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Article



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RESEARCH OF COORDINATION COMPOUNDS OF STRONTIUM NITRATE WITH A MIXED LIGAND

Abstract: Mixed-amide coordination compounds of strontium nitrate with thiocarbamide, acetamide, acetodiphenylamide, benzamide, and carbamide have been synthesized. The composition, identity, methods of coordination of the nitrate fragment, amide molecules were established, and the thermal behavior of the resulting coordination compounds was studied.

Key words: coordination compounds, synthesis, composition, physicochemical methods of analysis, IR absorption spectra, X-ray phase analysis.

Language: English

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Introduction

In modern coordination chemistry, in the section of solid state chemistry, metal complexes containing various N,O donor centers in the ligand environment occupy a special place. [1, p. 11]. Interest in them is due to the fact that the study of such metal complexes is developing in connection with their use as molecular magnets, catalytic systems, components of optical recording media, etc. They are good models for studying the problem of competitive coordination in the chemistry of complex compounds due to the specific effect of their environment on stereochemistry of polyhedra. Complex compounds of metals, having a number of specific properties, have found wide practical use in many sectors of the national economy. [2, p.40-43; 3, p.376-377]. Of particular interest among such complexes are polyamide compounds of metals with amides, which are biologically active substances. The use of

substances containing donor atoms of amides of aliphatic acids as ligands, in particular carbamide, thiocarbamide, acetamide, acetodiphenylamide, benzamide, promote the formation of complex compounds containing macroelements. [4;7,p.19]. A technology for obtaining complex compounds of transition metal salts with organic ligands has been developed, and the processes of formation of coordination compounds in solutions and solid phases have been determined. [8, p.376-377; 9,p.64-65]. The physicochemical properties of the synthesized coordination compounds have been studied. Despite the extensive experimental material on the study of complexes of transition metal salts with amides, there were no materials on homogeneous and mixed-ligand coordination compounds of alkaline earth metal nitrates with amides. Because, transition metals are considered as typical complexing agents, while

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alkaline earth metals are considered as substances difficult to form complex metals.

Material and methods.

To carry out the synthesis of coordination compounds, we have chosen the most efficient mechanochemical method, since it does not require scarce organic solvents and allows us to synthesize complexes of various compositions in high yield. The mechanochemical process of the interaction of metal nitrates and ligand molecules (urea, thiocarbamide, acetamide and acetodiphenylamide) is carried out by intensive grinding at room temperature in a ball mill of components taken in molar ratios of strontium nitrates and amides 1:1:1, respectively. This process was repeated 12 times. Molecules of carbamide (K), thiocarbamide (TK), acetamide (AA), acetodiphenylamide (ADP), benzamide (BA), and nitrate anion (NO₃) contain donor atoms and promote the formation of coordination compounds with metal ions. In [9,p.64-65; 11,p.199-200], coordination compounds of a number of metal nitrates with amides were synthesized and studied. In the literature, there is no information about polyamide coordination compounds of strontium nitrates. The synthesis was

carried out according to the procedure [12,p.489; 13,p.19].

Results and discussion

The complex of composition Sr(NO₃)₂·AA·BA·H₂O was synthesized by intensive stirring of 2.12 g (0.01 mol) Sr(NO₃)₂·1.1816 g (0.01 mol) acetamide and 1.21 g (0.01 mol) benzamide in a ball mill at room temperature for 0.15-0.20 hours. The product yield was 83.0%. 0.7628 g (0.01 mol) of thiocarbamide in a ball mill at room temperature for 0.15-0.20 hours. The product yield was 86.0%. 0.7628 g (0.01 mol) of thiocarbamide in a ball mill at room temperature for 0.15-0.20 hours. The product yield is 84.0%.

Analysis of the synthesized compounds for the content of magnesium and calcium was carried out according to [6,p.232;]. Nitrogen was determined by the Dumas method [12], carbon and hydrogen were determined by combustion in an oxygen stream (table. 1). To establish the individuality of the synthesized compounds, X-ray diffraction patterns were taken on a DRON-2.0 setup with a Cu anticathode [13,p.19;]. IR absorption spectra were recorded on spectrophotometers, IRTracer-100 from Shimadzu. IRTracer-100 (400-4000 cm⁻¹)

Table 1. Results of elemental analysis of mixed-amide coordination compounds of strontium nitrate

Compounds	Me, %		N, %		S, %		C, %		H, %		Empirical formula
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	
Sr(NO ₃) ₂ ·CH ₃ CONH ₂ ·C ₆ H ₅ CONH ₂ ·H ₂ O	21,3 4	21,4 6	13,4 7	13,6 6			26,1 4	26,3 4	3,3 3	3,4 1	SrN ₄ C ₉ H ₁₄ O ₉
Sr(NO ₃) ₂ ·CO(NH ₂) ₂ ·CS(NH ₂) ₂ ·H ₂ O	26,1 3	26,3 4	25,0 6	25,1 5	9,4 1	9,5 8	7,11 7	7,18 7	2,8 1	2,9 9	SrN ₆ C ₂ H ₁₀ S ₈ O ₈
Sr(NO ₃) ₂ ·CH ₃ CO(N C ₆ H ₅) ₂ CS(NH ₂) ₂ ·H ₂ O	17,5 1	17,6 3	16,7 2	16,8 3	6,3 2	6,4 1	35,9 7	36,0 7	3,7 3	3,8 1	SrN ₆ C ₁₅ H ₁₉ SO ₈

Frequencies were found in the IR absorption spectrum of a free urea molecule at 3443-ν_{as}(NH₂), 3347-ν_s(NH₂), 3255-2δ(NH₂), 1679-ν(CO), δ(NH₂), 1624-δ(NH₂), ν(CO), 1464-ν(CN), 1152-1057-ρ(NH₂), 1002-ν(CN), 789-δ(NH₂), 573-δ(NCO) and 559-δ(NCN). In the IR absorption spectrum of an uncoordinated thiocarbamide molecule, it has frequencies at 3380-ν_{as}(NH₂), 3276-ν_s(NH₂), 3178-2δ(NH₂), 1619-δ(NH₂), δ(HNC), 1474-ν(CN), 1413-ν(CS), 1084-ν(CN), 783-ρ(NH₂), 730-ν(CS), 631-δ(CS), δ(NCS), 487-δ(NCN) and 413-δ(NCS). In the IR absorption spectrum of AA, frequencies (cm⁻¹) were found at 3387-ν(NH₂), 3194-2δ(NH₂), 1670-ν(C=O), 1626-δ(NH₂), ν(CO), 1395-ν(CN), 1348-

δ(CH₃), 1154-ρ(NH₂), 1048-ρ(CH₃), 1005-ν(C-C), 875-ν(C-C), 582-δ(NCO) and 464-δ(CCN).

In the IR absorption spectrum of an uncoordinated benzamide (BA) molecule, frequencies were found at 3367-ν(NH₂), 3172-2δ(NH₂), 3059-ν(CH), 2885-ν(CH), 2779-ν(CH), 1955, 1893, 1810, 1659-ν(C=O), 1623-δ(NH₂), 1577-ν_K, 1450-ν_K, 1401-ν(CH), 1297, 1179, 1143-ν(NH₂), 1122, 1024, 918, 848, 812, 793, 685, 635, 529 and 411 cm⁻¹.

An analysis of the IR absorption spectra of non-coordinated molecules of urea, thiocarbamide, acetamide, acetadiphenylamide, benzamide, and their complex compounds with strontium nitrates showed that, with the transition to the coordinated state, the values of some frequencies of amide molecules

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change significantly. Due to the complexity of the IR absorption spectra of complex compounds of strontium nitrates with amides, we failed to attribute all the observed frequencies to the corresponding vibrations of the bond groups.

Comparison of IR absorption spectra of free molecules of carbamide and nitrocarbamide and complex compounds of compositions

$\text{Sr}(\text{NO}_3)_2 \cdot \text{CH}_3\text{CONH}_2 \cdot \text{C}_6\text{H}_5\text{CONH}_2 \cdot \text{H}_2\text{O}$
 $\text{Sr}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot \text{CS}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$
 $\text{Sr}(\text{NO}_3)_2 \cdot \text{CH}_3\text{CO}(\text{NC}_6\text{H}_5)_2 \cdot \text{CS}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ the coordination of carbamide and acetamide molecules through the oxygen atom of carbonyl groups was established (Fig 1,2,3).

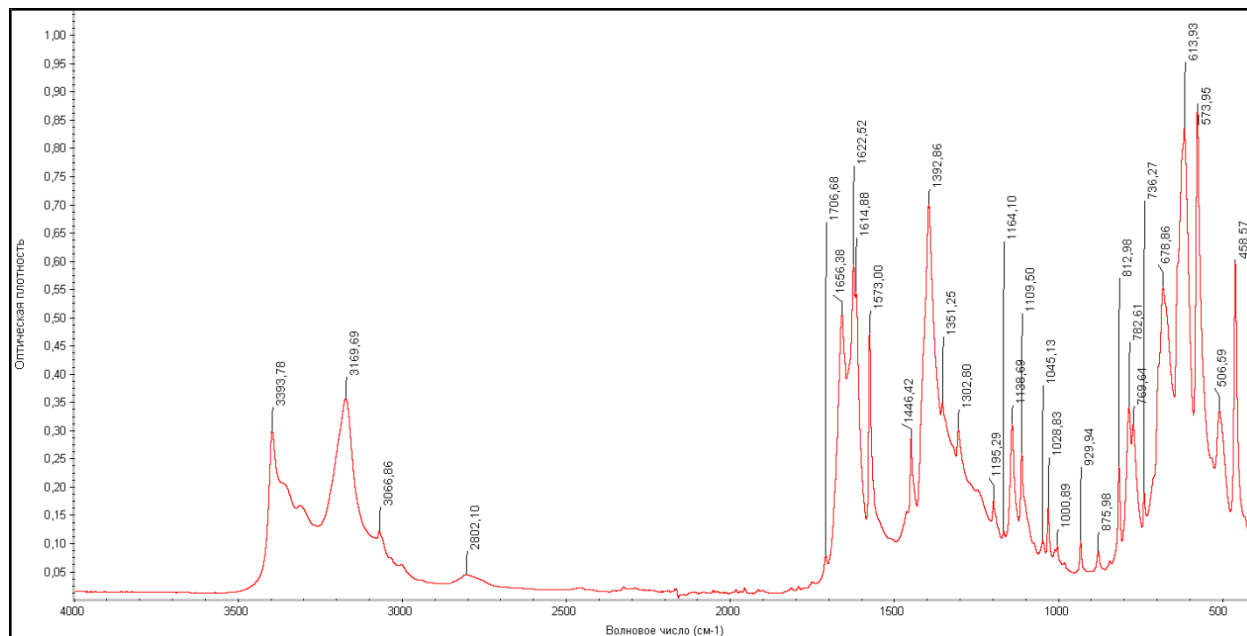


Fig. 1. IR-spectrum absorption mixed coordination compound nitrate strontium with acetamidom and benzamidom composition $\text{Sr}(\text{NO}_3)_2 \cdot \text{CH}_3\text{CONH}_2 \cdot \text{C}_6\text{H}_5\text{CONH}_2 \cdot \text{H}_2\text{O}$

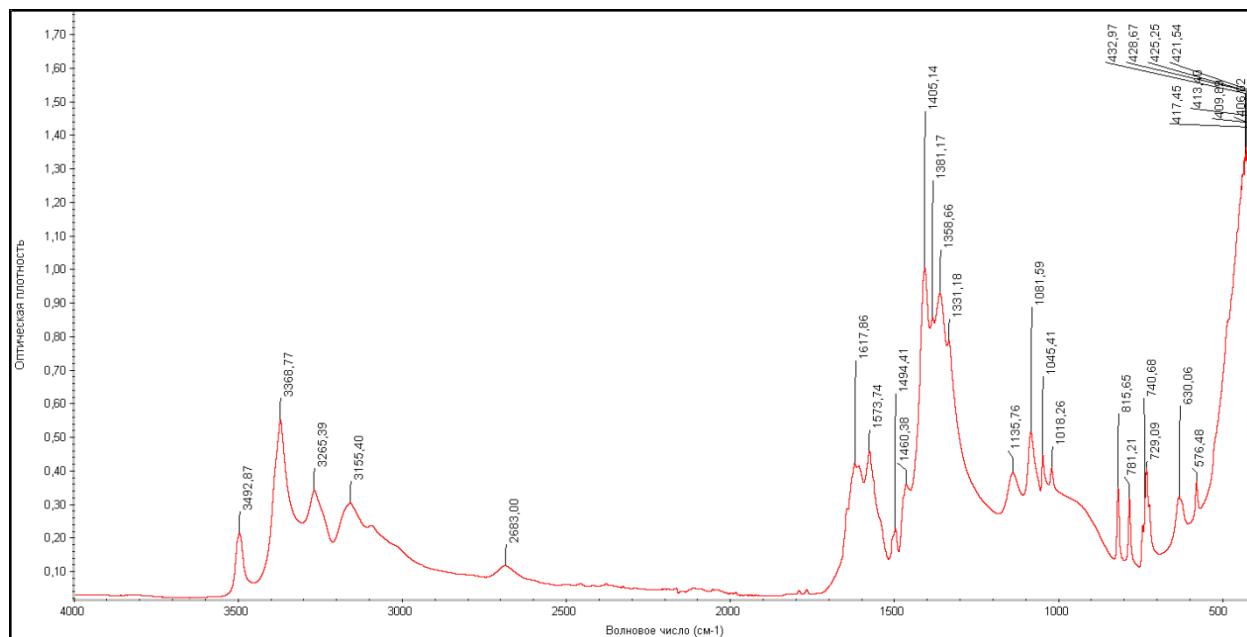


Fig.2. IR absorption spectrum of a mixed amide coordination compound of strontium nitrate with carbamide and thiocarbamide of the composition $\text{Sr}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot \text{CS}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$

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This is evidenced by a decrease in the frequency of the C=O bond by 17-48 cm⁻¹ and an increase in the frequency of the stretching vibration of the C-N bond by 7-20 cm⁻¹, respectively, in the cases of the coordinated state of carbamide and acetamide molecules. In the IR absorption spectra of the benzamide molecule, acetadiphenylamide, changes in

the characteristic frequencies are observed in the region of stretching vibrations of the C=O, C-N bond and ring vibrations. The observed changes in the characteristic bands indicate the coordination of organic molecules with strontium atoms through the oxygen atoms of carbonyl groups.

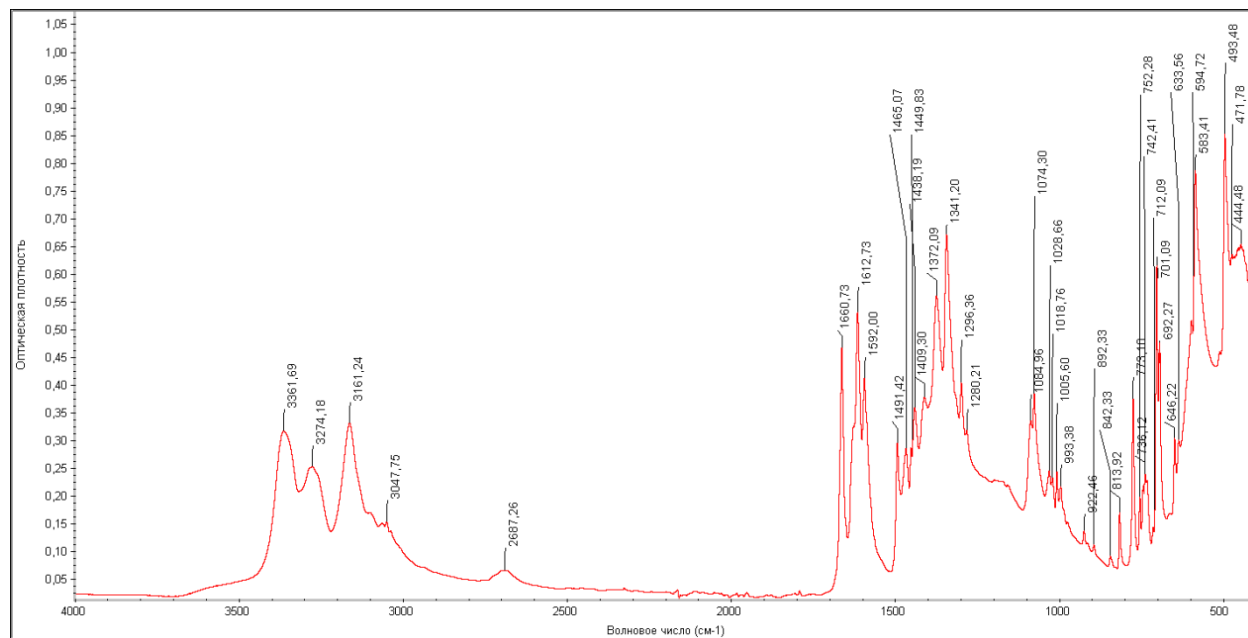


Fig.3. IR absorption spectrum of a mixed amide coordination compound of strontium nitrate with acetadiphenylamide and thiocarbamide of the composition $\text{Sr}(\text{NO}_3)_2 \cdot \text{CH}_3\text{CO}(\text{NC}_6\text{H}_5)_2\text{CS}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$

Comparison of interplanar distances and relative intensities of benzamide, acetamide, carbamide, thiocarbamide, acetadiphenylamide, nicotinamide and new complex compounds of strontium nitrates showed that they differ significantly from each other,

from similar ones and from the original compounds. Consequently, the synthesized coordination compounds have individual crystal lattices [83; c. 3-8, 84; c. 4-5, 85; c. 282-284, 86; c. 199-200] (table.2).

Table 2. Interplanar distances and relative intensities of the lines of the coordination compound of nitrate with amides

Compounds	d, Å	J, %	d, Å	J, %	d, Å	J, %	d, Å	J, %	d, Å	J, %
$\text{Sr}(\text{NO}_3)_2 \cdot \text{CH}_3\text{CONH}_2 \cdot \text{C}_6\text{H}_5\text{CONH}_2 \cdot \text{H}_2\text{O}$	6,21	24	3,39	33	2,77	17	2,11	19	1,621	14
	5,79	26	3,31	31	2,69	14	2,09	21	1,611	16
	5,26	28	3,28	100	2,65	16	2,02	14	1,590	14
	4,96	33	3,22	45	2,62	19	1,935	31	1,580	14
	4,80	28	3,09	26	2,59	21	1,907	12	1,556	14
	4,25	22	3,06	62	2,44	79	1,860	10	1,532	10
	4,17	14	3,00	24	2,34	21	1,789	14	1,460	14
	4,02	19	2,95	21	2,33	21	1,751	17	1,450	14
	3,75	19	2,89	21	2,25	22	1,699	14	1,413	12
	3,44	17	2,83	26	2,16	22	1,670	12	1,343	14
$\text{Sr}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot \text{CS}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$	6,79	27	4,20	41	2,57	35	2,09	35	1,595	16
	6,53	41	4,12	35	2,54	41	2,00	59	1,551	19
	5,96	68	3,92	19	2,47	41	1,943	35	1,542	22
	5,81	43	3,79	24	2,41	41	1,927	32	1,378	19

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Compounds	d, Å	J, %	d, Å	J, %	d, Å	J, %	d, Å	J, %	d, Å	J, %
	5,73	43	3,31	89	2,38	35	1,879	16	1,374	19
	5,52	49	3,04	100	2,33	27	1,860	19	1,344	16
	5,16	35	2,80	41	2,23	51	1,693	16	1,333	16
	4,96	54	2,73	24	2,17	41	1,653	19		
	4,86	54	2,66	24	2,13	22	1,639	19		
Sr(NO ₃) ₂ ·CH ₃ CO(N C ₆ H ₅) ₂ CS(NH ₂) ₂ ·H ₂ O	9,54	10	3,62	21	2,72	17	2,05	21	1,716	8
	9,18	11	3,41	27	2,69	17	2,01	6	1,657	10
	6,91	19	3,31	24	2,62	17	1,991	6	1,635	16
	6,53	17	3,24	100	2,58	12	1,938	5	1,551	6
	6,27	12	3,15	17	2,54	8	1,920	6	1,523	7
	4,88	83	3,07	37	2,48	7	1,882	7	1,483	5
	4,60	75	3,01	24	2,44	9	1,860	9	1,467	4
	4,25	9	2,91	12	2,38	17	1,816	8	1,385	6
	4,12	11	2,84	14	2,30	22	1,772	10	1,360	7
	4,02	18	2,80	12	2,20	14	1,759	7		
3,84	10	2,74	22	2,07	24	1,722	10			

Conclusion

Thus, on the basis of the studies carried out, it was established that the possibility of synthesizing mixed-ligand coordination compounds of strontium nitrate by a mechanochemical method was

established. The individuality of the synthesized compound was proved by physicochemical methods of analysis. The centers of coordination and the denticity of the acid residue are proven by IR spectroscopy data.

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