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X-Ray Phase and IR Spectroscopic Investigation of Homogeneous and Mixed Ligand Complex Compounds of Calcium Acetate

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Abstract: Homogeneous and mixed-ligand coordination compounds of calcium acetate with some amides have been synthesized. The composition, individuality, thermal behavior, methods of coordination of acetate groups and molecules of acetamide and nitrocarbamide have been established. The methods of coordination of organic ligands, the environment of the central ion, and the thermal behavior of the synthesized compounds have been proved by the methods of vibrational spectroscopy and thermal analysis. By comparing the interplanar distances and relative intensities of calcium acetate monohydrate and some amides, it is shown that the new coordination compounds differ from each other, as well as from the original components, therefore, the compounds have an individual crystal lattice.

Key words: synthesis, structure, X-ray phase analysis, IR spectral analysis, calcium acetate, formamide, acetamide, carbamide, tiocarbamide, nitrocarbamide, nicotineamide, benzoamide, nicotinic and benzoic acids.

In the world, with the development and expansion of agricultural industries, the requirements for chemical compounds that accelerate the growth of plants and increase their productivity are also increasing. Especially, one of the important tasks is to conduct targeted research on the synthesis of stimulants of complex action, and in this direction a lot of work has been done by leading scientists of the world, in particular, a lot of work has been carried out on the directed synthesis of metal complexes with a certain composition and structure to solve theoretical and practical problems of creating biologically active substances based on polydentate ligands and metal carboxylates.

In our Republic, in order to develop agricultural industries, much attention is paid to the production of new types of stimulants based on local raw materials that meet modern requirements. The Action Strategy for the Further Development of the Republic of Uzbekistan defines important tasks for “Deepening reforms and dynamic development of agricultural production, further strengthening the country’s food security, developing the production of environmentally friendly products, and significantly increasing the export potential of the agricultural sector”. In this area, based on local raw materials, the creation of environmentally friendly polyfunctional cheap drugs of a new type that increase the yield of agricultural crops, accelerate their growth and reduce water losses, is of great importance.

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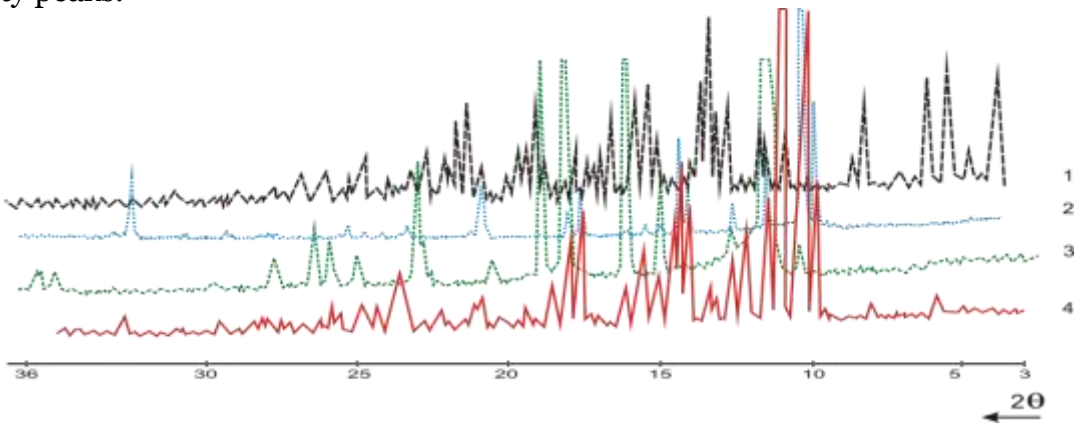
Analysis of scientific sources showed that despite the extensive experimental material on the study of complexes of metal carboxylates with amides, there is no information on determining the "composition-structure-property" relationship of coordination compounds of mixed-ligand calcium acetate and the patterns of their preparation and their application in practice .

Therefore, homogeneous and mixed-ligand complex compounds are individual chemical substances. By a similar comparison of the interplanar distances of the initial components and complex metal compounds, the synthesized compounds were identified. At the same time, peaks with an intensity of no more than 15% predominate in the diffraction patterns, which is evidence that the crystal lattices of the synthesized compounds are not completely formed. This is explained by the fact that during mechanochemical synthesis, the crystal lattice is destroyed and defects appear, which will act as reaction centers. As a result, the diffraction patterns are dominated by low-intensity peaks.



Drawing 1. Radiographs: 1-$CS(NH_2)_2$; 2-$CO(NH_2)_2$; 3-$Ca(CH_3COO)_2 \cdot H_2O$ и 4-$Ca(CH_3COO)_2 \cdot CO(NH_2)_2 \cdot CS(NH)_2 \cdot 0{,}5H_2O$

An analysis of the IR absorption spectra of non-coordinated molecules of formamide, acetamide, carbamide, thiocarbamide, nitrocarbamide, nicotinamide, benzamide, nicotinic and benzoic acid and their complexes with calcium acetate showed that with the transition to coordinated positions, the values of some frequencies of amide molecules change significantly. Due to the complexity of the IR absorption spectra of the complexes of the selected metals with amides, we were unable to attribute all the observed frequencies to the corresponding vibrations of the bond groups.

The IR absorption spectra of free molecules of formamide, acetamide, carbamide, thiocarbamide, nitrocarbamide, nicotinamide, benzamide, nicotinic and benzoic acid and their homogeneous and mixed-ligand coordination compounds with calcium acetate are presented. Table 1 shows the values of the characteristic frequencies (cm^{-1}) of some of the above compounds.

The IR absorption spectrum of a free formamide molecule is characterized by bands (sm^{-1}) at 3390, 3317 - ν (NH2), 3194- 2δ (NH2), 2888- ν (CH), 1709- ν (CO), 1615 - δ (NH2), 1391- δ (CH), 1316- ν (CN), 1052- r (NH2), 604- δ (OCN) [1].

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Table 1
Values of characteristic frequencies (cm^{-1}) in IR absorption spectra of free and coordinated molecules

Compound	ν(C=O)	ν(C=N)	ν(CS), δ(CS)	ν_k, δ(C=O)
$Ca(CH_3COO)_2•2HCONH_2•H_2O$	1692	1348		
$Ca(CH_3COO)_2•4HCONH_2•2,5H_2O$	1694	1389		
$Ca(CH_3COO)_2•4CO(NH_2)_2•0,5H_2O$	1678, 1634	1475, 1461		
$Ca(CH_3COO)_2•2\ CS(NH_2)_2$			725, 621	
$Ca(CH_3COO)_2•4NC_4H_5COOH$	1705			1606, 1031, 747

In the IR absorption spectrum of the free formamide molecule, two frequencies at 1709 and 1316 cm^{-1} correspond mainly to the stretching vibration of the C=O and C-N bonds. With the transition to a coordinated state, i.e. in complexes $Ca(CH_3COO)_2•2HCONH_2•H_2O$ and $Ca(CH_3COO)_2•4HCONH_2•2,5H_2O$ the C=O frequency values decrease by 17 and 15 sm^{-1}, while the C-N frequency value increases by 32 and 73 sm^{-1}. Such a change in frequencies indicates the coordination of formamide molecules with the calcium ion through the oxygen atom of the carbonyl group. By a similar comparison of the frequencies of the C=O and C=N bonds, the coordination of formamide molecules in mixed-amide complexes of the compositions
$Ca(CH_3COO)_2·HCONH_2·CH_3CONH_2·H_2O$
$Ca(CH_3COO)_2·HCONH_2·CO(NH_2)_2·0,5H_2O$ $Ca(CH_3COO)_2·HCONH_2·CS(NH_2)_2·2/3H_2O$
$Ca(CH_3COO)_2·HCONH_2·H_2NCONHNO_2·2H_2O$ $Ca(CH_3COO)_2·HCONH_2·NC_5H_4CONH_2·H_2O$
$Ca(CH_3COO)_2·HCONH_2·NC_5H_4CONH_2·H_2O$ $Ca(CH_3COO)_2·HCONH_2·C_6H_5CONH_2·H_2O$
$Ca(CH_3COO)_2·HCONH_2·NC_5H_4COOH·H_2O$

The IR absorption spectrum of acetamide showed frequencies (sm^{-1}) at 3387-ν(NH_2), 3194 - 2δ(NH_2), 1670 - ν(C=O), 1626 - δ(NH_2), ν(CO), 1395 - ν(CN), 1348 - δ(CH_3), 1154 - ρ (NH_2), 1048 - ρ(CH_3), 1005 - ν(C-C), 875 - ν(C-C), 582 - δ(NCO) и 464 - δ(CCN).

The IR absorption spectrum of a free acetamide molecule is characterized by several frequencies. Of these, at 1670 and 1395 sm^{-1} there are bands corresponding to the stretching vibrations of the C=O and C=N bonds. The first band decreases when the acetamide molecule is coordinated through the oxygen atom of the carbonyl group. In this case, the communication frequency value C=N is increased. Such changes were found in complexes with the compositions
$Ca(CH_3COO)_2·2CH_3CONH_2$
$Ca(CH_3COO)_2·CH_3CONH_2·4NC_5H_4CONH_2·H_2O$ $Ca(CH_3COO)_2·HCONH_2·CH_3CONH_2·H_2O$
$Ca(CH_3COO)_2·CH_3CONH_2·NC_5H_4CONH_2·0,5H_2O$ $Ca(CH_3COO)_2·CH_3CONH_2·CO(NH_2)_2·H_2O$
$Ca(CH_3COO)_2·CH_3CONH_2·CS(NH_2)_2·0,5H_2O$ $Ca(CH_3COO)_2·CH_3CONH_2·H_2NCONHNO_2$
$Ca(CH_3COO)_2·CH_3CONH_2·\cdot NC_5H_4CONH_2·0,5H_2O$

The IR spectrum of a free urea molecule (K) is characterized by bands at 3442- $\nu_{as}(NH_2)$, 3348-$\nu_s(NH_2)$, 3266-2 δ(NH_2), 1678- ν(C=O), δ(NH_2), 1623 δ(NH_2), ν(CO), 1464- ν(CN), 1154, 1059 ρ (NH_2), 999- ν(CN), 790- δ(NH_2), 582- δ(NCO) and 558 δ (NCN).

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In the IR absorption spectrum of a free carbamide molecule, along with other frequencies, two bands are observed, which confirm the presence of a coordination bond between the central ion and oxygen atoms of the carbamide molecule.

Frequencies were found in the IR absorption spectrum of thiocarbamide (TC) at 3382 - $\nu_{as}(NH_2)$, 3277 - $\nu_s(NH_2)$, 3176 - $2\delta(NH_2)$, 1673 - $\delta(NH_2)$, δ(HNC), 1473 - ν(CN), 1413 - ν(CS), 1083 - ν(CN), 783 - ρ (NH_2), 731 - ν(CS), 630 - δ(CS), δ(NCS), 487 - δ(NCN) and 420 - δ(NCS).

In the IR absorption spectrum of a free thiocarbamide molecule, three characteristic frequencies are observed at 1413-ν(CS), 730-ν(CS) and 631 sm^{-1} - δ(CS). In complex compounds of thiocarbamide, it is not possible to observe a change in the value of the frequency 1413 sm^{-1}- ν(CS), since it is overlapped by a wide band ν(COO) of the acetate group. However, in the low-frequency region of the spectrum, the frequencies of thiocarbamide molecules at 730 and 631 sm^{-1} decrease by 1-56 and 4-19 sm^{-1}, respectively, in the cases of homogeneous and mixed-amide complexes $Ca(CH_3COO)_2{\cdot}2CS(NH_2)_2$, $Ca(CH_3COO)_2{\cdot}4CS(NH_2)_2$, $Ca(CH_3COO)_2{\cdot}HCONH_2{\cdot}CS(NH_2)_2{\cdot}2/3H_2O$, $Ca(CH_3COO)_2{\cdot}CH_3CONH_2{\cdot}CS(NH_2)_2{\cdot}0{,}5H_2O$, $Ca(CH_3COO)_2{\cdot}CO(NH_2)_2{\cdot}$ $\cdot CS(NH_2)_2{\cdot}0{,}5H_2O$, $Ca(CH_3COO)_2{\cdot}CS(NH_2)_2{\cdot}H_2NCONHNO_2{\cdot}0{,}5H_2O$ and $Ca(CH_3COO)_2{\cdot}CS(NH_2)_2{\cdot}NC_5H_4CONH_2$. Such a change in frequencies in the spectrum can be explained by the coordination of the thiocarbamide molecule with the calcium ion through the sulfur atom.

In the IR absorption spectrum of an uncoordinated nitrocarbamide (NTC) molecule, frequencies were found at 3437- ν_{as} (NH_2), 3352- 2 δ (NH_2), 3182- ν (NH_2), 1704- ν (C=O), 1615- δ (NH_2), ν (CO), 1530 - ν_{as} (NO_2), 1466- ν (CN), 1340- ν_s (NO_2), 1108- ρ (NH_2), 1027- ν_s (CN), 785- δ (NH_2), 543- δ (NCO).

The IR absorption spectrum of a free nitrocarbamide molecule, along with other frequencies, has two characteristic frequencies at 1704-ν(CO) and 1460-ν(CN). These frequencies change when the nitrourea molecule is coordinated through the oxygen atom of the carbonyl group. The frequency of the stretching vibration of the C=O bond decreases, while ν(CN) increases. Similar changes were found in homogeneous and mixed amide complexes of compositions: $Ca(CH_3COO)_2{\cdot}2H_2NCONHNO_2$ $Ca(CH_3COO)_2{\cdot}4H_2NCONHNO_2{\cdot}H_2O$ $Ca(CH_3COO)_2{\cdot}HCONH_2{\cdot}H_2NCONHNO_2{\cdot}2H_2O$ $Ca(CH_3COO)_2{\cdot}CH_3CONH_2{\cdot}H_2NCONHNO_2$ $Ca(CH_3COO)_2{\cdot}CO(NH_2)_2{\cdot}H_2NCONHNO_2$ $Ca(CH_3COO)_2{\cdot}CS(NH_2)_2{\cdot}H_2NCONHNO_2{\cdot}0{,}5H_2O$ $Ca(CH_3COO)_2{\cdot}H_2NCONHNO_2{\cdot}NC_5H_4CONH_2{\cdot}0{,}5H_2O$

The IR spectrum of the uncoordinated nicotinamide (ANC) molecule has frequencies at 3366 - $\nu(NH_2)$, 3161 - $2\delta(NH_2)$, 3060 - ν(CH), 1680 - ν(C=O), 1619 - $\delta(NH_2)$, 1594 - $\nu_к$, 1574 - $\nu_к$, 1483, 1423 - $\nu_к$, δ(CCN), 1398,1342 - ν(CH), δ(CCN), 1200 - δ(CCN), 1143,1127 - $\nu(NH)_2$, δ(CCN), 1086 - δ(CCN), ν(CO), $\nu_к$, 1029 - $\nu_к$, δ(CCN), 986 - ν(CC), 831 - ν(CC), δ(CCC), 777,703 - δ(CCN), δ(CO), 624,604 - δ(CO), δ(CNC), 514 - δ(CO), δ(CCC).

In the IR absorption spectrum of the nicotinamide molecule, there are a sufficient number of frequencies, and the ν (ring) frequency is observed at 1593 sm^{-1}. Absorption bands at 1029-vk and 703 sm^{-1} (CCN), belonging to ring vibrations. Similar frequency changes are observed in homogeneous and mixed-amide complex compounds of the compositions – $Ca(CH_3COO)_2{\cdot}2NC_5H_4CONH_2{\cdot}H_2O$ $Ca(CH_3COO)_2{\cdot}4NC_5H_4CONH_2$ $Ca(CH_3COO)_2{\cdot}HCONH_2{\cdot}NC_5H_4CONH_2{\cdot}H_2O$ $Ca(CH_3COO)_2{\cdot}CH_3CONH_2{\cdot}NC_5H_4CONH_2{\cdot}0{,}5H_2O$ $Ca(CH_3COO)_2{\cdot}CO(NH_2)_2{\cdot}NC_5H_4CONH_2{\cdot}H_2O$ $Ca(CH_3COO)_2{\cdot}CS(NH_2)_2{\cdot}NC_5H_4CONH_2$ $Ca(CH_3COO)_2{\cdot}H_2NCONHNO_2{\cdot}NC_5H_4CONH_2{\cdot}0{,}5H_2O$

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These changes may indicate the coordination of nicotinamide with the calcium ion through the nitrogen heteroatom of the pyridine ring.

In the IR absorption spectrum of an uncoordinated benzamide molecule, frequencies were found at 3367 - ν(NH)$_2$, 3172 - 2δ(NH$_2$), 3059 - ν(CH), 2885 - ν(CH), 2779 - ν(CH), 1955, 1893, 1810, 1659 - ν(C=O), 1623 - δ(NH$_2$), 1577 - ν$_к$, 1450 - ν$_к$, 1401 - ν(CH), 1297, 1179, 1143 - ν(NH)$_2$, 1122, 1024, 918, 848, 812, 793, 685, 635, 529 и 411 sm^{-1}.

The nature of the coordination of acetate groups varies depending on the composition, the mutual arrangement of the acido- and apical ligands, and the presence of intramolecular hydrogen bonds.

The presented complex compounds have shown that in all cases the molecules of formamide, acetamide, carbamide and nitrocarbamide are coordinated through the oxygen atom of the carbonyl group. The thiocarbamide molecule is coordinated through the sulfur atom of the thio group. In the case of nicotinamide, heteroatomazote of the pyridine ring is involved in coordination with the calcium ion. Acetate fragments, depending on the composition, exhibit mono- or bidentate modes of coordination.

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