ISSN 2181-8622

Manufacturing technology problems

Scientific and Technical Journal Namangan Institute of Engineering and Technology

INDEX COPERNICUS INTERNATIONAL

Volume 9
Issue 2
2024

Google Scholar Crossref doi SLIB.UZ Scientific library of Uzbekistan

RESULTS OF MECHANOCHEMICAL SYNTHESIS OF METHYLENE BLUE COMPLEX WITH d-METALS

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Abstract: The article describes the mechanochemical synthesis of a complex based on methylene blue (MB) and cobalt(II) chloride and a description of the structure of the complex. The synthesis of the complexes was carried out by the mechanochemical method by mixing the reagents in a stoichiometric ratio in an agate mortar until a homogeneous mass was formed. Dimethylformamide (DMF) was added dropwise to the resulting reaction mixture until a homogeneous dark blue solution was formed. The crystals required for X-ray diffraction analysis were obtained by slow evaporation of the reaction solution over a week. The parameters of the crystals were analyzed by the X-ray structure method.The mechanochemical synthesis of the complexes was carried out by mixing the raw materials in stoichiometric proportions by grinding them in an agate mortar. DMF was added dropwise to the reaction mixture until a homogeneous dark blue solution was formed. The crystals required for X-ray diffraction analysis were obtained by evaporating the solution at room temperature for a week. The reaction yield was 85%. The mechanochemical synthesis of the $[MB]_2[CoCl_4]$ complex was proven based on X-ray diffraction analysis. The crystal required for X-ray diffraction determination of the structure was grown only from a DMF solution. It has been established that the synthesis of complexes based on transition metal chlorides and MB can be easily carried out using the mechanochemical method.

Keywords: mechanochemistry, synthesis, methylene blue, d-metal, cobalt(II) chloride, solvent, complex, crystal, X-ray structure, pseudotetrahedron, isostructure, cell, angle.

Introduction. "Mechanochemistry is a chemical reaction resulting from the direct absorption of mechanical energy" (IUPAC definition). There is a growing interest in developing a method to perform mechanochemistry in a solvent-free environment. Currently, scientists are investing more in creating clean and environmentally friendly reactions when combining solids with each other. Removing solvents during the reaction can have many positive effects. Solvents can also interfere with final product release due to solubility issues and coordination of the solvent with the metal ion, resulting in the need for solvent removal. In addition, avoiding solvents can minimize safety issues. This so-called green involves the development of a chemical approach to synthesis that is less wasteful, cost-effective, environmentally friendly and safe without the use of solvents [1].

The term mechanochemistry was first used in "Textbook of General Chemistry" published by Wilhelm Ostwald, professor of Riga Polytechnic School in 1885-1887. Among the forefathers of mechanochemistry are the American Matthew Currie-Lee and the English Michael Faraday. One of the first works in Russia was published by Flavian Flavitsky in 1902 in the "Journal of the Russian Society of Physico-Chemists".

When medicinal substances are crushed, micronization of the product occurs, as a result of which a number of positive properties appear in them (solubility, increased bioavailability, longer duration of action, etc.). It is very important to preserve such new properties of medicinal substances for a long time. Because freshly ground powders are

stored for a long time, the particle size increases, which means that the resulting healing efficiency is lost. This creates the problem of preserving the positive properties that appear when the medicinal substances are crushed. One of the solutions to this problem is the grinding of medicinal substances together with polymers. In this case, "entropy frozen" systems are formed, that is, very small particles of the medicinal substance (even at the molecular level) are dispersed within the polymer macromolecule. As a result, particle size increase and recrystallization, which occurs during storage of drugs, is prevented. Polymers stabilize the positive properties achieved in mechanical performance, facilitate dissolution and absorption of poorly soluble medicinal substances [2, 3].

As a result of plastic deformation of a solid, its shape and size change. Defects appear in the body, accumulate, and this causes changes in its physical and chemical properties. A set of defects can facilitate the chemical interaction of solids. Mechanically processed solids have an activation process, that is, during the grinding process, the particle size approaches a certain critical size. Mechanical activation not only increases the surface of the object, but also leads to the accumulation of defects in the entire volume of the crystal. This changes many of the physicochemical properties and reactivity of solids. In order to change the reactivity of solids in the desired direction, specific mechanical activation methods (reaction environment, impact energy, reaction time, temperature, impact appearance) should be used, because the chemical reactions of solids depend on various defects in the crystal according to the mechanism [4].

Ball, flow, rotor-flow, disintegrator, dismembrator, colloidal, planetary type mechanoreactors and mills are used for mechanical activation of substances, mechanical grinding and mechanosynthesis in solid phase processes. The working principles of the reactors are also different, and in most cases, the most suitable and convenient for carrying out the mechanosynthesis reaction are planetary-centrifugal type mechanoreactors. Because in these reactors, the impact force is given to the substances by means of spheres with a complex trajectory (percussive, crushing-sliding), and the impact force and time can be controlled [5].

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As a result of plastic deformation of a solid body, its shape and size change. Defects appear and accumulate in the body, and this causes changes in its physical and chemical properties. A set of defects can facilitate the chemical interaction of solids. There is a process of activation of mechanically processed solids, that is, during the grinding process, the particle size approaches a specific critical size. Mechanical activation not only

increases the surface of the object, but also leads to the accumulation of defects in the entire volume of the crystal. This changes many of the physico-chemical properties and reactivity of solids. In order to change the reactivity of solids in the desired direction, it is necessary to use specific mechanical activation methods (reaction environment, impact energy, reaction time, temperature, appearance of impact), because according to the mechanism of chemical reactions of solids depends on various defects in the crystal [7].

Aggregation processes that occur during mechanical processing of a mixture of inorganic salts and organic acids were investigated by physicochemical methods. It has been proven that neutralization reactions occur between benzoic, salicylic, acetylsalicylic, lemon, sebacin, indolelux, ascorbic acids and alkali metal carbonates.

$$RCOOH + M_2CO_3 \rightarrow RCOOM + MHCO_3$$

$$2RCOOH + M_2CO_3 \rightarrow 2RCOOM + H_2O + CO_2$$

$$RCOOH + MOH \rightarrow RCOOM + H_2O$$

Here M = Li, Na, K ions, RCOOH - benzoic, salicylic acetylsalicylic, citric, sebacin, indolyllux, ascorbic acids. Based on the above reactions, a mechanochemical technology for obtaining fast-dissolving "foaming" dry compositions for use in the food and pharmaceutical industries has been developed [8, 9].

IR-spectra of complexes of rutin with $FeSO_4$, starch, dextrin and urotropins obtained by mechanochemical method were studied. The frequency analysis of the spectra of rutin and related complexes showed that the alcohol and phenolic hydroxyl groups of rutin are the most active, and the carbonyl group is not involved in the formation of complexes. The rutin complex formed with $FeSO_4$ has a blue color, while the starting substances have other colors. This indicates that a complex compound was formed as a result of the reaction between Fe^{+2} d-element and rutin [10, 11].

Methodology & empirical analysis. Mechanochemistry studies the chemical and physicochemical changes of matter under the influence of deformation. Mechanochemical transformations are associated with the transition of a substance to a metastable chemically active state, as well as an increase in mass transfer due to the absorption of mechanical energy. One of the causes of chemical activation of deformation effect, friction is vibrational and electronic excited states of interatomic bonds, mechanical stress and broken bonds, including the appearance of various structural defects [12].

The increased interest in nanocrystalline materials has increased the activity to study them. At the same time, non-traditional methods of obtaining such materials play an important role, which may include the mechanical fusion method based on the use of ball grinding of a mixture of individual components included in their composition [13].

Synthesis of complexes was carried out by mechanochemical method by mixing reactants in a stoichiometric ratio until a thin mass was formed in an agate mortar. DMF was added dropwise to the resulting reaction mixture and the process continued until a homogeneous dark blue solution was formed.

Crystals required for X-ray structural analysis were obtained by slow evaporation of the reaction solution for one week. Crystal parameters were analyzed by X-ray structure.

Results. The mechanochemical method is to decompose polymers, synthesize intermetallics and ferrites, obtain amorphous alloys, and activate powder materials. A specific example of production using the mechanochemical method is the synthesis of (thermoelectric material) in a planar ball mill. This method provides mechanical processing of solids. Interesting mechanochemical ideas emerge in collaboration with experts in far-seeing fields. Thus, thanks to the scientists of the Institute of General and Experimental Biology of the Russian Academy of Sciences (Ulan-Ude), it was possible to discover such a completely unknown field as the technology of the production of medicines of ancient Tibetan medicine. Ancient pharmacists have been found to have used some mechanochemical approaches, especially in the production of medicines from metals. For the researchers, the result of repeating the technology from a treatise of thousands of years ago was surprising, in which a solid preparation of Silver was obtained, on which a "buffer" concentration of 1 mg/l of Silver was kept in solution (this is the recommended concentration for medical use).

It is very important to establish fundamental practices in the laboratory to determine the results of the research. As is common in experiments, parameter values must be determined that minimize the amount of waste, equipment use, and materials required to obtain the desired reactions.

Crystals of methylene blue (MB) and d-metal salts are brought to a soft, fluffy, flour form in the solid phase in agate mortar, as a result of which the substances are activated and plastic deformation occurs. Grinding of materials is accompanied by the breaking of chemical bonds, which predetermines the subsequent formation of new chemical bonds, that is, the occurrence of mechanochemical reactions. When grinding materials, the mechanical effect is pulsating; however, the generation of the tension field and its subsequent relaxation does not occur during the entire time the particles are in the reactor, but only when the particles collide and for a short time after that. The mechanical effect can be not only impulsive, but also local, because it does not occur in the entire mass of the solid, but only in the place where the stress field appears and then relaxes.

1) These are chemical reactions that occur during grinding or grinding of reagents used to produce products in very small samples with little or no solvent.

2) The observation of chemical reactions between solids during mechanical grinding has made great progress throughout history and continues to do so. Development with the invention of better technologies such as orbital ball mills. Reactions with metal salts can be consistently monitored and analyzed using visual observation, solid infrared spectroscopy, and elemental analysis.

3) Then, reactions of metal salts with organic ligands can be carried out. They are observed and compared to determine their mutual reactivity. With this approach, these reactions become a safer and more cost-effective method for the synthesis of coordination compounds.

Synthesis of complexes. For the synthesis of $[MB]_2[CoCl_4]$ crystal, 82 mg (0.2 mmol) of methylene blue pentahydrate – $[MB]Cl{\cdot}5H_2O$ and 23.8 mg (0.1 mmol) of $CoCl_2{\cdot}6H_2O$ salt were mixed by the mechanochemical method, in which the solvent had a negative

effect on the reaction process. influence was ruled out. The reagents $CoCl_2 \cdot 6H_2O$ (23.80 mg, 0.1 mmol) and $[MB]Cl \cdot 5H_2O$ (82 mg, 0.2 mmol) were mixed in a 1:2 stoichiometric ratio on an agate mortar until a thin mass was formed. 5.0 mL of DMF was added dropwise to the reaction mixture and the process was continued until a homogeneous dark blue solution was formed.

Elongation ellipsoids are drawn at the 50% probability level. The sparsely populated disordered Cl(4B) atom was excluded. Symbols A and B denote independent $[MB]^+$ cations.

Table 1. Bond lengths (d) and bond angles (ω) in structure (I).

ATOM	ATOM	*D*, Å	ATOM	ATOM	*D*, Å	ATOM	ATOM	*D*, Å
CO	Cl1	2.263(3)	N10A	C11A	1.33(1)	C72A	N7A	1.47(1)
CO	Cl2	2.265(3)	C9B	C8B	1.33(1)	C32B	N3B	1.46(1)
CO	Cl3	2.257(3)	C7A	N7A	1.36(1)	C6A	C7A	1.41(1)
CO	Cl4	2.242(4)	C7A	C8A	1.44(1)	C14A	N10A	1.35(1)
C72B	N7B	1.47(1)	N7B	C71B	1.44(1)	C14A	C9A	1.44(1)
N3A	C31A	1.46(1)	N7B	C7B	1.35(1)	C6B	C12B	1.36(1)
N3A	C3A	1.35(1)	C8B	C7B	1.43(1)	C6B	C7B	1.40(1)
N3A	C32A	1.46(1)	S5B	C12B	1.73(1)	C11A	C12A	1.44(1)
C11B	C9B	1.41(1)	S5B	C13B	1.73(1)	C4B	C3B	1.41(1)
C11B	C12B	1.47(1)	S5A	C12A	1.73(1)	C4B	C13B	1.38(1)
C11B	N10B	1.32(1)	C8A	C9A	1.34(1)	C1B	C14B	1.44(1)
C13A	C6A	1.38(1)	N3B	C31B	1.47(1)	N10B	C14B	1.35(1)
C13A	C14A	1.42(1)	N3B	C3B	1.34(1)	C14B	C13B	1.42(1)
C13A	S5A	1.72(1)	C2A	C3A	1.40(1)	C12A	C4A	1.38(1)
C2B	C1B	1.34(1)	C2A	C1A	1.37(1)	C11A	C1A	1.40(1)
C2B	C3B	1.42(1)	C3A	C4A	1.40(1)	C71A	N7A	1.48(1)

Crystals available for X-ray structure analysis were obtained by slow evaporation of the reaction solution for one week. Details of the resulting crystal parameters and X-ray structure studies are given below. The yield of the reaction is 85%.

DMFA

$$CoCl_2 \cdot 6H_2O + 2[MB]Cl \cdot 5H_2O \rightarrow [MB]_2CoCl_4 + 16H_2O$$

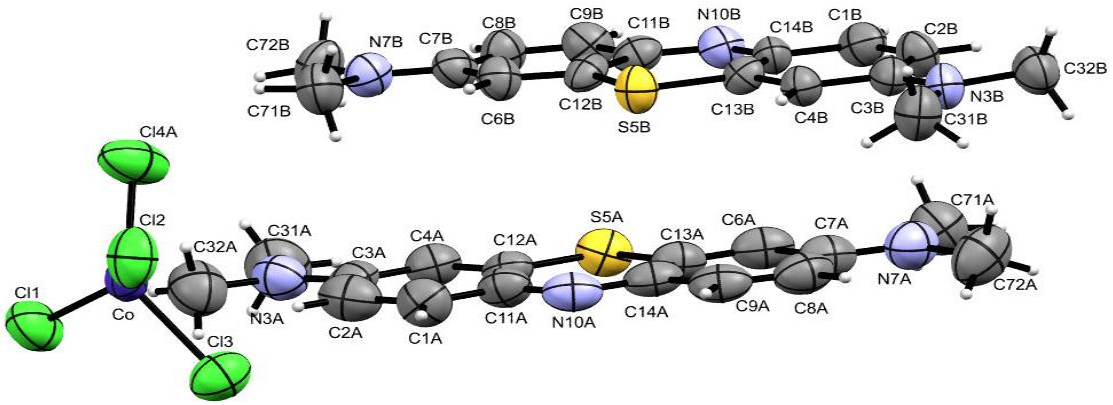

Figure 1. Molecular structure and atomic numbering scheme of compound I.

$[MB]_2[CoCl_4]$ (I) - Co^{2+} va Cu^{2+} cations have similar ionic radii, so they formed similar complexes with MBCl. Similar to the $[MB]_2[CuCl_4]$ (II) complex, it forms pseudotetrahedral, isostructural complexes. Cell parameters of both crystals are the same: a=15,1404(7), b=14,9566(4), c=16,5237(8) Å, β=115. 279(6) °, for crystal I V=3383,5(3) $Å^3$; For crystal II a=15,1327(5), b=14,9456(3), c=16,5175(5), β=115,236(4), V=3379,18(19) $Å^3$.

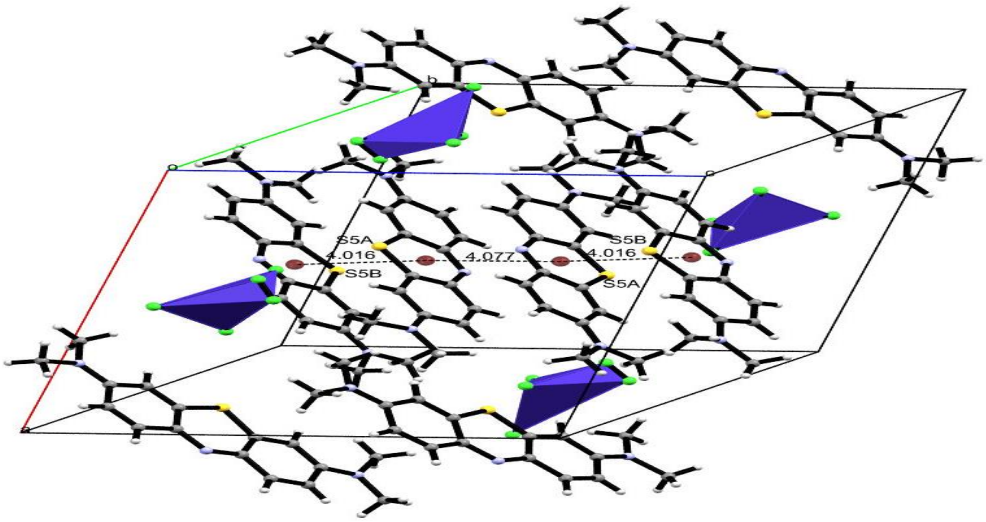

Figure 2. π-π stacking fragment and center-to-center distances in crystal structure I.

Conclusions. According to the obtained results, X-ray analysis of the crystal structure of the complex compound $[MB]_2[CoCl_4]$ allows to determine the structure of the substance. Figure 3.4 shows the structure of the complex crystal and its arrangement in the cell. When water was used as a solvent, the complex precipitated as a crystalline hydrate. When acetone, methyl alcohol, ethyl alcohol are used, due to the rapid evaporation of these solvents, salt and MB crystals fell to the bottom of the mortar. Visual examination using a microscope showed that the mixture consists of crystals of the initial substances. It was studied that DMFA is a convenient solvent, and it was found that the convenience of the mechanochemical method in performing the synthesis of transition metal chlorides with MB, this result definitely depends on the composition of complex compounds of metal ions and MB.

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