

Structural variations in the organo-potassium derivatives of triphenylmethane with PMDTA: a new modification of $[\text{Ph}_3\text{CK} \cdot (\text{N},\text{N},\text{N}',\text{N}'',\text{N}''')\text{-pentamethyldiethylenetriamine}]_n$

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Abstract

The metalation of triphenylmethane (Ph_3CH) with potassium metal in toluene and PMDTA ($\text{N},\text{N},\text{N}'',\text{N}'''$ -pentamethyldiethylenetriamine) at 111 °C affords red crystals of $[\text{Ph}_3\text{CK} \cdot \text{PMDTA}]_n$ (1). X-ray analysis reveals that the single crystal structure of 1 is different to the one shown previously. Here a polymeric zigzag chain instead of a discrete molecule was observed. Crystal data (Mo K α radiation) at -100 °C for 1: $a = 9.872(2)$, $b = 18.917(4)$, $c = 29.047(6)$ Å, $\beta = 97.63(3)^\circ$, monoclinic space group Cc , $R = 0.0449$ ($F^2 > 2\sigma(F^2)$), $wR_2 = 0.1420$.

Keywords: Organo-potassium compounds; Triphenylmethyl anion; Crystal structure; Solvation effects

1. Introduction

The organometallic chemistry of the heavier Group I elements (K, Rb, Cs) has attracted increased interest in recent years [1–4]. Much of the X-ray structure investigations on this class of compounds has been based on the triphenylmethyl anion [1–4]. Interactions between metal cations and delocalized carbanions depend on the size of the cations and on any additional donor ligands which may be present [1,3,4]. Whether the organic triphenylmethyl moiety should be regarded as a 'carbanion' or not is yet to be resolved. Large polarizable cations like K⁺ are significantly less charge-localizing than Li⁺ and therefore they often show multihapto interactions [5]. Semi-empirical MNDO calculations on the potential energy surface of $\text{Ph}_3\text{CK} \cdot$ ligand systems show a rather flat potential energy surface [3]. This may result in different modifications for a given anion–ligand–cation system [6].

In this paper we report the X-ray crystal structure of a new modification of $[\text{Ph}_3\text{CK} \cdot \text{PMDTA}]_n$ (1).

2. Experimental details

All experiments were performed under anaerobic and anhydrous conditions using standard Schlenk and needle/septum techniques. The toluene was dried over sodium–potassium alloy and distilled under argon prior to use. Triphenylmethane, potassium and PMDTA (Aldrich) were used without purification. Potassium was always used in excess to dry the solvent, the ligand and the acidic hydrocarbon.

2.1. Synthesis of $[\text{Ph}_3\text{CK} \cdot \text{PMDTA}]_n$ (1)

About 1 g potassium (25 mmol), 2.44 g triphenylmethane (10 mmol), 2.1 ml PMDTA (1.73 g, 10 mmol) and 50 ml toluene were mixed in a 100 ml Schlenk flask. The mixture was refluxed at 111 °C for four days under rapid stirring, giving a red solution and precipitate. Toluene was added until all the product was dissolved and separated from the excess potassium by filtering the cold solution. Subsequent cooling of the solution to 5 °C gave dark-red well-defined prisms suitable for single crystal X-ray diffraction measurements after three days. A second crop of crystals was obtained after adding hexane to the solution. Overall yield: 3.1 g (68%). Anal. Found: C, 73.56; H, 8.62; N, 9.34. $\text{C}_{56}\text{H}_{76}\text{N}_6\text{K}_2$ Calc.: C, 73.80; H, 8.41; N, 9.22%.

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Table 1

Crystal data, data collection and refinement of the structure of **1**

<i>Crystal data</i>	$[\text{Ph}_3\text{CK} \cdot \text{PMDTA}]_n$
<i>a</i> (Å)	9.872(2)
<i>b</i> (Å)	18.917(4)
<i>c</i> (Å)	29.047(6)
β (°)	97.68(3)
<i>Z</i>	4
Volume (Å ³)	5376(3)
Crystal system	monoclinic, <i>Cc</i> (9)
Density, ρ_{calc} (g cm ⁻³)	1.126
<i>Data collection</i>	
$2\theta_{\text{max}}$	50
Radiation	Mo K α
Wavelength (Å)	0.71069
Temperature (°C)	-100
Unique reflections	4612
Observed reflections	2787
Observation criterion	$I > 2.0\sigma(I)$
Absorption correction	None
μ (cm ⁻¹)	2.2, azimuthal scans indicated no need for absorption correction
<i>Solution and refinement</i>	
Solution method	direct methods (SHELXS-86)
Program	teXsan
Method of refinement	full-matrix (SHELXL-93)
Number of parameters	588
<i>R</i>	0.0449
<i>R_w</i>	0.1420
<i>S</i>	1.02
Max., av. shift/error	-0.09, 0.00
Residuals, min./max. (e Å ⁻³)	-0.37/0.27
<i>F</i> (0,0,0)	1392
H atoms	constrained (see text)
Non-hydrogen atoms	all anisotropic
Disorder	minor disorder: C12, C13, C14; no disorder model applied

2.2. X-ray structure determination of **1**

The data collection for the structure determination was performed on a Rigaku AFC7R diffractometer at

173 K using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystals were coated with paraffin oil and mounted with a glass fibre on the goniometer. 25 high angle reflections were used to determine the unit cell and an orientation matrix for data collection. Table 1 shows the details of data collection and structure refinement. Table 2 shows the atomic coordinates and Table 3 selected bond lengths and angles. Fig. 1 shows a view and atom labelling for $[\text{Ph}_3\text{CK} \cdot \text{PMDTA}]_n$ (**1**). The intensities of three representative reflections were measured every 150 reflections. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS [8] within the teXsan [9] package) and refined by full-matrix least-squares on F^2 with SHELXL [10]. All non-hydrogen atoms were refined anisotropically (SHELXL). All hydrogen atom positions were constrained with C-H 1.0 Å and free torsional rotation of methyl groups, and their isotropic thermal parameters were calculated with the respective carbon atom multiplied by 1.2 (for aromatic carbons), 1.3 (for methylene carbons) and 1.5 (for methyl carbons). A minor disorder in three carbon atoms of ligand PMDTA **1** is evident (C12, C13, C14). Refinement with two positions for each atom gave no significant improvement.

3. Results and discussion

There are several different ways to prepare potassium alkyl compounds. Many years ago triphenylmethylchloride was treated with alkaline amalgam [11] and deprotonation of the CH acidic triphenylmethane was effective with molten alkaline metals [12]. Recently 'model super base' mixtures, 'super bases', 'complex bases' or LICKOR-reagents have been used to generate potassium organic compounds ([3] and literature cited therein). Here we have used a method already described elsewhere [1], viz. the reaction of potassium metal with

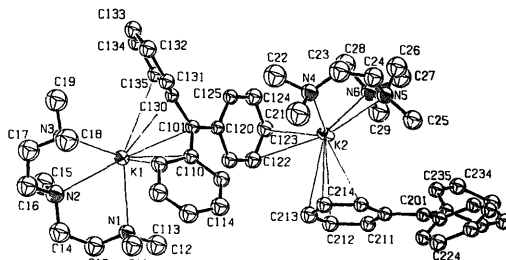


Fig. 1. View of $[\text{Ph}_3\text{CK} \cdot \text{PMDTA}]_n$ (**1**) showing atom labelling. Isotropic displacement parameters (or thermal ellipsoids for K) are at 30% probability level and hydrogen atoms are omitted for clarity (PLATON [7]).

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1

Atom	x	y	z	U_{eq}^a
K(1)	-371(1)	1855(1)	825(1)	42(1)
K(2)	3148(1)	71(1)	3047(1)	41(1)
N(1)	-970(7)	3388(3)	564(2)	55(2)
N(2)	-2547(8)	2145(4)	69(3)	70(2)
N(3)	-2904(6)	1137(3)	879(2)	44(1)
N(4)	5665(6)	-758(3)	3141(2)	46(2)
N(5)	5068(6)	277(3)	3892(2)	46(2)
N(6)	3742(6)	1549(3)	3309(2)	44(2)
C(11)	300(12)	3646(6)	433(4)	98(3)
C(12)	-1338(15)	3868(6)	917(4)	114(5)
C(13)	-1957(18)	3400(6)	149(5)	179(10)
C(14)	-2699(17)	2908(6)	-35(5)	142(6)
C(15)	-2107(11)	1797(6)	-338(4)	90(3)
C(16)	-3869(10)	1825(5)	169(4)	78(3)
C(17)	-3668(9)	1112(5)	412(3)	66(2)
C(18)	-3608(10)	1557(5)	1202(3)	76(3)
C(19)	-2768(9)	410(4)	1061(3)	61(2)
C(21)	6313(8)	-404(5)	2778(3)	63(2)
C(22)	5526(11)	-1509(5)	3016(3)	75(3)
C(23)	6515(9)	-673(5)	3595(3)	71(3)
C(24)	6438(8)	45(5)	3805(3)	67(3)
C(25)	4588(9)	-135(5)	4268(3)	63(2)
C(26)	5055(9)	1032(4)	4021(3)	63(2)
C(27)	5016(9)	1552(5)	3629(3)	68(2)
C(28)	2592(10)	1855(5)	3518(4)	78(3)
C(29)	3890(11)	1991(5)	2897(3)	75(3)
C(101)	1281(6)	1908(3)	1828(2)	33(2)
C(110)	1(7)	2074(4)	2025(2)	37(2)
C(111)	-889(7)	2627(4)	1847(3)	48(2)
C(112)	-2096(8)	2782(4)	2034(3)	59(2)
C(113)	-2492(8)	2394(5)	2399(3)	69(3)
C(114)	-1622(8)	1852(4)	2583(3)	57(2)
C(115)	-418(7)	1698(4)	2410(2)	43(2)
C(120)	1886(7)	1204(3)	1854(2)	32(1)
C(121)	1097(7)	566(3)	1888(2)	38(2)
C(122)	1676(8)	-97(4)	1919(2)	43(2)
C(123)	3081(8)	-198(4)	1923(2)	44(2)
C(124)	3883(7)	401(4)	1887(2)	43(2)
C(125)	3308(7)	1080(4)	1859(2)	36(2)
C(130)	2054(6)	2495(3)	1642(2)	34(2)
C(131)	2146(7)	3184(4)	1848(2)	44(2)
C(132)	2935(8)	3723(4)	1688(3)	52(2)
C(133)	3667(8)	3615(4)	1315(3)	50(2)
C(134)	3558(7)	2957(4)	1095(2)	43(2)
C(135)	2787(6)	2417(4)	1253(2)	36(2)
C(201)	154(6)	-1135(3)	4301(2)	32(2)
C(210)	1046(6)	-798(4)	3860(2)	34(2)
C(211)	736(6)	-1179(4)	3435(2)	39(2)
C(212)	227(7)	-866(4)	3017(2)	43(2)
C(213)	-46(6)	-134(4)	2987(2)	44(2)
C(214)	257(7)	258(1)	3395(2)	43(2)
C(215)	795(6)	-47(3)	3810(2)	36(2)
C(220)	1282(6)	-803(3)	4735(2)	34(2)
C(221)	2162(7)	-906(3)	5163(2)	37(2)
C(222)	1898(8)	-600(3)	5579(2)	42(2)
C(223)	769(8)	-175(4)	5610(2)	48(2)
C(224)	-109(7)	-56(4)	5202(3)	54(2)
C(225)	131(7)	-35(1)	4781(2)	45(2)
C(230)	2274(6)	-181(3)	4309(2)	33(2)
C(231)	2265(7)	-2333(3)	4664(2)	38(2)

Table 2 (continued)

Atom	x	y	z	U_{eq}^a
C(232)	2966(7)	-2965(4)	4672(2)	41(2)
C(233)	3744(8)	-3147(4)	4316(3)	50(2)
C(234)	3807(7)	-2645(4)	3967(3)	47(2)
C(235)	3135(6)	-2011(4)	3966(2)	38(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Selected bond lengths (\AA) and angles ($^\circ$) for 1

K(1)–N(3)	2.869(6)
K(1)–N(2)	2.911(6)
K(1)–N(1)	3.034(6)
K(1)–C(101)	3.146(6)
K(1)–C(150)	3.364(6)
K(1)–C(135)	3.370(6)
K(1)–C(222)#	3.406(7)
K(1)–C(111)	3.408(8)
K(1)–C(223)#	3.457(8)
K(1)–C(110)	3.483(7)
K(2)–N(5)	2.920(6)
K(2)–N(4)	2.921(6)
K(2)–N(6)	2.936(6)
K(2)–C(213)	3.159(6)
K(2)–C(214)	3.172(7)
K(2)–C(123)	3.297(7)
K(2)–C(212)	3.377(7)
K(2)–C(122)	3.417(7)
K(2)–C(215)	3.425(6)
K(2)–C(21)	3.440(8)
C(101)–C(120)	1.457(9)
C(101)–C(110)	1.489(9)
C(101)–C(130)	1.489(9)
C(201)–C(210)	1.452(8)
C(201)–C(220)	1.457(8)
C(201)–C(230)	1.475(9)
N(3)–K(1)–N(2)	64.5(2)
N(3)–K(1)–N(1)	108.9(2)
N(2)–K(1)–N(1)	62.1(2)
N(5)–K(2)–N(4)	62.5(2)
N(5)–K(2)–N(6)	64.6(2)
N(4)–K(2)–N(6)	110.5(2)
C(120)–C(101)–C(110)	122.4(6)
C(120)–C(101)–C(130)	118.3(6)
C(110)–C(101)–C(130)	119.0(6)
C(111)–C(110)–C(115)	115.0(6)
C(125)–C(120)–C(121)	113.6(6)
C(135)–C(130)–C(131)	114.3(6)
C(210)–C(201)–C(220)	120.2(6)
C(210)–C(201)–C(230)	119.8(5)
C(220)–C(201)–C(230)	120.0(5)
C(211)–C(210)–C(215)	113.3(6)
C(221)–C(220)–C(225)	113.2(6)
C(231)–C(230)–C(235)	112.1(6)

Symmetry transformations used to generate equivalent atoms: # $x, -y, z + \frac{1}{2}$.

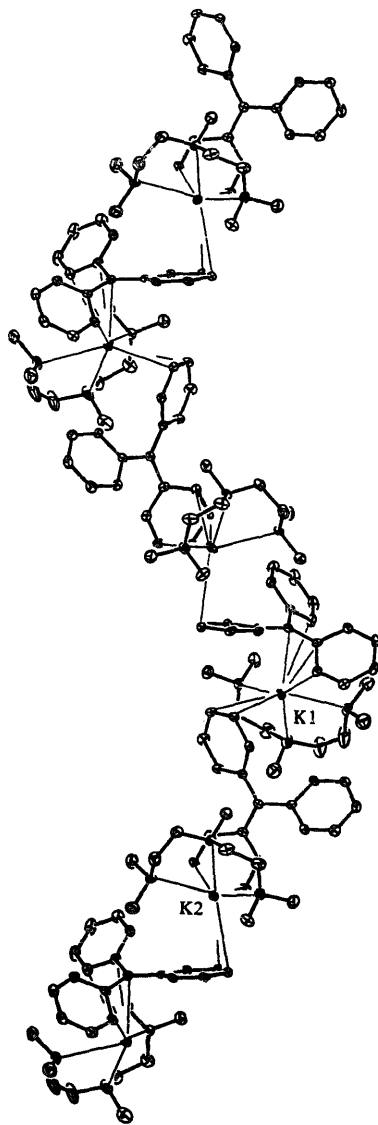


Fig. 2. PLATON drawing [7] of the zigzag chain of [Ph,CK · PMDTA], (1); hydrogen atoms are omitted for clarity.

triphenylmethane and PMDTA in boiling toluene which on cooling to 5°C and with the addition of hexane has yielded the potassium complex $[\text{Ph}_3\text{CK} \cdot \text{PMDTA}]_n$ (1) in a new modification (Eq. (1)). The earlier reaction was in benzene with crystallization at 7°C [1] from the same solvent.



Compound 1 crystallizes in the monoclinic space group *Cc* with two formula units of $[\text{Ph}_3\text{CK} \cdot \text{PMDTA}]$ in the asymmetric unit. There are two significantly different cation–ligand–anion moieties in the lattice which form an infinite one-dimensional zigzag chain (Fig. 2). The first potassium atom, K1, is bound by PMDTA 1 (N1–3), almost like in the discrete molecules in Ref. [1], albeit with slightly longer K–N distances (see Table 3). It is also bound by carbon atoms of the triphenylmethyl anion, viz. C101 at 3.145 Å, which is the shortest K–C distance as expected on residual charge considerations, and neighbouring C130 (3.363 Å), C135 (3.370 Å) and C110 (3.481 Å), C111 (3.408 Å) atoms. There are additional K–C interactions with the peripheral carbon atoms of one phenyl ring of the second triphenylmethyl anion (C222: 3.405 Å, C223: 3.457 Å). Overall the environment for the potassium atom K1 is similar to that for the sodium atom in $[\text{Ph}_3\text{CNa} \cdot \text{TMEDA}]_n$ (TMEDA = N,N,N',N'-tetramethylethylenediamine) [13].

The environment for the second potassium atom K2 looks like that for the rubidium atom in $[\text{Ph}_3\text{CRb} \cdot \text{PMDTA}]_n$ [3]. There are no interactions with the central carbon atoms of either of the two triphenylmethyl anions. Besides the connected three nitrogen atoms of ligand PMDTA 2 (N4–6), the only other interactions are with peripheral carbon atoms of one of each triphenylmethyl anion (C122 3.418 Å, C123 3.297 Å, anion 1; C212 3.377 Å, C213 3.159 Å, C214 3.172 Å, C215 3.425 Å, anion 2). It is noteworthy that the distance to one of the terminal carbon atoms of the PMDTA ligand 1 is only 3.440 Å (in the first modification of $[\text{Ph}_3\text{CK} \cdot \text{PMDTA}]$ there are three short distances to terminal carbon atoms of the PMDTA ligand at 3.128, 3.226 and 3.276 Å [1]). Perhaps there are also other interactions to this carbon atom [14].

Anion 2 shows no interaction of the central carbon C201 and the neighbouring *ipso* carbon atoms C210, C220, C230 with a potassium cation, this leads to a bond shortening compared with anion 1 (anion 1: C101–C110 1.489 Å, C101–C120 1.457 Å, C101–C130 1.489 Å; anion 2: C201–C210 1.452 Å, C201–C220 1.456 Å, C201–C230 1.476 Å, see also Refs. [1,3]). The phenyl rings show a considerable angle contraction at the *ipso* position (anion 1: C111–C110–C115 114.9°,

C121–C120–C125 113.7°, C131–C130–C135 114.5°; anion 2: C211–C210–C215 113.3°, C221–C220–C225 113.3°, C231–C230–C235 112.2°), notably the contraction in the second anion is a little bit stronger than in the first anion, which is probably due to higher negative charge in this moiety [3]. The two central carbon atoms C101 and C201 show *sp*²-hybridization and therefore angles of about 120° (anion 1: C110–C101–C120 122.4°, C110–C101–C130 119.00°, C120–C101–C130 118.3°; anion 2: C210–C201–C220 120.21°, C210–C201–C230 119.8°, C220–C201–C230 120.0°). Unlike anion 1, anion 2 is less disturbed by a cation interaction at the central carbon atom that results in almost perfect 120° angles at this atom. Exact assignment of coordination numbers and hapticities is not useful in the compounds discussed here, because the distances from the metal to the ligands and anions are rather long.

The calculated density in this modification (1.126 g cm⁻³) is less than in the modification of the discrete molecule (1.187 g cm⁻³). That means that packing effects would favour the discrete molecule.

Acknowledgements

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