ELSEVIER

Journal of Molecular Structure 526 (2000) 159–163

Journal of
MOLECULAR
STRUCTURE

www.elsevier.nl/locate/molstruc

Studies of reaction heats and structures of complexes formed between macro compounds and $SbCl_5$ in CCl_4

G. Schroeder[a], B. Gierczyk[a], V. Rybachenko[b], B. Brzezinski[a,*]

[a]*Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*
[b]*Institute of Physical Organic and Coal Chemistry, National Academy of Sciences, R. Luxemburg 70, 340114 Donetsk, Ukraine*

Received 14 January 2000; accepted 11 February 2000

Abstract

The heats of reactions between the acyclic and cyclic macro-compounds are determined. The values can be used as a measure of the donor abilities of the macro ligands. Formation of two types of complexes between the macro compounds and $SbCl_5$ is established. The acyclic macro-compounds form 1:1 complexes, whereas the macrocyclic compounds only 1:2 complexes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Reaction heat; Supramolecular chemistry; Macrocyclic compounds; Tris(oxaalkyl)-phosphates; Tris(oxaalkyl)-phosphines; Tris(oxaalkyl)-silanes; $SbCl_5$

1. Introduction

Recently, we have studied the complexation of some acyclic macro-compounds as well as crown ethers with protons and cations such as Li^+, Na^+ and K^+, by spectroscopic methods [1–9]. These studies have demonstrated that within the complexes all the cations fluctuate in multi-minima potentials showing the so-called proton and cation polarisabilities due to these fluctuations [10–14].

It is well known that the enthalpy of the interaction between $SbCl_5$ (Lewis acid) electron donors (solvents or atoms including free electron pair) makes the scale of Gutmann's Donor Numbers, DN [15,16]. The scale is supplemented by the data obtained from ^{13}C NMR and the ionisation of the PhC–Cl bond in the measured solvent.

In this paper formation and structures of the complexes of some cyclic and acyclic macro-compounds with $SbCl_5$ are studied by the calorimetric titration in the aprotic solvent, CCl_4.

2. Experimental

Crown ethers and tris(3,6-diazaheptyl)amine were used as commercial products (Aldrich). The esters of inorganic acids: $P(OR)_3$ and $OP(OR)_3$ were prepared according to previously described procedures [17].

2.1. Synthesis of phenyl-tris(oxaalkyl)silanes

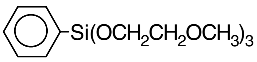
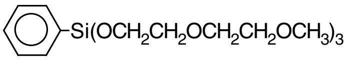
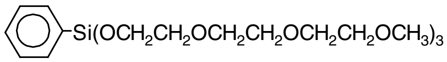
Phenyl-tris(oxaalkyl)silanes were obtained in reactions of phenyltrichlorosilane with a corresponding poly(ethylene glycol) monomethyl ether. To a solution of poly(ethylene glycol) monomethyl ether (0.25 mol) in ethyl ether (100 cm^3) cooled to 0°C, phenyltrichlorosilane (0.08 mol) was added

---

[*] Corresponding author. Tel.: + 48-61-869-9181; fax: + 48-61-865-8008.
E-mail address: bbrzez@main.amu.edu.pl (B. Brzezinski).

PII: S0022-2860(00)00464-6

Table 1
Boiling points and yields of phenyl-tris(oxaalkyl)silanes

Compound	Boiling point (°C/mmHg)	Yield (%)
 $C_6H_5-Si(OCH_2CH_2OCH_3)_3$	181–183/1.2	92
 $C_6H_5-Si(OCH_2CH_2OCH_2CH_2OCH_3)_3$	245–247/1.1	90
 $C_6H_5-Si(OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3)_3$	255–258/0.2	85

dropwise over 2 h under continuous stirring. The solvent was removed on a rotary evaporator. The products were purified by vacuum distillation and their purity was controlled by GC and NMR techniques. The boiling points and yields are given in Table 1.

2.2. Calorimetric measurements

The reaction heats were determined following the procedure given in Refs. [18,19] by the titration of macro-compounds with $SbCl_5$, both dissolved in CCl_4.

3. Results and discussion

The dependencies of the observed enthalpy on C_{SbCl_5}/C_{ligand} or C_{ligand}/C_{SbCl_5} for two examples of the acyclic and cyclic macro-compounds (two types of ligands) are shown in Fig. 1a and b, respectively. Fig. 1a shows that in the case of acyclic macro-compounds

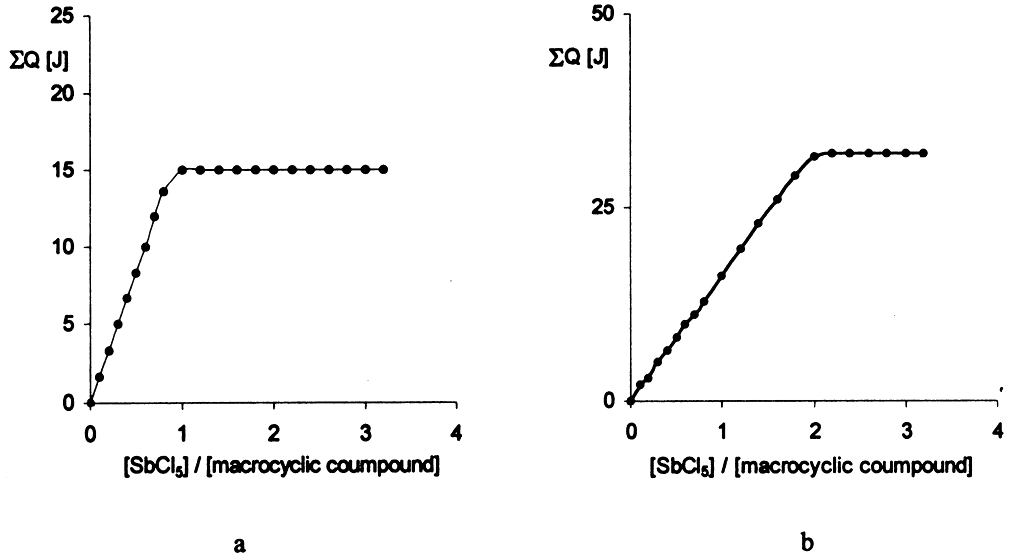
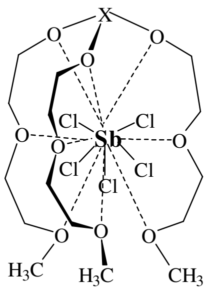
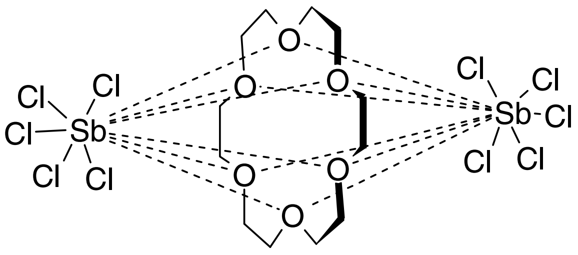


Fig. 1. Calorimetric titration curves for: (a) $PhSi(OCH_2CH_2OCH_3)_3$ (2×10^{-3} M) by $SbC1_5$ in $CC1_4$; (b) cyclamene (2×10^{-3} M) by $SbC1_5$ in $CC1_4$.



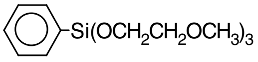
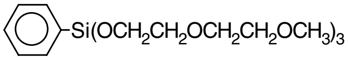
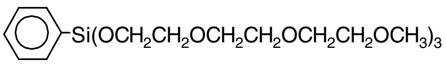
1:1 COMPLEX (X= P, O=P, Si or N)



1:2 COMPLEX

Scheme 1.

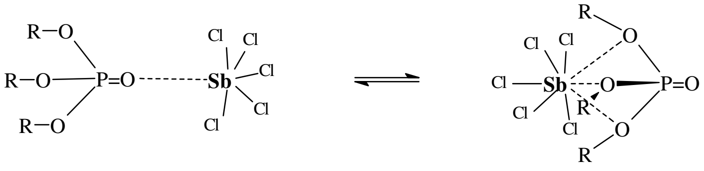
Table 2
Heats of interactions of macro-compounds with $SbCl_5$ in CCl_4-solution (1:1 complexes)

Macro-compounds	$-\Delta H$ (kJ mol^{-1})
$P(OC_2H_5)_3$	108 ± 5
$P[OCH_2CH_2OCH_3]_3$	188 ± 4
$P[OCH_2CH_2OCH_2CH_2OCH_3]_3$	265 ± 9
$O{=}P(OC_2H_5)_3$	102 ± 5
$O{=}P[OCH_2CH_2OCH_3]_3$	118 ± 7
$O{=}P[O{-}(CH_2CH_2O)_7CH_3]_3$	132 ± 9
$O{=}P[O{-}(CH_2CH_2O)_{12}CH_3]_3$	143 ± 16
	181 ± 6
	268 ± 15
	356 ± 16
$N(CH_2CH_2OCH_2CH_2OCH_3)_3$	360 ± 20

only 1:1 complexes with $SbCl_5$ are formed. In the case of cyclic macro-compounds only 1:2 complexes ($Cl_5Sb \leftarrow Donor \rightarrow SbCl_5$) are formed (Fig. 1b). The structures of these two types of complexes are shown in Scheme 1.

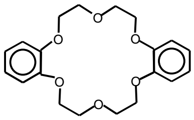
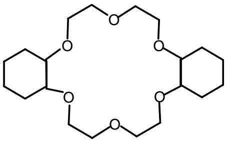
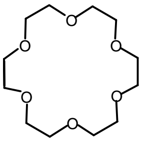
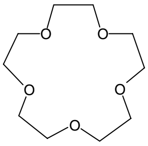
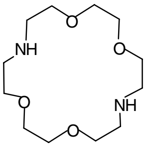
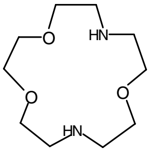
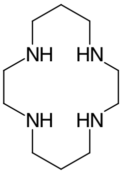
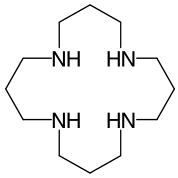
The heats of the reactions between acyclic and cyclic ligands with $SbCl_5$ are summarised in Tables 2 and 3, respectively.

Table 2 shows three families of ligands: tris(oxaalkyl)phosphines, tris(oxaalkyl)phosphates and tris(oxaalkyl)silanes. In each family, ΔH values increase with increasing chain length of oxaalkyl groups. Furthermore, for two types of ligands, i.e. tris(oxaalkyl)phosphines and tris(oxaalkyl)silanes, the ΔH values are comparable for the chains of comparable lengths. The results indicate that the lengths of oxaalkyl chains determine the complex formation between them and $SbCl_5$. Completely different ΔH values were observed in the complexation reaction of tris(oxaalkyl)phosphates by $SbCl_5$. These values are much lower and the increase of ΔH with increasing lengths of the chains is also much lower, indicating the existence of an equilibrium in which not only the chains, but also the P=O bonds are ligands for the $SbCl_5$ molecule (Scheme 2 (the equilibrium in 1:1 complexes formed



Scheme 2.

Table 3
Heats of interactions of macrocyclic compounds with $SbCl_5$ in CCl_4 solution (1:2 complexes)

Macrocyclic compound	$-\Delta H$ (kJ mol^{-1})	Macrocyclic compound	$-\Delta H$ (kJ mol^{-1})
	232 ± 6		240 ± 10
	257 ± 10		278 ± 10
	405 ± 10		410 ± 15
	384 ± 14		336 ± 10

between tris(oxaalkyl)phosphates and $SbCl_5$ molecules)). The same is true in the case of cryptands.

Table 3 demonstrates that in the case of macrocyclic compounds including only five or six oxygen atoms, the ΔH values of the formation of 1:2 complexes with $SbCl_5$ molecules are comparable. Thus, the number of the oxygen atoms does not play an important role in the complexation.

In conclusion this paper is the first to report the donor numbers of acyclic and cyclic macrocompounds.

Acknowledgements

The authors kindly acknowledge the financial support of the State Committee for Scientific Research KBN, grant 3 TO9A 03413. Prof V.I. Rybachenko also thanks the financial support of the J. Mianowski Fund for Science Development in Poland.

References

[1] J. Olejnik, B. Brzezinski, G. Zundel, J. Mol. Struct. 271 (1992) 157.
[2] B. Brzezinski, G. Zundel, J. Olejnik, J. Mol. Struct. 300 (1993) 573.
[3] B. Brzezinski, G. Schroeder, A. Rabold, G. Zundel, J. Phys. Chem. 99 (1995) 8519.
[4] B. Brzezinski, G. Schroeder, J. Mol. Struct. 441 (1998) 43.
[5] B. Brzezinski, G. Zundel, J. Phys. Chem. 98 (1994) 2271.
[6] B. Brzezinski, G. Zundel, J. Chem. Soc. Faraday Trans. I 81 (1985) 2375.
[7] F. Bartl, B. Brzezinski, B. Rózalski, G. Zundel, J. Phys. Chem. 102 (1998) 5234.

[8] B. Brzezinski, F. Bartl, G. Zundel, J. Phys. Chem. 101 (1997) 5607.

[9] G. Schroeder, B. Leska, B. Gierczyk, K. Eitner, G. Wojciechowski, B. Rózalski, F. Bartl, B. Brzezinski, J. Mol. Struct. 508 (1999) 129.

[10] G. Zundel, in: P. Schuster, G. Zundel, C. Sandorfy (Eds.), The Hydrogen Bond—Recent Development in the Theory and Experiments, vol. II, North Holland, Amsterdam, 1976, p. 15 (chap. 15).

[11] G. Zundel, in: A. Müller, H. Ratajczak, W. Junge, E. Diemann (Eds.), Electron and Proton Transfer in Chemistry and Biology, Elsevier, Amsterdam, 1992, pp. 313–327.

[12] G. Zundel, Edv. Chem. Phys. (2000) (in press).

[13] M. Eckert, G. Zundel, J. Mol. Struct. 181 (1988) 141.

[14] D. Borgis, G. Tarjus, H. Azzouz, J. Chem. Phys. 97 (1992) 1390.

[15] V. Gutmann, The Donor–Acceptor Approach to Molecular Interactions, Plenum, New York, 1978.

[16] V. Gutmann, Electrochim. Acta 21 (1976) 661.

[17] G. Schroeder, B. Gierczyk, B. Leska, J. Includ. Chem. 35 (1999) 327.

[18] V.I. Rybachenko, G. Schroeder, E.B. Titow, Żurnal Ob.Chem. 66 (1996) 1007.

[19] V.I. Rybachenko, E.B. Titow, Żurnal Fiz. Chem. 77 (1997) 248.