

Preparation and crystal structure of 2,4-dimethylpentadienyl-potassium tetramethylethylenediamine complex

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Abstract

The compound, 2,4-dimethylpentadienylpotassium tetramethylethylenediamine, was obtained by reaction of 2,4-dimethylpentadiene with metallic potassium in tetrahydrofuran (THF) in the presence of tetramethylethylenediamine (TMEDA) at -78°C . Its crystal structure was determined by a low temperature X-ray diffraction study. The crystal is monoclinic with space group $P2_1/n$, a 11.322(4), b 9.242(3), c 15.956(5) Å, β 106.70(3) $^{\circ}$, and $Z = 4$. The final R value is 0.055 for 964 observed reflections. The 2,4-dimethylpentadienyl anion adopts the planar U conformation. The potassium cations, each with a chelating TMEDA molecule attached, are linked by bridging anions while the anions are connected to the bridging cations with the average bond distances K–C(1,5), K–C(2,4) and K–C(3), of 3.123, 3.216 and 3.248 Å, respectively, to form a puckered chain. The structure of the complex is compared with those of 2,4-dimethylpentadiene complexes of transition metals and the bonding within the complex is described.

Introduction

Pentadienylmetal chemistry has developed rapidly during the past few years [1] and many transition metal complexes with pentadienyl ligands have been synthesized. Metal complexes of 2,4-dimethylpentadienyl (2,4- C_7H_{11}) ligands, also known as the "open metallocenes", have similarities to those of cyclopentadienyl ligands, so that a number of structural studies have been carried out. Up to now the crystal structure of 2,4-dimethylpentadienylpotassium [2] has not been determined owing to difficulties in the preparation of crystals suitable for data collection, even though it is widely used as a reagent for the preparation of 2,4- C_7H_{11} derivatives. In order to study the metal complex conformation and bonding patterns we have prepared the

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crystals of 2,4-dimethylpentadienylpotassium tetramethylethylenediamine (TMEDA) and determined its crystal structure at low temperature.

Experimental

1. Preparation of the crystal

Metallic potassium was added to a mixed solvent of tetrahydrofuran (THF) and triethylamine, the solution was cooled to -78°C , and then 2,4-dimethyl-1,3-pentadiene was added, work-up was by the procedure in ref. 2. Once the reaction was complete, petroleum ether was added and the solution was cooled to induce crystallization. Removal of the solvent gave the product, which was washed twice with petroleum ether. THF and TMEDA were added and the mixture was allowed to stand at room temperature to form the TMEDA complex. Finally, crystals of 2,4-dimethylpentadienylpotassium tetramethylethylenediamine complex were obtained on cooling the solution. The crystal is extremely air-sensitive.

2. Determination of crystal structure

A crystal of the approximate dimensions $0.4 \times 0.2 \times 0.1$ mm was selected under the protecting conditions of a dry and low temperature nitrogen atmosphere. The unit cell parameters were determined and X-ray intensity data were collected on a Nicolet R3m/E four-circle diffractometer with graphite-monochromated Mo- K_{α} radiation, ω scan mode and scan speeds variable from 4.88 to $29.30^{\circ}/\text{min}$. The low temperature device, LT-1, which kept the sample in a cooling stream of nitrogen, was used and the temperature was maintained at about -80°C during data collection. A total of 2378 reflections were collected within the range of $3^{\circ} < 2\theta < 45^{\circ}$. The intensity of one check reflection was monitored every 68 reflections. No obvious change was observed in the intensity of the check reflections, which shows that the crystal is stable during data collection. The intensities were corrected for Lorentz polarization factors but not for absorption. The crystal data are listed in Table 1.

The crystal structure was solved by the heavy-atom method. The coordinates of the K atom derived from the Patterson analysis were used to calculate the Fourier map. Successive Fourier syntheses gave the positions of all non-hydrogen atoms. The atomic coordinates and anisotropic temperature factors for all non-hydrogen atoms were refined by used block-diagonal least-squares. Nine hydrogen atoms were located on a difference Fourier map and the other hydrogen atom positions were calculated from theoretical models. Further refinements led to final values of $R = 0.055$ and $R_w = 0.057$ for 964 unique observed reflections with $I > 2.5\sigma(I)$.

All calculations were performed using SHELXTL programs.

Table 1

Crystal data

$\text{C}_{13}\text{H}_{27}\text{N}_2\text{K}$	Mol.wt. 250.47
Monoclinic system	Space group $P2_1/n$
a 11.322(4) Å	b 9.242(3) Å
c 15.956(5) Å	β 106.70(3) $^{\circ}$
V 1599.2 Å ³	$Z = 4$
D_c 1.04 g cm ⁻³	μ 3.05 cm ⁻¹ (Mo- K_{α} λ 0.71069 Å)

Results and discussion

The coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 2 and the coordinates of the hydrogen atoms are listed in Table 3. Bond distances and bond angles are given in Tables 4 and 5.

The K^+ cations, each with a chelating TMEDA molecule attached, alternate with $[2,4-C_7H_{11}]^-$ anions. Two cations are linked by a bridging anion while two anions are connected to a bridging cation, thus forming a chain along *b*. Figure 1 shows a fragment of the chain. The $2,4-C_7H_{11}$ complexes of the transition metals with d^x electrons are quite similar to their cyclopentadienyl sandwich complexes, but those of the alkali metals generally have a puckered chain. This difference is obviously dependent on the electronic structure and the oxidation state of the metal.

In the $2,4-C_7H_{11}$ potassium complex, the K–C bond distances are in the range 3.069 to 3.276 Å with a mean of 3.185 Å. Compared with the $2,4-C_7H_{11}$ complexes of V [3], Cr [3] and Fe [4], it can be seen that the difference between the ionic radii of alkali and those of the transition metals is about 0.5 Å, and the difference between the M–C bond distances is about 1 Å. This indicates that transition metals have smaller ionic radii and a higher positive charge, which causes stronger polarization of the M–C bond. By contrast the weak polarization of K^+ ion gives rise to highly ionic M–C bond. Furthermore, the cyclooctatetraenyl dianion in $(C_8H_8)K_2 \cdot 3THF$ [5] is bonded to each K^+ ions, on either side of the ring, with an average K–C bond distance of 2.971 Å, which is shorter than the K–C bond distance in our molecule by 0.214 Å. It also shows the higher ionic character of the $2,4-C_7H_{11}$ potassium complex.

The $2,4-C_7H_{11}$ ligand adopts the planar U conformation in line with the prediction based on the *ab initio* calculation [1c]. The C–C bond distances fall in two sets, viz. the internal C–C bond distances, C(2)–C(3) and C(3)–C(4), average 1.427 Å; and the external C–C bond distances, C(1)–C(2) and C(4)–C(5), average

Table 2

Coordinates ($\times 10^4$) and equivalent temperature factors ($\text{\AA}^2 \times 10^3$) for the non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
K	3130(1)	6798(2)	6915(1)	37(1)
C(1)	3804(6)	9401(8)	8263(5)	44(3)
C(2)	3015(6)	8609(7)	8601(4)	36(3)
C(3)	1763(6)	8265(8)	8213(4)	41(3)
C(4)	977(6)	8566(7)	7344(4)	36(3)
C(5)	1219(7)	9351(7)	6696(4)	43(3)
C(6)	3566(7)	7969(9)	9521(4)	52(3)
C(7)	–298(6)	7900(8)	7157(5)	49(3)
N(1)	5410(6)	7375(8)	6466(4)	50(3)
N(2)	2988(6)	7707(7)	5117(4)	55(3)
C(8)	5224(8)	7312(11)	5528(5)	70(4)
C(9)	4140(8)	8064(13)	4983(6)	83(5)
C(10)	6283(9)	6267(11)	6910(6)	83(5)
C(11)	5852(9)	8765(11)	6847(7)	79(5)
C(12)	2538(9)	6292(10)	4756(6)	79(4)
C(13)	2088(9)	8816(11)	4720(5)	85(5)

Table 3

Coordinates ($\times 10^4$) of the hydrogen atoms

Atom	x	y	z
H(1a)	4648	9539	8597
H(1b)	3503	9818	7690
H(3)	1370	7743	8580
H(5a)	601	9460	6144
H(5b)	2015	9788	6788
H(6a)	4354	8551	9808
H(6b)	3774	6882	9545
H(6c)	2923	8156	9853
H(7a)	-223	6834	6991
H(7b)	-853	8447	6627
H(7c)	-679	7951	7670
H(8a)	5999	7744	5409
H(8b)	5144	6238	5348
H(9a)	4073	7852	4338
H(9b)	4275	9156	5101
H(10a)	5924	5287	6649
H(10b)	6277	6325	7553
H(10c)	7176	6361	6877
H(11a)	5940	8851	7506
H(11b)	5169	9454	6503
H(11c)	6675	9038	6734
H(12a)	3058	5416	5049
H(12b)	2443	6279	4095
H(12c)	1680	6238	4856
H(13a)	2297	9837	4978
H(13b)	1281	8467	4830
H(13c)	1980	8843	4057

1.367 Å. The difference of 0.060 Å between internal and external C-C bond distances is clearly larger than those in transition metal complexes. This fact points to the more double bond character for the external bond and the weaker interaction

Table 4

Bond distances (Å)

K-C(1)	3.170(7)	K-C(1') ^a	3.069(7)
K-C(2)	3.202(7)	K-C(2')	3.230(7)
K-C(3)	3.219(8)	K-C(3')	3.276(7)
K-C(4)	3.168(7)	K-C(4')	3.264(6)
K-C(5)	3.152(7)	K-C(5')	3.102(7)
K-N(1)	2.920(7)	K-N(2)	2.950(6)
C(1)-C(2)	1.378(11)	C(2)-C(3)	1.411(9)
C(3)-C(4)	1.443(8)	C(4)-C(5)	1.353(10)
C(2)-C(6)	1.539(9)	C(4)-C(7)	1.518(10)
C(8)-C(9)	1.460(12)	N(1)-C(8)	1.451(11)
N(1)-C(10)	1.458(11)	N(1)-C(11)	1.448(12)
N(2)-C(9)	1.420(12)	N(2)-C(12)	1.461(11)
N(2)-C(13)	1.456(11)		

^a C(1') is generated by transformation: $0.5 - x, -0.5 + y, 1.5 - z$. It is similar for other atoms.

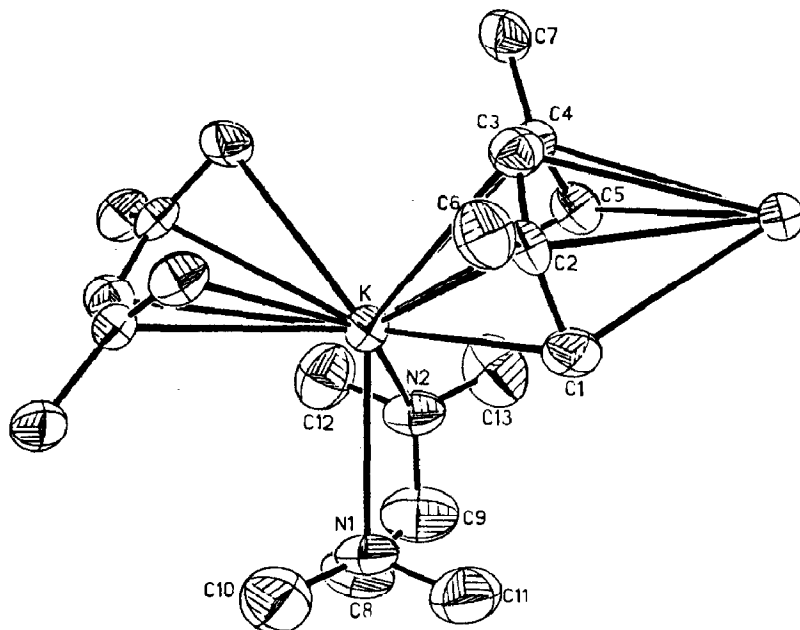
Table 5

Bond angles ($^{\circ}$)

C(1)–C(2)–C(3)	129.1(6)	C(2)–C(3)–C(4)	130.0(7)
C(3)–C(4)–C(5)	129.3(6)	C(1)–C(2)–C(6)	116.6(6)
C(3)–C(2)–C(6)	114.3(7)	C(5)–C(4)–C(7)	117.2(6)
C(3)–C(4)–C(7)	113.5(6)	N(1)–C(8)–C(9)	116.3(8)
N(2)–C(9)–C(8)	116.8(9)	C(8)–N(1)–C(10)	110.5(7)
C(8)–N(1)–C(11)	113.5(7)	C(8)–N(1)–K	111.7(5)
C(10)–N(1)–C(11)	108.4(6)	C(10)–N(1)–K	106.1(6)
C(11)–N(1)–K	106.4(6)	C(9)–N(2)–C(12)	112.4(8)
C(9)–N(2)–C(13)	109.3(7)	C(9)–N(2)–K	114.6(4)
C(12)–N(2)–C(13)	109.7(6)	C(12)–N(2)–K	92.5(5)
C(13)–N(2)–K	117.3(5)	N(1)–K–N(2)	60.9(2)

between ligand and metal in this complex than those in the transition metal complexes. In $V(2,4-C_7H_{11})_2$ the average bond angle of C(1)–C(2)–C(3) and C(3)–C(4)–C(5) is 124.9° , for C(2)–C(3)–C(4) is 130.2° and the C(1)–C(5) distance is 3.05 Å. In our structure they are 129.2° , 130° and 3.26 Å, respectively. Thus it seems that the 2,4- C_7H_{11} ligand arranges itself in such a way at the C(2) and C(4) atoms, depending on the ionic radius of the metal so as to optimize metal-ligand overlap.

Figure 2 depicts the projection of the structure onto the plane of the K atoms, which zigzag to give a K–K–K angle of 120.3° . The planes of N(1)–N(2)–K and

Fig. 1. Structure of $(2,4-C_7H_{11})K \cdot TMEDA$.

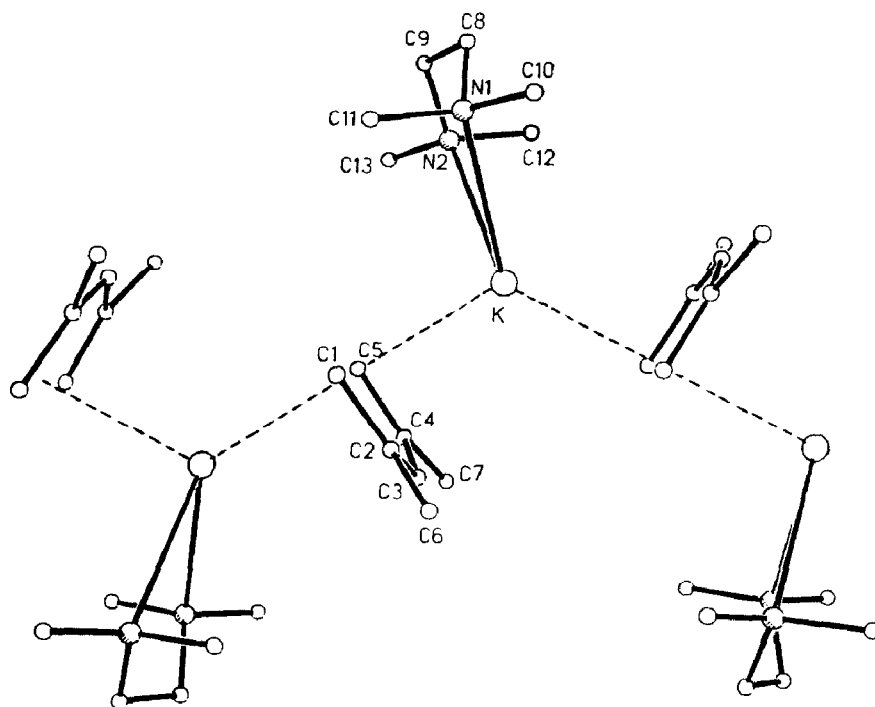


Fig. 2. Projection of structure on the plane of K atoms.

2,4-C₇H₁₁ are almost perpendicular to the K atom plane. In the structure of Nd(2,4-C₇H₁₁)₃ [6], the Nd–C(3) distance is the shortest and that of Nd–C(1,5) is intermediate, is attributable to a resonance hybrid in which the negative charge is localized somewhat more on the C(3). However, in our study the K–C(3) distance is the longest (3.248 Å) while that of K–C(1,5) is the shortest (3.123 Å). This seems to be due to a geometric factor. It has been noted that the point at which the K–K axis intersects the plane formed by C(1),C(2),C(3),C(4) and C(5) deviates, from the center of mass defined by these atoms, toward the C(1)–C(5) side by 0.85 Å, so that the 2,4-C₇H₁₁ can be accommodated only between the two K atoms on the side of C(1)–C(5), owing to obstruction by the TMEDA molecule. This may in part cause the crystal to be unstable.

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