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SYNTHESIS AND PROPERTIES OF THE 1/1 COMPLEX OF 1,4,7,10,13,16-HEXAOXACYCLOOCTADECANE WITH POTASSIUM PERCHLOROTRIPHENYLMETHIDE

J. VECIANA, J. RIERA, J. CASTAÑER,

Instituto de Química Orgánica Aplicada (CSIC), C. Jorge Girona Salgado 18–26, 08034 Barcelona (Spain)

and N. FERRER

Departamento de Física del Estado Sólido, Facultad de Física, Universidad de Barcelona, Av. Diagonal 645, 08028 Barcelona (Spain)

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Summary

The 1/1 complex of 1,4,7,10,13,16-hexaoxacyclooctadecane with potassium perchlorotriphenylmethide has been prepared by reaction, in the presence of 18-crown-6, of $(C_6Cl_5)_3CH$ with KOH or reduction of radical $(C_6Cl_5)_3\dot{C}$ with K metal. Its structure as revealed by X-ray diffraction can be described as a separated ion pair of a $(C_6Cl_5)_3C^-$ carbanion and a potassium ion coordinated with the 18-crown-6; the carbanion has sp^2 hybridization and there is weak negative charge delocalization into the aromatic ring. The electronic spectra of alkaline salts of $(C_6Cl_5)_3C^-$ in various media provides evidence about the nature of the species present in solution. Electron-transfer reactions of $(C_6Cl_5)_3C^-$ with O_2 and several organic acceptors are described. Thermal decomposition of the solid crowned salt under an inert atmosphere involves decomplexation of the 18-crown-6 and a one-electron-transfer from the carbanion to the potassium counterion.

Introduction

It is known that, because of steric effects, the radicals, carbanions and carbenium ions of the perchlorotriphenylmethyl (PTM) series are exceptionally stable [1–3] compared with their unshielded counterparts [4].

Synthesis of perchlorotriphenylcarbanion (PTM^-) salts has been carried out by treatment of αH-pentadecachlorotriphenylmethane (**2**) [1], with base, or by reduction of perchlorotriphenylmethyl radical (PTM) [1,2]. Remarkable features of carbanion PTM^- are its resistance or inertness toward water and O_2 in homogeneous Me_2SO solutions. Evenso, alkaline salts of carbanion PTM^- cannot be isolated in solid form, although they are stable in solution, since during removal of the solvent (Et_2O) they decompose, mainly giving the PTM radical. However, when

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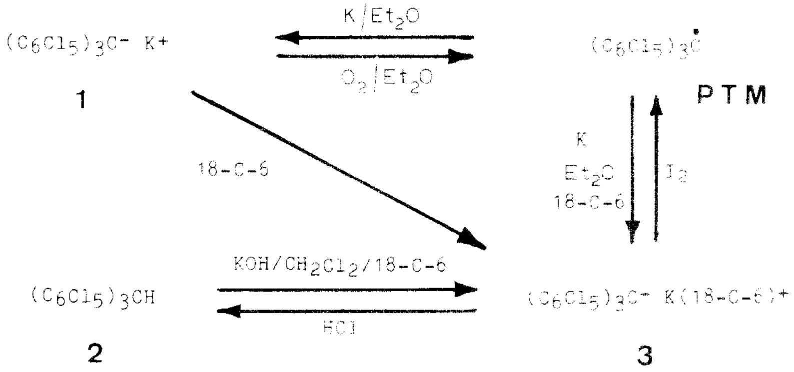


SCHEME 1

the counterion is tetraalkylammonium, the salt can be isolated easily. This higher stability compared with that of the alkaline salts has been attributed to the inability of the quaternary ammonium ions to act as electron acceptors [2]. Crown ethers and cryptates are strong complexing agents for alkaline ions [5] and their use has led to the isolation of very unstable crystalline ionic species such as (2.2.2 crypt)Na$^+$Na$^-$ [6], and even the electride (18-C-6)Cs$^+$e$^-$ [7].

We describe below the synthesis, isolation and properties of potassium salts of carbanion PTM$^-$ in which the metal is 1/1 complexed with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-C-6). Some properties of the uncrowned alkaline salts of PTM$^-$ are also reported.

Results and discussion

Radical PTM reacts with potassium metal in Et$_2$O or tetrahydrofuran (THF) at room temperature, with a vigorous shaking, giving a wine-red solution of the potassium salt of carbanion PTM$^-$ (**1**). This conversion is quantitative, as confirmed by hydrolysis to αH-compound **2** with aqueous HCl. Upon adding 18-C-6 to the Et$_2$O solution, a good yield of the corresponding K(18-C-6) salt (**3**) precipitates out as garnet crystals with a bronze luster. This crowned salt can be prepared more conveniently by treating radical PTM with potassium metal in Et$_2$O or the αH-compound **2** with KOH in CH$_2$Cl$_2$, in the presence of 18-C-6.

Salt **3** has been characterized by elemental analyses, IR, UV-VIS and ^{1}H NMR spectroscopy, oxidation with I$_2$ to radical PTM and hydrolysis with aqueous HCl to αH-compound **2** (quantitative yield). It is insoluble in aliphatic hydrocarbons and in CCl$_4$, slightly soluble in Et$_2$O, and soluble in CH$_2$Cl$_2$, CHCl$_3$, THF, acetone, methanol and ethanol.

X-Ray structure

The X-ray structure of crowned salt **3** has been determined [8] and a perspective view is shown in Fig. 1. The central, anionic carbon atom and the three ring carbons connected to it are in a plane (sp^2 hybridisation). The molecule is propeller-shaped as expected, two rings being more tilted (45°) than the other (40°) with respect to the plane of the trivalent carbon. This marked tilting, and the normal bond length

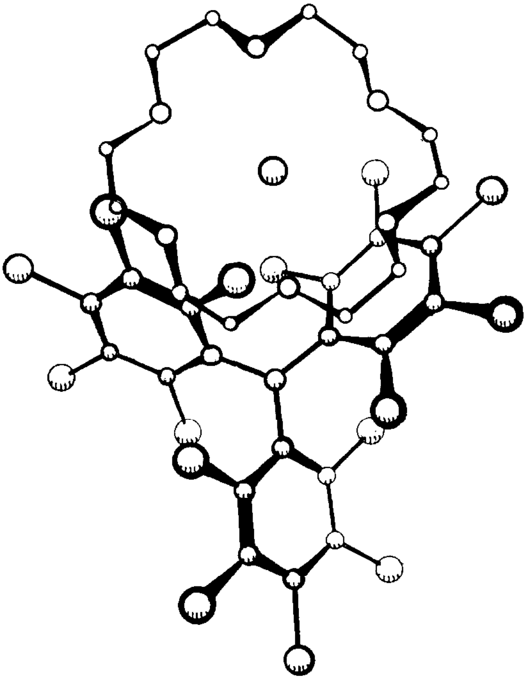


Fig. 1. Projection of the structure of crowned salt **3** on the *b–c* plane.

observed between the trivalent and the aromatic carbons (1.46 Å), indicates that there is only weak negative charge delocalization into the aromatic rings. The average distance between two vicinal *ortho*-chlorines (4.0 Å; Van der Waals radii of two chlorines, 3.6 Å) shows clearly the steric shielding of the trivalent carbon. The potassium counterion is coordinated with the six oxygen atoms of the macrocyclic polyether, and it is not centered on the top of the propeller, but slightly displaced toward the less tilted ring and one of the others. In the unit cell, the two K^+ ions are located far away (6.35 and 9.40 Å) from the trivalent carbon atoms (where most of the negative charge resides) of the two PTM^- carbanions, indicating that this bulky carbanion has little tendency to coordinate as counter-ion and that the salt can be described as a separated ion pair. The minimum distances between vicinal PTM^- ions involve a *meta*-chlorine atom of one PTM^- and a *meta* and *para* carbon atom of the other (3.4 and 3.6 Å, respectively). These short distances suggest an interaction between this chlorine atom and the π-electron system of the closest ring of the vicinal PTM^- [9]. Such an interaction might be responsible for the conductivity behaviour of salt **3** (see later).

Magnetic susceptibility behaviour

Crowned salt **3** is diamagnetic, but it has a residual paramagnetism which obeys the Curie–Weiss law in the range 77–390 K (6×10^{20} spins mol^{-1}; χ_{dia}, -0.480×10^{-6}; θ $-2.3°$ K), even when it is prepared from αH-compound **2**. Accordingly, the ESR spectrum of polycrystalline samples of salt **3** shows, at high gain, a symmetrical signal (g 2.0023; line width 5.4 G) with weak satellites (a 25 G), whose intensities

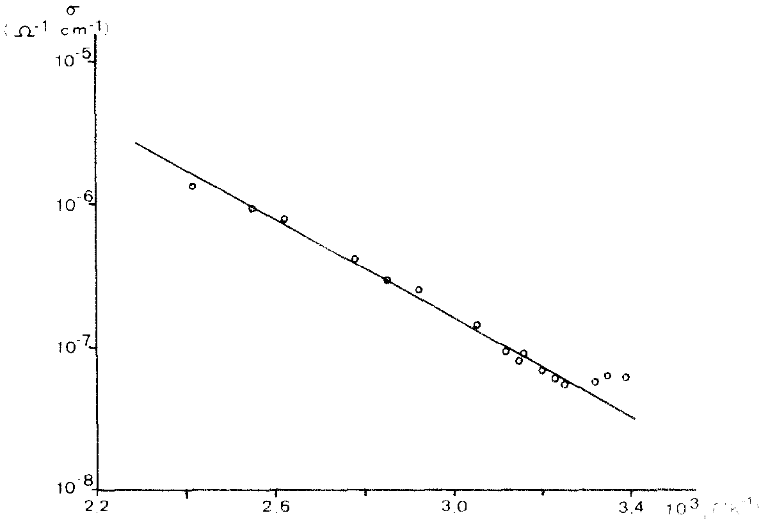


Fig. 2. Temperature dependence of the specific conductivity (Ω^{-1} cm^{-1}) of crowned salt **3**. $r = 0.9927$.

vary reversibly with temperatures up to 200°C. These paramagnetic characteristics can be attributed to the presence of small amounts of radical PTM, as confirmed by the UV-VIS and EPR spectra of salt **3** in solution.

Conductivity properties

Conductivity measurements on compressed pellets of crowned salt **3** have been performed (σ 25°C, 6×10^{-8} Ω^{-1} cm^{-1}). Ohm's law is obeyed; the current does not change with time and a reversal of the polarity reverses immediately the current. These results are consistent with electronic conduction. In the range 35–142°C there is a reversible variation of conductivity with temperature (Fig. 2), reflecting semiconductor behaviour, with an activation energy of 0.35 eV.

The presence of the PTM radical as an impurity in salt **3** has an important influence on the conductivity phenomena. Thus ground mixtures of radical PTM (σ 25°C, 1×10^{-12} Ω^{-1} cm^{-1}) and salt **3** have a slightly increased conductivity (σ 25°C, 10^{-7} to 10^{-5} Ω^{-1} cm^{-1}), which reaches a maximum for a 1/1 mixture. Similar behaviour has been reported for ground mixtures of tetracyanoquinodimethane (TCNQ) and K^+(18-C-6)TCNQ$^-$, and was explained in terms of reduction of the Coulomb repulsion force between mobile electrons caused by the presence of neutral TCNQ [10]. Some attempts to prepare crystals of pure mixed valence complex of type $(PTM)_n(K^+(18\text{-}C\text{-}6)PTM^-)_m$ from solutions of its components in CH_2Cl_2 were unsuccessful.

Electronic spectra

The UV-VIS spectrum of carbanion PTM$^-$ displays a shoulder of medium intensity around 274 nm and a symmetrical, intense broad band with the maximum in the range 504–513 nm. In Et_2O or THF this band is bathochromically shifted (17–28 nm) with respect to that of the non-chlorinated analogue (the triphenylmethide anion) [11]. Displacements of this type are normal for perchloroaromatic

TABLE 1

SOLVENT EFFECT ON THE UV-VIS SPECTRUM OF CARBANION PTM^- λ, nm (ε, l mol^{-1} cm^{-1} $\times 10^{-3}$)

Salt	Solvent [a]					
	Et_2O	THF	CH_2Cl_2	Me_2SO/Et_2O	Me_2SO/THF	H_2O/THF
1 [b]	504 (3.1)	513 (3.3)		513 (2.6)	513 (2.8)	513 (3.3)
3	509 (3.3)	513 (3.4)	513 (3.3)			

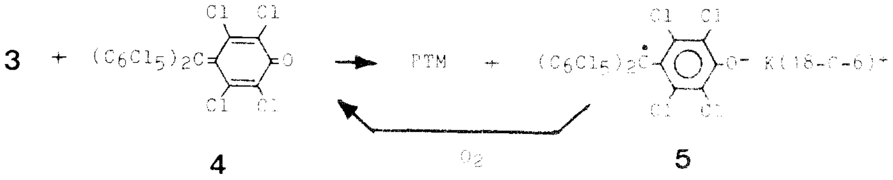
[a] Solvent mixtures are 1/9. [b] The solutions of **1** were prepared by reaction of radical PTM with potassium metal; ε values were calculated from the weight of this radical.

compounds [12]. The wavelength maxima and extinction coefficients of salts **1** and **3** in various solvents are shown in Table 1. The following facts are observed in the absorption maximum of salt **1**: (i) There is a bathochromic shift (9 nm) on going from Et_2O to THF. (ii) The presence of 18-C-6 polyether or Me_2SO in Et_2O causes a bathochromic shift of 5 or 9 nm, respectively. (iii) The presence of 18-C-6 polyether, Me_2SO or water has no effect on the absorption maximum in THF. These spectral features suggest that K^+ PTM^- (**1**) in Et_2O exists predominantly as contact ion pairs, and in the other solvents, predominantly as solvent separated ion pairs and/or free ions, as K^+(18-C-6)PTM^- (**3**) does even in Et_2O. In order to obtain further evidence for contact ion pairs of salt **1**, we tried to prepare solutions of Li^+ and Na^+ salts of carbanion PTM^- in Et_2O, since it is known that for contact ion pairs the absorption maxima show important bathochromic shifts on changing the cation from Li^+ to K^+ [11]. Unfortunately, treatment of radical PTM with Li metal, n-butyllithium or t-butyllithium and with Na metal or NaH in Et_2O did not give the desired Li^+ and Na^+ salts. Negative results were also obtained when α*H*-compound **2** was treated with LiOH or NaOH in Et_2O. In this connection it is mentioned that these salts can be obtained (λ 513 nm; ε 32000 l mol^{-1} cm^{-1} in both cases) in THF (a solvent with more solvating power) by treating radical PTM with the corresponding metals.

Chemical behaviour

In contrast to solid triphenylmethide salts [4], crowned salt **3** is stable toward water either in the solid state or in solution (UV-VIS spectrum in THF/H_2O). This striking difference correlates with the acidities of triphenylmethane (pK_a 30) [13] and α*H* compound **2** (estimated pK_a ca. 7) [14].

As ion pairing and solvation can have large influences on the kinetics of electron transfer reactions [15], the reactions of potassium salts **1** and **3** with O_2 and organic acceptors were studied. No significant electron transfer took place with crowned salt **3** in O_2 saturated solutions of Et_2O, THF or CH_2Cl_2 (UV-VIS spectra, 2 h). Salt **1** is also stable (UV-VIS spectra, 2 h) in O_2 saturated solutions of THF, Me_2SO/THF (1/9) or H_2O/THF (1/9); but, it gives radical PTM in an O_2 saturated solution of Et_2O (isosbestic points at 300 and 400 nm), radical PTM being formed in 80% yield in 12 min. It is apparent that the reactivity of carbanion PTM^- toward O_2 is higher in conditions which favour contact ion pairs, as observed for bis(9-fluorenyl)phenylmethide [16]. This enhanced reactivity is attributed to a greater stabilization by K^+ of the (more concentrated) negative charge in the transition state than in the reactant carbanion. Such a low stabilization by K^+ of the reactant carbanion, in bis(9-fluo-



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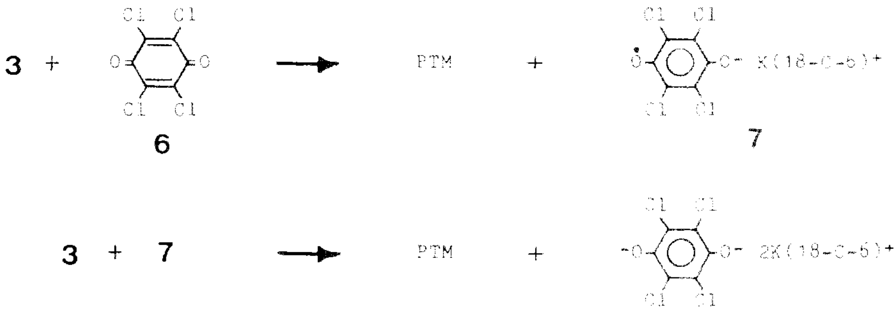

SCHEME 3

renyl)phenylmethide is due to the high delocalization of its negative charge [16], while in PTM^- it can be attributed to the steric shielding of the central carbon which hinders the approach of the K^+ counterion.

Carbanion PTM^- (salt **3** in CH_2Cl_2) reacts with an equimolecular amount of perchlorodiphenylmethyl radical (PDM) to give (UV-VIS spectrum) radical PTM quantitatively. It also reacts rapidly with 1 mol of perchlorofuchsone (**4**) or chloranil (**6**) in CH_2Cl_2 to give excellent yields of radical PTM and the corresponding radical anions **5** and **7**. Radical anion **5** was identified by its UV-VIS absorption at 742 nm [3b], and reversion to fuchsone **4** by passing the crude reaction solution through silica gel in air [3b]. Radical anion **7** was detected by the EPR technique: when the reaction was carried out in the EPR cavity two well separated featureless lines (integrated area 1/1) were observed, one due to radical PTM (*g* 2.0023), and the other to the K^+(18-C-6) salt of radical anion **7** (*g* 2.0052; line width, 0.81 G); a similar *g*-value has been reported for uncomplexed K^+ salts of radical anion **7** [17]. Since it has also been found that 1 mol of crowned salt **3** reacts with 0.5 mol of chloranil (**6**) to give an almost quantitative (98%) yield of radical PTM, we conclude that radical anion **7** can also oxidize carbanion PTM^- to radical PTM.

Carbanion PTM^- (salt **1** in THF, and salt **3** in Et_2O, THF or CH_2Cl_2) does not undergo one-electron transfers to benzophenone, fluorenone, 1,4-dinitrobenzene, perchlorobenzophenone and perchlorofluorenone (UV-VIS spectra, 2 h). However, the reverse reaction takes place in the case of benzophenone, since 1 mol of potassium ketyl **8** reacts immediately with radical PTM in THF containing 18-C-6, yielding crowned salt **3** quantitatively. The results obtained on electron transfer reactions of carbanion PTM^- with O_2 and organic acceptors, in media where the predominant species are solvent-separated ion pairs and/or free ions, are in general agreement with the oxidation potential of PTM^- ($E_{1/2}$ −0.28 V vs. SCE in Me_2SO) [14], and the known reduction potentials of the acceptors.

$$\mathbf{3} + (C_6H_5)_2C{=}O \ \underset{\longleftarrow}{\not\longrightarrow}\ PTM + (C_6H_5)_2C\text{-}\dot{O}^{-}\ K^{+}$$

8

SCHEME 4

Thermal behaviour

When solid **3** is kept at 280°C under purified Ar it decomposes without melting, evolves 18-C-6 and gives mainly the PTM radical.

Non-isothermal thermogravometric analysis of salt **3** (Fig. 3) up to 350°C shows that this salt begins to lose 18-C-6 at 250°C, and the process is completed at about 290°C. (A 25.2% weight loss was observed in an isothermal TG curve of salt **3** at 287°C, Fig. 3; calcd., 24.9%). Above 290°C further weight loss is observed, due to the sublimation and decomposition of the PTM radical formed. This has been confirmed by TG analysis of pure radical PTM, which sublimes and decomposes giving radical perchloro-9-phenylfluorenyl at about 300°C [1].

The formation of paramagnetic species in the thermal decomposition of salt **3** has also been detected by ESR. An irreversible increase of the intensity (×2000) of the initial weak signal was observed when a polycrystalline sample of salt **3** was heated at 285°C under purified Ar for 30 min. The resulting ESR signal, recorded at −160°C (Fig. 4), consists of a strong asymmetric band in the $g = 2$ region, and a very weak band in the $g = 4$ region, characteristic of a triplet species. The band at $g = 2$ has an intensity proportional to $1/T$, which is characteristic of a triplet in the ground state. Since the main products of the thermal decomposition of salt **3** are 18-C-6 and radical PTM, and the reaction was carried out with a rigorous exclusion of O_2, it is suggested that in such thermal decomposition there is decomplexation of the 18-C-6 from K^+ and an electron transfer from PTM^- carbanion to its counterion (K^+), to give the radical pair $PTM^{\bullet}K^{\bullet}$.

In this connection it is noteworthy that Pauling concluded that in alkaline metal halides, stretching of an ionic bond should produce radicals if the ionization

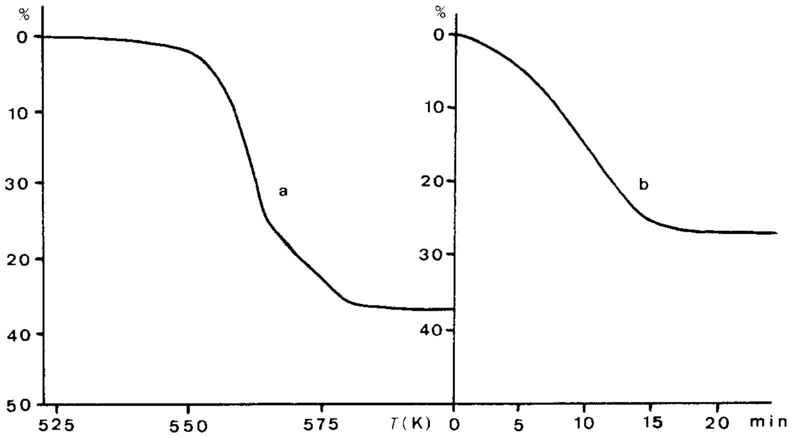

Fig. 3. (a) Non-isothermal TG curve of crowned salt **3** at 1.25°C min^{-1}. (b) Isothermal TG curve of crowned salt **3** at 560 K.

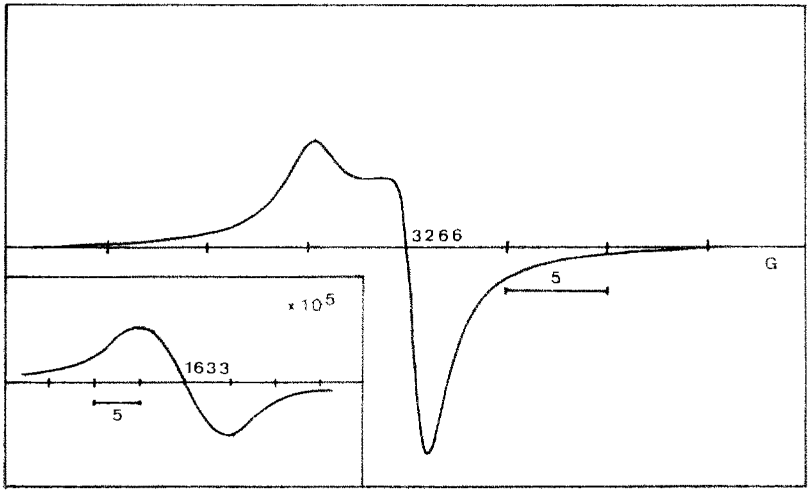

Fig. 4. ESR spectrum of crowned salt **3** after heating at 285°C for 30 min, recorded at − 160°C.

potential (*IP*) of the metal exceeds the electron affinity (*EA*) of the atom forming the anion [18]. Baughan et al. [19] calculated that the ionic bond stretch needed to produce $Na^{\cdot}$ and $CH_3^{\cdot}$ in $Na^+ CH_3^-$ is only 0.9 Å.

The electron affinity of radical PTM can be roughly estimated to be about 52 kcal mol^{-1}, as given by the corresponding calculated value for triphenylmethyl radical (36 kcal mol^{-1}) [20] plus the difference between the oxidation potentials of triphenylmethide and PTM^- (0.71 V = 16 kcal mol^{-1}) [14]; those potentials were determined under similar conditions, where the predominant species are free ions [21]. This estimated *EA* value of radical PTM is considerably smaller than the *IP* of potassium (99.7 kcal mol^{-1}) [18], and so, it is reasonable to assume that when decomplexation of 18-C-6 in salt **3** takes place, because of steric shielding of PTM the resulting ions cannot approach close enough to gain the necessary lattice energy to overcome the *IP* − *EA* difference. Consequently, the failure to obtain solid salt **1** from salt **3** can be attributed to the steric shielding of the α-carbon of PTM^-. Finally it is concluded that the thermodynamic stabilities of solid salt **3** and the uncrowned alkaline salts of PTM^- in THF or Et_2O solutions, arise from the large energy of solvation of the metal ion by the ethers [21,22], which is greater than the *IP* − *EA* energy term. Related arguments were used to explain the thermal decomposition of sodium amyl [23], the ionicity of solid (2,2,2-cryptate)$Na^+ Na^-$ (24), and the charge transfer phenomena in solid $TCNQ^-$ salts with organic counterions [25].

Experimental

General methods

The m.p. was determined with a Kofler microscope. The IR, UV-VIS, ^1H NMR and ESR spectra were recorded with Perkin–Elmer 682, Beckmann Acta M-VI, Perkin–Elmer R-12B and Varian E4 spectrometers, respectively. The magnetic susceptibilities were measured in helium with a Varian 4-inch magnet with constant-force caps, and a Cahn RG electrobalance. The thermogravimetric analyses were carried out with a Perkin–Elmer TGS-2 system, under N_2 (40 cm^3 min^{-1}), with a 3–4 mg sample. The heating rate in the non-isothermal experiments was 1.25°C min^{-1}. Conductivity measurements on solid samples were made with a PAR 136 digital electrometer with applied voltages corresponding to electric fields from 10^4 to 2.5×10^5 V m^{-1}. The measurements were carried out on ground crystals of the samples, compressed to pellets, which were sandwiched between two metallic blocks with gold faces. The system was placed in a heated container in which the temperature and pressure between the metallic blocks could be controlled. The conductivities were measured under pressures exceeding 4×10^7 Pa, where saturation of the conductivity was observed.

The solvents Et_2O and THF were freshly distilled from Na under N_2 in presence of benzophenone ketyl. CH_2Cl_2 was distilled from P_2O_5 under N_2 and stored over molecular sieves. Handling of the radicals and carbanions was carried out in the dark under Ar. The spectra given in Table 1 were obtained at sample concentrations of $3–8 \times 10^{-5}$ *M*. The stabilities of carbanion PTM^- with organic acceptors (monitored by UV-VIS spectroscopy) were examined at concentrations of $3–5 \times 10^{-5}$ *M* and with a two- to threefold excess of the acceptor.

1/1 Complex 18-C-6-potassium perchlorotriphenylmethide (3)

(a) From potassium perchlorotriphenylmethide (1) solution. An excess of potassium (in lumps) was added to a solution of radical PTM (0.119 g, 0.16 mmol) in Et_2O (100 ml), and the mixture was shaken vigorously for 20 h. The resulting wine-red solution of carbanion **1** was filtered into an Ar filled flask containing 18-C-6 (0.048 g, 0.18 mmol) and then left to stand overnight. The large crystals formed were separated, washed with Et_2O and dried, to give crowned salt **3** (0.121 g, 73%), garnet crystals with bronze luster, m.p. 280°C (dec); IR (KBr) 2905 m, 1500m, 1360s, 1330m, 1105s, 960m, 720m, 690m, 640m, 610m, 515m cm^{-1}; UV-VIS, see Table 1; ^1H NMR ($CDCl_3$) δ, 3.63 (s). Anal. Found: C, 35.2; H, 2.2; Cl, 49.8. $C_{31}H_{24}Cl_{15}KO_6$ calcd.: C, 35.0; H, 2.3; Cl, 50.0%.

(b) From PTM radical. An excess of potassium (in lumps) was added to a solution of radical PTM (0.103 g, 0.13 mmol) and 18-C-6 (0.046 g, 0.17 mmol) in Et_2O (250 ml), and the mixture was shaken for 20 h. The excess of potassium was removed, and the microcrystalline precipitate was filtered, washed with Et_2O, and recrystallized (CH_2Cl_2/pentane, 1/5) to give pure crowned salt **3** (0.130 g, 71%).

(c) From αH compound 2. Finely powdered KOH (2.39 g) was added to a solution of αH-compound **2** (3.00 g, 3.9 mmol) and 18-C-6 (1.16 g, 4.4 mmol) in CH_2Cl_2 (150 ml), and the mixture was stirred for 20 h. The excess of KOH was filtered off and the solution was concentrated to give pure crowned salt **3** (1.86 g). The mother liquors were diluted with pentane (150 ml), yielding more **3** (1.94 g) (90% overall yield).

Hydrolysis of crowned salt 3

Aqueous 2*N* HCl (5 ml) was added to a solution of salt **3** (0.072 g) in CH_2Cl_2 (20 ml), and the mixture was stirred for 1 h. The organic layer was decanted, washed with water, dried, and evaporated. The residue was chromatographed (silica gel; hexane) to give the αH compound **2** (0.050 g, 98%).

Oxidation of crowned salt 3

(a) With p-chloranil (6). CH_2Cl_2 (10 ml) was added to a mixture of salt **3** (0.110

g, 0.10 mmol) and *p*-chloranil (**6**) (0.014 g, 0.05 mmol), and the resulting brown solution was stirred for 4 h then quenched with aqueous $1N$ HCl (25 ml). The organic layer was decanted, washed with water, dried, and evaporated. The red residue was purified by chromatography on silica gel (hexane) giving radical PTM (0.077 g, 98%).

(b) With perchlorofuchsone (4). This oxidation was performed as in (a) above (salt **3**, 0.140 g; fuchsone **4**, 0.107 g). Column chromatography of the product (silica gel: hexane/$CHCl_3$) yielded radical PTM (0.098 g, 98%) and fuchsone **4**, the latter being formed by air oxidation of its anion radical **6** (0.091 g, 85%).

(c) With iodine. This oxidation was performed as in (a) (salt **3**, 0.119 g; iodine, 0.352 g). The excess of iodine was removed by washing with aqueous $NaHSO_3$. Radical PTM was obtained (0.084 g, 99%).

Thermal decomposition of crowned salt 3

Two round bottom flasks, containing salt **3** (0.207 g) and concentrated H_2SO_4 (4 ml), respectively, were connected through a tube provided with a 3-way stopcock for selection of vacuum or argon supply. The acid was degassing three times by the freeze-pump-thaw technique, and the system filled after each cycle with rigorously purified argon (passed through a pyrogallol solution). Then salt **3** was heated at 280°C for 2 h; darkening of the solid, and evolution of a colorless liquid took place. The resulting black-reddish solid was cooled and quenched by transferring the H_2SO_4. The suspension formed was added to cracked ice. Extraction with $CHCl_3$ followed by washing, drying and evaporation, of the extract left a residue, which upon column chromatography (silica gel, hexane) gave a red powder (0.128 g) containing radical PTM (66%) and αH compound **2** (20%) (UV-VIS spectroscopy). The colorless liquid evolved was trapped (-70°C) in a separate experiment and identified as 18-C-6 (47%).

References

1 M. Ballester, J. Riera, J. Castañer, C. Badía and J.M. Monsó, J. Am. Chem. Soc., 93 (1971) 2215.

2 M. Ballester and G. De La Fuente, Tetrahedron Lett., (1970) 4509.

3 (a) M. Ballester, J. Riera and A. Rodriguez, Tetrahedron Lett., (1970) 3615; (b) M. Ballester, J. Riera, J. Castañer, A. Rodriguez, C. Rovira and J. Veciana, J. Org. Chem., 47 (1982) 4498.

4 (a) M.A. Coles and F.A. Hart, Chem. and Ind. 30 (1968) 423; (b) H. Koster and E. Weiss, J. Organomet. Chem., 168 (1979) 273; (c) J.J. Brooks and G.D. Stucky, J. Am. Chem. Soc., 94 (1972) 7333.

5 M. Hiraoka, Crown Compounds, Their Characterization and Applications, Studies in Organic Chemistry, Vol. 12; Elsevier, Amsterdam, 1982, p. 67–150.

6 F.J. Teham, B.L. Barnett and J.L. Dye, J. Am. Chem. Soc., 96 (1974) 7203.

7 D. Issa and J.L. Dye, J. Am. Chem. Soc., 104 (1982) 3781.

8 C. Miravitlles, E. Molins, X. Solans, G. Germain and J.P. Declercq, J. Incl. Phenom., 3 (1985) 27.

9 C.K. Prout and B. Kamenar, in Foster (Ed.), Molecular Complexes, Vol. 1, Elek. Science; London, 1973, p. 151–204.

10 M. Morinaga, T. Nagami, Y. Kanda, T. Matsumoto, K. Matsukoa and H. Mikawa, Bull. Chem. Soc. Japan, 53 (1980) 1221.

11 E. Buncel and B. Menon, in E. Buncel, T. Dorst, (Eds.), Comprehensive Carbanion Chemistry, Part A: Elsevier, New York, 1980, p. 97–120.

12 M. Ballester and J. Castañer, J. Am. Chem. Soc., 82 (1960) 4259.

13 W.S. Mathews, J.E. Bares, J.E. Bartmess, F.G. Bordwell, F.J. Confort, G.E. Brucker, Z. Margolin, R.J. McCallum, G.J. McCallum and N.R. Vainer, J. Am. Chem. Soc., 97 (1975) 7006.

14 K.P. Butin, I.M. Taha and O.A. Reutov, Izv. Akad. Nauk, SSSR. Ser. Khim., (5) (1978) 1011.

15 R.D. Guthrie, in E. Buncel (Ed.), Comprehensive Carbanion Chemistry, Part A Elsevier, New York, 1980 p. 197–271.

16 J.G. Pacifici, J.F. Garst and E.G. Janzen, J. Am. Chem. Soc., 87 (1965) 3014.

17 Landolt-Börnstein. II. Magnetic Properties of Free Radicals", Vol. 9; H. Fisher and K.H. Hellewge (Eds.), Part d1, p. 231–235.

18 L. Pauling, The Nature of the Chemical bond, Cornell University Press, New York, 1944.

19 E.C. Baugham, M.G. Evans and M. Polanyi, Trans. Farad. Soc., 37 (1941) 377.

20 G. Kothe, A. Stürve and H. Baumgärtel, Tetrahedron Lett., 28 (1972) 5957.

21 M. Szwarc and J. Jagur-Grodzinski, in M. Szwarc, (Ed.), Ions and Ion Pairs in Organic Reactions, Vol. 2; John Wiley; New York, 1974, p. 1–150.

22 T. Yanabe, K. Hori, K. Akagi and K. Fukui, (a) Tetrahedron, 35 (1979) 1065; (b) idem, ibid, 39 (1983) 67.

23 M. Avery, Solid Organometalic Metal Reagents; Gordon and Breach; New York, 1964; p. 1–18.

24 M.H. Cohen, J. Jortner, J.C. Thompson, J. Chem. Phys., 63 (1975) 3741.

25 J.B. Torrance, Acc. Chem. Res., 12 (1979) 79.