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Research Article

Keywords: Crystalline cyamelurate synthesis, Kinetic control of reactions, Crystal Structures, s-, p- and d-Metals.

DOI: https://doi.org/10.21203/rs.3.rs-550116/v1

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Metal cyamelurates: structural diversity caused by kinetic and thermodynamic controls

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Abstract

The kinetic control of chemical reactions makes it possible both to isolate metastable substances with properties different from those of thermodynamically stable phases, and to obtain information useful for studying the crystal nucleation and further transformations of metastable phases into stable ones. Metal cyamelurates are suitable subjects for kinetic control in synthesis due to their easy crystallization and short reaction times. In this work cobalt, manganese, magnesium, copper, aluminum, chromium, calcium and lead cyamelurates were obtained and their crystal structures were determined. Most syntheses at room temperature take place under kinetic control, and this often leads to a mixture of phases. KM(C₆N₇O₃)·5H₂O (M=Co(II), Mn(II)) powders consisted of one crystalline compound. An increase in temperature leads to thermodynamic control, which is proved by registration of Mn(C₆N₇O₃H)·5H₂O and KMg(C₆N₇O₃)·5H₂O crystalline phases. It was possible to isolate Ca(C₆N₇O₃H)·6H₂O and Pb(C₆N₇O₃H)·3H₂O from the mixture by washing samples with a weak acid solution. As a result of the work, five different structural types were obtained, including KCu(C₆N₇O₃)·2H₂O and KM(C₆N₇O₃H)₂·6H₂O (M=Al, Cr(III)). Despite the diversity of salts obtained as a result of thermodynamic or kinetic control, practically the same building blocks form the crystal structure of cyamelurates. The hypothesis of nucleation in a colloidal micelle with electric double layer can be applied to the compounds listed above.

Keywords Crystalline cyamelurate synthesis, Kinetic control of reactions, Crystal Structures, s-, p- and d-Metals.

Introduction

Cyameluric acid was first obtained more than 170 years ago, but its structure was determined by Pauling almost 90 years after the discovery of the acid [1]. Nevertheless heptazine derivatives are still fractionally investigated [2]. The
crystal structures of poorly soluble salts of cyameluric acid have hardly been studied as well. It was previously shown [3] that the formation of a thermodynamically stable crystalline modification of zinc cyamelurate, [Zn(H₂O)₆][Zn(H₂O)₄(C₆N₇O₃H)₂] [4], proceeds in several stages: (i) formation of the initial metastable phase, [ZnK₂(H₂O)₈(C₆N₇O₃H)₂], from building blocks existing in aqueous solutions of precursors; (ii) transformation of the initial metastable phase into the second phase, [Zn(H₂O)₅(C₆N₇O₃H)], via complexation reaction; (iii) hydrate isomerization of the latter into the final thermodynamically stable product. It was suggested [3] that the synthesis of zinc, nickel, and iron cyamelurates occurs in double electric micelles, which act as nanoreactors.

It was found [3] that cyamelurate ligands donate only oxygen atoms to the inner spheres of metal complexes, despite the potential for the formation of bonds of nickel or zinc with nitrogen atoms of cyamelurate ions. This possibility follows from the tautomerism of cyameluric acid [5-7], the widespread occurrence of nickel or zinc amino complexes, and the ability to form chelate cycles with the simultaneous participation of oxygen and nitrogen atoms.

The closest analogue of cyameluric acid (heptazine or tri-s-triazine derivative), cyanuric acid (1,3,5-triazine derivative) provides nitrogen atoms to the inner spheres of nickel or copper complexes [8-10]. In barium cyanurate [11], anions form four-membered metalloccycles through oxygen and nitrogen atoms or attach to the metal ion only via oxygen atoms. In calcium cyanurate, only oxygen-metal coordination bonds are present [12], but four-membered metalloccycles are formed by cyanurate ligands and lead atom [13-14].

The property of the triazine ring to attach metal atoms by lone electron pairs of nitrogen atoms is used in covalent triazine frameworks to obtain hybrid materials in which metal ions and noble metal nanoclusters can be attached to nitrogen atoms of triazine rings. This results in efficient photocatalysts [15-22]. Various heptazine derivatives also exhibit catalytic properties, and one of the known materials is graphite-like C₃N₄ [23].

There is very little information on the syntheses, crystal structures, and properties of soluble cyameluric acid salts. A few papers are available on cyamelurates of lithium, sodium, potassium, rubidium, cesium [24-26]; strontium [27], zinc-ammonium and calcium-ammonium cyamelurates, as well as cyamelurates of the copper(II) ammonia complex [28] and guanidinium [29]. Two phases of ammonium cyamelurates were synthesized, and their crystal structures were determined [23]. All these substances are readily soluble in water and form single crystals suitable for single-crystal X-ray diffraction. Synthesis procedure and crystal structure of cyamelurates [M(H₂O)₆][M(H₂O)₄(C₆N₇O₃H)₂], where M=Mn(II), Co(II), Ni(II), Zn(II) (all four compounds are isostructural), are described in [4]. We classified them as thermodynamically stable for the reasons stated in our previous article [3]. The crystal structures described below are metastable and obtained under kinetic control with rare exceptions (see below).
Kinetic control was used to isolate intermediate metastable phases preceding the appearance of thermodynamically stable compounds.

As a result of a reaction proceeding under thermodynamic control, the main product is the most stable among all possible products. On the other hand, kinetic control leads to the products with the highest reaction rates. In cases where the most rapidly formed product is not the most stable, kinetic control makes it possible to isolate metastable phases from the reaction system. Often, by changing the reaction conditions, either kinetic or thermodynamic product can be obtained. High temperatures and reaction times (as much as equilibration catalysts) are favorable for thermodynamic products, but low temperatures, short reaction times and high concentrations are used to isolate metastable products.

In a work [30], the synthesis conditions were slightly different from that of samples in the work [4], and diverse results were obtained: similar powder patterns of nickel and zinc cyamelurates clearly differed from the powder pattern of manganese cyamelurate, and the chemical composition of manganese cyamelurate contained potassium, while Zn(II), Ni(II), Co(II) cyamelurates did not contain stoichiometric amounts of potassium [30].

Many forms of cyameluric acid give rise to a variety of its derivatives: cyameluric acid is known to have 17 tautomers [5-7]. Crystals with composition K$_3$($C_6N_7O_3$)·3H$_2$O [24] are derived from the trihydroxo-tautomer of cyameluric acid. An aqueous solution of this salt, according to our experience, has a pH of about 10. After acidification of the potassium cyamelurate solution to pH=7.5, K$_2$($C_6N_7O_3$H)·H$_2$O crystallizes from the solution [25]. Cyamelurate ions in this compound are derived from the monocarbonyl tautomer. Further acidification of the potassium cyamelurate solution to pH=4.5 leads to the formation of K($C_6N_7O_3$H$_2$)·2H$_2$O crystals [25] in which the anion is formed by the cyameluric acid dicarbonyl tautomer.

In this work, we report on the synthesis and crystal structures of cobalt, manganese, magnesium, copper, aluminum, chromium, calcium and lead cyamelurates. Within the framework of the requirements for the study of reactions, carried out under kinetic control, the conditions for the synthesis of cyamelurates were chosen so that the desirable quality X-ray powder diffraction patterns were obtained for the best conditions for solution and refinement of the crystal structures of the powders.

**Experimental**

**Materials**

Melamine (99,8%, GE), KOH (puriss., Labtech), Co(NO$_3$)$_2$·6H$_2$O (98,0%, Sigma-Aldrich), Cu(NO$_3$)$_2$·2.5H$_2$O (98,0%, Sigma-Aldrich), Mn(NO$_3$)$_2$·4H$_2$O (97,0%, Sigma-Aldrich), Mg(NO$_3$)$_2$·6H$_2$O (pur., LLC Reaktiv), Al(NO$_3$)$_3$·9H$_2$O
Synthesis of melon

The bulk melon was prepared according to [31]. The final product is light-yellow powder: C, % - 34.73; H, % - 2.05; N, % - 61.79 (chemical formula \( \text{C}_3\text{N}_{4.57}\text{H}_{2.12} \), which corresponds to the results of [32]).

Synthesis of potassium cyamelurate

Potassium cyamelurate (\( \text{K}_3\text{C}_6\text{N}_7\text{O}_3 \)) was obtained by refluxing melon powder in aqueous KOH solution (2.5 molar) for several hours as described in [27]. The reaction mixture was exposed to hot filtration. After cooling to 0 °C colorless precipitate was filtered and washed with ethanol, acetone and dried in air at 180 °C.

Synthesis of KM(C\( \text{C}_6\text{N}_7\text{O}_3 \))\( \cdot\)5H\( \text{H}_2\text{O} \) (M=Co(II), Mn(II))

Dry potassium cyamelurate was used in the synthesis. Solution of 0.36 mmol of \( \text{K}_3(\text{C}_6\text{N}_7\text{O}_3) \) in 5 mL H\( \text{H}_2\text{O} \)-was added to solution of 0.54 mmol of \( \text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) in 5 mL H\( \text{H}_2\text{O} \); or 0.52 mmol of \( \text{K}_3(\text{C}_6\text{N}_7\text{O}_3) \) in 5 mL H\( \text{H}_2\text{O} \)-and 0.78 mmol of \( \text{Mn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O} \) in 5 mL H\( \text{H}_2\text{O} \) were mixed in just the same manner upon stirring for 8-10 minutes at room temperature. pH of mother liquor was around 4-5. Light pink (Co) and colorless (Mn) precipitates were centrifuged (3-5 min, 3000 rpm), were washed twice with distilled water and dried in air. Compound \( \text{KCo(C}_6\text{N}_7\text{O}_3\text{)}\cdot5\text{H}_2\text{O} \) is indicated below as (1).

Our attempts to reproduce the synthesis of \( [\text{M(H}_2\text{O)}_6]\text{[M(H}_2\text{O)}_4(\text{C}_6\text{N}_7\text{O}_3\text{H)}_2] \) (M=Ni(II), Zn(II)) described in [4] were unsuccessful and led to the phases we already received [3]. However, in one of our experiments with manganese cyamelurate, we found a phase identical to \( [\text{Mn(H}_2\text{O)}_6]\text{[Mn(H}_2\text{O)}_4(\text{C}_6\text{N}_7\text{O}_3\text{H)}_2] \) [4]. In this synthesis, a hot aqueous solution of potassium cyamelurate was poured into a hot solution of manganese nitrate and the mixture was boiled with stirring for about 10 minutes. The increased reaction temperature inevitably led to an equilibrium crystalline form of manganese cyamelurate, which confirms our opinion on the thermodynamic equilibrium of the compounds synthesized in [4], stated earlier [3].

Synthesis of KMg(C\( \text{C}_6\text{N}_7\text{O}_3 \))\( \cdot\)5H\( \text{H}_2\text{O} \)

Potassium cyamelurate solution (0.25 mmol in 7 mL H\( \text{H}_2\text{O} \)) was added to the magnesium nitrate solution (0.38 mmol in 3 mL H\( \text{H}_2\text{O} \)) upon stirring and heating for 10 minutes (pH of mother liquor is equal 5-6). Colorless precipitate formed gradually. It was centrifuged (5 min, 3000 rpm), was washed with distilled water and dried in air. X-ray diffraction showed that the compound is isostructural to the potassium-cobalt cyamelurate.
A similar synthesis of magnesium cyamelurate without heating led to a mixture of phases (Fig. S1).

**Synthesis of KCu(C₆N₇O₃)·2H₂O**

0.223 g of K₃(C₆N₇O₃)·3H₂O and 0.235 g of Cu(NO₃)₂·2.5H₂O (0.666 mmol and 1.4 mmol respectively) were mixed with 10 mL H₂O upon stirring for 8-10 minutes. Light purple precipitate was centrifuged (3-5 min, 3000 rpm), was washed twice with distilled water and dried in air. Compound KCu(C₆N₇O₃)·2H₂O is indicated below as (2).

**Synthesis of KM(C₆N₇O₃H)·6H₂O (M=Al, Cr(III))**

The synthesis was carried out by adding a solution of K₃C₆N₇O₃·3H₂O (0.25 mmol in 4 mL H₂O) to aluminum nitrate solution (0.25 mmol in 6 mL H₂O) upon stirring (pH mother liquor was equal 4-5). Since the rate of precipitation was low, the reaction were carried out both under heating and at room temperature in search of the best synthesis conditions. The resulting precipitates were centrifuged (3-5 min, 3000 rpm), washed with distilled water and dried in air at room temperature. According to the results of X-ray studies, the powders synthesized at different temperatures are similar and contain only one crystalline phase, the composition of which corresponds to KAl(C₆N₇O₃H)·6H₂O. This compound is indicated below as (3). A clearer resolution of the diffraction peaks was obtained by washing the final product with dilute hydrochloric acid.

Chromium(III) derivative was obtained similarly to the above method, but without heating. K₃C₆N₇O₃ solution (0.25 mmol in 4 mL H₂O) was poured into Cr(NO₃)₃ solution (0.25 mmol in 5 mL H₂O). At the end of the synthesis, the pH of the mother liquor was in the range of 5-6. The resulting gray precipitate was centrifuged in order to separate from the mother liquor (3000 rpm, 2-5 min) and was washed twice with distilled water. To avoid the loss of crystallization water, the product was dried in air at room temperature. Elevated temperatures in the synthesis of chromium cyamelurate lead not to an improvement in the diffraction pattern, but to an amorphous insoluble powder.

**Synthesis of Ca(C₆N₇O₃H)·6H₂O**

Potassium cyamelurate solution (0.25 mmol in 7 mL H₂O) was added to the calcium nitrate solution (0.39 mmol in 4 mL H₂O) upon stirring and heating for 10 minutes (pH of mother liquor is equal 6-7). Colorless precipitate formed was centrifuged (5 min, 3000 rpm), washed twice with distilled water and dried in air. Since the calcite phase was detected in the sample, it was additionally washed with diluted solution of HCl. Compound Ca(C₆N₇O₃H)·6H₂O is indicated below as (4).

An attempt to synthesize calcium cyamelurate without heating was also made. The sample was washed only with water. This resulted in a different powder diffraction picture. The results of the powder X-ray diffraction (PXRD) are shown in Figure S2.
Synthesis of Pb(C₆N₇O₃H)·3H₂O

Potassium cyamelurate solution (0.25 mmol in 7 mL H₂O) was added to the lead nitrate solution (0.38 mmol in 3 mL H₂O) upon stirring and heating for 10 minutes (pH of mother liquor is equal 5). Instantly formed colorless precipitate was centrifuged (5 min, 3000 rpm), washed twice with distilled water and dried in air. The diffraction pattern wasn’t appropriate for indexing so the powder was washed with a weak hydrochloric acid solution. Compound Pb(C₆N₇O₃H)·3H₂O is indicated below as (5).

An attempt to synthesize lead cyamelurate without heating and without acid washing was made. The results of the PXRD are shown in Figure S3.

Characterization

**Powder X-ray Diffraction.** Powder X-ray diffraction measurements were carried at ambient conditions at two laboratory diffractometers – Huber G670 Guinier camera (CoKα₁ radiation) for (1) and EMPYREAN (PANalytical, Ni-filtered CuKα₁ radiation) for another samples. Data collection details for (1) – (5) are given in Tables S1 and S2. Unit cell dimensions were determined using three indexing programs: TREOR90 [33], ITO [34], and AUTOX [35, 36]. The unit cell parameters and space groups were tested with the use of the Pawley fit [37] and confirmed by the crystal structure solution. We came to the crystal structures for (1) – (5) by using a simulated annealing technique [38]. The model used for the cyamelurate molecule, in a direct space search without H atoms, was taken from the literature [23]. A bond-restrained Rietveld refinement implemented within MRIA [39] was applied to the above results. In the refinements, preferred orientation approximated with a March-Dollase formalism [40] and anisotropic line broadening [41] were taken into account. H atoms in all structures were positioned geometrically (O−H 0.85–0.89 Å) and not refined. Rietveld plots for all structures after the final refinements are shown in Figures S4 – S8.

Crystal structures of (1) – (5) were deposited in the Cambridge Structural Database [42], CCDC numbers are 2008696 for (1), 2008695 for (2), 2084859 for (3), 2084860 for (4), 2084861 for (5).

**Chemical analysis** turned out to be ineffective for determining the compositions of the obtained polycrystalline samples due to presence of unknown amorphous phase; therefore, the chemical compositions of the crystalline phases were determined solely by the results of X-ray diffraction analysis.

Results
Crystal structure of metal cyamelurates

The crystal structures and compositions of (1) – (5) were determined by solution the crystal structures using PXRD data. The crystalchemical analysis of the solved structures revealed the structural blocks that make up the crystals of the obtained compounds.

Crystal structure of potassium-cobalt cyamelurate

A fragment of the crystal structure of potassium-cobalt(II) cyamelurate [KCo(H$_2$O)$_5$C$_6$N$_7$O$_3$] is shown in Figure 1.

![Crystal structure diagram](image)

**Fig. 1** A fragment of the structure (1). Symmetry codes: i = 0.5-x, -0.5+y, 0.5-z; ii = -x, -1-y, 1-z; iii = -1.5+x, -0.5-y, 0.5+z; iv = -0.5-x, -0.5+y, 0.5-z; v = -1+x, -1+y, z.

The cobalt cation is coordinated by four water molecules (O4, O5, O6, O7) and two oxygen atoms O1, O3i of the cyamelurate anion along the vertices of the octahedron. As a result, a flat zigzag chain is formed, in which the cyamelurate
ions alternate with the cobalt atoms connecting them (Fig. S9). The potassium cation is located between the layers formed by flat zigzag chains, and binds these chains into a three-dimensional structure. The first coordination sphere of the potassium atom includes nine oxygen atoms located at a distance of no more than 3.2 Å from the potassium cation. They form a one-capped square antiprism. Five oxygen atoms belong to water molecules, and four – to the cyamelurate anions. Each oxygen atom of anions is a bonding bridge between potassium and cobalt cations (O1, O3), or between two potassium cations (O2). Oxygen atoms of water molecules (O4, O5, O6, O7) also bind potassium and cobalt cations. In addition to the Coulomb forces and coordination and hydrogen bonds between the anions, the \(\pi-\pi\) interaction also takes place (cyamelurate anions are packed in piles, similar to rods, Fig. S9). Looking ahead, we note that similar interactions are present in other compounds under consideration (see below).

**Registration of the \([\text{Mn(H}_2\text{O)}_6][\text{Mn(H}_2\text{O)}_4(\text{C}_6\text{N}_7\text{O}_3\text{H)}_2]\) crystalline phase**

The synthesis of manganese cyamelurate at elevated temperatures resulted in a phase identical to that described in the literature \([\text{Mn(H}_2\text{O)}_6][\text{Mn(H}_2\text{O)}_4(\text{C}_6\text{N}_7\text{O}_3\text{H)}_2]\) [4].

To refine the structure of the substance obtained by us according to the structure published in the literature, the Rietveld method was used. The calculation results are shown in Table 1 and Figure 2.

**Table 1.** Parameters of the manganese cyamelurate unit cells

| Unit cell parameters | Manganese cyamelurate (this work) | Manganese cyamelurate ([4]) |
|----------------------|----------------------------------|-----------------------------|
| \(a\)               | 7.0763(4)                        | 6.9844(4)                   |
| \(b\)               | 8.6438(6)                        | 8.7175(5)                   |
| \(c\)               | 9.8805(7)                        | 10.0198(6)                  |
| \(\alpha\)          | 79.208(4)                        | 79.079(2)                   |
| \(\beta\)           | 81.567(5)                        | 81.581(2)                   |
| \(\gamma\)          | 85.802(5)                        | 84.507(2)                   |
**Fig. 2** Experimental (black) and difference (red) profiles. The vertical blue bars denote the calculated positions of diffraction peaks.

**Crystal structure of potassium-copper(II) cyamelurate**

Figure 3 shows the structure of a fragment of \([\text{KCu(H}_2\text{O)}_2\text{C}_6\text{N}_7\text{O}_3]\) crystals.
Fig. 3 A fragment of the structure (2). Symmetry codes: i = 0.5-x, 0.5-y, 1-z; ii = x, -y, z; iii = -0.5+x, 0.5-y, -1+z; iv = -x, y, -z; v = 0.5-x, 0.5+y,1-z; vi = 0.5-x, -0.5+y,1-z.

The cations and anion of this compound are on the crystallographic elements of symmetry, namely: the potassium cation (0, y, 0) is on the 2 axis; copper cation (.25, .25, .5) is in the center of the inversion; and the crystallographic plane m (x, 0, z) passes through the O2, N1, C3, C4 atoms of the anion.

There are significant differences in the coordination of both alkali and transition metals in comparison with the structure (1). The copper atom has a coordination number 4. The coordination polyhedron is square, which is typical for bivalent copper cations. In this case, not only the oxygen atoms of water molecules, but also the nitrogen atoms of cyamelurate ions are included in the coordination sphere of the copper atom. The coordination number of an alkali metal, based on the same criteria for entering the coordination sphere (distance K–L<3.2 Å, where L is a ligand) is 8, not 9, as for compound (1): oxygen and nitrogen atoms of cyamelurate anions and water molecules located along the vertices of a quadrangular prism.

Cyamelurate ions are linked in pairs by π-π interactions (Fig. S10a). The crystal consists of flat chains in which Cu(H2O)2 fragments alternate with
cyamelurate ions (Figure S10a). The planar chains are linked to each other via potassium cations and the distance between the parallel chains is equal to 3.57 Å. (Figure S10b).

**Crystal structure of potassium-aluminum hydrocyamelurate**

A fragment of structure (3) is shown in Fig. 4. The aluminum and chromium(III) hydrocyamelurates were found to be isostructural (Fig. S11). The composition of the chromium salt crystals corresponds to the formula [Cr(H₂O)₆][K(C₆N₇O₃H)₂].

![Fig. 4](image)

**Fig. 4** A fragment of the structure (3). Symmetry codes: i = -1+x, y, z; ii = x, -1+y, -1+z; iii = -1-x, 2-y, 2-z; iv = -1+x, 1+y, 1+z; v = -x, 2-y, 3-z; vi = -x, 2-y, 2-z; vii = 1+x, y, z; viii = x, 1+y, 1+z; ix = 1-x, 2-y, 2-z; x = 1-x, 1-y, 1-z; xi = -x, 1-y, 1-z.

(C₆N₇O₃H)²⁻ anions are connected in infinite planar chains via hydrogen bonding N5–H5…O1, where i = -1+x, y, z. Such chains form parallel stacks and potassium and aluminum cations are located between them (Fig. S12). The aluminum aqua complex [Al(H₂O)₆]³⁺ has the geometry of a regular octahedron (the deviation of the O–Al–O angles from right angles does not exceed 2.1°). The potassium atom is surrounded by six oxygen and two nitrogen atoms of cyamelurate ions along the vertices of a centrosymmetric eight-vertex structure, similar to a distorted cube.

**Crystal structure of calcium hydrocyamelurate**
A fragment of structure \([\text{Ca(H}_2\text{O)}_6]\text{C}_6\text{N}_7\text{O}_3\text{H}\) is shown in Figure 5.

**Fig. 5** A fragment of the structure (4). Symmetry codes: i = 2-x,-y,1-z; ii = 2-x,-y,-z; iii = -1+x,y,z; 1+x,y,z; iv = 1+x,y,z.

In the structure of compound (4), hydrocynamelurate anions, due to the strong hydrogen bond N5–H5...O1\text{iii}, are arranged in an infinite chain along the a-axis according to the 'head-tail' principle, similar to structure (3). Through π-π interaction neighboring anionic chains form anionic walls, between which calcium cations are located. The distance between parallel chains of anions in one stack is equal to 3.17 Å. Each calcium cation is surrounded by eight water molecules along the vertices of a distorted two-cap trigonal prism. Adjacent calcium coordination polyhedra have common edges (O4 / O4\text{ii}) and (O9 / O9\text{i}), as a result of which endless zigzag chains of polyhedra are formed along the c axis between the anionic walls (Fig. S13).

**Crystal structure of lead(II) hydrocynamelurate**

Structure of [Pb(H\text{O})_2\text{C}_6\text{N}_7\text{O}_3\text{H}·H\text{2O}] is shown in Figure 6.
In structure (5), hydrocyamelurate anions form chains via O1...H4\textsuperscript{ii}–N4\textsuperscript{ii} hydrogen bonds. Walls of anions are built from these chains by means of π–π interactions, as in (3) and (4). Each lead cation forms three four-membered metalloccycles with three anions lying in the same plane with the cation producing endless ribbons (Fig. S14a). Below and above this plane, the cation is coordinated by two water molecules (O5, O6) and an oxygen atom O2\textsuperscript{i}. Thus, the coordination number of the lead cation in this structure is 9. The structure also contains a solvate water molecule, which, through hydrogen bonds, stabilizes the anions in the plane of the ribbon. The distance between two parallel ribbons is equal 3.04 Å and the distance between adjacent layers – 3.16 Å (Fig. 14b).

**Discussion**

An unexpected result should be noted: when mixing hot precursor solutions in the synthesis of manganese(II) cyamelurate, a crystalline phase was obtained, identical to that described in [4], while at room temperature, even observing all the synthesis conditions used in [4], we could not reproduce this synthesis.

As stated earlier [3], we consider crystals of isostructural zinc, nickel, cobalt, and manganese hydrocyamelurates [4] to be thermodynamically stable. These single crystals turned out to be of a size sufficient for single-crystal X-ray diffraction analysis, and, therefore, they were obtained under the conditions of a reversible reaction leading to a thermodynamically equilibrium phase. The
synthesis of manganese cyamelurate in hot water was carried out in order to check the result of the reaction under conditions close to thermodynamic equilibrium, which is facilitated by high temperatures. Precipitation from a hot solution of a phase similar to that synthesized in the work [4] confirmed the acceptability of our hypothesis that the synthesis of compounds $\text{[M(H}_2\text{O)}_6]_2\text{[C}_6\text{N}_7\text{O}_3\text{H}_2]}$ (M=Mn(II), Co(II), Ni(II), Zn(II), [4]) proceeds under thermodynamic control.

It is known [25] that the equilibrium of the cyameluric acid tautomers depends on the pH of the medium: crystallization from an alkaline medium leads to salts with the $(\text{C}_6\text{N}_7\text{O}_3^{-})$ anion, the $(\text{C}_6\text{N}_7\text{O}_3\text{H})^2-$ anion is formed in a neutral, and $(\text{C}_6\text{N}_7\text{O}_3\text{H}_2^-)$ anion – in an acidic (pH~4.5) medium. Although $\text{KM(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot6\text{H}_2\text{O}$ (M=Co(II), Mn(II)) crystals are formed at pH 4–5, no hydrogen atoms in the anions were found. Comparing the composition and reaction conditions of thermodynamic samples [4] with potassium-cobalt and potassium-manganese cyamelurates noted in this article, we concluded that the latter are metastable. The formation of the metastable phases (in [3] and in this work) can be explained by the ability of metal cyamelurates to easily form diverse crystalline modifications under kinetic control.

$\text{KMg(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot5\text{H}_2\text{O}$ that isostructural to potassium-cobalt cyamelurate crystallizes at elevated temperatures to get single-phase powder. We suppose that $\text{KMg(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot5\text{H}_2\text{O}$ is a thermodynamic product and the unknown phase of magnesium cyamelurate (Fig. S1) is a kinetic product. Vice versa, since the $\text{KAl(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot6\text{H}_2\text{O}$ crystals were always isolated as single-phase at different temperatures, that compound can be considered thermodynamically stable.

The synthesis of calcium and lead(II) cyamelurates at elevated temperatures, on the contrary, led to a mixture of crystalline phases (Fig. S4, S5). Washing with a dilute solution of hydrochloric acid made it possible to isolate single-phase powders $\text{Ca(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot6\text{H}_2\text{O}$ and $\text{Pb(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot3\text{H}_2\text{O}$. The hydrochloric acid most likely shifted the equilibrium from unknown calcium and lead salts in favor of hydrocyamelurates.

Calcium hydrocyamelurate $\text{Ca(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot6\text{H}_2\text{O}$ precipitated as a minor among the mixture of crystalline and amorphous phases. A product of the same reaction at room temperature washed with water has completely different composition Fig. S4. Lead hydrocyamelurate $\text{Pb(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot3\text{H}_2\text{O}$ precipitates both at room and at elevated temperatures and mixtures of different phase compositions are formed in both syntheses (Fig. S5). By obtaining this phase (or mixture of phases) at a relatively low temperature, it can be assumed that metastable phases precipitate at room temperature.

In a $\text{Ca(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot6\text{H}_2\text{O}$ crystal structure two building blocks are distinguished: hydrated polynuclear calcium complexes and anions of cyameluric acid keto-tautomer $(\text{C}_6\text{N}_7\text{O}_3\text{H})^{2-}$. Similar building blocks but with monomeric six-water cationic aquacomplexes can be identified in the structures of $\text{K}_2\text{Zn(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot8\text{H}_2\text{O}$ [3] and $\text{KM(C}_6\text{N}_7\text{O}_3\text{H)}_2\cdot6\text{H}_2\text{O}$ (M=Al, Cr(III)).
Pb(C₆N₇O₃H)·3H₂O crystals do not contain lead aquacomplexes and consist of polynuclear complexes, in which cyamelurate ions perform both bidentate cyclic and bridging functions, connecting lead ions. Pb(C₆N₇O₃H)·3H₂O phase is obtained in a mixture with unknown crystalline phases both at room temperature and upon heating (Fig. S5).

Since the initial ratio of reagents M²⁺:C₆N₇O₃⁻ (M=Mn(II), Co(II), Mg, Cu(II), Ca, Pb(II)) is equal to 3:2 and the obtained crystalline salts contain an anion and a cation in the ratio of 1:1, all compounds were formed with an excess of subsequent metal nitrate in the dispersion medium. An excess of aluminum and chromium(III) cations also takes place, since there are two anions per cation in the compound, and the precursor ratio was 1:1. It can be assumed that metal ions created a dense layer of an electric double layer in micelles, i.e. nucleation of KM(C₆N₇O₃)·5H₂O (M=Co(II), Mn(II), Mg), KCu(C₆N₇O₃)·2H₂O, KM(C₆N₇O₃H)₂·6H₂O (M=Al, Cr(III)), Ca(C₆N₇O₃H)·6H₂O and Pb(C₆N₇O₃H)·3H₂O proceeds similarly to nucleation of zinc hydrocyamelurates, described previously in [3].

**Conclusion**

Syntheses of cyamelurates of many metals take place at room temperature under kinetic control. By raising the temperature, thermodynamic control of the reactions can be established. This is clearly seen in the example of manganese(II) salts obtained at room temperature and by heating the initial reagent solutions.

As in the case of zinc cyamelurates [3], the hypothesis of nucleation in a colloidal micelle with electric double layer can be also applied to the above mentioned salts of cyameluric acid.

Despite the variety of salts of cyameluric acid obtained as a result of thermodynamic or kinetic control, practically the same building blocks form the crystal structure of cyamelurates. In crystals (3), (4), (5) hydrocyamelurate anions form anionic walls, which are interconnected by cations and hydrogen bonds. Cyamelurate anions form either anionic rods (π-π stacking) in compound (1) or π-π dimers surrounded by cations in compound (2).

**Declarations**

**Funding** This work was supported by Russian Foundation for Basic Research (grant 20-08-00097) and by M.V. Lomonosov Moscow State University Program of Development.

**Conflicts of interest** The authors have no conflicts of interest to declare that are relevant to the content of this article.
**Data availability** The datasets generated and analyzed during the current study are available in Cambridge Crystallographic Data Centre, CCDC numbers 2008696, 2008695, 2084859, 2084860, 2084861. [https://www.ccdc.cam.ac.uk/].

**Code availability** not applicable

**Author’s contribution** A. S. Isbjakowa, chemical syntheses and analyzes, writing of manuscript; V. V. Chernyshev, powder methods of crystal structure determinations V. A. Tafeenko, crystal-chemical analysis; L. A. Aslanov, setting a scientific problem and choosing objects of research, supervision of research, analysis of results, writing of manuscript.

**Ethical approval** All ethical standards mentioned in Instructions for Authors are fulfilled.

**Consent to participate** All authors agreed with participation in research and publication of the results.

**Consent for publication** All authors agreed with the content and all gave explicit consent to submit to Structural Chemistry Journal. All authors obtained consent from the responsible authorities at the institute/ organization where the work has been carried out, before submission. All listed authors have approved the manuscript before submission, including the names and order of authors;
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A fragment of the structure (1). Symmetry codes: i = 0.5-x, -0.5+y, 0.5-z; ii = -x, -1-y, 1-z; iii = -1.5+x, -0.5-y, 0.5+z; iv = -0.5-x, -0.5+y, 0.5-z; v = -1+x, -1+y, z.
Figure 2

Experimental (black) and difference (red) profiles. The vertical blue bars denote the calculated positions of diffraction peaks.
Figure 3

A fragment of the structure (2). Symmetry codes: i = 0.5-x, 0.5-y, 1-z; ii = x, -y, z; iii = -0.5+x, 0.5-y, -1+z; iv = -x, y, -z; v = 0.5-x, 0.5+y,1-z; vi = 0.5-x, -0.5+y,1-z.
Figure 4

A fragment of the structure (3). Symmetry codes: 

\begin{align*}
i &= -1+x, y, z; \\
ii &= x, -1+y, -1+z; \\
iii &= -1-x, 2-y, 2-z; \\
iv &= -1+x, 1+y, 1+z; \\
v &= -x, 2-y, 3-z; \\
vi &= -x, 2-y, 2-z; \\
vi &= 1+x, y, z; \\
\text{vii} &= 1+y, 1+z; \\
\text{viii} &= 1-x, 2-y, 2-z; \\
\text{ix} &= 1-x, 1-y, 1-z; \\
\text{x} &= -x, 1-y, 1-z.
\end{align*}
Figure 5

A fragment of the structure (4). Symmetry codes: i = 2-x,y,1-z; ii = 2-x,-y,-z; iii = -1+x,y,z; 1+x,y,z; iv = 1+x,y,z.
Figure 6

A fragment of the structure (5). Symmetry codes: i = 1-x, -y, 1-z; ii = x, y, 1-z; iii = x, 0.5-y, 0.5+z.

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