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THE FORMATION AND MOLECULAR STRUCTURE OF ACETYLCYCLOPENTADIENYLSODIUM·TETRAHYDROFURANATE

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Summary

Acetylcyclopentadienylsodium has been isolated in crystalline form as a THF adduct from a reaction between cyclopentadienylsodium and methyl acetate in THF solution. The product has been characterized by means of a single-crystal X-ray diffraction study. $\{[C_5H_4CMeO]Na\cdot THF\}_n$ crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters a 6.698(3), b 16.095(4), c 10.661(3) Å, β 92.93(3)° and D_c 1.17 g cm^{-3} for $Z = 4$. Least-squares refinement led to a final R value of 0.080 based on 661 independent observed reflections. The coordination sphere around each sodium atom consists of the oxygen atoms from two C_5H_4CMeO ligands, the oxygen atom of the THF molecule, and an ion contact pair between the sodium and the five ring carbon atoms of the C_5H_4CMeO ligand.

Introduction

Alkali metal salts of cyclopentadiene (metal cyclopentadienides) have been of great synthetic and theoretical interest to chemists for many years. That one of the methylene hydrogens of cyclopentadiene is directly replaceable by an alkali metal was originally demonstrated by Thiele in 1900—1901, when he reacted granulated potassium metal dispersed with cyclopentadiene to produce cyclopentadienylpotassium, C_5H_5K [1]. In 1953—1954, the utility of alkali metal cyclopentadienides (especially C_5H_5Na in THF) in the formation of η^5-cyclopentadienyl derivatives of the transition metals was first demonstrated by several research groups [2—6], and this synthetic technique remains the most versatile and widely applicable route to this important class of organometallic compounds up to the present time. The structure and bonding of alkali metal

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salts of cyclopentadiene have likewise been of considerable theoretical interest, dating back to classical studies by Hückel [7,8].

In spite of the importance of alkali metal cyclopentadienides in organic, organometallic and theoretical chemistry, remarkably only one crystallographic study has been undertaken in this area, namely the structure of $C_5H_5Na \cdot$TMEDA [9]. Very recently, we have reported that reactions of C_5H_5Na with various organic esters lead in good yield to a series of functionally-substituted cyclopentadienylsodium derivatives, including acetyl-(I) [10], formyl-(II) [10], carbomethoxy-(III) [10], and nitrocyclopentadienylsodium (IV) [11] (I, R = $C(O)CH_3$; II, R = CHO; III, R = $COOCH_3$; IV, R = NO_2). The synthetic utility of these reagents in organometallic chemistry has aptly been demonstrated [10—13]. In the present paper, we describe a detailed synthetic route to acetylcyclopentadienylsodium (I), and the results of a single-crystal X-ray diffraction study on a THF adduct of I which demonstrate it to have a unique bridging structure.

Experimental

Preparation of acetylcyclopentadienylsodium · THF

All operations were conducted under prepurified nitrogen. Into a 500-ml, three-neck roundbottom flask fitted with a reflux condenser, nitrogen inlet and outlet valves was placed sodium sand (4.60 g, 0.20 mol). THF (200 ml) was next added, followed by freshly cracked cyclopentadiene (20.0 ml, 0.24 mol) in four portions. After all the sodium had reacted, methyl acetate (23.8 ml, 0.30 mol) was added and the reaction mixture heated to reflux for 11 h. Upon cooling to room temperature, off-white crystals of acetylcyclopentadienylsodium·THF suitable for X-ray diffraction studies separated out of solution. The crystals were collected under nitrogen, washed with several portions of ether, and finally dried under vacuum (0.1 Torr) to give 18.2 g (70%) of product.

X-ray data collection, structure determination, and refinement for $\{[C_5H_4CMeO]Na \cdot THF\}_n$

Single crystals of the air-sensitive compound were sealed under nitrogen in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($\theta > 20°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table 1.

Data were collected on the diffractometer by the ω-2θ scan technique [14]. A summary of data collection parameters is given in Table 1. The intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu = 1.18$ cm^{-1}).

Calculations were carried out with the SHELX [15] system of computer programs. Neutral atom scattering factors for Na, O, and C were taken from Cromer and Waber [16]. Scattering factors for H were from ref. 17.

The positions of the non-hydrogen atoms were revealed by application of the direct methods program MULTAN [18]. Refinement with isotropic temperature factors led to a reliability factor of $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.135$. Scrutiny of a difference Fourier map showed electron density in accordance

TABLE 1

CRYSTAL DATA AND SUMMARY OF INTENSITY DATA AND STRUCTURE REFINEMENT

Compound		$\{[C_5H_4CMeO]Na\cdot THF\}_n$
Molecular weight		202.2
Space group		$P2_1/c$
Cell constants	a	6.698(3) Å
	b	16.095(4) Å
	c	10.661(3) Å
	β	92.93(3)°
Cell vol		1147.8 Å^3
Molecules/unit cell		4
ρ (calcd.)		1.17 g cm^{-3}
μ (calcd.)		1.18 cm^{-1}
Radiation		Mo-K_α
Max crystal dimensions		0.25 × 0.43 × 0.89 mm
Scan width		0.80 + 0.20 tan θ
Standard reflections		0, 10, 0 004
Decay of standards		±2%
Reflections measured		1055
2θ range		4—36°
Reflections collected		661
No. of parameters varied		145
GOF		1.57
R		0.080
R_w		0.080

TABLE 2

FINAL FRACTIONAL COORDINATES FOR $\{[C_5H_4CMeO]Na\cdot THF\}_n$

Atom	x/a	y/b	z/c
Na	0.3120(5)	0.5265(2)	0.0949(3)
O(1)	0.658(1)	0.5101(4)	0.1113(7)
O(2)	0.285(1)	0.6721(4)	0.1061(7)
C(1)	0.960(2)	0.4809(7)	0.225(1)
C(2)	1.024(2)	0.4113(7)	0.1548(9)
C(3)	1.206(2)	0.3855(7)	0.210(1)
C(4)	1.256(2)	0.436(1)	0.315(1)
C(5)	1.108(2)	0.4927(7)	0.327(1)
C(6)	0.775(2)	0.5217(7)	0.206(1)
C(7)	0.714(2)	0.5836(8)	0.304(1)
C(8) [a]	0.413(3)	0.716(1)	0.019(2)
C(9)	0.332(4)	0.797(1)	—0.002(2)
C(10)	0.094(3)	0.791(1)	0.043(2)
C(11)	0.094(3)	0.717(1)	0.130(1)
C(12) [b]	0.447(8)	0.735(3)	0.086(5)
C(13)	0.29(1)	0.816(4)	0.071(6)
C(14)	0.21(1)	0.810(4)	0.093(7)
C(15)	0.178(6)	0.734(3)	0.164(4)
H(1)[C(2)]	0.9440	0.3820	0.0811
H(2)[C(3)]	1.2925	0.3370	0.1824
H(3)[C(4)]	1.3785	0.4316	0.3772
H(4)[C(5)	1.1020	0.5388	0.3961
H(5)[C(7)]	0.8438	0.6091	0.3438
H(6)[C(7)]	0.6004	0.6106	0.3469
H(7)[C(7)]	0.7069	0.6062	0.2126

[a] Atoms C(8)—C(11) have occupancy factors of 0.749. [b] Atoms C(12)—C(15), 0.251.

with disorder of the carbons of the THF ligand. The approximate disorder was deduced to be 75—25% and subsequent refinement of the occupancy factors led to 0.749 and 0.251. R_1 was now 0.103. Conversion to anisotropic thermal parameters of all except the 0.251 occupancy atoms led to $R_1 = 0.089$. The hydrogen atoms of the cyclopentadienyl ring were placed in calculated positions 1.00 Å from the bonded carbons and the three methyl hydrogen atoms were found on a difference Fourier map. The hydrogen atom positional and thermal parameters were not refined. Additional cycles of refinement led to final values of $R_1 = 0.080$ and $R_2 = 0.080$. The largest parameter shifts in the final cycle of refinement were less than 0.02 of their esd's. A final difference Fourier showed no feature greater than 0.4 $e^-/Å^3$. The standard deviation of an observation of unit weight was 1.57. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final positional parameters are given in Table 2 [19].

Results and discussion

The sodium atom environment and the numbering scheme are presented in Fig. 1. The sodium atom is coordinated through the oxygen atom to two C_5H_4CMeO units forming a dimer (Fig. 2). The two halves of the dimer are related crystallographically by $(1 - x, 1 - y, -z)$, and one THF ligand is coordinated to each sodium atom. When one considers the ionic contact between the sodium atom and the cyclopentadienyl groups, the dimers are in fact linked into polymeric chains along the a axis. A portion of the latter is shown in Fig. 3.

(Continued on p. 85)

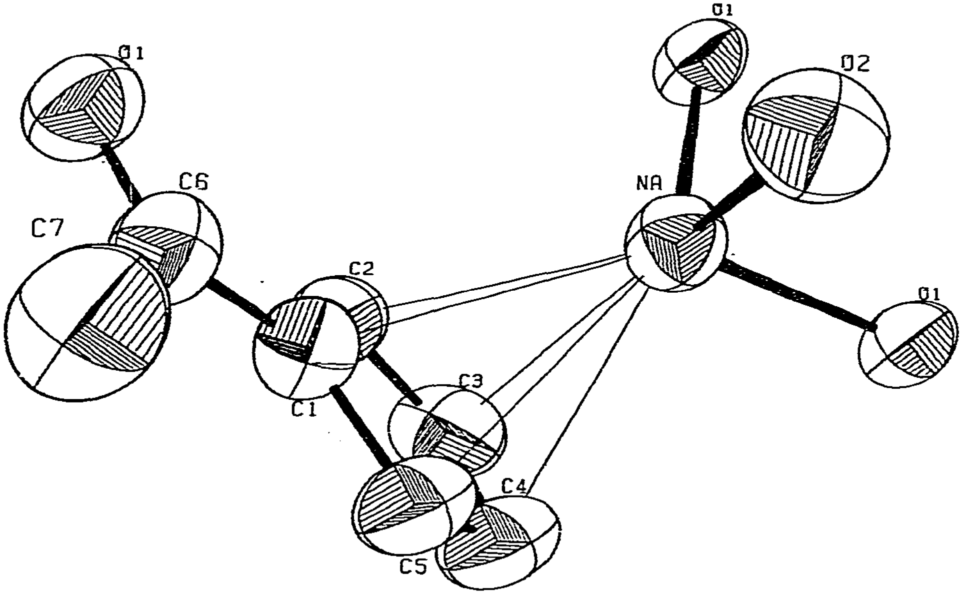

Fig. 1. Sodium atom environment and atom numbering scheme for $\{[C_5H_4CMeO]Na\cdot THF\}_n$. The atoms are represented by their 50% probability ellipsoids for thermal motion.

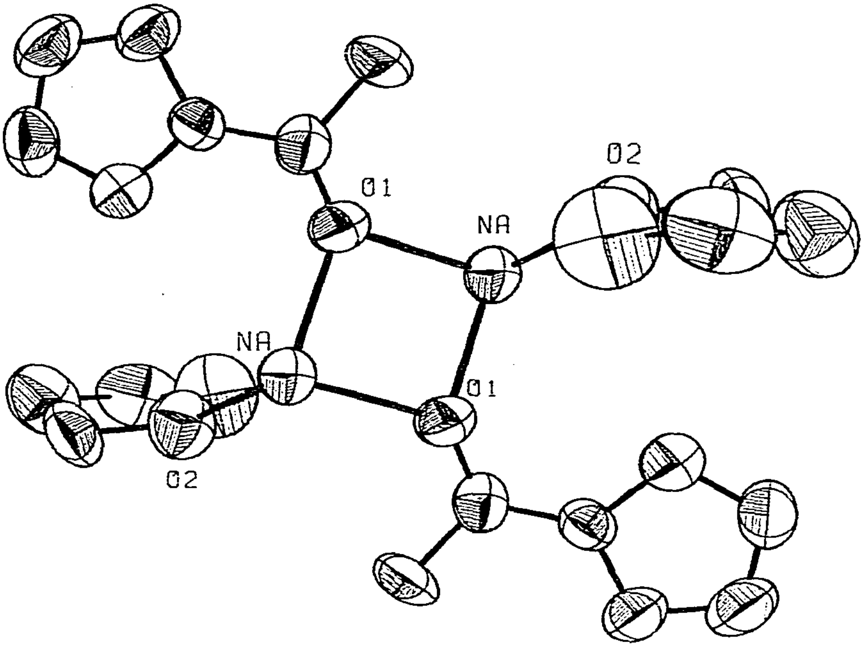

Fig. 2. View of $\{[C_5H_4CMeO]Na\cdot THF\}_n$ showing the dimeric unit of the polymeric configuration.

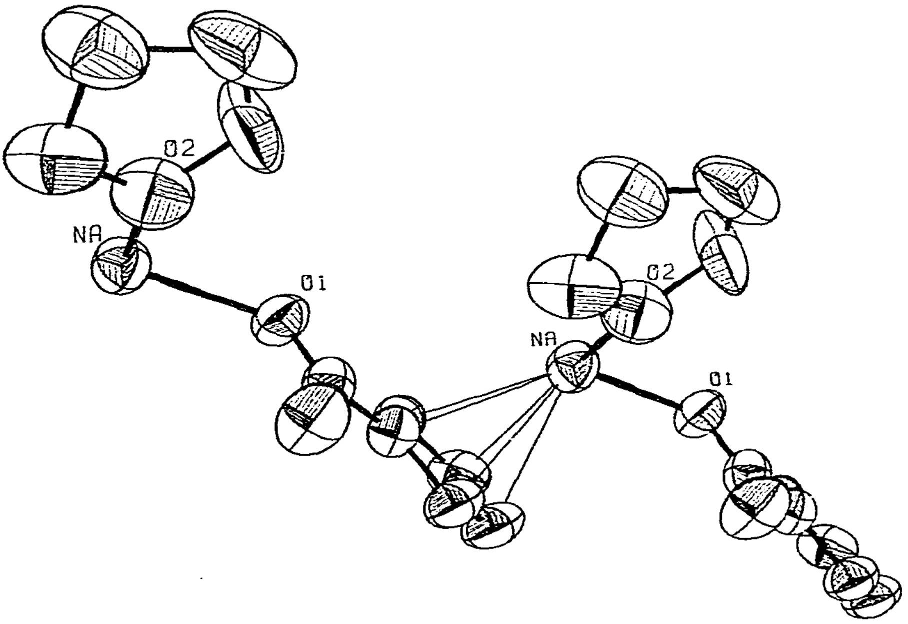

Fig. 3. Fragment of the structure of $\{[C_5H_4CMeO]Na\cdot THF\}_n$ centered on the organic ligand. The mode of polymerization of the dimeric units is illustrated.

TABLE 3

BOND DISTANCES AND ANGLES FOR $\{[C_5H_4CMeO]Na\cdot THF\}_n$

Atoms	Distance (Å)	Atoms	Distance (Å)
Na—O(1)	2.329(8)	Na—O(2)	2.354(8)
Na—O(1)	2.295(8)	O(1)—C(6)	1.26(1)
O(2)—C(8)	1.48(2)	O(2)—C(11)	1.50(2)
C(1)—C(2)	1.43(1)	C(1)—C(5)	1.44(1)
C(1)—C(6)	1.41(1)	C(2)—C(3)	1.39(1)
C(3)—C(4)	1.41(1)	C(4)—C(5)	1.35(1)
C(6)—C(7)	1.52(1)	C(8)—C(9)	1.42(2)
C(9)—C(10)	1.69(3)	C(10)—C(11)	1.52(2)
Na—C(1)	2.89(1)	Na—C(2)	2.77(1)
Na—C(3)	2.69(1)	Na—C(4)	2.80(1)
Na—C(5)	2.94(1)		

Atoms	Angle (°)	Atoms	Angle (°)
O(1)—Na—O(2)	100.9(3)	O(1)—Na—O(1)	84.7(3)
O(1)—Na—O(2)	108.4(3)	Na—O(1)—C(6)	128.4(7)
Na—O(2)—C(8)	114(1)	Na—O(2)—C(11)	123.7(8)
C(8)—O(2)—C(11)	114(1)	C(2)—C(1)—C(5)	107(1)
C(2)—C(1)—C(6)	125(1)	C(5)—C(1)—C(6)	128(1)
C(1)—C(2)—C(3)	107(1)	C(2)—C(3)—C(4)	109(1)
C(3)—C(4)—C(5)	109(1)	C(1)—C(5)—C(4)	108(1)
O(1)—C(6)—C(1)	124(1)	O(1)—C(6)—C(7)	118(1)
C(1)—C(6)—C(7)	118(1)	O(2)—C(8)—C(9)	108(2)
C(8)—C(9)—C(10)	105(1)	C(9)—C(10)—C(11)	104(1)
O(2)—C(11)—C(10)	104(1)		

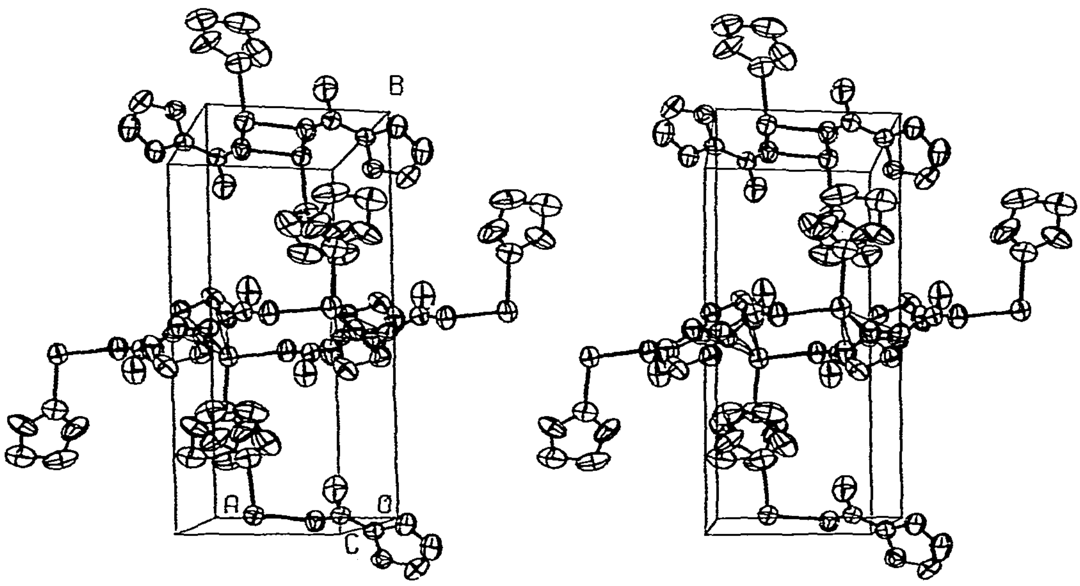

Fig. 4. Stereoscopic view of the unit cell contents of $\{[C_5H_4CMeO]Na\cdot THF\}_n$.

The two independent Na—O(1) bond distances are 2.329(8) and 2.295(8) Å (Table 3). The Na—O(2) contact (THF ligand) is 2.354(8) Å. All three distances are shorter than the 2.426 Å Na—O separation in $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$ [20], but agree well with the 2.354 Å average Na—O distance in $[Na(THF)_2]_2$-$[AlMe_2C_{14}H_{10}]_2$ [21]. Thus, the less sterically crowded sodium environment in the title compound may allow a closer Na—O contact.

The cyclopentadienyl carbon atoms of the C_5H_4CMeO ligand and the sodium atom are separated by distances that range from 2.69(1) to 2.94(1) Å. This is consistent with the 2.92(1) Å Na—C separation found for $Na(C_5H_5)(Me_2NCH_2$-$CH_2NMe_2)$ [9], the only other compound which demonstrated a similar ionic linkage [22].

The five carbon atoms of the C_5H_4CMeO ligand forming the cyclopentadienyl ring are planar to within 0.02 Å [19]. The oxygen atom lies in the plane, but the methyl group deviates by 0.31 Å away from the plane. C(6) deviates 0.09 Å from the plane in the same direction as the methyl group. A stereoscopic view of the unit cell packing is presented in Fig. 4.

Acknowledgements

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