Ion–Molecule Reactions of Thiourea Macrocyclic Derivatives with Ions of Acetylacetonates of some Rare-Earth Elements in Gaseous Phase

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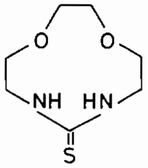
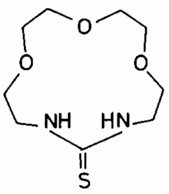
Various cations are easily included into the coordination sphere of the cyclic polyethers [1]. In some cases macroheterocyclic derivatives containing nitrogen atoms along with oxygen atoms in the cycle may be the effective complexing agents [2].

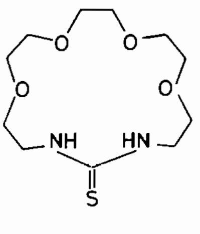
Mass-spectral data on chelation in the gaseous phase may be used for testing the possibility of macrocyclic molecules for cation extraction. Earlier [3] we registered 1:1 complexes of crown ethers with ions containing thallium atoms, which were close analogues of the corresponding particles in the condensed phase. In the present paper, in order to investigate their chelating ability, the ion–molecule reactions of macrocyclic derivatives of thiourea (L^1–L^4) with charged products of destruction under electron impact of acetylacetonates of the rare-earth elements $(acac)_3M$, where M = La, Pr, Nd, Sm and Yb, were studied.



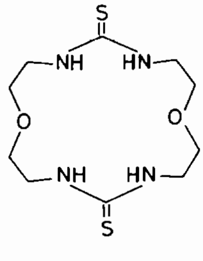
L^1



L^2



L^3



L^4

Mass-spectra data for trisacetylacetonates of La and Nd are in good agreement with the literature [4, 5]. Mass-spectra of these compounds as well as those of Pr, Sm, and Yb complexes are shown in Table I.

Relative intensities of peaks of significant ions in the case of M = Pr are close to those in the spectra of La and Nd.

In the case of heavier elements the decrease in contribution of acac MOH^+, $[(acac-H)M]^+$ and MO^+ ions is observed. At the same time, intensities of peaks at $acacM^+$ and MOH^+ ions containing M atoms in oxidation state +2 increase considerably. Besides molecular ions $(acac)_3M^+$ and the products of their intramolecular fragmentation, there are at pressures above 10^{-4} torr cluster ions of general formula $(acac)_nM_2$ (where n = 3–5). The formation of these ions is the result of ion-molecular reactions of neutral complex molecules with positively charged fragments containing atoms of rare-earth elements [6, 7].

In the mass spectra obtained during the simultaneous evaporation of trisacetylacetonate complexes and organic ligand molecules (L) into the ion source of the mass-spectrometer, all studied ions, as well as ions corresponding to macrocyclic molecular ions and the products of their destruction, are present.

In addition, in the combined mass-spectra there are some peaks that are not in the spectra of the components. Mass numbers and isotope relations of these ions correspond to $[(acac)_2ML]^+$ and $[(acac)ML-H]^+$ compositions where L is the neutral molecule of the macrocycle. At simultaneous evaporations of $(acac)_3Nd$ with L^3 and L^4 the formation of $[(acac)NdL^3-H]^+$ (m/z 518) and $[(acac)NdL^4-H]^+$ (m/z 532) was observed. The formation of these ions may be the result of the corresponding ion-reagent addition to neutral macrocyclic molecules. Apparently, such a mechanism takes place in the case of $(acac)_2M^+$ ions:

$$(acac)_2M^+ + L \longrightarrow [(acac)_2ML]^+$$

It might be suggested that the reaction of the $(acac-H)M^+$ addition to L results in the $[(acac)ML-H]^+$ ion formation. In order to clarify the possible mechanism of formation of these ions we have obtained low energy (12eV) mass-spectra of trisacetylacetonates and their mixtures with macrocyclic ligands. Low energy spectra contain as a rule only molecular and $(acac)_2M^+$ ions (Table I). Nevertheless the formation of $[(acac)ML-H]^+$ ions also occurs in these conditions. Hence, these ions are the products of the following reaction:

$$(acac)_2M^+ + L \longrightarrow [(acac)ML-H]^+ + Hacac$$

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TABLE I. Monoisotopic Mass Spectra[a] of Rare Earth Trisacetylacetonates, $(acac)_3M$, and Products of Ion–Molecule Reactions[b] with Macrocyclic Thiourea Derivatives L^1 and L^2 [c].

M	La		Pr		Nd		Sm		Yb	
Ion	m/z	int.	m/z	int.	m/z	int.	m/z	int.	m/z	int.
$(acac)_3M^+$	436	17	438	8 (50)	439	11 (40)	449	10 (53)	471	18 (64)
$(acac)_2M^+$	337	55	339	44 (48)	340	45 (51)	350	54 (46)	372	55 (25)
$[(acac)_2M - H]^+$	336	5	338	5 (2)	339	6 (8)	349	1 (–)	371	1 (–)
$[(acac)_2M - H_2O]^+$	319	1	321	1	322	2	332	1	354	2
$acacMOH^+$	255	15	257	16	258	14	268	8	290	4
$acacM^+$	238	2	240	3	241	4	251	10	273	16 (2)
$[acacM-H]^+$	237	4	239	7	240	7	250	6	272	3
MOH^+	156		158		159		169	7	191	4
MO^+	155	5	157	16	158	12	168	3	190	
$(acac)_2M^+L^1$	527	25	529	95	530	75	540			d
$[(acac)ML^1 - H]^+$	427	100	429	100 d	430	100 d	440	100 d		
$(acac)_2M^+L^2$	d		573	10 (30)	574	d (10)	584	(10)	606	8 (10)
$[(acac)ML_2 - H]^+$			473	100 (100)	474	(100)	484	100 (100)	506	100 (100)

[a] m/z Values are given for isotopes ^{139}La, ^{141}Pr, ^{142}Nd, ^{152}Sm, ^{174}Yb. Intensities are expressed as percentages of the total intensity of the metal-containing ions peaks. Data on low energy (12eV) mass spectra are given in brackets. [b] Intensities of ion-molecule reaction products are given as the % of the most intensive products, their intensities being less than 1% of the $(acac)_2M^+$ ions intensity. [c] The experiment was not carried out.

Oxidation state +3 is the most characteristic of rare earth elements, the complexes of which are studied in the present paper. According to the conception of valency change [4] significant ions such as $(acac)_2M^+$ and $(acac - H)M^+$ in mass spectra of $(acac)_3M$ contain lanthanide atoms in the $M(III)^+$ form. As only these particles form complexes with macrocyclic derivatives (L^1–L^4) it may be suggested that the necessary conditions for forming a stable complex in the gaseous phase is the presence of a positively charged lanthanide atom in stable oxidation state +3. In the case of iron trisacetylacetonate $(acac)_2Fe^+L^2$ (m/z 488) and $[(acac)FeL^2 - H]^+$ (m/z 388) ions, where the atom of transition metal is in oxidation form +3, and ions $[(acac)FeL^2]^+$ (m/z 389) containing Fe atoms in stable oxidative state +2 are present. This observation is also in good agreement with data for formation of crown ether complex with thallium containing ions in the gaseous phase [3].

Thus, the present results confirm our suggestion on the formation of complexes of some thiourea macrocyclic derivatives with ions containing rare earth atoms. The presence of metal atoms in stable oxidation state +3 is necessary for the formation of such particles in the gaseous phase.

Experimental

Thiourea macrocyclic derivatives were synthesized according to [8]. Mass-spectra were obtained on Varian MAT 112 and AEI-MS-30 instruments with electron energy 70 and 12 eV. Ion-molecule reactions were carried out with sample evaporation from one (MS-30) and two (MAT 112) direct inlet systems. Monoisotopic spectra were calculated using the 'Aelita' programme [9].

References

1 J.-M. Lehn, *Struct. Bonding* (Berlin), *16*, 1 (1973).
2 T. I. Kirichenko, A. V. Bogatsky and N. G. Lukyanenko, *Dokl. Acad. Nauk SSSR*, *255*, 340 (1980).
3 A. A. Koridze, D. V. Zagorevskii and Yu. S. Nekrasov, *Izv. Acad. Nauk SSSR, Ser. Chim.*, 1921 (1982).
4 S. M. Schildcrout, *J. Phys. Chem.*, *80*, 2834 (1976).
5 S. M. Schildcrout, R. E. Sievers and R. W. Moshier, *J. Am. Chem. Soc.*, *90*, 4006 (1968).
6 C. G. Macdonald and J. S. Shannon, *Aust. J. Chem.*, *19*, 1545 (1966).
7 N. V. Zakurin, Yu. S. Nekrasov, M. D. Reshetova and A. Yu. Vasil'kov, *Inorg. Chim. Acta*, *76*, L161 (1983).
8 A. V. Bogatsky, N. G. Lukyanenko and T. I. Kirichenko, *Zh. Organ. Chim.* (SSSR), *16*, 1301 (1980).
9 Yu. N. Sukharev and Yu. S. Nekrasov, *Org. Mass Spectrom.*, *11*, 1232 (1976).