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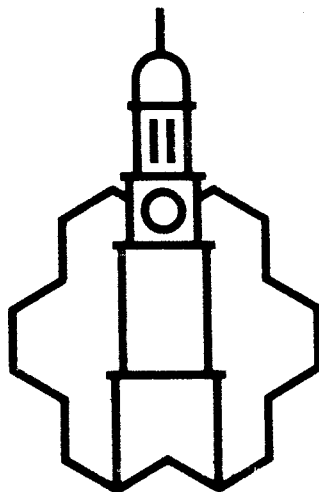


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V. P. Solovyov, N. N. Strakhova, O. A. Raevsky

Institute of Physiologically Active Compounds, Acad. Sci. USSR,
Chernogolovka, 142432CALORIMETRIC AND IR SPECTROSCOPIC STUDY OF THE INTERACTION
IN CH_3CN OF BENZO-CROWN-ETHERS WITH NH_4NCS , LiNCS , KNCS , NaNCS
AND $\text{Ca}(\text{NCS})_2$ SALTS.

Stoichiometry of complexes and $\log \beta_i$, ΔH_i , and ΔS_i ($i=1,2$) values for the interaction of the benzo-crown-ethers and its derivatives



with NH_4NCS , LiNCS , KNCS , NaNCS and $\text{Ca}(\text{NCS})_2$ salts in acetonitrile at 293K were determined by a calorimetric titration and IR spectrophotometry technique.

The number of complexes in solution, their stoichiometry, stability constants $\log \beta_i$, enthalpies ΔH_i , and entropies ΔS_i were determined. For a study of solution equilibria the computer programs using some statistical tools for reliability of designing the best equilibrium model of the systems were written.

The calculated thermodynamic values is surveyed in Table.

The influences of macrocyclic ring size, functionality of the groups R (Ac - acetyl, PhCO - benzoyl), and some physical properties of cations and ligands on complex formation are discussed.

Table *).

Ligand	Salt	Method	$\log \beta_i$	ΔH_i	ΔS_i
B18C6	LiNCS	Cal	1.8 (1)	5.5	53
	NaNCS	Cal	4.71 (1)	-17.2	32
	KNCS	Cal	4.75 (1)	-22.2	15
	$\text{Ca}(\text{NCS})_2$	Cal	<5.2 (1)	-18.1	<38
	NH_4NCS	Cal	4.07 (1)	-18.5	16
B15C5	LiNCS	Cal	3.20 (1)	-17.5	3
	NaNCS	Cal	4.02 (1)	-23.5	-2
	KNCS	Cal	3.58 (1)	-25.5	-17
			6.35 (2)	-53.2	-57

	NH ₄ NCS	Cal	2.16 (1)	-19.2	23
			4.13 (2)	-58.2	-116
	Ca(NCS) ₂	Cal	4.20 (1)	-26.5	-8
			5.80 (2)	-13.5	66
AcB15C5	NaNCS	Cal	3.72 (1)	-20.1	4
	KNCS	Cal	2.86 (1)	-22.5	-21
			5.82 (2)	-53.8	-69
	NH ₄ NCS	Cal	2.14 (1)	-21.6	31
			4.58 (2)	-15.0	-63
	Ca(NCS) ₂	Cal	3.90 (1)	-21.0	2
PhCOB15C5	NaNCS	Cal	3.60 (1)	-20.4	1
	KNCS	Cal	3.32 (1)	-23.6	-16
			5.98 (2)	-51.6	-59
	NH ₄ NCS	Cal	2.07 (1)	-22.6	35
			4.35 (2)	-45.2	-68
	Ca(NCS) ₂	Cal	3.90 (1)	-21.0	2
B12C4	LiNCS	Cal	1.05 (1)	-18.6	-42
			2.80 (2)	-2.2	46
	NaNCS	Cal	1.88 (1)	-17.8	-24
			4.50 (2)	-37.6	-40
	NaNCS	IR	1.65 (1)	-	-
			4.93 (2)	-	-
	KNCS	Cal	1.76 (1)	-13.1	-27
			2.84 (2)	-29.8	-46
	NH ₄ NCS	Cal	1.60 (1)	-10.4	-4
			3.15 (2)	-12.4	19
	NH ₄ NCS	IR	1.51 (1)	-	-
			3.14 (2)	-	-
	Ca(NCS) ₂	Cal	3.23 (1)	-22.6	-14
			4.78 (2)	-25.6	6
	Ca(NCS) ₂	IR	2.80 (1)	-	-
			4.76 (2)	-	-
AcB12C4	NaNCS	Cal	1.7 (1)	-13	-28
			3.57 (2)	-45	-83
	Ca(NCS) ₂	Cal	2.18 (1)	-29.4	-57

*) Thermodynamic values given for reactions $M + L \rightleftharpoons ML$ (1), and $M + 2L \rightleftharpoons ML_2$ (2).

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