A Precise Low-Temperature Crystal Structure of Bis(cyclopentadienyl)beryllium

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Abstract

The crystal structure of bis(cyclopentadienyl)beryllium has been redetermined at 128(3) K. The crystals are monoclinic, space group $P2_1/n$, with unit cell a 5·993(5), b 7·478(4), c 8·978(5) Å, β 85·94(6)°, and Z 2. The essential 'slip-sandwich' structure previously reported is confirmed. The beryllium is disordered between two equivalent sites. In each site it is centrally bonded to one ring and peripherally bonded to the other. There is a small alternation in the C–C distances in the crystallographically equivalent rings towards a cyclopentadiene geometry. From the bond lengths and angles the peripherally bonded cyclopentadienyl ring appears to be bonded to the beryllium with a largely sp² hybridized carbon. This indicates only a small perturbation of the delocalized π-electron structure of the cyclopentadienyl ring and accounts for the reported Raman spectrum of the compound.

Introduction

'Beryllocene' is the lightest member of the ferrocene family of compounds, $M^{II}(C_5H_5)_2$. Despite many studies on the molecule since its preparation in 1959,[1] there is no consistent description of its structure and bonding. A C_{5v} structure with the beryllium atom asymmetrically located between planar, parallel cyclopentadienyl rings was suggested from the first electron diffraction study of the vapour.[2] This interpretation has recently been revised,[3] however, in view of the results of X-ray diffraction studies,[4,5] which indicate a 'slip-sandwich' structure. In the 'slip-sandwich' the cyclopentadienyl rings remain parallel but are offset. The beryllium atom is centrally bonded to one of the cyclopentadienyl rings (pentahapto). It is peripherally bonded to the second ring, however, located closest to a single carbon atom of that ring. In contrast with the X-ray results, the Raman spectrum was recently described as inconsistent with a monohapto cyclopentadienyl ring.[6] In view of these

[1] Fischer, E. O., and Hofmann, H. P., *Chem. Ber.*, 1959, **92**, 482.
[2] Almenningen, A., Bastiansen, O., and Haaland, A., *J. Chem. Phys.*, 1964, **40**, 3434.
[3] Almenningen, A., Haaland, A., and Lusztyk, J., *J. Organomet. Chem.*, 1979, **170**, 271.
[4] Wong, C. H., Lee, T. Y., Chao, K. J., and Lee, S., *Acta Crystallogr., Sect. B*, 1972, **28**, 1662.
[5] Wong, C., Lee, T. Y., Lee, T. J., Chang, T. W., and Liu, C. S., *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 667.
[6] Lusztyk, J., and Starowieyski, K. B., *J. Organomet. Chem.*, 1979, **170**, 293.

uncertainties and because the previous low-temperature X-ray structure[4] was based on film data and consequently imprecise, we have redetermined the structure at 128(3) K by means of diffractometer methods. The 'slip-sandwich' structure is confirmed and some details of the bonding are revealed by the precise bond lengths.

Experimental

Data Collection

A crystal was grown in a glass capillary to prevent aerial oxidation. Lattice parameters at $-145(3)°C$ were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined by scans performed on an Enraf–Nonius CAD4 four-circle diffractometer employing graphite monochromated Mo $K\alpha$ radiation.

Crystal data.—$C_{10}H_{10}Be$; formula weight 139·19; monoclinic, space group $P\,2_1/n$; $a\ 5·993(5)$, $b\ 7·478(4)$, $c\ 8·978(5)$ Å, $\beta\ 85·94(6)°$; $D_c\ 1·151$ g cm^{-3}; $V\ 401·3$ Å^3, $Z\ 2$, μ(Mo $K\alpha$) 0·32 cm^{-1}, λ(Mo $K\alpha$) 0·7107 Å, $F(000)$ 148 electrons.

Intensity data were collected in the range $1·2 < \theta < 22°$ using a $(\omega-\frac{1}{3}n\theta)$ scan where n, optimized by peak analysis, was 6. The ω scan angles and horizontal counter apertures employed were $(1·20+0·35\tan\theta)°$ and $(2·40+0·5\tan\theta)$ mm respectively. Data reduction and application of Lorentz and polarization corrections were carried out by using program SUSCAD.[7] In view of the low absorption coefficient no correction for absorption was performed. Of the 432 independent reflections collected 357 with $I > 2·5\sigma(I)$ were considered 'observed' and used in the calculations.

Structure Solution and Refinement

The structure was solved by the automatic direct methods routine for centrosymmetric structures of the SHELX program.[8] Only the five carbon atoms were located initially; refinement of these with anisotropic thermal parameters and calculation of a difference map revealed the beryllium and hydrogen atoms. The disordered beryllium was included in the model in two equivalent sites each with an occupancy of 0·5 and refined with anisotropic thermal parameters while the hydrogen atoms were refined with isotropic thermal parameters. Attempts to refine H(5) at two sites each with half occupancy failed and refinement of this atom with anisotropic thermal parameters did not reveal any significant ($>1\sigma$) deviation from sphericity.

Full-matrix least-squares techniques were used to refine all positional and thermal parameters, an overall scale factor and an empirical isotropic extinction parameter x, $[F_o' = F_o(1-0·0001xF_o^2/\sin\theta)]$. Refinement converged (all shifts $<0·05\sigma$) with x 0·040(7), R 0·035 and $R_w = 0·037$.* A weighting scheme, applied and refined, converged at $w = 1·43/(\sigma^2F_o+0·00054F_o^2)$. A final difference map was structurally featureless with the largest peak less than 0·2 e Å^{-3} in height.†

All calculations were performed by using the SHELX[8] system of programs and all scattering factors (neutral Be for Be^{2+}) and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography.[9]

Description of the Structure

The structure confirms as correct the solution obtained at 153 K by using photographic data.[4] Positional parameters are given in Tables 1 and 2 and bond lengths and angles in Tables 3 and 4.

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* $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $R_w = \Sigma(|F_o|-|F_c|w^{1/2}/\Sigma(|F_o|w^{1/2})$.
† Structure factors are available on application to the Editor-in-Chief, Editorial and Publications Service, CSIRO, 314 Albert Street, East Melbourne, Vic. 3002.

[7] SUSCAD—'Data Reduction Program for the CAD4 Diffractometer' University of Sydney, 1976.
[8] Sheldrick, G. M., SHELX-76 'Program for Crystal Structure Determination' 1976.
[9] Ibers, J. A., and Hamilton, W. C., (Eds), 'International Tables for X-Ray Crystallography' Vol. 4, pp. 99, 148 (Kynoch Press: Birmingham 1974).

Table 1. Non-hydrogen atomic coordinates

Atom	10^4x	10^4y	10^4z
C(1)	6045(4)	1745(3)	8279(3)
C(2)	4801(4)	702(3)	7343(3)
C(3)	2566(4)	571(3)	7988(2)
C(4)	2410(4)	1523(3)	9316(2)
C(5)	4600(4)	2236(3)	9548(3)
Be	4694(10)	−282(9)	9358(6)

Table 2. Hydrogen positional and thermal parameters

Atom	10^3x	10^3y	10^3z	U_{11} (Å)
H(1)	762(4)	204(3)	812(3)	4(1)
H(2)	533(4)	11(3)	641(3)	4(1)
H(3)	136(4)	−16(3)	758(2)	3(1)
H(4)	99(3)	166(3)	1001(2)	2(1)
H(5)	495(4)	306(3)	1030(3)	3(1)

Table 3. Bond distances

Atoms	d (Å)	Atoms	d (Å)
H(1)–C(1)	0·957(25)	C(2)–C(1)	1·395(4)
C(5)–C(1)	1·424(3)	Be–C(1)	1·940(7)
H(2)–C(2)	0·978(26)	C(3)–C(2)	1·410(4)
Be–C(2)	1·950(6)	H(3)–C(3)	0·988(22)
C(4)–C(3)	1·386(3)	Be–C(3)	1·930(6)
H(4)–C(4)	1·017(21)	C(5)–C(4)	1·431(3)
Be–C(4)	1·913(6)	H(5)–C(5)	0·952(27)
Be–C(5)	1·891(6)	Be$\cdots$Be′	1·303(12)
C(1)$\cdots$Be′	2·400(6)	C(2)$\cdots$Be′	3·014(6)
C(3)$\cdots$Be′	2·984(6)	C(4)$\cdots$Be′	2·347(6)
C(5)–Be′	1·826(6)		

Table 4. Bond angles (degrees)

Atoms	Angle	Atoms	Angle
C(2)–C(1)–H(1)	126·0(14)	C(5)–C(1)–H(1)	125·7(14)
C(5)–C(1)–C(2)	108·2(2)	H(2)–C(2)–C(1)	128·2(14)
C(3)–C(2)–C(1)	108·2(2)	C(3)–C(2)–H(2)	123·6(14)
H(3)–C(3)–C(2)	124·8(13)	C(4)–C(3)–C(2)	108·7(2)
C(4)–C(3)–H(3)	126·3(13)	H(4)–C(4)–C(3)	125·8(12)
C(5)–C(4)–C(3)	108·0(2)	C(5)–C(4)–H(4)	126·1(12)
C(4)–C(5)–C(1)	106·7(2)	H(5)–C(5)–C(1)	126·3(14)
H(5)–C(5)-C(4)	126·0(14)		

ORTEP[10] plots of the complex showing lateral and plan views are given in Figs 1 and 2. The least-squares plane through the five carbon atoms ($-0\cdot2462x + 0\cdot8290y - 0\cdot5022z = -3\cdot6702$) gives the following deviations: C(1) $0\cdot012$, C(2) $-0\cdot005$, C(3) $-0\cdot005$, C(4) $0\cdot012$, C(5) $-0\cdot015$, H(1) $0\cdot005$, H(2) $-0\cdot038$, H(3) $-0\cdot072$, H(4) $0\cdot021$, H(5) $0\cdot099$, Be $-1\cdot505$ Å. Since the error in a typical carbon site is $0\cdot0024$ Å and in a hydrogen site $0\cdot024$ Å these values show that C(5) and H(5) deviate significantly from the plane formed by C(1)–C(4). The plane through C(1), C(2), C(3) and C(4) ($0\cdot2493x + 0\cdot8217y - 0\cdot5125z = -3\cdot7576$) gives the following deviations: C(1), C(2), C(3) and C(4) $0\cdot000$, C(5) $-0\cdot038$, H(1) $-0\cdot011$, H(2)
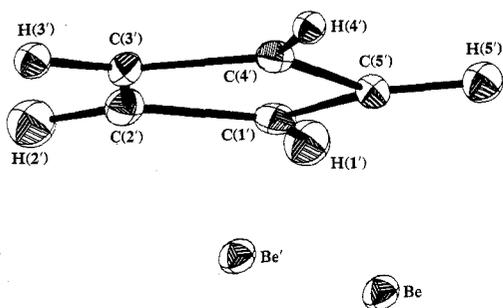
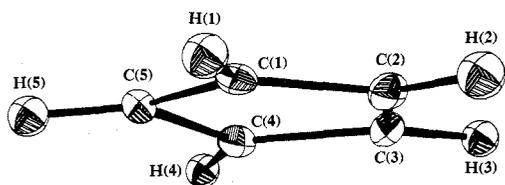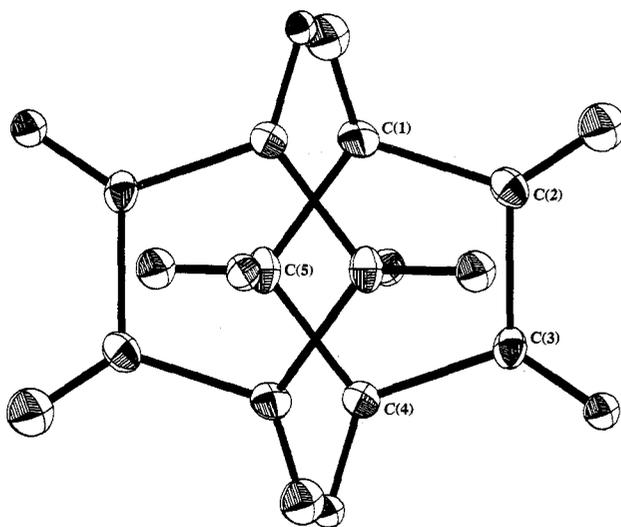**Fig. 1.** Lateral view of the beryllocene molecule.

Fig. 2. Plane view of the beryllocene molecule.

[10] Johnson C. K., ORTEP 'Thermal Ellipsoid Plotting' 1965.

−0·023, H(3) −0·057, H(4) 0·005, H(5) 0·064, Be −1·513 Å. Thus C(5) is moved closer to the beryllium while H(5) is bent away, both indicative of a significant C(5)–Be bonding interaction. Also bond lengths from C(5) to C(1) and C(4) are significantly longer than all others within the cyclopentadienyl ring.

Fig. 3 shows a packing diagram of the contents of the unit cell. The orientation of the molecules is such that the parallel arrangement of the two cyclopentadienyl rings within each molecule does not seem to be determined by packing forces.
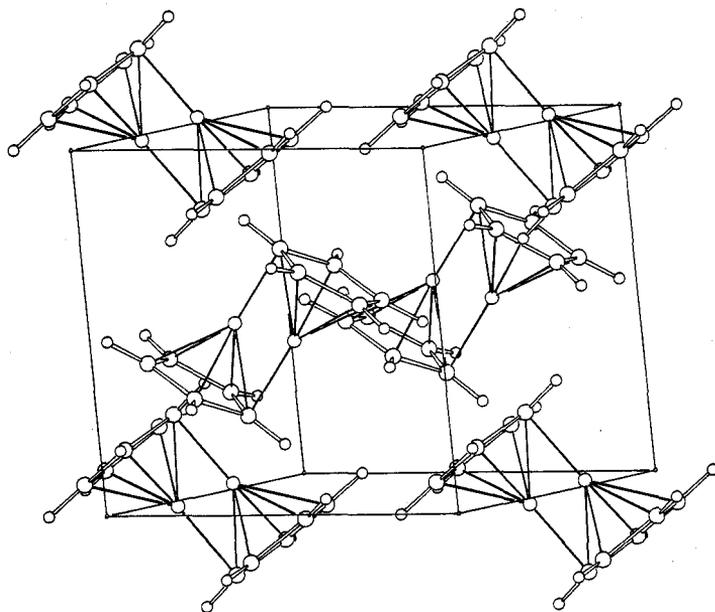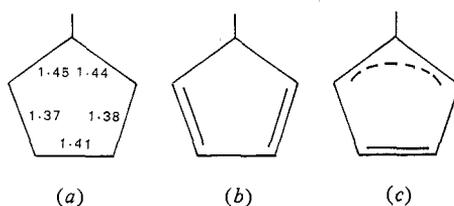

Fig. 3. Packing diagram of the unit cell.

Fig. 4.
(a) Estimated C—C bond lengths in the peripheral ring;
(b) monohapto cyclopentadiene structures;
(c) trihapto allyl-ene cyclopentadienyl structure.

(a)   (b)   (c)

Discussion

The disorder of the beryllium Be atoms between two crystallographically equivalent sites means that the observed cyclopentadienyl ring is the mean between centrally bonded and peripherally bonded cyclopentadienyl rings. In order to obtain a geometry for the ordered structure an additional assumption must be made. We assume that the centrally bonded ring with fivefold symmetry has a C–C bond length of 1·41 Å, equal to the average of the five observed C–C distances. The geometry of the peripherally bonded ring can then be calculated from twice the difference between the observed and the average C–C distances. This leads to the values given in Fig. 4a.

The alternation in bond lengths is clearly consistent with a peripherally bonded ring with partial diene character (Fig. 4b), and inconsistent with a trihapto ring with allyl character (Fig. 4c). The alternation in bond lengths is far less, however, than occurs in cyclopentadiene[11] itself (1·34 Å to 1·51 Å), or in other σ-bonded cyclopentadienyl complexes such as silylcyclopentadiene,[12] $SiH_3(C_5H_5)$ (1·39 Å to 1·50 Å), and germylcyclopentadiene,[13] $GeH_3(C_5H_5)$ (1·35 Å to 1·48 Å). Our hypothesis is that the delocalized π-electron structure of the cyclopentadienyl ring is only partly localized towards a σ-bonded cyclopentadiene structure in beryllocene.

This hypothesis is consistent with the small bond angles between beryllium and the ring [Be–C(5)–C(1), 94·4° and Be–C(5)–C(4), 91·4°]. In cyclopentadiene,[11] in contrast, the H(5)–C(5)–C(1) angle is 111·9°, in silylcyclopentadiene[12] Si–C(5)–C(1) is 106·6°, and in germylcyclopentadiene[13] Ge–C(5)–C(1) is 106·3° (vapour) and 106·9° and 108·5° (crystal). In these three cases the angle is close to that expected for sp^3 hybridization of the carbon bonded to the metal. In beryllocene, in contrast, the angle is close to that expected for sp^2 hybridization of the ring carbon, with the bond to beryllium involving a $p\pi$-orbital.

The bonding in beryllocene is not unique among metal cyclopentadienyl compounds. Tris(cyclopentadienyl)indium has a polymeric structure with bridging and terminal cyclopentadienyl groups.[14] The terminal cyclopentadienyl ligands are peripherally bonded with C–C bond length alternations around the ring similar to those observed in beryllocene. The mean In–C–C angle is 97°.

The structural evidence thus suggests that for some peripherally bonded cyclopentadienyl ligands the ring retains a largely π-delocalized character. The negative charge is only partly localized on the carbon directly bonded to the beryllium. This accounts then for the absence of characteristic diene features in the Raman spectrum of beryllocene.[6] It suggests that there is a continuum of bonding types from strictly σ-bonded monohapto cyclopentadiene to centrally bonded pentahapto cyclopentadienyl rings.

Acknowledgment

[11] Damiani, D., Ferretti, L., and Gallinella, E., Chem. Phys. Lett., 1976, 37, 265.
[12] Bentham, J. E., and Rankin, D. W. H., J. Organomet. Chem., 1971, 30, C54.
[13] Barrow, M. J., Ebsworth, E. A. V., Harding, M. M., and Rankin, D. W. H., J. Chem. Soc., Dalton Trans., 1980, 603.
[14] Einstein, F. W. B., Gilbert, M. M., and Tuck, D. G., Inorg. Chem., 1972, 11, 2832.