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Mechanochemical Synthesis in Chemistry of Cluster Systems

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Abstract

Mechanochemical reactions for the synthesis of cluster compounds of higher boranes, carboranes, and transition metal complexes with structural metal chalcogenide cluster fragments containing [Nb_2], [W_3] and [Mo_3] are reviewed. These are typical systems in cluster chemistry. Reactions were performed by mechanical activation (MA) of mixtures of starting crystalline substances in hermetically sealed vibratory ball mills. A brief overview of basic definitions and concepts of cluster chemistry and mechanochemistry is presented. The results of studies on six types of mechanochemical reaction on cluster compounds are summarized. Published data on the experimental technique for reactions performed under conditions of MA are given. MA can change the structure or composition of the cluster nucleus, or lead to elimination of structural cluster fragments from coordination polymers; it can also lead to exchange of the ligand surroundings of the nucleus-forming atoms, and to formation of discrete molecules or ionic saltlike compounds containing clusters. Solid-phase redox reactions on transition metal atoms can take place during formation of heteroatomic metallocarboranes.

INTRODUCTION

Cluster chemistry is an actively developing field of chemistry where most complex substances are being created for use in fundamental research in inorganic and coordination chemistry. In the course of these studies, valuable functional properties of cluster compounds may be revealed, which make them useful in catalysis, electronics, biochemistry, synthesis of new types of cluster materials, etc. Obviously, this direction cannot develop without novel effective synthetic procedures to obtain new and known cluster compounds. The classical procedures are based on reactions in solutions and melts and are often too complex and time-consuming; they do not always lead to reasonably high yields of target products and demand the use of specific pure solvents [1, 2]. It is reasonable, therefore, to examine feasibility of mechanically initiated (*i.e.*, mechanochemical) solid-phase reactions for the synthesis of several characteristic cluster systems that rule out the use of solvents and lead to facile synthesis of these systems. Mechanochemical reactions have not been fully investigated in cluster chemistry, and no reviews have been published. This work is an attempt to summarize published data on mechanochemical reactions in cluster systems, complementing this information with new original results.

For discussion of results and experimental techniques we employ the classical definitions of clusters and mechanochemical processes. Thus Cotton's definition of cluster compounds is "compounds containing discrete groups of metal (element) or non-metal atoms directly bonded to one another" Another definition taken from the explanatory dictionary [3] runs: "Cluster compounds are complex compounds where the role of the central atom is played by a three-dimensional cell of directly bonded metal atoms". The cluster groups of metal atoms may be combined with ligands. Therefore, structural changes in clusters during reactions can take place for both cluster atoms and ligands. Polyatomic cluster systems can be formed from atoms other than metal atoms. Thus higher boranes and their derivatives can form cluster structures from boron atoms and appropriate heteroatoms. Examples are provided by $B_nH_n^{2-}$ type anions, where n = 5–12, in particular $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, carboranes (12) $B_{10}C_2H_{12}$, adduct complexes $B_{10}H_{12}L_2$ (Lewis bases), and metallocarboranes $SnB_9C_2H_{11}$ and $[M(B_9C_2H_{11})_2]^-$, where M(III) = Fe, Co, Ni, Cr. Due to the diversity of compositions and generality of structures of boranes and their derivatives, cluster chemistry of these compounds may be extended to clusters of metal atoms because these two types of cluster systems have a number of structural features in common [4].

Mechanochemistry is a rapidly developing field of modern chemistry. Mechanochemical processes occur by mechanical activation (MA) of solid mixtures of starting substances. The mechanisms of these reactions are complex, not always liable to investigation by conventional procedures. MA of reagent mixtures is generally performed in mills of various types. For solid-phase reactions of clusters during MA, we use the definition from review [5]: “Mechanochemical reactions are reactions initiated by deformation, attrition, or cleavage of solids”. This definition reflects the complex nature of mechanochemical transformations in solids, deformation, attrition, and cleavage being very diverse processes. Each of these processes or their combinations can initiate chemical transformations leading to different results. Among macroscopic consequences of MA are mixing of components, decreased dimensions of particles (fractionation, dispersion), increased surface of solid reagents, and increased number of contacts between particles [6–8]. Diffusion transfer of substances over the surface of solids is much faster than the same process in the bulk of the sample. Moreover, in crystals MA can induce phase transitions with accumulation of various structural defects. According to modern knowledge, defect formation is the major factor that changes the reactivity of solids and mechanochemical reactions themselves [6–9]. These general theoretical principles and consequences of MA also hold for solid-phase mechanochemical reactions on complex cluster systems.

This review summarizes the results of studies on the following types of solid-phase mechanochemical reactions:

1) synthesis of the *closo*-$SnB_9C_2H_{11}$ metallocarborane cluster by a sequence of two reactions using MA with the salt and the *nido*-$B_9C_2H_{12}^{2-}$ anion, NaH, and $SnCl_2$;

2) structural rearrangement of the $[B_{10}H_{12}]$ open *arachno*- borane cluster in the $B_{10}H_{12}(NH_3)_2$ nonionic adduct complex into closed polyhedral anion *closo*-$B_{10}H_{10}^{2-}$;

3) synthesis of anionic bis(dicarbollylic) “sandwich” complexes $[M(B_9C_2H_{11})_2]^-$ [M = Co(III), Fe(III), Cr(III)], which are derivatives of *ortho*-carborane(12);

4) synthesis of saltlike complexes with $[M_3Q_7Br_6]^{2-}$ cluster anions (M = W, Mo; Q = S, Se) containing $[M_3]$ trigonal clusters;

5) synthesis of the $[Mo_3S_7Dtc_3]^+$ cation containing the [Mo3} cluster, Dtc = $(C_2H_5)NCS_2^-$, and $[Mo_3S_7]^{4+}$ as the central structural fragment;

6) extraction of $Nb_2O_4^{4+}$ cluster nuclei from $[Nb_2Q_4Br_4]_\infty$ layered polymer compounds to form discrete cluster anions (Q is chalcogen).

For full description and comparison purposes, the appropriate sections of this review give data on the classical synthetic procedures and on the structure and properties of the compounds.

EXPERIMENTAL PROCEDURES AND METHODS OF INVESTIGATION

The proper choice of conditions and apparatuses is essential to MA in each particular case [5, 7–9]. A classification of apparatuses for MA according to the type of operation is given in [5]. All known types of apparatus fall into three categories according to the character of the physical process underlying MA of solids: cleavage, attrition, or shear in the crystal lattice. The specifics of experiments on mechanochemical synthesis of the cluster compounds mentioned above demands that dry oxygen-free atmosphere or vacuum be treated in the working zone of the apparatus. For studies of reactions of cluster systems under conditions of MA and appropriate apparatus is a vibrator ball mill, which had been successfully used by the authors over years for synthesis of B_2H_6 and borane derivatives [10–14]. The chamber of the mill is a steel cylinder hermetically closed with a flanged cap mounted on it and having a vacuum valve for air evacuation or gas release. The chamber was filled to 50–70 % of its volume with milling steel balls 3–6 mm in diameter. The samples of the starting reagents were loaded into this packing, and the chamber was closed with the cap. The thus equipped cylinder was mounted vertically on an eccentric type vibrator set into motion by an electric motor. The adjustable vibrator allows one to vary the frequency and amplitude of mill vibrations. The ball packing of the vibrator undergoes vertical vibrations, thus activating the reagent mixture. The chamber of the mill was placed, if necessary, into a heated air thermostat where the temperature may be kept at a level from room temperature to 120 °C. To measure the gas volume resulting in the reaction the chamber was connected via a flexible tube and a valve to a gasometer apparatus for continuously monitoring the reaction. Typical synthetic conditions: mill capacity 100 cm^3; ball mass 100 g; ball diameter 6 mm; vibration frequency 23 Hz, amplitude 6 mm; 4–10.5 g samples of the mixtures of the starting solid reagents. The target volatile substances formed by MA were extracted from the mixture with selected solvents and purified by recrystallization. A vibratory reactor of a titanium alloy packed with tungsten carbide balls was occasionally employed to avoid undesirable side reactions, sometimes arising from the use of steel apparatuses.

Mechanochemical reactions were used to synthesize new cluster compounds along with known ones. The classical synthetic procedures, as well as compositions, structural characteristics, and spectral data have been published in original works cited herein. These data are used for product identification and comparisons.

MECHANOCHEMICAL REACTIONS ON CLUSTER SYSTEMS

Synthesis of $SnB_9C_2H_{11}$

It was shown [15] that a cluster compound 1-stanna-2,3-dicarba-*closo*-dodecaborane (II) ($SnB_9C_2H_{11}$) may be obtained by mechanochemical synthesis. The molecule of this derivative of *ortho*-carborane(12), $B_{10}C_2H_{12}$, is an icosahedral cluster with two C–H and nine B–H fragments and one Sn(II) atom at the vertices. The Sn(II) atom is coordinated to three B and two C atoms lying in the pentagonal cross section plane of the icosahedron (Fig. 1) [16]. The compound is nonionic; it dissolves in C_6H_6 and its analogs and sublimes in vacuum at 140 °C.

Traditional liquid-phase synthesis follows the scheme [16]

$$B_9C_2H_{12}^- + H^- = B_9C_2H_{11}^{2-} + H_2 \quad (1)$$

$$B_9C_2H_{11}^{2-} + SnCl_2 = SnB_9C_2H_{11} + 2Cl^- \quad (2)$$

Synthesis is conducted in pure THF and benzene, in an inert atmosphere. Each stage takes at least 24 h. Reaction (1) is neutralization of a weak H-acid with a strong Lewis acid H- introduced in the form of NaH. Reaction (2) involves addition of Sn(II) to the *nido*-$B_9C_2H_{11}^{2-}$ ionic cluster to form a neutral icosahedral cluster *closo*-$SnB_9C_2H_{11}$ (see Fig. 1). Mechanochemical synthesis of this target compound was performed by MA of a mixture of crystalline reagents; the general scheme of this reaction is

$$\begin{aligned} &CsB_9C_2H_{12}\,(\text{sol.}) + NaH\,(\text{sol.}) + SnCl_2\,(\text{sol.}) \\ &\quad = SnB_9C_2H_{11}\,(\text{sol.}) + NaCl + CsCl + H_2 \quad (3)\end{aligned}$$

The reaction was performed in a vibratory mill under above-indicated conditions of MA. Excess amounts of NaH (28–100 %) and $SnCl_2$ (12–100 %) were added to the reaction mixtures, the total mass of reagent mixtures being 7–9.3 g. The full time of MA was 4–10 h at room temperature of the mill case (20–25 °C). According to the data of gasometric measurements of the produced amount of H_2, stage (1) gives yields of 60–75 % after 4–5 h. The $SnB_9C_2H_{11}$ product was isolated from the reaction mixture by vacuum sublimation at 140 °C. Alternatively, the substance was extracted with hot toluene with further evaporation of the solvent. Reaction (3) gave yields of 3.2–5.2 % based on $CsB_9C_2H_{12}$. The optimum yield of 5.2 % was obtained when reagents were simultaneously charged according to scheme (3) with excess amounts of NaH and $SnCl_2$ (90 and 17 %, respectively) and MA was conducted for 3–4 h. These results gave a

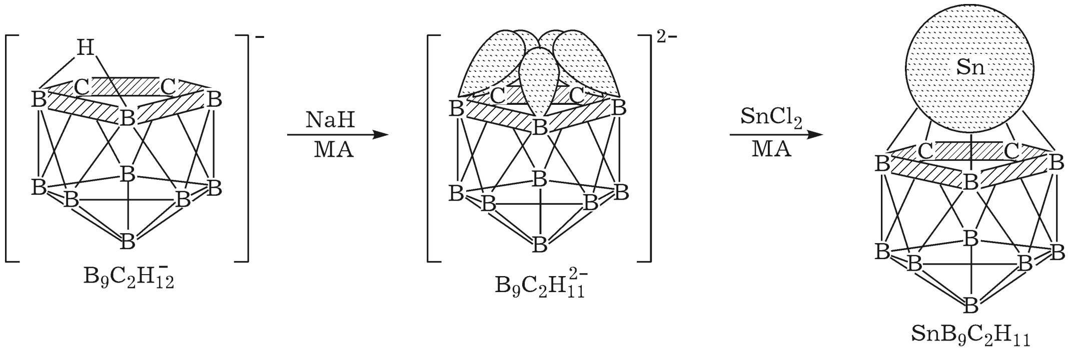


Fig. 1. Formation of the $SnB_9C_2H_{11}$ *closo*-cluster from a salt with the $B_9C_2H_{12}^{2-}$ anion by reaction (3).

convincing proof of feasibility of complex multistage solid-phase reactions or cluster systems that occur either on the ligand (1) or on the cluster nucleus (2) [15].

Structural rearrangement of the $[B_{10}H_{12}]$ arachno-cluster of the $B_{10}H_{12}(NH_3)_2$ nonionic complex into the closo-$B_{10}H_{10}^{2-}$ anion

The nonionic compound $B_{10}H_{12}(NH_3)_2$, *i.e.*, 6,9-bis-(ammonia)-*arachno*-dicarborane(12) belongs to the class of the known cluster derivatives of dicarborane(14) of $B_{10}H_{12}L_2$ type, where L is a Lewis base of medium strength [17–19]. The classical synthetic procedure for this compound is a reaction of NH_3 with $B_{10}H_{14}$ in aromatic hydrocarbons [17]. In its molecular structure, the $[B_{10}H_{12}]$ open cluster is combined with ten terminal and two bridging H atoms. The NH_3 molecules are bonded to the sixth and ninth atoms of the borane cluster *via* σ bonds involving the N atom, which is the donor of an electron pair. $B_{10}H_{12}L_2$ typically undergoes substitution reactions of L bases with stronger (L^*) bases and the reaction that forms a closed polyhedral anion of decahydro-*closo*-decaborate (2-), *i.e.*, $B_{10}H_{10}^{2-}$ with a structure of a two-capped square antiprism, and results in elimination of the bridging H atoms [17, 18]. It was of interest to examine which of the two interactions is possible under conditions of MA. Mechanochemical reaction of $B_{10}H_{12}(NH_3)_2$ with a pyridinium salt $C_5H_5N \cdot HCl$ has been studied [20]. A standard mill was employed; conditions: 25 °C, activation time 8 h, 50 % excess of pyridinium hydrochloride PyCl in the mixture. The reagents were found to react according to the scheme

$$B_{10}H_{12}(NH_3)_2\,(\text{sol.}) + 2\text{Py}\cdot\text{HCl}\,(\text{sol.}) \rightarrow [\text{PyH}^+]_2B_{10}H_{10}^{2-}\,(\text{sol.}) + 2NH_4Cl \quad (4)$$

Water extraction gave a salt with the $B_{10}H_{10}^{2-}$ anion, and the NH_4^+ cation was identified by analytical methods. IR spectroscopy data confirmed the formation of the $B_{10}H_{10}^{2-}$ anion. The spectrum of the resulting mixture has all typical absorption bands in the ranges, cm^{-1}: 625, 1029, 1085 (vibrations of the B atoms of the cluster) and 2470, 2532 (B–H stretching vibrations in the equatorial and apical positions of the B atoms of the cluster, respectively) [21]. Thus it was shown that MA in the presence of PyH^+ transforms the *arachno*-$[B_{10}H_{12}]$ cluster into the closo-structure of the $B_{10}H_{10}^{2-}$ anion with elimination of two bridging H atoms of the ligand to form the NH_4^+ cation (4).

Synthesis of bis(dicarbollyl) complexes $[M^{III}(B_9C_2H_{11})_2]^-$

Bis(dicarbollyl) “sandwich” complexes of cobalt, iron, and chromium of $[M(B_9C_2H_{11})_2]^-$ type were synthesized by Hawthorne *et al.* [18, 22]; these are metallocarborane derivatives. They represent some kind of analogues of metallocenes $M(C_5H_5)_2$ in which the $B_9C_2H_{11}^{2-}$ anion is analogue of the $C_5H_5^-$ ligand and is π bonded to the M atom. Thus the transition metal M atom is π bonded to the B_3C_2 open pentagonal planes of atoms of the two $B_9C_2H_{11}^{2-}$ anions, completing their configurations to two icosahedra (as done by the Sn(II) atom, see Fig. 1) sharing the M vertex. The M(III) atom has a coordination number of 10. Bonding of this type occurs by a reaction similar to (2). The classical methods for the synthesis of bis(dicarbollyl) complexes are based on reactions in polar organic solvents (THF, ethers, *etc.*) or in 25 % aqueous NaOH at 100 °C (for the case of the Co complex) in an inert atmosphere. It was shown [23] that salts with the $[M(B_9C_2H_{11})_2]^-$ anions may be obtained by solid-phase mechanochemical synthesis from a mixture of reagents: dithallium salt of 1,2-dicarbollide dianion $Tl_2(1,2\text{-}B_9C_2H_{11})$ with anhydrous Co(II), Fe(III), Cr(III) chlorides. Mechanochemical reactions were performed in a 50 cm^3 steel reactor filled with steel balls 12 mm in diameter (mass 130 g). The reactor was charged with samples of the appropriate metal chloride and $Tl_2(B_9C_2H_{11})$ with a total mass of 2.0–3.3 g with stoichiometric excess of chlorides 5–45 %. For mechanical activation the reactor was vibrated at a frequency of 28 Hz and an amplitude of 11 mm for 30 min. The desired products were isolated from the reaction mixture by dissolution in acetone; the solution was filtered, and the tetramethylammonium salt of metallocarborane was precipitated with a solution of the Me_4N^+ cation salt; the precipitate was purified by recrystallization and examined by analytical and spectral methods. The composition and the nature of the $(Me_4N)[M(B_9C_2H_{11})_2]$ products received strong evidence.

The scheme of mechanochemical reactions for the synthesis of Fe(III) and Cr(III) complexes is

$$MCl_3\ (sol.) + 2Tl_2(B_9C_2H_{11})\ (sol.) = Tl\,[M(B_9C_2H_{11})_2]\ (sol.) + 3TlCl \qquad (5)$$

The yields of the target products of reaction (5) are 62–70 %.

The Co(III) complex is synthesized according to a more complex scheme:

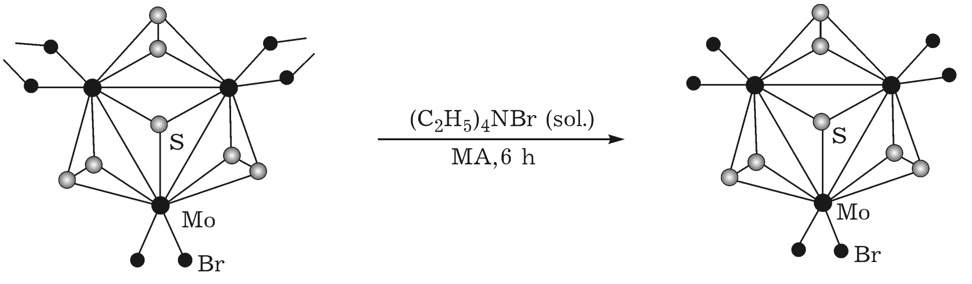
$$3CoCl_2\ (sol.) + 4Tl_2(B_9C_2H_{11})\ (sol.) = 2Tl[Co(B_9C_2H_{11})_2]\ (sol.) + 6TlCl + Co \qquad (6)$$

The presence of the Co metal was confirmed analytically. Reaction (6) is accompanied by a redox disproportionation stage according to the scheme 3Co(II) → 2Co(III) + Co^0. This stage also takes place during synthesis according to the classical route in solutions [22]. The yield of the target product of reaction (6) is 74 %.

The results of the study reported in [23] provide strong evidence that solid-phase reactions during MA ensure incorporation of transition metal heteroatoms in the structures of carborane clusters, forming complex systems of coordination and other bonds. These reactions may be accompanied by redox processes leading to cluster derivatives of metallocarboranes.

Synthesis of $[M_3Q_7Br_6]^{2-}$ anion salts

Known thiohalide cluster anions $[M_3Q_7Br_6]^{2-}$ contain in their structures trigonal metal clusters $[M_3]$ combined with ligands [1, 2, 24]. Typical compositions of these anions include M = W, Mo; Q = S, Se, forming $[M_3Q_7]^{4+}$ cluster fragments. The M atoms are in the oxidation state (+4). The general formula of the anion for M = Mo and Q = S is $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]^{2-}$. The scheme of the structure is presented in Fig. 2. Two structural types of sulfur atom are present. The first type is apical (μ_3-S): the S atom is bonded to the three vertices of the $[Mo_3]$ triangle. The second type (μ_2-S_2) is bridging, with bridging pairs S_2 of atoms. Each pair is linked with two Mo atoms. The Br atoms are linked in pairs with the Mo atoms. The



$[Mo_3S_7Br_2Br_{4/2}]_n$ (sol.)

$[(C_2H_5)_4N]_2[Mo_3S_7Br_6]$ (sol.)

Fig. 2. Transformation of the polymer structure of the $[Mo_3]$ cluster derivative containing the "terminal" and "bridging" bromine atoms into the salt structure with a discrete $[Mo_3S_7Br_6]^{2-}$ anion [reaction (8)].

structurally diverse Q atoms exhibit different reactivities during substitutions. In the given anions, the bromine atoms are readily replaced by other ligands. This is of interest for selective syntheses.

The $[M_3S_7Br_4]_n$ polymer products where the $[M_3S_7]^{4+}$ clusters are linked by the bridging bromine atoms are the starting materials for syntheses of compounds with $[M_3]$ clusters (see Fig. 2). The polymers are obtained by heating mixtures of approximately stoichiometric amounts of M, S, and Br_2 in sealed evacuated ampules at 300–400 °C for 40–100 h [24, 25]. The following reaction can serve as an example:

$$3Mo + 7S + 2Br_2 \rightarrow [Mo_3S_7Br_4]_n \text{ (polymer)} \quad (7)$$

Polymer products of this type are rather inert in reactions (in particular, in depolymerizations), resulting in discrete ions containing $[M_3]$ clusters. Depolymerization was generally accomplished by prolonged heating in concentrated acids or melts, leading to low yields and poor reproducibility of results. These difficulties were eliminated by using solid-phase reactions under conditions of MA [24, 25], for example:

$$[Mo_3S_7Br_4]_n \text{ (sol.)} + 2n Et_4NBr \text{ (sol.)} = n[Et_4N]_2^+[Mo_3S_7Br_6]^{2-} \text{ (sol.)} \quad (8)$$

The reaction was performed in a standard apparatus described above using a 10.5 g charge of a mixture of reagents with a 100 % stoichiometric excess of Et_4NBr. The target product of reaction (8) was isolated by dissolving the product in acetonitrile; then it was crystallized from a mixture of acetonitrile and diethyl ether. The maximal yield of $[Et_4N]_2[Mo_3S_7Br_6]$ (74 %) was obtained by MA for 5 h [25]. Similar results were achieved in syntheses of cluster complexes with M = W, Q = Se by reaction (8) [24]. The products were defined by chemical and analytical methods, IR and Raman spectroscopy, X-ray diffraction and X-ray phase methods.

The results of this part of our study have demonstrated feasibility of a rather complex solid-phase transformation of cluster systems by MA. This transformation involves depolymerization of an inorganic polymer, subsequently forming a discrete $[M_3Q_7Br_6]^{2-}$ type anion. The latter may be used for preparative syntheses of its derivatives.

Synthesis of the $[Mo_3S_7Dtc_3]^+$ cation

As is known [26, 27], liquid-phase reaction of $[Et_4N]_2[Mo_3S_7Br_6]$ with $Na[(C_2H_5)_2NCS_2]$, *i.e.*, with NaDtc in acetonitrile may be used to obtain saltlike complexes $[Mo_3S_7Dtc_3]Dtc$ and $[Mo_3S_7Dtc_3]Br$. It was of interest to examine if these compounds could be obtained by mechanochemical solid-phase reactions, that is, it was of interest to perform a reaction of substitution of Br atoms at Mo atoms by the bidentate (at S atoms) Dtc ligand, transforming the cluster anion into the cation form without sacrificing the $Mo_3S_7^{4+}$ trigonal cluster fragment.

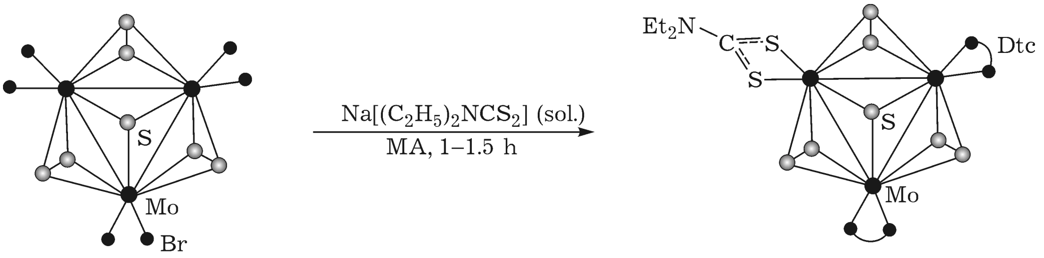
Mechanochemical synthesis of $[Mo_3S_7Dtc_3]Dtc$ was accomplished by the reaction [28]

$$[Et_4N]_2[Mo_3S_7Br_6] \text{ (sol.)} + 4NaDtc \text{ (sol.)} = [Mo_3S_7Dtc_3]Dtc \text{ (sol.)} + 2Et_4NBr \text{ (sol.)} + 4NaBr \text{ (sol.)} \quad (9)$$

The reaction with MA was carried out in a vacuum ball mill with a 100 m^3 reactor packed with steel balls 6 mm in diameter (mass 200 g); vibration frequency of the reactor 23 Hz, amplitude 6 mm. The reagents used included $NaDtc \cdot 3H_2O$ of pure grade and $[Et_4N]_2[Mo_3S_7Br_6]$ prepared by the (mechanochemical) procedure of [25]. Anhydrous NaDtc was obtained by heating the reagent in vacuum at 75 °C for 6 h until constant mass was achieved. The charge of the reagent mixture was 4.5 g, NaDtc being in excess of 85 % with respect to the stoichiometric amount. The reactor with the charged reagents was evacuated. The time of MA was 1.5 h. The powder produced by MA was washed from the balls with water. The precipitate was filtered off and washed with water, ethanol, and acetonitrile. The isolated product, $[Mo_3S_7Dtc_3]Dtc$, was dried in vacuum at 75 °C and recrystallized from DMSO. The yield of the target product was 93 %. The composition and nature of the product were confirmed by analytical, IR, and Raman methods (Fig. 3) [28].

When hydrated $NaDtc \cdot 3H_2O$ was used in the synthesis and the MA time was decreased (to no more than 1 h), the product mixture contained significant amounts of $[Mo_3S_7Dtc_3]Br$; *i.e.*, a reaction

$$[Et_4N]_2 [Mo_3S_7Br_6] \text{ (sol.)} + 3NaDtc \text{ (sol.)} = [Mo_3S_7Dtc_3]Br \text{ (sol.)} + 2Et_4NBr \text{ (sol.)} + 3NaBr \text{ (sol.)} \quad (10)$$



$[(C_2H_5)_4N]_2[Mo_3S_7Br_6]$ (sol.)

$[Mo_3S_7(Dtc)_3]Dtc$ (sol.)

Fig. 3. Scheme of structure transformation from the $[Mo_3S_7Br_6]^{2-}$ cluster anion into the $[Mo_3S_7(Dtc)_3]^+$ cation [reaction (9)].

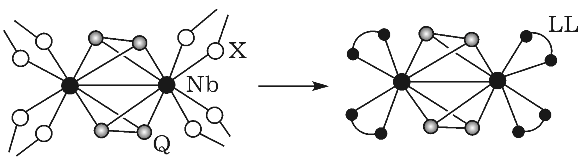
took place. Other partial substitution products can form as well.

A more complex compound, $[Mo_3S_7Dtc_3][Co(B_9C_2H_{11})_2]$, containing two types of cluster: $[Mo_3]$ and $B_9C_2H_{11}^{2-}$ carborane ligands coordinated to the cobalt atom were synthesized using the $[Mo_3S_7Dtc_3]Dtc$ cluster complex obtained by mechanochemical reaction [29].

Synthesis of binuclear chalcogenide bridging complexes of niobium

Binuclear chalcogenide cluster complexes of niobium form a large family of inorganic compounds. In the mid-1960s, polymer compounds whose structure and composition are described by the crystal-chemical formula $[Nb_2(\mu\text{-}S_2)_2(\mu\text{-}X)_{8/2}]_\infty$ were obtained by the reaction $Nb + S_2Cl_2$ or $Nb + S + X_2$ ($X = Br$, I). The structure involves a stable cluster group $Nb_2S_4^{4+}$ with a Nb–Nb single bond and two disulfide bridging ligands ($\mu\text{-}S_2$). In the range of moderate temperatures (300–500 °C), these phases are obviously thermodynamically stable, as indicated by the possibility of their synthesis from other substances (with preserved total stoichiometry) by reactions $Nb + S + NbX_4$ or $Nb_3Cl_8 + S$ (300 °C) [1, 30]. The products of the general formula NbQ_2X_2 ($Q = S$, Se; $X = Cl$, Br, I) could be convenient “starting” compounds in cluster chemistry of niobium chalcogenide. Because of their structure (coordination polymers with pseudooctahedral Nb_2S_4 fragments linked by X atoms into 3*D* frameworks), however, these phases are extremely inert with respect to liquid-phase depolymerization. To isolate cluster fragments from them, one employs high-temperature liquids including KNCS, NaCN melts, acetonitrile solutions of PPh_3, *etc.* [30]. These conditions often lead to complex mixtures of products. To overcome these difficulties we have developed a mechanochemical procedure for solid-phase synthesis of niobium chalcogenide complexes. Under conditions of MA, the coordination polymer of the general formula NbQ_2X_2 ($Q = S$, Se; $X = Cl$, Br, I) reacts with the appropriate ligand L. The ligand may be mono- (L) or bidentate (LL). As a result, the cluster fragments are cut out of the coordination polymer to form ionic or molecular complexes (Fig. 4). This reaction was performed under MA conditions in a vibratory reactor of a titanium alloy using tungsten carbide balls. The use of steel apparatuses and balls leads to undesirable side reactions. The mechanochemical reaction between $NbSe_2Br_2$ (polymer) and KNCS forms a water-soluble selenide cluster $K_4[Nb_2(Se_2)_2(NCS)_8]$. in high yields. The selenium atoms were not replaced by the sulfur atoms, as was the case with synthesis in KNCS melt.

Examples of synthesis under MA conditions are as follows:



$[Nb_2(Q_2)_2X_{8/2}]_n$

$[Nb_2(Q_2)_2(LL)_4]^{2(1-m)}$
(*m* is the charge
on the ligand)

Fig. 4. General scheme of synthesis of binuclear chalcogenide clusters from polymer complexes under conditions of MA in a vibratory mill [reactions (11) and (12)]. $Q = S$, Se; $X = Cl$, Br; LL is a chelating ligand.

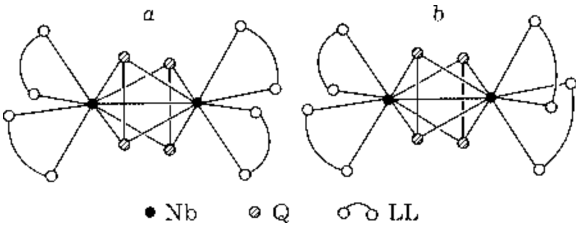


Fig. 5. Centrosymmetric C_{2h} (*a*) and noncentrosymmetric D_2 (*b*) geometrical isomers of $[Nb_2(Q_2)_2(LL)_4]$ formed by mechanochemical reaction (12), where LL is a chelating ligand, and Q is chalcogen.

1) reaction with monodentate L:

$$Nb_2Q_4Br_4 \text{ (sol., polymer)} + 8KNCS \text{ (sol.)} \rightarrow K_4[Nb_2Q_4(NCS)_8] \text{ (sol.)} + 4KBr \text{ (sol.)} \quad (11)$$

2) reaction with bidentate LL:

$$Nb_2Q_4Br_4 \text{ (sol., polymer)} + 4K_2C_2O_4 \text{ (sol.)} \rightarrow K_4[Nb_2Q_4(C_2O_4)_4] \text{ (sol.)} + 4KBr \text{ (sol.)} \quad (12)$$

Mechanochemical reaction was employed for effective syntheses of many chelate complexes of $[Nb_2(Q_2)_2(LL)_4]$ type. Examples are new selenide clusters with ionic and molecular structure $K_4[Nb_2(Se_2)_2(C_2O_4)_4] \cdot 4H_2O$, $[Nb_2(Se_2)_2(acac)_4]$, and $[Nb_2(Se_2)_2(i\text{-}PrOCS_2)_4]$. ^{1}H, ^{12}C, ^{31}P, and ^{77}Se NMR spectroscopy in solution was used to prove that the products were two geometrical isomers of idealized C_{2h} and D_2 symmetry that differ only in the relative orientation of the chelate cycles at the two ends of the molecule (Fig. 5). Synthesis under conditions of MA of solids yields isomers in a nearly statistical ratio of 1 : 1. However, the dominant product that crystallized from solution was the centrosymmetric isomer.

Thus studies on mechanochemical reactions leading to binuclear niobium chalcogenide bridging complexes with a stable $Nb_2O_4^{4+}$ cluster group indicated that MA can be effectively used to cut this cluster fragment out of the starting coordination polymers. At subsequent stages, this fragment reacts with mono- or bidentate L ligands to form series of compounds. The $Nb_2(\mu\text{-}Se_2)_2^{4+}$ selenide fragment was shown to be stable under conditions of MA.

CONCLUSIONS

The original and published data revised in this paper have demonstrated for the first time that solid-phase mechanochemical reactions are applicable to the synthesis of cluster compounds of varying nature and composition. Complex cluster compounds with discrete molecular or ionic structures have been synthesized by reactions under conditions of MA. Cluster derivatives of boranes and metallocarboranes [14, 15, 20, 23] and the derivatives of chalcogenide clusters of transition metal atoms (M) with $[M_2]$ and $[M_3]$ (M = W, Mo, Nb) structural cluster fragments [24–26, 8] were synthesized mechanochemically. For reactions initiated by MA, hermetic vibratory ball mills are applicable; principles of operation and design of these mills are described in [10–14].

The results for every type of reaction on cluster systems are briefly discussed in the corresponding sections of this review. Two major types of mechanochemical reactions have been accomplished. Reactions of the first type are those where the composition and structure of the cluster fragments are changed by introducing heteroatoms or removing the ligand [reactions (1)–(6)]. Reactions of the second type involve extraction of the cluster structural fragments from coordination polymers and modification of the ligand surroundings of the cluster atoms [reactions (8)–(12)]. The latter reactions [for example, reaction (8)] form saltlike and molecular compounds. Replacement of the ligand surroundings of the M atoms in clusters with the $[M_3]$ fragment sometimes changes the nature of the cluster component of the complex from anionic to cationic [reactions (9), (10)]. Finally, during formation of heteroatomic cluster derivatives of metallocarboranes, solid-phase redox processes can take place on transition metal atoms [reaction (6)]. The real mechanisms and the theoretical aspects of processes that occur during MA are actually unknown because of their complexity and the lack of appropriate equipment for experiment. Cluster mechanochemistry is yet in its infancy. The available empirical data, however, are useful in syntheses of compounds from the given class. Mechanochemistry of cluster systems itself must be the object of further development in view of the obvious advantages of mechanochemical methods of synthesis.

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