitted for clarity. There are no intermolecular distances below 3.0 Å.

radii and reflects a typical strongly polar σ-bond. In monomeric linear $BeCl_2$ however, the bonds are much shorter, being 1.75 Å; if it is assumed that there is only σ-bonding in the molecule, then there would be considerable polarisation of the Be–Cl bond towards chlorine, with two unoccupied *p* orbitals on beryllium and two filled *p* orbitals on both chlorine atoms [9]; back donation by a π interaction seems likely, and this would explain the marked shortening of the Be–Cl bond. In CpBeCl the cyclopentadienyl ligand is a stronger π electron donor than chlorine, and this gives rise to very effective π-bonding with beryllium *p* orbitals. The strong π type bonding of Cp ring and smaller positive charge [10] on beryllium atom lowers the π type Be–Cl interaction, resulting in a Be–Cl bond length intermediate value between that in four and two coordinated beryllium species. In the gas phase a Be–Cl distance of 1.837(6) Å was found for CpBeCl by electron diffraction [1] but the relatively large errors in both diffraction studies precludes a detailed comparison of the vapour and solid state structures.

The pentahapto bonding in compounds of this type has been discussed by Jutzi [11], Schleyer, Streitwieser et al. [12]. Although not precisely located, the hydrogen atoms of the cyclopentadienyl ring show a slight tendency to bend towards the beryllium atom, in agreement with theoretical predictions [12].

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