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THE STRUCTURE OF DICYCLOPENTADIENYLZINC

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Summary

Dicyclopentadienylzinc, $(C_5H_5)_2Zn$, crystallizes in the monoclinic system, space group $P2_1/c$ ($Z = 8$). Cell dimensions are: *a* 14.046(1), *b* 8.640(1), *c* 15.828(2) Å; *β* 113.03(1)°. The structure consists of infinite chains of zinc atoms with bridging cyclopentadienyl groups. In addition, each zinc atom carries a terminal cyclopentadienyl group. The chains, which run parallel to the *a*-axis, contain two crystallographically independent zinc atoms in the order ...12211221... The cyclopentadienyl groups bridging between zinc atoms of the same type are located over centers of symmetry and therefore disordered. The cyclopentadienyl group bridging between Zn(1) and Zn(2) is normal. It appears that both σ- and π-type interactions contribute to the cyclopentadienyl–zinc bonds.

Introduction

Dicyclopentadienyl compounds of transition metals typically have a ferrocene-like sandwich structure. Electron-deficient cyclopentadienides of the Main Group metals, on the other hand, tend to form polymers with bridging cyclopentadienyl groups. Although exceptions to both rules are known [1,2], the trend is fairly consistent. The element zinc occupies a borderline position between the transition metals and the Main Group metals, and this naturally poses the question of whether the structure of Cp_2Zn will in any way be intermediate between both categories of cyclopentadienyl compounds.

E.O. Fischer [3], who first prepared Cp_2Zn, proposed a ferrocene-like sandwich structure (with a predominantly ionic ring–metal interaction) on the basis of the similarity of the IR spectra of Cp_2Zn and Cp_2Mg. Lorberth [4] suggested a structure with centrally σ-bound Cp rings (which amounts to the same thing) on the basis of the equivalence of all Cp protons in the ^1H NMR spectrum of the compound.

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Burlitch, in his review of zinc-transition metal compounds [5], used the formulation (η^1-Cp)$_2$Zn, probably by analogy with the *monohapto* structure currently accepted for Cp_2Hg [6].

In our study of cyclopentadienylzinc-transition metal compounds [7], we have encountered several examples of η^5-bound Cp(Zn) groups. An η^5-bound Cp group also occurs in gaseous CpZnMe [8]. In the solid state, however, the compound forms polymeric chains of zinc atoms separated by bridging cyclopentadienyl groups [9]. We have determined the structure of Cp_2Zn by X-ray diffraction analysis, and found it to be related to, but more complicated than, the structure of CpZnMe.

Results and discussion

Details of the data collection and structure refinement are summarized in Table 1. Fractional atomic coordinates are given in Table 2; bond lengths are given in Table 3 and selected bond angles in Table 4. Cp_2Zn crystallizes in the monoclinic system, space group $P2_1/c$ ($Z = 8$). The structure consists of infinite chains of zinc atoms with bridging cyclopentadienyl groups; in addition, each zinc atom carries a terminal Cp group. The chains, which run parallel to the *a*-axis, contain two crystallographi-

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TABLE 1

FRACTIONAL ATOMIC PARAMETERS OF NON-HYDROGEN ATOMS OF DICYCLOPENTADIENYLZINC

Atom	x/a	y/b	z/c
Zn(1)	0.0294(2)	0.2126(3)	0.4000(1)
Zn(2)	0.3854(2)	0.2017(3)	0.4014(2)
C(11)	0.198(2)	0.177(4)	0.357(2)
C(12)	0.175(2)	0.132(4)	0.427(3)
C(13)	0.212(2)	0.235(6)	0.493(2)
C(14)	0.249(2)	0.359(3)	0.465(2)
C(15)	0.240(2)	0.325(3)	0.372(2)
C(21)	−0.173(3)	0.287(3)	0.248(2)
C(22)	−0.075(3)	0.327(4)	0.262(2)
C(23)	−0.029(1)	0.421(3)	0.335(2)
C(24)	−0.117(3)	0.456(3)	0.359(2)
C(25)	−0.195(2)	0.373(4)	0.307(2)
C(31)	0.489(2)	0.410(9)	0.370(2)
C(32)	0.477(3)	0.262(4)	0.333(4)
C(33)	0.399(3)	0.294(6)	0.245(2)
C(34)	0.373(2)	0.437(7)	0.237(2)
C(35)	0.430(5)	0.512(4)	0.317(5)
C(41)	−0.063(3)	0.02(1)	0.432(3)
C(42)	−0.036(3)	0.12(1)	0.505(3)
C(43)	0.045(3)	0.06(1)	0.575(3)
C(44)	0.069(3)	−0.08(1)	0.546(3)
C(45)	0.002(3)	−0.10(1)	0.458(3)
C(51)	0.428(3)	0.043(4)	0.518(2)
C(52)	0.422(3)	−0.063(4)	0.453(2)
C(53)	0.518(3)	−0.079(4)	0.452(2)
C(54)	0.584(3)	0.016(4)	0.517(2)
C(55)	0.528(3)	0.091(4)	0.558(2)

TABLE 2

CRYSTAL DATA AND DETAILS OF THE STRUCTURE REFINEMENT OF DICYCLOPENTADIENYLZINC

Crystal data	
Formula	$C_{10}H_{10}Zn$
Mol. wt	195.56
Crystal system	monoclinic-*b*
Space group	No. 14, $P2_1/c$
a (Å)	14.046(1)
b (Å)	8.640(1)
c (Å)	15.828(2)
β (°)	113.03(1)
V (Å^3)	1767.8(4)
Z	8
D_{calc} (g cm^{-3})	1.469
F_{000}	800
μ(Mo-K_α) (cm^{-1})	27.84
Crystal size (mm)	0.13×0.18×0.5
Data collection	
θ_{min}, θ_{max} (°)	0.1 20.0
Radiation	Mo-K_α (Zr-filtered), 0.71069 Å
$\omega/2\theta$ scan (°)	$0.40+0.35\tan\theta$
Max. time/refl. (min)	1.0
Horizontal and vertical aperture (mm)	3, 2
Reference reflection	020
Total data	3327
Total unique	1398
Observed data ($I > 2.5\sigma(I)$)	937
Refinement	
No. of refined parameters	178
Weighting scheme	$w^{-1}=(\sigma^2(F)+0.0015F^2)/1.19$
Final $R_F = \Sigma\|F_0-\|F_c\|\|/\Sigma F_0$	0.064
Final $R_{wF} = [\Sigma w(F_0-\|F_c\|)^2/\Sigma w F_0{}^2]^{1/2}$	0.066
Rms deviation of refl. of unit wt.	3.31

TABLE 3

BOND DISTANCES BETWEEN NON-HYDROGEN ATOMS IN DICYCLOPENTADIENYLZINC (Å) [a]

Zn(1)–C(12)	2.04(3)	Zn(2B)–C(54)	2.22(4)	C(31)–C(32)	1.39(8)
Zn(1)–C(13)	2.41(3)	Zn(2B)–C(53)	2.43(4)	C(32)–C(33)	1.42(7)
Zn(1)–C(23)	2.08(3)	C(11)–C(12)	1.33(6)	C(33)–C(34)	1.29(8)
Zn(1)–C(22)	2.33(4)	C(12)–C(13)	1.32(6)	C(34)–C(35)	1.36(8)
Zn(1)–C(41)	2.27(7)	C(13)–C)14)	1.33(5)	C(35)–C(31)	1.28(8)
Zn(1)–C(42)	2.33(5)	C(14)–C(15)	1.46(5)		
Zn(1A)–C(44)	2.21(6)	C(15)–C(11)	1.39(4)		
Zn(2)–C(15)	2.19(3)	C(21)–C(22)	1.35(5)		
Zn(2)–C(11)	2.46(2)	C(22)–C(23)	1.36(4)		
Zn(2)–C(32)	2.04(6)	C(23)–C(24)	1.46(4)		
Zn(2)–C(31)	2.48(6)	C(24)–C(25)	1.29(4)		
Zn(2)–C(51)	2.19(4)	C(25)–C(21)	1.32(5)		
Zn(2)–C(52)	2.41(4)				

[a] Symmetry code: A = $-x,-y,1-z$; B = $1-x,-y,1-z$.

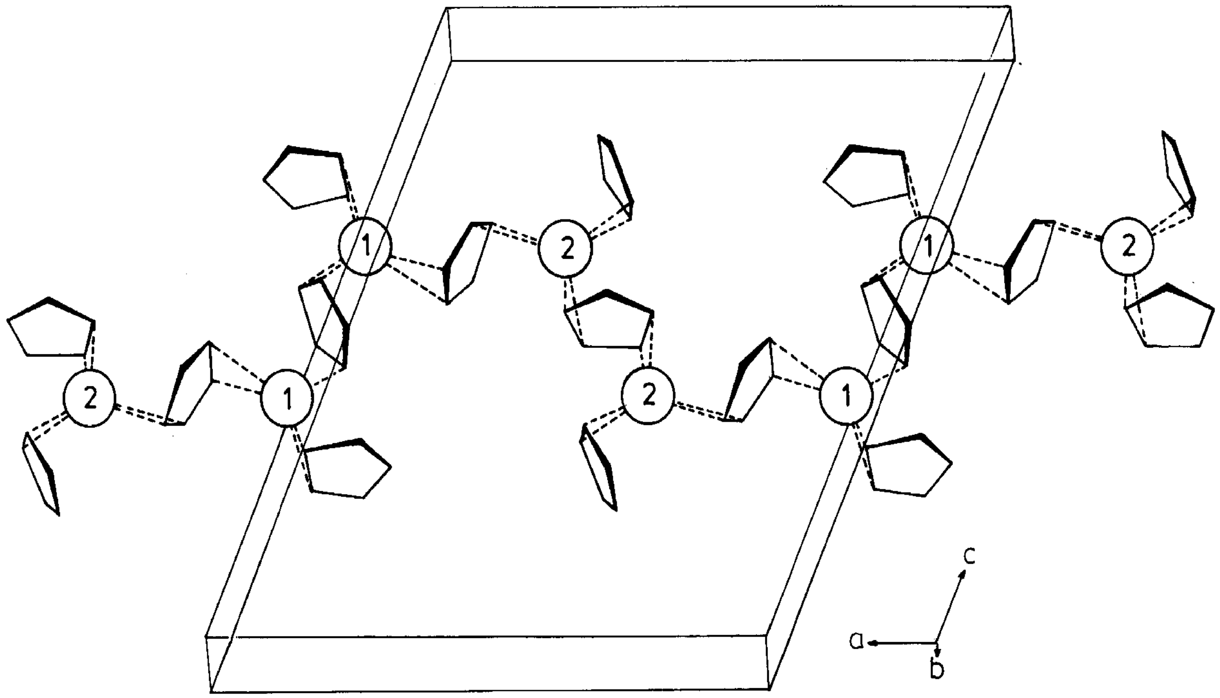

Fig. 1. Schematic drawing showing four units of the chain structure of Cp_2Zn. Only one conformation of each disordered Cp ring is shown. Dotted lines indicate zinc–carbon distances of < 2.50 Å.

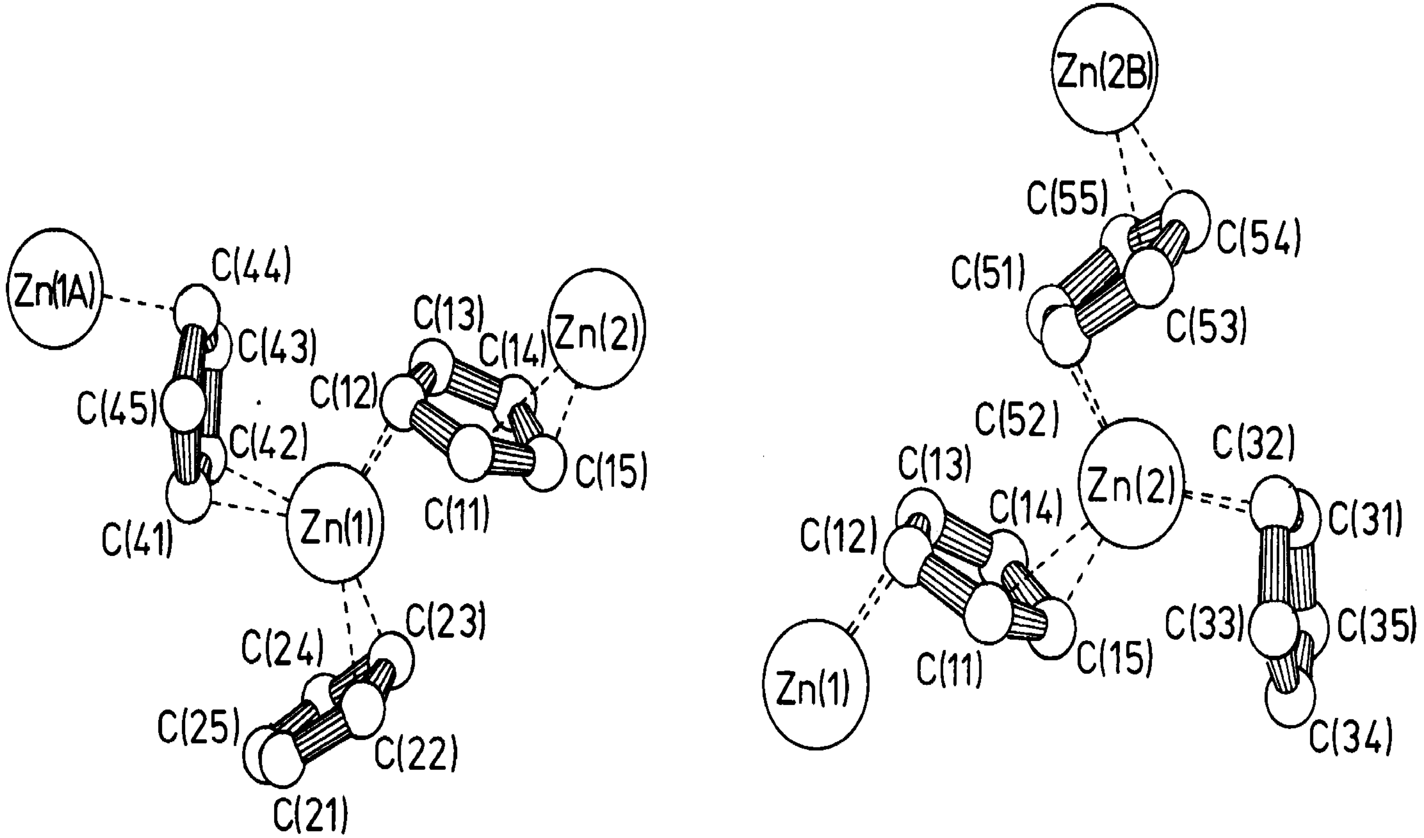

Fig. 2. PLUTO drawings of the coordination spheres of the zinc atoms of Cp_2Zn. Only one conformation of the disordered Cp(4) and Cp(5) rings is shown. Dotted lines indicate zinc–carbon distances of < 2.50 Å (Hydrogen atoms have been omitted for clarity). For symmetry code see Table 3.

TABLE 4

SELECTED BOND ANGLES FOR DICYCLOPENTADIENYLZINC (°)

C(12)–Zn(1)–C(23)	125(1)	C(21)–C(22)–C(23)	114(3)
C(12)–Zn(1)–C(41)	109(2)	C(22)–C(23)–C(24)	100(2)
C(23)–Zn(1)–C(41)	126(2)	C(23)–C(24)–C(25)	108(3)
C(15)–Zn(2)–C(32)	119(2)	C(24)–C(25)–C(21)	114(3)
C(15)–Zn(2)–C(51)	114(1)	C(25)–C(21)–C(22)	104(3)
C(32)–Zn(2)–C(51)	126(2)	C(31)–C(32)–C(33)	99(4)
C(11)–C(12)–C(13)	108(3)	C(32)–C(33)–C(34)	111(4)
C(12)–C(13)–C(14)	112(3)	C(33)–C(34)–C(35)	109(4)
C(13)–C(14)–C(15)	106(3)	C(34)–C(35)–C(31)	106(5)
C(14)–C(15)–C(11)	103(3)	C(35)–C(31)–C(32)	115(4)
C(15)–C(11)–C(12)	111(3)		

cally independent zinc atoms in the order ...12211221... The cyclopentadienyl groups bridging between zinc atoms of the same type are located over centers of symmetry and therefore disordered. The Cp group bridging between Zn(1) and Zn(2) is normal. A schematic drawing showing four units of the chain structure is presented in Fig. 1. The approximately trigonal environments of the zinc atoms are illustrated more clearly in Fig. 2.

Neither the terminal nor the bridging Cp groups are bound to zinc in a purely η^1-fashion. This is clearly illustrated by the appearance of several rather short "non-bonded" Zn–C distances (e.g. Zn(1)–C(13) 2.41(3), Zn(2)–C(11) 2.46(2), Zn(1)–C(22) 2.33(4) Å). The bonding situation can best be described as "$\eta^{2.5}$", similar to that in CpZnMe [9]. Accordingly, it appears that both σ- and π-type interactions contribute to the zinc–Cp bonds. This will be discussed in more detail in a forthcoming paper.

The structures of many metal cyclopentadienides can be rationalized on the basis of both the radius of the metal atom and the binding mode of the Cp groups, more space around the metal being occupied by increasingly delocalized metal–Cp bonds. In, for example, the series Mg < Zn < Mn < Ca ≃ Pb, the metal ion radius increases on going from Mg to Pb. In Cp_2Mg, which has a sandwich structure [1], the metal is surrounded by only two η^5-bound Cp groups. The next larger metal, zinc, can accomodate three Cp groups, although none of these is η^5-bound. In Cp_2Mn [2], which like Cp_2Zn forms polymeric chains, already one η^5-bound Cp group is present but the other two are less delocalized like in the case of zinc. Cp_2Pb [10] again forms polymeric chains and the lead is now surrounded by three η^5-bound Cp groups. Cp_2Ca [11] forms a three-dimensional network in which each calcium is surrounded by two η^5-bound Cp groups, one η^3-bound group, and one η^1-bound group, i.e. four in all. As regards space requirements, such an environment will be comparable to the threefold η^5-coordination around lead in Cp_2Pb.

Experimental

General remarks

All experiments were carried out under dry, oxygen-free nitrogen. Solvents were carefully purified, dried and distilled under nitrogen. Solutions were handled with syringes.

Synthesis of dicyclopentadienylzinc

Cp_2Zn was prepared by the method described by Lorberth [4]. To a solution of 118 g $Zn(N(SiMe_3)_2)_2$ in 100 ml of diethyl ether was added 100 ml of freshly distilled cyclopentadiene and the mixture was stirred for 4 h. In most cases, the mixture abruptly turned milky-white after ca. 40 min but sometimes this took appreciably longer. The course of the reaction can be monitored by checking the amount of zinc amide remaining in solution by ^1H NMR spectroscopy. After completion of the reaction, the ether was decanted and the colourless, solid residue was washed twice with ether and twice with pentane, than dried in vacuo to yield 44 g (73%) of pure, colourless, microcrystalline Cp_2Zn.

Single crystals suitable for X-ray analysis were obtained by slow sublimation in vacuo (140°C/10^{-2} mmHg).

Data collection and structure refinement for Cp_2Zn

A colourless crystal suitable for data collection was sealed under nitrogen in a Lindemann capillary and transferred to an Enraf-Nonius CAD 4F diffractometer. The automatic CAD 4F search program produced a set of reflections which could not be indexed on the basis of a reasonable unit cell. If some of the weaker reflections were ignored, a consistent indexing scheme could be found on the basis of the unit cell mentioned in Table 2. The presence of additional non-indexable reflections was attributed to twinning (which was later confirmed by Weissenberg photographs), although no external signs of twinning were visible. Unit cell dimensions and standard deviations were determined in the usual way from the setting angles of 19 carefully centered reflections [12]. The space group was determined as $P2_1/c$, and the data belonging to one hemisphere ($+h$, $\pm k$, $\pm l$) were collected in the $\omega/2\theta$-scan mode with use of Zr-filtered Mo-K_α radiation. The two sets of equivalent reflections were merged with a consistency-index of 0.07, supporting the adopted monoclinic symmetry assignment. In view of the poor quality of the data set, no absorption correction was attempted.

The structure was solved by standard Patterson and Fourier techniques and refined by blocked full-matrix least-squares techniques. Anisotropic thermal parameters were used for the zinc atoms and for the carbon atoms of the ordered Cp rings. The disordered rings were refined as rigid pentagons (d_{CC} 1.36 Å) with independent isotropic thermal parameters. The hydrogen atoms were placed at calculated positions and were divided into two groups (those belonging to the ordered and to the disordered Cp rings), each of which was assigned one overall variable isotropic thermal parameter. Weights were introduced in the final refinement stages. Neutral-atom scattering factors were taken from ref. 13 and corrected for anomalous dispersion [14].

Supplementary data (all positional and thermal parameters, bond lengths and bond angles, and a listing of structure factor amplitudes) are available from the authors.

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References

1 W. Bünder and E. Weiss, J. Organomet. Chem., 92 (1975) 1.

2 W. Bünder and E. Weiss, Z. Naturforsch. B, 33 (1978) 1235.

3 E.O. Fischer, H.P. Hoffmann and A. Treiber, Z. Naturforsch. B, 14 (1969) 599.

4 J. Lorberth, J. Organomet. Chem., 19 (1969) 189.

5 J.M. Burlitch, in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Vol. 6. Pergamon Press, Oxford, 1982, p.1004.

6 F.A. Cotton and T.J. Marks, J. Am. Chem. Soc., 91 (1969) 7281; E. Maslowsky and K. Nakamoto, Inorg. Chem., 8 (1969) 1108.

7 P.H.M. Budzelaar, J. Boersma, G.J.M. van der Kerk, A.L. Spek and A.J.M. Duisenberg, Inorg. Chem., 21 (1982) 3777; P.H.M. Budzelaar, J. Boersma and G.J.M. van der Kerk, Angew. Chem. Int. Ed. Engl., 22 (1983) 329; P.H.M. Budzelaar, K.H. den Haan, J. Boersma, G.J.M. van der Kerk and A.L. Spek, Organometallics, 3 (1984) 156; P.H.M. Budzelaar, A.A.H. van der Zeijden, J. Boersma, G.J.M. van der Kerk, A.L. Spek and A.J.M. Duisenberg, Organometallics, 3 (1984) 159.

8 T.C. Bartke, A. Bjørseth, A. Haaland, K.M. Marstokk and H. Møllendal, J. Organomet. Chem., 85 (1975) 271.

9 T. Aoyagi, H.M.N. Shearer, K. Wade and G. Whitehead, J. Organomet. Chem., 146 (1978) C29.

10 C. Panattoni, G. Bombieri and U. Croatto, Acta Crystallogr., 21 (1966) 823.

11 R. Zerger and G. Stucky, J. Organomet. Chem., 80 (1974) 7.

12 F.A.J.J. van Santvoort, H. Krabbendam, A.L. Spek and J. Boersma, Inorg. Chem., 17 (1978) 388.

13 D.T. Cromer and J.B. Mann, Acta Crystallogr., A24(1968)321.

14 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.