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18-CROWN-6 ETHER COMPLEXES WITH ARALKYLAMMONIUM PERCHLORATES
Thermochemical properties

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Abstract

Thermochemical properties of crown ether complexes have been studied by simultaneous TG-DTA (thermogravimetric analysis–differential thermal analysis) coupled with a mass spectrometer, DSC (differential scanning calorimetry) and hot stage microscopy (HSM).

The examined complexes contain benzylammonium- [BA], (*R*)-(+)-α-phenylethylammonium- [(*R*)-PEA], (*R*)-(+)- and (*S*)-(–)-α-(1-naphthyl)ethylammonium perchlorate [(*R*)-NEA and (*S*)-NEA] salts as guests. In the cases of BA and (*R*)-PEA an achiral pyridono-18-crown-6 ligand [P18C6], and in the case of (*R*)-NEA and (*S*)-NEA a chiral (*R,R*)-dimethylphenazino-18-crown-6 ligand [(*R,R*)-DMPh18C6] was used as host molecule to obtain four different crown ether complexes.

In all cases, the melting points of the complexes were higher than those of both the host and the guest compounds. The decomposition of the complexes begins immediately after their melting is completed, while the BA and (*R*)-PEA salts and the crown ether ligands are thermally stable by 50 to 100 K above their melting points. During the decomposition of the salts and the four complexes strongly exothermic processes can be observed which are due to oxidative reactions of the perchlorate anion. Ammonium perchlorate crystals were identified among the decomposition residues of the salts.

P18C6 was observed to crystallize with two molecules of water. The studied complexes of P18C6 did not contain any solvate.

BA was observed to exhibit a reversible solid-solid phase transition upon heating.

The heterochiral complex consisting of (*S*)-NEA and (*R,R*)-DMPh18C6 shows a solid-solid phase transition followed by two melting points. HSM observations identified three crystal modifications, two of them simultaneously co-existing.

Keywords: ammonium perchlorate, crown ether complexes, decomposition, DSC, HSM, primary organic ammonium perchlorates, TG-MS

Introduction

Macrocycle complexes

Macrocycles are chelate forming rings built up of more than 8 atoms and containing at least 3 donor-atoms [1]. Their complexes can have high stability due to the so-

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called macrocyclic effect, which is a chelate effect strengthened by the stabilizing effects of the cyclic structure [2]. Their applications are based on their ability to selectively form complex structures [3–5].

Detailed knowledge of the properties of the complexes and the way they are formed are required for using them effectively in different applications and for the further development of desired supramolecular structures. Thermoanalytical methods are widely used in the studies of macrocyclic compounds and their complexes. They are successfully applied in the studies of thermal decomposition, desolvation processes and phase transitions of polymorphic modifications. Combining the results of different thermoanalytical methods and using coupled techniques makes the undoubtful identification of the observed processes and their investigation from different points of view.

Thermal decomposition of ammonium perchlorates

The mechanism and different factors influencing the thermal decomposition of ammonium perchlorate have previously been extensively studied because of the intrinsic chemical interest [6, 7]. Its later application as oxidizer in solid propellants also stimulated this research.

Unlike ammonium perchlorate, which is a relatively stable compound, alkyl-substituted ammonium perchlorates are highly explosive materials as their crystals contain both the oxidizer and the fuel part. Their thermal decomposition is a strongly exothermic process [8, 9].

The molecular fragments developing during the decomposition of alkyl-substituted ammonium perchlorates giving rise to the most intensive peaks in the mass spectra are the m/e=16 (CH_4^+, O^+, NH_2^+), 28 ($C_2H_4^+$, CO^+, N_2^+), 44 (CO_2^+, N_2O^+) [8, 9].

During the thermal decomposition of monomethylammonium perchlorate NH_4ClO_4 is formed. When the mass loss is 55%, monomethylammonium perchlorate is completely decomposed and converted to ammonium perchlorate [10]. Monomethylammonium perchlorate decomposes in two different ways. In the first case via a proton transfer mechanism it dissociates to methylamine and perchloric acid, and in the other case with the breaking of the carbon-nitrogen bond ammonia and the unstable methyl perchlorate are formed. The perchloric acid and the ammonia react to give ammonium perchlorate [8, 10]. Such product could not be observed in the cases of the di-, tri- and tetramethyl-substituted ammonium perchlorates [8]. For di- and trimethylammonium perchlorates the methyl group transfer is not characteristic, so ammonia is not formed. In the case of tetramethylammonium perchlorate the proton transfer mechanism is impossible so perchloric acid is not present.

Polymorphism of ammonium perchlorate

Ammonium perchlorate like alkali metal perchlorates has two polymorphic modifications [11, 12]. Its stable crystal form is orthorhombic at room temperature and cubic above 513 K [6, 7, 11, 12]. The crystallographic phase transition is due to the order-disorder transformation of the perchlorate anion, the ammonium cation begins free rotation even below room temperature [6]. (It is possible that there exists a third crystal modification below 83 K [6].)

Polymorphism is also characteristic of alkyl-substituted ammonium perchlorates [8, 13]. Mono-, di-, trimethyl- and monoethylammonium perchlorates have three different polymorphs [8, 10, 14, 15]. The first transition at lower temperature is due to the breaking of hydrogen bonds of the type N–H…O, which allows a higher mobility for the perchlorate anions. The transition at higher temperature is related to the molecular motion of the cations [14–16]. Tetramethylammonium perchlorate has two different polymorphic modifications [15], with no possibility for the formation of N–H…O type hydrogen bonding.

Experimental

Materials

Pyridono-18-crown-6 (P18C6) [17] and (*R,R*)-dimethylphenazino-18-crown-6 ((*R,R*)-DMPh18C6) [18] ligands as well as their complexes formed with benzylammonium- (BA) [17] and (R)-(+)-α-phenylethylammonium perchlorates ((*R*)-PEA) [17] or with (*R*)-(+) and (*S*)-(–)-α-(1-naphthyl)ethylammonium perchlorates ((*R*)-NEA and (*S*)-NEA) [4] respectively (Fig. 1), were prepared as previously described.

Instruments

The TG/DTA-MS coupled measurements have been carried out using TA Instruments SDT 2960 simultaneous TG/DTA unit connected through a heated silica capillary inlet to a Balzers Instruments Thermostar GSD 300T quadrupole MS.

The DSC measurements were performed with TA Instruments DSC 2920.

A Leica MZ6 polarizing microscope with Leica Heating Stage 350 was used to perform HSM investigations. The transformation processes of the investigated samples were recorded with a JVC GCX3 digital camera.

The X-ray powder diffractograms were taken on a Freiburger Präzisionsmechanik (Carl Zeiss) HZG4 X-ray diffractometer.

Methods

Using TG/DTA-MS equipment the heating rate was 5 K min^{-1} in the 300 to 570 K temperature interval. The mass spectrometer was used in scan mode with 0.2 s scan time, so the mass spectra recorded between *m*/*e* 15 to 95 have been taken every 16 s. The measuring cell was purged with helium gas with 120 mL min^{-1} flow rate.

In general, DSC measurements were performed up to the temperatures of decomposition of the samples with 5 K min^{-1} heating rate.

The NH_4ClO_4 solid decomposition product of the salts was investigated with DSC. BA was heated up to 570 K with 10 K min^{-1} heating rate and cooled down to room temperature then reheated to 540 K with 5 K min^{-1} heating rate. (*R*)-PEA was heated until 530 K with 10 K min^{-1} heating rate and cooled down to room tempera-

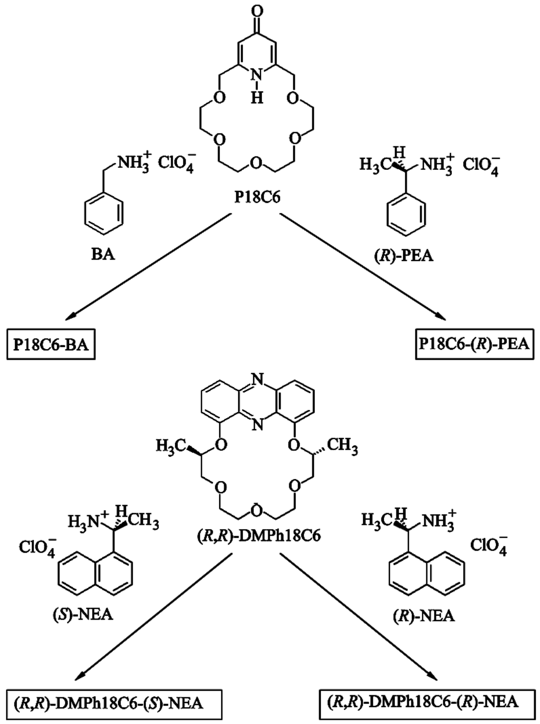


Fig. 1 Formulas of the compounds used in this study

ture, then reheated to 530 K with 5 K min^{-1} heating rate. (*R*)-NEA was heated until 540 K with 5 K min^{-1} heating rate.

The X-ray powder diffraction analyses were carried out at the CuK_{α} line at room temperature. The accelerator voltage was 30 kV, the current strength 25 mA. The powder diffractogram of the decomposition products of (*R*)-NEA was recorded. (*R*)-NEA was heated with HSM to the peak temperature of the exothermic decomposition (490 K) and cooled down to room temperature. The black carbonized decomposition products were analyzed by X-ray powder diffraction, in the $2\Theta=2°–64°$ range. The powder diffractogram of the dehydrated form of P18C6 was also recorded in the $2\Theta=2°–44°$ range.

Results and discussions

Thermal decomposition and stability of the complexes

The investigated aralkylammonium perchlorate salts and their complexes contain the oxidizing perchlorate anion therefore highly exothermic processes are characteristic in their decomposition. The thermal decompositions of the crown ethers are endothermic. The decomposition processes were investigated with TG/DTA-MS and DSC methods in order to get insights into the stability of the complexes (Table 1, Fig. 2).

TG/DTA measurements performed up to 570 K showed an exothermic decomposition in the ca. 460–570 K temperature range. During this step the mass loss is 40

Table 1 Thermoanalytical data

Sample	Melting point (onset)/K	Melting enthalpy/ kJ mol^{-1}	Thermal stability	First stage of the exothermic decomposition	
				Peak temperature/K	Mass loss/m/m%
P18C6	394.8	29.8	to 490 K	no	
BA	404.4	16.7	to 510 K	570	60
P18C6-BA	468.1	64.0	to melting	510	60
(*R*)-PEA	369.1	13.7	to 480 K	520	40
P18C6-(*R*)-PEA	428.6	51.5	to melting	520	70
(*R*,*R*)-DMPh18C6	432.8	41.4	to 500 K	no	
(*R*)-NEA	460.0	27.1	to melting	490	40
(*R*,*R*,)-DMPh18C6-*(R)*-NEA	500.9	51.7	to melting	530	40
(*R*,*R*,)-DMPh18C6-(*S*)-NEA	471.5 480.1		to 480 K	530	40

to 60%. For BA this step is seen as sharp peak both on the DTG and DTA curves. In the case of (*R*)-PEA and (*R*)-NEA the decomposition occurs in two steps, that give flatter DTA peaks at lower temperatures than for BA, and also the mass loss is lower. For the complexes of P18C6 the temperature of this exothermic decomposition is lower and the mass loss is greater than for the complexes of DMPh18C6.

During the exothermic decomposition of the complexes molecular fragments originating from both the crown ethers and the salts can be observed (Table 2). The break up of the complexes is instantly followed by the thermal decomposition of both components. During the melting of the complexes an endothermic decomposition step with a mass loss of a few percents can be observed. The enthalpy of the latter process merges with the melting enthalpy of the complexes, and therefore the observed melting enthalpy becomes much higher (>50 kJ mol^{-1}) than usual. This process occurs at lower temperatures than the oxidative reactions of the perchlorate anion and presumably has different mechanism. The decomposition products of this very first step could not be detected with the aid of mass spectrometry.

In the case of the complexes of the achiral pyridono crown ether, the melting points of the complexes are much higher than those of both the host (P18C6) and the guest (BA and (*R*)-PEA) compounds (Table 1). However, the first endothermic decomposition step for the complexes begins immediately after their melting is completed, while the salts and the crown ether are thermally stable up to ca. 100 K above their melting points until the exothermic decomposition caused by the perchlorate anion. Thus one can say that the complexation decreases the thermal stability of the components, since the melting points of the complexes are by 20 to 60 K lower than the temperatures of thermal decomposition of the free ligand and the salts. The temperatures of the exothermic decomposition of the complexes are lower than those of the free components. In the case of P18C6-BA the decrease is significant (ca. 60 K: Table 1, Fig. 2) while in the case of P18C6-(*R*)-PEA, it is only a few K (Table 1). In the mass spectra of the P18C6-BA and P18C6-(*R*)-PEA complexes the molecular fragments originating from the BA and (*R*)-PEA salts give sharp peak at the begin-

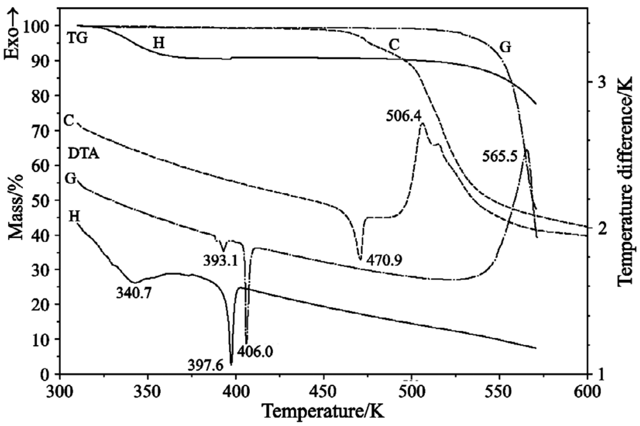


Fig. 2 Thermoanalytical curves (TG and DTA) of P18C6 ether (host-H), BA salt (guest-G) and their complex: P18C6-BA (complex-C) showing the exothermic decomposition processes due to the presence of the perchlorate anion

ning of the decomposition and the fragments coming from the P18C6 crown ether make a drawn-out peak in time from the beginning of the thermal decomposition until the end of the first stage. The decomposition of the complexes starts with the decomposition of the salts. This is followed by the decomposition of the crown ether, which is a longer process (Tables 2, 3).

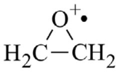
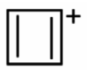
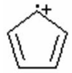
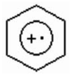
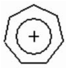
The complexes of the chiral crown ether [(*R*,*R*)-DMPh18C6] also decompose immediately after melting, while the crown ether is stable by 70 K above its melting point. The decomposition of the salt [(*R*)-NEA] begins when its melting is complete (opposite to BA and (*R*)-PEA). (*R*)-NEA can be regarded as more stable when complexed, since the decomposition temperature of the complex is by 20 to 40 K higher than that

Table 2 Mass spectroscopy results

Sample	Mass numbers of the molecular fragments detected during thermal decomposition (*m*/*e*)	K*
P18C6	36 38 39 44 51 58 65 88 91	490
BA	17 18 28 32 37 38 39 44 51 63 65 77 91	510
P18C6-BA	17 18 28 32 36 37 38 39 44 51 58 63 65 77 88 91	470
(*R*)-PEA	17 18 28 32 37 38 39 44 51 63 65 77 89 91	480
P18C6-(*R*)-PEA	17 18 28 32 36 37 38 39 44 51 58 63 65 77 88 91	430
(*R*,*R*)-DMPh18C6	17 18 28 32 36 38 39 40 44 58 64	500
(*R*)-NEA	17 18 28 32 36 38 39 44 51 63 65 77 87 91	460
(*R*,*R*,)-DMPh18C6 -(*R*)-NEA	17 18 20 22 28 32 36 37 38 39 40 44 51 58 63 65 77 87 91	500
(*R*,*R*,)-DMPh18C6 -(*S*)-NEA	17 18 20 22 28 32 36 37 38 39 40 44 51 58 63 65 77 87 91	470

*Initial temperature of the thermal decomposition

Table 3 Presumed structure of the most intense molecular fragments

Inorganic fragments					
m/*e*=17 OH^+, NH_3^+	*m*/*e*=18 H_2O^+, NH_4^+	*m*/*e*=28 $C_2H_4^+$, CO^+, N_2^+	*m*/*e*=32 O_2^+	*m*/*e*=44 CO_2^+, N_2O^+	
Linear organic fragments					
m/*e*=44 $H_3C-CH=NH_2^+$	*m*/*e*=58 $H_2C=CH-O^{+\bullet}-CH_3$	*m*/*e*=63 and *m*/*e*=65 $Cl-CH=NH^{+\bullet}$ (and protonated forms)			
Cyclic organic fragments					
m/*e*=44 	*m*/*e*=39 	*m*/e=51 	*m*/*e*=65 	*m*/*e*=77 	*m*/*e*=91 

of the salt itself (Table 1). The exothermic decompositions of the two diastereomeric complexes are very similar. In the mass spectra of the (*R*,*R*,)-DMPh18C6-(*R*)-NEA and (*R*,*R*,)-DMPh18C6-(*S*)-NEA complexes, molecular fragments that appear are not present neither in that of the DMPh18C6 crown ether, nor of the (*R*)-NEA salt (Table 2). The MS peaks of the molecular fragments originating from the salts are sharp and those of the crown ether are drawn-out. Their decomposition starts at the same temperature.

Crystalline NH_4ClO_4 as the decomposition product of the primary aralkylammonium perchlorate salts

During the exothermic decomposition of the aralkylammonium perchlorate salts (BA, (*R*)-PEA and (*R*)-NEA) a solid crystalline decomposition product is formed which is not detectable in the case of the complexes. While heating the samples with HSM until the peak temperature of the exothermic decomposition of the samples, crystal seeds are formed followed by the growth of dendritic crystals. The habit of these crystals is the same for all investigated aralkylammonium perchlorate salts.

Powder diffraction analyses performed on the decomposition products of (*R*)-NEA show that the only crystalline component in the solid residue is NH_4ClO_4 as it was found by Nambiar *et al.* in the case of methylammonium perchlorates [10]. Powder diffraction data were compared to ICDD cards number 8–451 and 43–648, and found to agree well.

NH_4ClO_4 has an enantiotropic solid-solid phase transition at 513 K [ICDD 2–232, 6, 11, 12] that can be observed as an endothermic peak on the DTA and DSC records of the decomposed aralkylammonium pechlorate salts. The decomposition products of BA were produced with DSC after heating to 570 K. During the reheating the only observable peak was an endothermic change at 518 K with relatively low enthalpy change (29.3 J g^{-1}), which is probably due to the solid-solid phase transition of NH_4ClO_4. The same experiments were made on (*R*)-PEA, and the endothermic peak appeared at

517 K during the second run. Since the exothermic decomposition of (*R*)-NEA (490 K) takes place below the temperature of the polymorphic phase transition of NH_4ClO_4, the endothermic peak appears at 515 K already in the first run.

Explanation of the difference in the thermal behaviour of the complexes and the free salts on the basis of single-crystal diffraction data

In the crystal lattice of the ammonium pechlorate salts the aralkylammonium cation and the perchlorate anion are close to each other, while in the complexes they are separated. In the complexes the aralkylammonium cation is connected via tripod-like hydrogen bonding to the nitrogen atom of the heterocyclic unit and to the two alternating ether oxygen atoms of the crown ether. In the case of P18C6 the perchlorate anion is connected to the oxygen atom of the hydroxypyridino unit of the crown ether [17] (the pyridono and the hydroxypyridino forms are in a tautomeric equilibrium). In the complexes of DMPh18C6 the perchlorate anion is situated in the gaps of the crystal lattice [4]. The difference between the thermal behaviour of the complexed compounds and the salts can be due to the separation of the perchlorate anion from the ammonium cation in the complexes, which prevents the formation of ammonium perchlorate.

Dehydration process of the pyridono-18-crown-6 (P18C6) ether

The P18C6 ether was observed to undergo a dehydration process (Fig. 3). The TG measurements show 9.5% mass loss in the 300 to 380 K temperature range. This proportion corresponds to ca. 2 moles of water. In this temperature range the intensity of the peak *m*/*e*=18 is significantly increased on the mass spectra which proves that the leaving crystal solvent is water. Dehydration is observable also with HSM method. Covering the crystals with silicone oil, water bubbles develop from the sample.

The crystal structure of the crown ether previously determined by single crystal X-ray diffraction [19] also contains crystal water, but with only 1 molecule of water per molecule of crown ether. The water molecule in this structure connects two

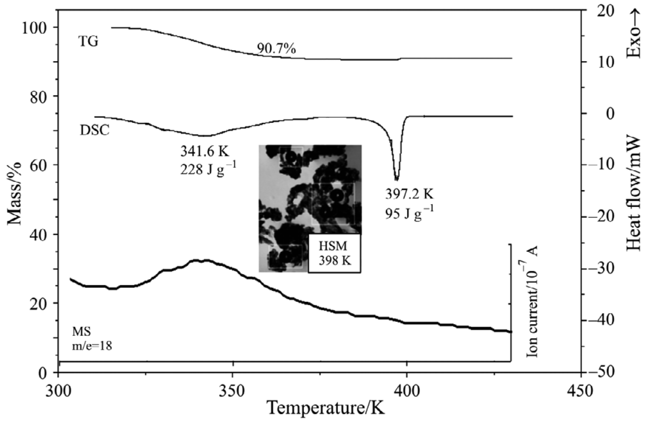


Fig. 3 Thermoanalytical curves (TG, HSM image and DSC) and mass spectral records showing the loss of crystal water of the P18C6 ether as a result of heating

crown ether molecules related by a two-fold screw axis via hydrogen-bonds to the double-bonded oxygen atom of the pyridone ring.

The powder diffractogram of the crystals used for the thermal studies has been recorded. It does not agree with that calculated from the determined crystal structure of P18C6 monohydrate, so it can be regarded as a different crystal modification. Thus P18C6 ether has a second crystal modification that contains 2 mole equivalents of water. It is likely that in the dihydrate the second molecule of water is located in the cavity of the crown ether where polar molecules can easily fit.

The crystal structure of the sulfur analogue of the crown ether (where the double bonded oxygen atom of the pyridono unit is substituted by a sulfur atom) is also known and two molecules of water can be observed for one molecule of the thiopyridono crown ether [20]. The first molecule of water is bonded in a similar way to the double bonded sulfur atom of the thiopyridono ring, as to the double bonded oxygen atom of the pyridono unit in the P18C6 crown ether. (The position of the second hydrogen atom in the water molecule has not been determined.) The measured powder diffractogram of P18C6 agrees well with the one calculated from the single crystal X-ray diffraction data of this thiopyridono analogue.

The P18C6 ether was crystallized from acetone presumably as the monohydrate and during the storage took up the second molecule of crystal water. Immediately after crystallisation the melting point of the monohydrate was 377–378 K and months later it shifted to 397–398 K which is the melting point of the dihydrate (HSM measurements). Presumably the water molecule connected to the double-bonded oxygen or sulfur atom of the crown ether is required for the formation of the crystalline structure as it connects together the crown ether molecules around the symmetry axis. The crown ether can take up a second water molecule to its cavity if there is enough moisture in its surrounding.

Polymorphism of benzylammonium perchlorate (BA) salt

The solid-solid phase transition of the BA salt (Fig. 4) appears on the DTA and DSC curves as an endothermic peak. The transformation takes place at 391 K but the equi-

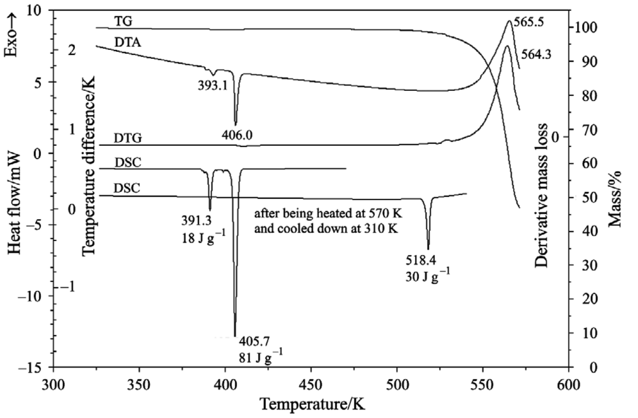


Fig. 4 Thermoanalytical curves (TG, DTG, DTA, DSC) showing the solid-solid phase transition of BA salt

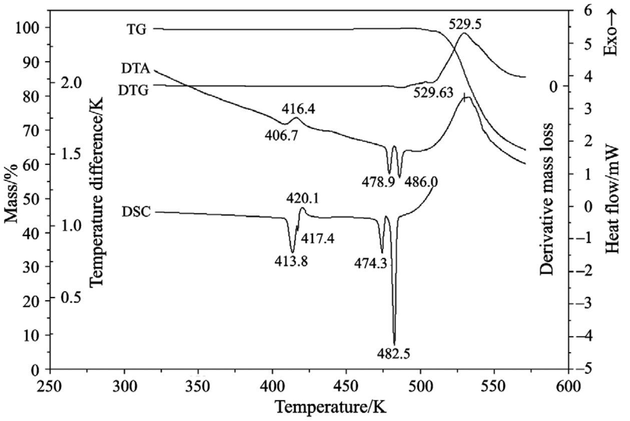


Fig. 5 Thermoanalytical curves (TG, DTG, DTA, DSC) showing the complex mechanism of the phase transitions of (*R*,*R*)-DMPh18C6-(*S*)-NEA complex

librium temperature changed by a few K during the storage. If the crystals are cooled below the equilibrium temperature they transform back to the modification that is stable at lower temperature and if the sample is reheated the phase transition takes place again. The phase transition process and also the transformation backward could be observed with the aid of HSM.

Polymorphism of the complex of (R,R)-dimethylphenazino-18-crown-6 ether with (S)-naphthylethylammonium perchlorate ((R,R)-DMPh18C6-(S)-NEA complex)

DTA and DSC results show the polymorphism of the (*R,R*)-DMPh18C6-(*S*)-NEA complex (Fig. 5). This solid-solid phase transition is a complex process proceeding in two endothermic steps followed by an exothermic one between 410 and 420 K. At 474.2 K and at 482.5 K two melting temperatures can be measured. HSM studies have been used to clear up the complex processes taking place in the sample during the heating. Therefore we conclude that at least 3 different polymorphs exist for this complex molecule two of them simultaneously co-existing.

The other diastereomer of the complex does not show polymorphic phase transition.

Conclusions

The melting points of the investigated complexes were higher than those of both the host and the guest compounds. The decomposition of the complexes begins immediately after their melting is completed, while the benzylammonium perchlorate, (*R*)- phenylethylammonium perchlorate salts and the crown ether ligands are thermally stable by 50 to 100 K above their melting points. During the decomposition of the salts and the four complexes strong exothermic processes can be observed which are due to oxidative reactions of the perchlorate anion. Ammonium perchlorate crystals were identified among the decomposition residues of the perchlorate salts with X-ray powder diffraction and DSC.

Beyond the above stated conclusions the lesson learned from this study is that each of the compounds needs to be individually analysed since polymorphism, solvate formation and decomposition processes are likely to occur.

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References

1 L. F. Lindoy, The chemistry of ligand complexes; Cambridge University Press 1989. Cambridge, Great Britain

2 J. W. Steed and J. L. Atwood, Supramolecular Chemistry; John Wiley & Sons Ltd. 2000. Chichester, England

3 Z. Köntös, P. Huszthy, J. S. Bradshaw and R. M. Izatt, Tetrahedron Asymmetry, 10 (1999) 2087.

4 T. Gérczei, Zs. Böcskei, Gy. Keserű, E. Samu and P. Huszthy, Tetrahedron Asymmetry, 10 (1999) 1995.

5 M. Józwiak and H. Piekarski, J. Therm. Anal. Cal., 69 (2002) 291.

6 A. G. Keenan and R. F. Siegmund, Quart. Rev. Chem. Soc., 23 (1969) 430.

7 P. W. M. Jacobs and H. M. Whitehead, Chem. Rev., 69 (1969) 551.

8 P. R. Nambiar, V. R. Pai Verneker and S. R. Jain, J. Thermal Anal., 8 (1975) 15.

9 T. K. Thomas and U. S. Nandi, J. Thermal Anal., 18 (1980) 21.

10 P. R. Nambiar and P. R. Pai Verneker, J. Thermal Anal., 7 (1975) 587.

11 H. Braekken and H. Harang, Z. Krist., 75 (1930) 538.

12 V. R. Pai Verneker and K. Rajeshwar, Thermochim. Acta, 13 (1975) 305.

13 M. Stammler, R. Bruener, W. Schmidt and D. Orcutt, Adv. X-Ray Anal., 9 (1966) 170.

14 S. Jurga and H. W. Spiess, Ber. Bunsenges Phys. Chem., 89 (1985) 763.

15 S. Jurga, Phys. Stat. Sol. (A), 81 (1984) 77.

16 S. Jurga, J. Seigler, R. Blinc and H. W. Spiess, Phys. Lett. (A), 116 (1986) 295.

17 J. Gelencsér, N. Báthori, M. Czugler, P. Huszthy and M. Nógrádi, Tetrahedron Asymmetry, 14 (2003) 2803.

18 P. Huszthy, E. Samu, B. Vermes, G. Mezey-Vándor, M. Nógrádi, J. S. Bradshaw and R. M. Izatt, Tetrahedron, 55 (1999) 1491.

19 J. S. Bradshaw, Y. Nakatsuji, P. Huszthy, B. E. Wilson, N. K. Dalley and R. M. Izatt, J. Heterocycl. Chem., 23 (1986) 353.

20 J. S. Bradshaw, P. Huszthy, H. Koyama, S. G. Wood, S. A. Strobel, R. B. Davidson, R. M. Izatt, N. K. Dalley, J. D. Lamb and J. J. Christensen, J. Heterocycl. Chem., 23 (1986) 1837.