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On the Formation and Decomposition of the Melonate Ion in Cyanate and Thiocyanate Melts and the Crystal Structure of Potassium Melonate, $K_3[C_6N_7(NCN)_3]$

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The synthesis of potassium melonate, $K_3[C_6N_7(NCN)_3]$, by reaction of a potassium thiocyanate melt with the polymer melon $[C_6N_7(NH)(NH_2)]_n$ is an established, though poorly understood, reaction. We have modified the original approach by using salt melts containing Na^+ ions and/or cyanate ions to yield the respective melonate salts. These melonates, however, are not the final reaction products. We have identified them to decompose in cyanate melts to form tricyanomelaminates at higher temperatures and prolonged reaction times. This is the first selective decomposition reaction leading from heptazines to triazines. The progress of the reactions was studied by using thermal analysis, thus allowing the exact determination of reaction temperatures and weight losses. With the data at hand we are now able to gain better insight into the formation and properties of alkali melonates while establishing new synthetic routes to these compounds. We were able to isolate crystals of anhydrous potassium melonate directly from a thiocyanate melt. The structure of this compound was solved by single-crystal X-ray-diffraction. The new reaction conditions involving cyanates on the one hand avoid the release of CS_2 and are no longer highly corrosive to most metallic reaction vessels and on the other hand these reagents provide new, cheap, and convenient access to melonates and tricyanomelaminates.

Introduction

Potassium hydromelonate or simply potassium melonate $\{K_3C_9N_{13} = K_3[C_6N_7(NCN)_3]\}$ was first synthesized by Gmelin in 1835[1] starting from elemental sulfur and potassium hexacyanoferrate.[2] Liebig subsequently spent considerable effort on investigating melonates.[3] Accordingly, potassium melonate can alternatively be prepared from potassium thiocyanate and $SbCl_3$ or $BiCl_3$ or by the reaction of melon, a polymeric compound with idealized formula $[C_6N_7(NH)(NH_2)]_n$,[4] with molten potassium thiocyanate, thus generating a more facile approach for this compound.

Hydromelonates or melonates are salts of the corresponding hydromelonic acid $H_3C_6N_7(NCN)_3$, which has not been validly proven so far to be isolable as such due to polymerization issues (though some claims have been made in the literature[11,7]). The name hydromelonic acid is derived from the assumption that this compound was a hydrate of melon, as it was reported to evolve water and transform into melon upon heating. Thus, melon was initially wrongly believed to be the anhydride of hydromelonic acid. It must be noted that alternative spellings (e.g., "mellonates") or expressions (e.g., "cyamelon"[5] for hydromelonic acid) were commonly used during the 19th century. The melonate ion can be described as tricyanamido-*s*-heptazine or tricyanomelem [with melem being triamino-*s*-heptazine, $C_6N_7(NH_2)_3$]. The tricyanomelaminates $[C_3N_3(NCN)_3]^{3-}$ are comparable chemical compounds based on the cyanuric nucleus $[C_3N_3]$ instead of the cyameluric nucleus $[C_6N_7]$ (cf. Scheme 1). These compounds have already been studied in detail by preceding works.[6,8] In the literature, it has been claimed that tricyanomelaminates are available by reaction of melamine and thiocyanate melts (with melonates being a major byproduct).[7] However, a synthesis based on trimerization of dicyanamides[8] was predominantly employed for the preparation of the majority of tricyanomelaminates described so far. Unfortunately, ion-exchange steps are often required, as not many different dicyanamide salts are readily available and only alkali dicyanamides yield well-defined tricyanomelaminates by this approach.[6]

Especially, nonmetal tricyanomelaminates were discussed as precursors for carbon nitride materials.[9] Thus, melonates are a promising class of compounds for this purpose as well. This is mainly due to the fact that the latter compounds contain the heptazine nucleus, a structural element that is largely believed to be the dominating building block in graphitic carbon nitride ($g\text{-}C_3N_4$).[7,10]

In addition to the potassium salt, copper $\{Cu_3[C_6N_7(NCN)_3]_2\}$,[7] sodium $\{Na_3[C_6N_7(NCN)_3]\cdot 5H_2O\}$,[11] and

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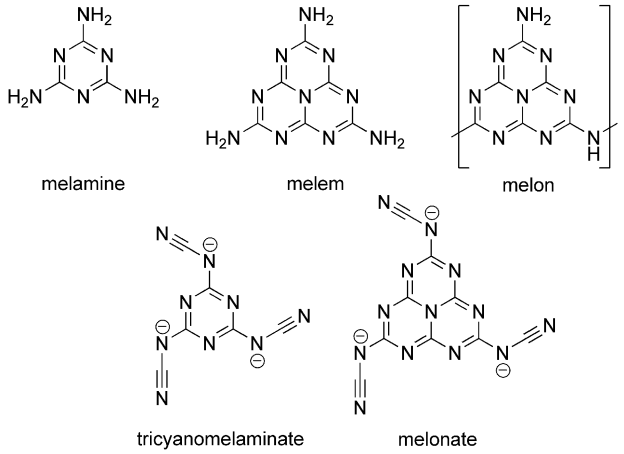


Scheme 1. Molecular structure of some prominent *s*-heptazine- or *s*-triazine-based species. Formulas only display one select resonance structure.

silver melonate $\{Ag_3[C_6N_7(NCN)_3]\cdot 6NH_3\}$[11] have been described in the literature. Several other salts have been mentioned by Finkel'shtein et al.[12] Potassium melonate, however, remained the only melonate salt thoroughly investigated for a remarkable period of time. Until very recently, no structural data of melonates have been available. So far, only the pentahydrate of potassium melonate has been studied by single-crystal X-ray diffraction.[13] Recently, rubidium and cesium melonate $\{Rb_3[C_6N_7(NCN)_3]\cdot 3H_2O$, $Cs_3[C_6N_7(NCN)_3]\cdot 3H_2O\}$ and a protonated calcium melonate $\{Ca[HC_6N_7(NCN)_3]\cdot 7H_2O\}$ were synthesized and investigated with regard to their structure and properties.[14] The lithium melonate $\{Li_3[C_6N_7(NCN)_3]\cdot 6H_2O\}$, another novel melonate salt, was also reported recently.[15] Though the chemistry of potassium melonate was intensively studied during the mid 19th century its molecular structure remained unclear for a long period of time. It was not until the 1930s that Pauling et al. proposed a correct constitution of the melonate ion based on quantum chemical considerations.[16] The mechanism behind the formation of melonate salts however remains unresolved. This contribution intends to gain further insight into the formation of the melonate anion in salt melts while investigating the influence of reaction conditions and starting materials. In this context we have also been able to solve the crystal structure of anhydrous potassium melonate that has been obtained directly from a thiocyanate melt.

Results and Discussion

Experimental Overview

The most commonly used procedure for the preparation of $K_3[C_6N_7(NCN)_3]$ was described by Redemann et al.,[17] where melon has been successively added to molten KSCN. The reaction occurs upon heating with a Bunsen burner and carbon disulfide is evolved, which instantly ignites, as the reaction is carried out in air. Because it is difficult to balance a reaction equation by assuming the products to be only melonate, CS_2, and NH_3 (which is easily detectable by the alkaline reaction of the evolved gasses), some products resulting from decomposition reactions or even some further starting materials must also be involved. Recent works have assumed a reaction equation with formation of KNH_2 and K_2NH [Equation (1)].[13]

$$C_6N_7(NH)(NH_2) + 6\ KSCN \rightarrow K_3[C_6N_7(NCN)_3] + 3\ CS_2 + KNH_2 + K_2NH \quad (1)$$

The formation of these products could however not be experimentally verified. This remains the only balanced reaction equation ever given for the title reaction. H_2S or sulfides possibly play a role as reaction products as well. A slight smell of H_2S can often be detected during the course of the reaction and many reaction procedures given in the literature include steps to purify the product from sulfides.

We have made the interesting discovery that the method of preparing the thiocyanate melts using a Bunsen burner is actually quite a smart choice. When the reaction mixtures are heated in a laboratory furnace oxidation of the thiocyanate forming the respective sulfate is a troublesome side reaction as long as the reaction is performed in air. This is however hardly observed when a Bunsen burner is used, as the temperature gradient derived from the use of this heat source seems to protect the melt from oxidation because the surface is significantly cooler than the lower part of the reaction vessel. The oxidation problem can also be avoided by using an inert gas atmosphere or by conducting the reaction on a scale of 50 to 100 g (as is described in most literature procedures), thus reducing the proportion of surface to volume.

We tried to broaden the applicability of the reaction by investigating the behavior of melon in cyanate melts. Such a reaction procedure would eliminate or mitigate some unfavorable aspects of the original setup like the evolution of CS_2, sensitivity to oxidation by air, or the corrosive behavior of the melt towards metals as a result of the formation of the respective metal sulfides. Most fortunately, the reaction protocol used for KSCN melts can be easily applied to KOCN melts as well. As we were able to yield potassium melonate this way we decided to study the reaction in more detail to determine other possible alterations of the reaction setup. We also changed the cation component of the melts by employing Na^+. Upon addition of melon, NaSCN melts show a behavior much like the one of KSCN melts, finally yielding sodium melonate. For NaOCN, however, the situation is somewhat more complicated as we will describe below. We observed the formation of tricyanomelaminate ions in this case and for KOCN melts at higher temperatures as well.

Thermal Analysis

A major shortcoming of most research provided on the synthesis of melonates so far is the lack of exact data on the reaction conditions and the progress of the reaction. Temperatures have only been given very roughly by refer-

ring to optical assessments of the reaction process, like the presence or absence of red heat when observing the Bunsen burner heated reaction. Some more detailed temperatures are given by Kroke et al.,[13] but do not cover all reaction conditions discussed in this work. We have thus conducted a series of thermoanalytical experiments to provide more detailed information on the course of the reaction. We additionally collected thermograms of each salt as a reference to allow us to distinguish between the thermal events of the pure melt and the reactivity of the mixture. As can be seen, the salts melt at their respective melting points, which are in agreement with given literature values.[18–21] Decomposition of the melts take place commencing in the higher region of the temperature range studied (cf. Figures 1 and 2). The decomposition of the potassium (thio)cyanate melts has been shown to yield cyanides and elemental sulfur/oxygen [cf. Equations (2) and (3)],[21] whereas different decomposition routes have been reported for NaOCN [Equation (4)].[20]

$$KOCN \rightarrow KCN + 1/2\ O_2 \quad (2)$$

$$KSCN \rightarrow KCN + S \quad (3)$$

$$5\ NaOCN \rightarrow 3\ NaCN + Na_2CO_3 + CO_2 + N_2 \quad (4)$$

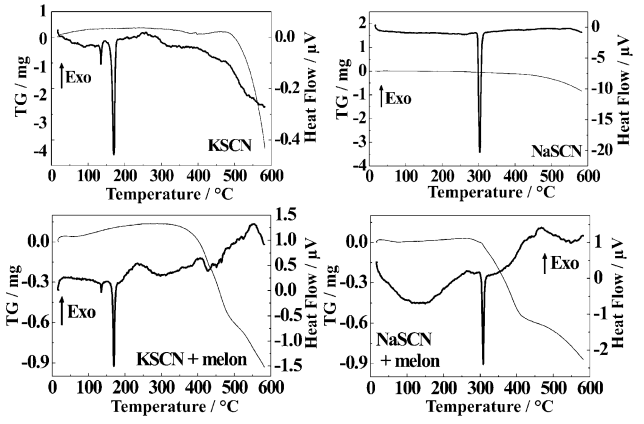


Figure 1. Thermograms for pure thiocyanate melts (top) and melon/thiocyanate mixtures (bottom). Heat flow curves are drawn in bold, TG curves are drawn in narrow.

Reaction mixtures with molar ratios of 4 (SCN^-/OCN^-) to 1 (melon) were used for all experiments. The molar mass of the idealized melon monomer was used for stoichiometric calculations in this regard. Small samples were chosen for mixtures containing SCN^- because of the deteriorating effect of the CS_2 evolved during the course of the reaction on the platinum parts of the DTA rod.

We first studied the thermal behavior of both sodium and potassium thiocyanate/melon mixtures by using thermal analysis (cf. Figure 1). The principal course of the reaction is identical for both salts, whereas the temperatures vary. No reaction takes place below the melting point of the thiocyanates. The endothermic heat flow signal observed in reactions involving KSCN at ca. 133 °C (literature values

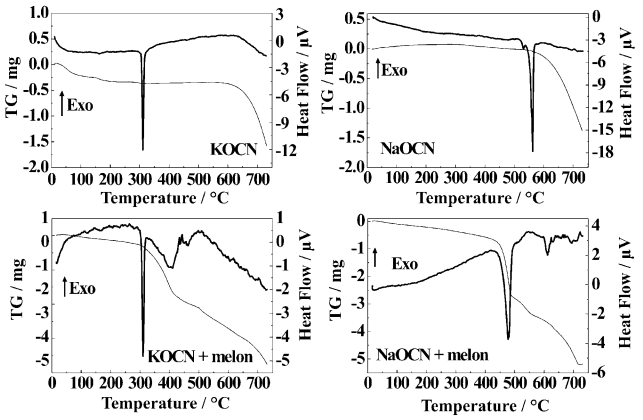


Figure 2. Thermograms for pure cyanate melts (top) and melon/cyanate mixtures (bottom). Heat flow curves are drawn in bold, TG curves are drawn in narrow.

range between 140 and 146 °C[21]) has to be attributed to the order–disorder transition observed for this compound and is followed by melting at about 165 °C (ref.[18] 173 °C). The reaction itself onsets around 400 °C (calculated from the TG curve). Unfortunately, the heat flow signal could not be well resolved due to kinetic aspects (probably slow reaction rates) and limited sample sizes. No plateau is reached after this reaction and a slow weight loss is observable until decomposition of the melt itself commences at around 500 °C.

For NaSCN mixtures, melting is observed at 304 °C (literature values vary significantly and are reported between 287[20] and 323 °C[18]). Unlike the observations for KSCN melts, reaction takes place almost immediately after the melt has formed (onset based on TG at 322 °C) and is concluded at around 420 °C. The onset of decomposition of a pure NaSCN melt starts earlier (≈450 °C) than is the case for KSCN.

After identification of reaction temperatures, experiments were conducted for identical SCN^-/melon mixtures at these distinct temperatures by using a muffle furnace. By these experiments, the initial weight loss could be clearly associated with the formation of the melonate salts. The nature of the decomposition reactions associated with the weight loss of the melonate-containing melts could however not be elucidated this way because of the negative effect of the oxidation reactions. An intense blue color was detectable for all melts containing SCN^- during the course of the reaction. However, the blue intermediate could not be preserved and the melts lost color, even if they were rapidly quenched by using liquid nitrogen.

As we were able to yield potassium melonate by reaction of melon with molten potassium cyanate, we also decided to study this reaction in more detail using thermal analysis (cf. Figure 2). The potassium cyanate/melon mixtures show a melting signal of KOCN at 305 °C slightly lower than the pure salt as a result of melting point depression. At about 368 °C an endothermic reaction associated with weight loss occurs. The mixture gradually loses more weight upon heating. At above 650 °C, the degradation of the melt itself

commences, thus further increasing the weight loss. As a result of the slowness of the process no individual reactions could be resolved in the heat flow signal in this temperature range.

On the basis of these findings a couple of reactions in a muffle furnace were conducted by using identical mixtures of melon and KOCN at select temperatures. Thus optical assessment of the reaction mixture was allowed and the products of different reaction steps could be isolated. Taking all data into account the course of the reaction can be understood in some detail. A cyanate melt can only dissolve a very limited quantity of melon. At first no reaction is observed. A comparably fast reaction yielding potassium melonate is observed quite early. This reaction is accompanied by evolution of gases noticeable by a temporarily foaming of the melt. This step is usually concluded in a matter of no more than a few minutes. If the melt is heated well beyond the initial reaction temperature and maintained at that temperature for a prolonged time no melonate can be observed any longer upon cooling to room temperature. However, potassium tricyanomelaminate has formed instead. Because this conversion happens quite slowly, we assign it with the gradual weight loss found in the TG curve.

The situation is somewhat different when sodium cyanate is used in comparison to all other mixtures studied. The melting point of NaOCN is significantly higher than that of KOCN and thus well beyond the reaction temperatures observed for the formation of $K_3[C_6N_7(NCN)_3]$ in KOCN melts. We have measured a melting point of 549 °C, whereas literature values of 550 °C have been reported.[19] We detected a rather weak endothermal event (onset at 520 °C) overlapping with the melting signal, for which we have been unable to find any reference. This signal is probably related to a phase transition of some sort. For the reactive mixture an endothermic reaction associated with a notable weight loss is observed around 458 °C, thus much lower than the actual melting point of pure sodium cyanate. In a control experiment at the given temperature the sodium cyanate/melon mixture partially melts, yielding a product of gum-like consistency (at the respective temperature). Evolution of gases is also easily detectable. We have not been able to unequivocally identify the nature of these gases. We, however, consider CO_2, NH_3, and H_2O to be the most plausible gaseous species evolved.

This product solidifies again upon further heating and stays solid well beyond the melting point of pure NaOCN. No melting occurs below 601 °C. The melting of the mixture at that temperature is also associated with the degradation of the C/N species only leaving NaOCN after a prolonged time at this temperature.

Sodium tricyanomelaminate is the only product we were able to isolate from mixtures of NaOCN and melon so far. This can be rationalized by comparison to the experiments conducted for the potassium salt. Because of the high melting point of NaOCN, a reaction can only occur at temperatures high enough to favor the degradation of melonates into tricyanomelaminates, thus rendering sodium melonate not accessible by this reaction.

Sodium melonate was reported to crystallize from water forming a pentahydrate.[11] We would like to note that our analytical results of this compound yielded from NaSCN melts during this work are more in line with a hexahydrate (cf. Table 1).

Table 1. Elemental analysis of sodium melonate.

	N / wt.-%	C / wt.-%	H / wt.-%	Na / wt.-%	Drying loss / wt.-%[a]
Observed	38.69	22.70	2.75	14.36	23.6
$Na_3[C_6N_7(NCN)_3]\cdot 5H_2O$	40.53	24.06	2.24	15.35	20.0
$Na_3[C_6N_7(NCN)_3]\cdot 6H_2O$	38.97	23.13	2.59	14.76	23.1
$Na_3[C_6N_7(NCN)_3]\cdot 7H_2O$	37.52	22.28	2.91	14.21	26.0

[a] Calculated for complete solvent loss and measured by DTA/TG.

The DTA/TG diagram of sodium melonate shows that the dehydrated compound is stable until about 640 °C. Above this temperature it melts and decomposes.

Structural Analysis of Anhydrous $K_3[C_6N_7(NCN)_3]$

When a hot, fully reacted melt containing potassium melonate in potassium thiocyanate was slowly cooled to room temperature, crystals of anhydrous potassium melonate were obtained.[22] This compound is moderately hygroscopic, forming the pentahydrate if subjected to air for a prolonged time. However, the formation of the hydrate is favored by the hygroscopic nature of the melt itself; thus, the crystals quickly decay when not separated from the melt. As can be proved by powder XRD, the crystals collected from the melt display the same structure as the anhydrous melonate prepared by drying of the pentahydrate.

Potassium melonate crystallizes in the monoclinic space group $P2_1/c$. Consisting of a cyameluric nucleus typical for all heptazines that is substituted by three cyanamide groups, the molecular structure of the melonate ion is as expected (cf. Scheme 1). The asymmetric unit comprises two different melonate anions, as two different rotamers of the $[C_6N_7(NCN)_3]^{3-}$ ion are stabilized alongside each other in the solid state (cf. Figure 3). One of them is of slightly distorted C_{3h} symmetry, allowing the three N–C≡N groups to maintain maximum distance from each other and essentially maintaining the planarity of the molecule. The other rotamer brings two cyanamide groups into closer proximity, thus deviating from planar geometry by tilting N21–C16≡N26 notably out of the plane. This conformation thus only slightly resembles C_s – the symmetry the idealized planar molecule would exhibit. The occurrence of similar rotamers was also reported for tricyanomelaminates. Examples are: C_s[23] and C_{3h}.[8c] To the best of our knowledge, no tricyanomelaminate expressing both rotamers of its anion side by side has been described so far. Hydrated potassium melonate crystallizes displaying the higher symmetric rotamer alone.[13] Our data thus show that for melonates the C_s conformation can be assumed and that as both conformations can exist alongside each other it is not significantly disfavored with respect to the C_{3h} rotamer. The rotation of the cyanamide groups only seems to result in minor ener-

getic preferences, thus allowing coordination and packing effects to determine the resulting molecular conformation (Figure 4).

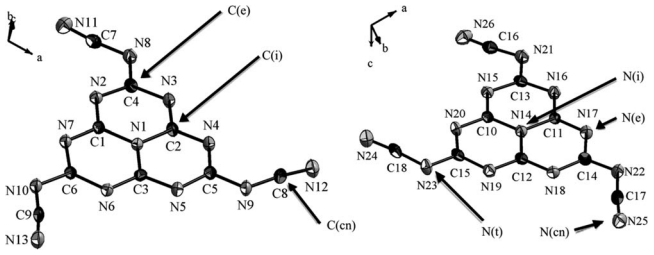


Figure 3. Molecular structure of the two rotamers of the melonate ion derived from single-crystal XRD. Ellipsoids are drawn at the 50% probability level. Chemically equivalent atoms are labeled in accordance to the depicted formalism.

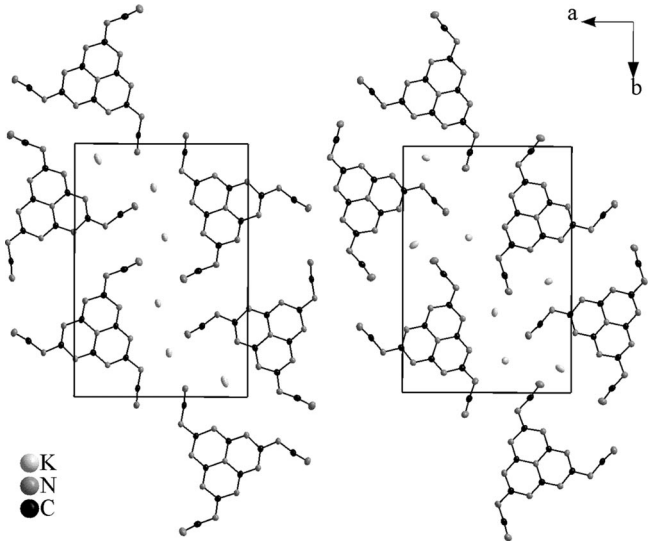


Figure 4. Two different layers of melonate anions in $K_3[C_6N_7(NCN)_3]$. Each layer contains only one rotamer of the anion. Viewed along the *c* axis. Molecules in other layers are omitted for clarity.

Bond lengths and angles between chemically equivalent atoms are found to be almost identical. Unless noted otherwise, only averaged values are used in the following discussion (cf. Table 2). The cyameluric nucleus resembles that found in the pentahydrate and in other heptazines. It is almost planar, all angles are close to 120°. Similarly with other melonates, the bond lengths between the central nitrogen atom and the neighboring carbon atoms are notably longer than the other bonds in the nucleus that have bond lengths between those expected for C–N single and double bonds. The cyanamide groups are almost linear with an average angle of 173.4° at the central carbon atom. The average C≡N bond length is 1.158 Å. The melonate anions are stacked perpendicular to *c* at a distance of 3.28 Å (one quarter of *c*). The K^+ ions are located between these stacks. This nicely illustrates that π-stacking becomes the predominant structure-directing interaction, because hydrogen bonding is impossible. Taking recent works on interactions between aromatic molecules[24] into account we, however, do not expect a significant energetic preference of melonate stacks. This finding is comparable to the situation reported for triazidoheptazine,[25] whereas trichloroheptazine[10a,26] expresses short N···Cl contacts rather than π stacks (Figure 5).

Table 2. Distances and angles between selected chemically equivalent atoms in $K_3[C_6N_7(NCN)_3]$. For atom assignments please refer to Figure 3.

Distances / Å		Angles / °	
N(i)–C(i)	1.393–1.407	C(i)–N(i)–C(i)	119.3–120.4
C(i)–N(c)	1.316–1.342	N(i)–C(i)–N(c)	119.2–120.3
N(c)–C(e)	1.349–1.368	N(c)–C(i)–N(c)	120.3–121.0
C(e)–N(e)	1.329–1.348	C(i)–N(c)–C(e)	116.8–118.1
N(e)–C(cn)	1.313–1.335	N(c)–C(e)–N(e)	124.8–125.2
C(cn)–N(cn)	1.155–1.163	C(e)–N(e)–C(cn)	116.3–118.9
		N(e)–C(cn)–N(cn)	172.3–175.2

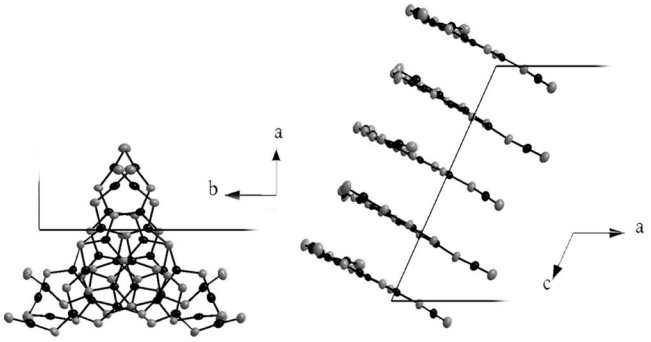


Figure 5. Stacking of melonate ions found in $K_3[C_6N_7(NCN)_3]$. Viewed along the *c* axis (left) and the *b* axis (right). Only one stack is shown; other unit cell contents are omitted for clarity.

The K^+ ions are coordinated by five to seven nitrogen atoms in asymmetric coordination spheres. All nitrogen positions, except the central atom of the cyameluric nucleus, take part in the coordination of potassium. Potassium-nitrogen distances are relatively long, ranging from 2.802 to 3.179 Å.

Comparing the structure of anhydrous $K_3[C_6N_7(NCN)_3]$ with the other melonate salts (Li, Rb, Cs, Ca) published recently,[14,15] it is evident that the molecular structure of the melonate anion is very similar in these cases as well. All these compounds, however, only display C_{3h}-like rotamers. The most prominent difference is the existence of H-bonding networks in hydrated or protonated salts.

Mechanistic Considerations

Detailed mechanistic considerations regarding the reaction of melon in thiocyanate melts have not come to our attention. With the data at hand, it is hardly possible to devise a mechanism explaining the described reactivity free of doubt or room for alternative assumptions. We think, however, that as some important discoveries have been

made, reaction mechanisms can thus be discussed to a certain extent. To provide a basis for mechanistic considerations we would like to discuss some possible explanations for the formation of melonate salts as follows.

The synthesis can be performed with a variety of starting materials. Though it is not necessary that the mechanism for OCN^- and SCN^- melts be similar, we would, however, like to make this assumption as a first hypothesis. In order to assess the plausibility of certain products, we performed some experiments regarding the reactions of thiocyanate melts towards certain species we considered likely to occur as intermediates in a reaction mechanism (cf. Supporting Information). All experiments were conducted under the same conditions used for the classic syntheses of potassium melonate, as most data is available for this reaction.

When discussing the following mechanisms one must be aware of the fact that they include two assumptions not to be confirmed at the moment. The first one is that the heptazine core is retained during the formation of melonates, and reactivity can thus be explained by cleavage of the polymer chain of melon and derivatization of the amino groups. The second hypothesis is that the reactive component is thiocyanate itself and not some other species formed by the decomposition of the melt or any other in situ activation step. When one considers the possibilities of the SCN^- (or OCN^-) ion for attacking melon, some species seem likely to occur during the reaction (cf. Scheme 2). A nucleophilic substitution at the hepazine core could possibly occur to yield a (thio)cyanate (Scheme 2, route a) or an iso(thio)cyanate species (Scheme 2, route b). We cannot offer any convenient explanation how the thiocyanate presented in route a could transform into a cyanamide group of a melonate anion. We thus do not consider such a mechanism to be a good explanation for the observed reactivity. It could however be an initial source of NH_2^- anions for other mechanistic routes.

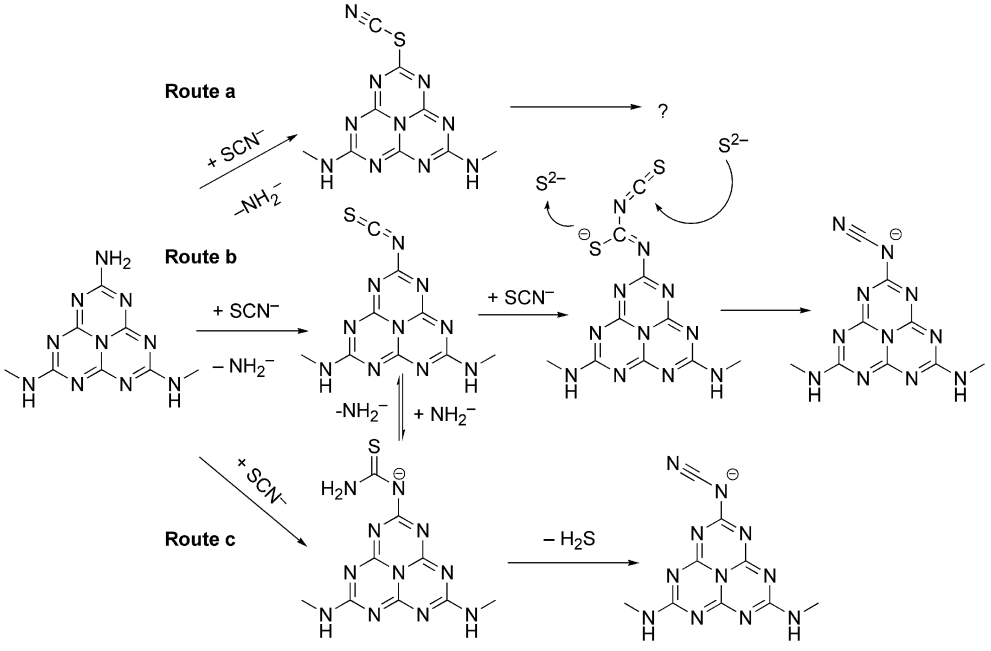
The isothiocyante (Scheme 2, route b) could possibly react to form a cyanamide by first consuming a second equivalent of SCN^- and afterwards releasing CS_2 in the presence of sulfides. The addition of SCN^- to a NH_2 group forming a thiourea intermediate that could decompose into a NCN^- group and H_2S (Scheme 2, route c) might also be possible.

Cleavage of the polymer chain of melon is most likely explained by possible nucleophilic substitution of the NH groups, allowing a reaction comparable to route b (Scheme 2) to be followed. This would probably result in the following reaction [Equation (5)] taking place for route c (Scheme 2).

$$C_6N_7(NH)(NH_2) + 4\ KSCN \rightarrow K_3[C_6N_7(NCN)_3] + CS_2 + KHS + H_2S \quad (5)$$

The reaction equation offered by Kroke et al. [cf. Equation (1)] would result from reaction route b (Scheme 2) taking place.

The evolution of CS_2 needs to be explained by the mechanism, as it is constantly observed under all reaction conditions involving thiocyanates no matter whether melon, melem, or other C/N/H compounds (like melamine) are present. The fact that a SCN^- melt evolves CS_2 when treated with melem and not melon shows that route c (Scheme 2) cannot offer a complete explanation of the observed reactivity. Otherwise, only H_2S should have been detected in such a case, as cleavage of the polymeric melon could not result in other reactions possibly yielding CS_2. As we have not detected any CS_2 upon adding a source of sulfides ($Na_2S{\cdot}H_2O$) to a KSCN melt under comparable con-



Scheme 2. Possible mechanisms for the observed reactivity of the thiocyanate anion towards melon. Routes b and c explain the formation of cyanamide groups.

ditions, we consider the reaction of H_2S with the thiocyanate melt eventually evolving the CS_2 gas to be unlikely.

Route b (Scheme 2) also has its setbacks, as the postulated NH_2^- (and NH^{2-} if one takes cleavage of the heptazine chain into account) species certainly are reactive towards melon and/or the melt and additional steps thus should be necessary to explain their further reactions. Also, a source of the sulfide ions discussed in the mechanism needs to be explained to suggest the likelihood of such a reaction. In addition, we have not observed melon to fully react with 6 equivalents of KSCN as would be expected on the basis of assuming route b (Scheme 2) to take place. A combination of both mechanisms could perhaps be possible. In such a case, H_2S from route c (Scheme 2) could react with NH_2^- from route b (Scheme 2) to yield S^{2-} and NH_3, and thus generating sufficient amounts of sulfides.

As was initially stated, melonates were also found under conditions lacking heptazine-based C/N/H species as starting materials. In this regard, it must be mentioned that Liebig initially yielded many triazine and heptazine species by pyrolysis of an ammonium thiocyanate melt (which was actually a mixture of potassium thiocyanate and ammonium chloride).[27] One can thus offer two basic types of explanations for this finding. One is that heptazines, like melon or melem, are formed from suitable precursors (like NH_4SCN) in these mixtures and subsequently transferred into melonates. The other is that melonates are assembled, bypassing the formation of melem or melon. This would, however, also indicate that a reaction route, in which heptazines were initially broken down into species like cyanamides and melonates were reassembled from such, could be possible. In fact such a course of reaction seems quite likely.

If one were to assume that potassium amide, for example, liberated by route a or b [Scheme 2; cf. Equation (1)], would react with residual melon, one could think of a decomposition, ultimately leading to potassium cyanamide [Equation (6)].

$$C_6N_7(NH)(NH_2) + 12\ KNH_2 \rightarrow 6\ K_2CN_2 + 9\ NH_3 \quad (6)$$

The cyanamide could react further with melon to yield melonate through nucleophilic substitution reactions at the heptazine core [cf. Equation (7)].

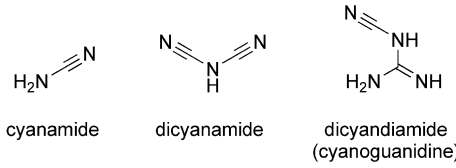
$$3\ K_2CN_2 + C_6N_7(NH)(NH_2) \rightarrow K_3[C_6N_7(NCN)_3] + K_2NH + KNH_2 \quad (7)$$

A combination of all these reactions [Equations (1), (6), and (7)] would result in Equation (8). In such a way, the fate of NH^{2-} and NH_2^- offered in Equation (1) could be explained by the degradation of melon.

$$5\ C_6N_7(NH)(NH_2) + 12\ KSCN \rightarrow 4\ K_3[C_6N_7(NCN)_3] + 6\ CS_2 + 5\ NH_3 \quad (8)$$

The finding that melonates can yield tricyanomelaminates in cyanate melts also takes a certain amount of explanation. Tricyanomelaminates are usually synthesized from dicyanamides, typically at temperatures around 600 °C. Apart from this initially described synthetic route to tricyanomelaminates, reactions starting from mixtures of cyanides [$Hg(CN)_2$ + (Na/K)CN],[11,28] cyanamides and dicyandiamide [$Na_2(NCN)$ + $H_4C_2N_4$],[11] dicyandiamide salts like $Na(H_3C_2N_4)$,[29] or melon and $NaNH_2$[28] have already been mentioned (cf. Scheme 3 for structures of the molecules mentioned). The occurrence of melonates as intermediates has, however, not been mentioned in any of these works. The thermal decomposition of melonates has been determined to occur beyond 516 °C (for $K_3C_9N_{13}$).[13] In this context, it becomes evident that under the conditions of the transformation of potassium melonate into potassium tricyanomelaminate in molten KOCN, which we have conducted at 500 °C, the starting material is on the border of its thermal stability. We thus consider it likely that melonate initially decomposes into smaller, probably acyclic ions like cyanamides, dicyanamides, or dicyandiamides (or a mixture of such). These species can subsequently form tricyanomelaminates much like the mixtures described above. It is possible to devise a balanced reaction equation for this decomposition involving no more starting materials than potassium melonate and potassium cyanate [cf. Equation (9)]. We, however, are not able to give proof or mechanistic details for this equation.

$$3\ K_3[C_6N_7(NCN)_3] + 6\ KOCN \rightarrow 5\ K_3[C_3N_3(NCN)_3] + 3\ CO_2 \quad (9)$$



Scheme 3. Structures of some small acyclic C/N/H molecules.

The source of the blue color still remains to be determined. On the basis of our work we would like to contribute that this intermediary coloring of the melt only occurs for SCN^- melts, whereas OCN^- melts do not show this phenomenon and that an intense blue color can temporarily occur upon addition of several compounds to a SCN^- melt.

On the basis of the thermal condensation leading from melamine to melem and melon, one may believe that heptazine-based molecules are always favored over triazines when the temperature is increased. The reactivity leading to tricyanomelaminates in cyanate melts shows that accepting this to be a general principle applicable under all circumstances, however, is a rash assumption. As the properties of salt melts are fundamentally different to those within a sealed glass ampoule used for condensation reactions, many conclusions previously drawn do not necessarily apply to reactions in a melt. Under the conditions studied in this work, polymeric heptazines are transformed into molecular heptazine species and upon further heating into molecular triazine species. In some sense, this is the inversion of the reactivity known to take place in sealed glass ampoules at higher temperatures.

Conclusions

The present work illustrates some modifications usable for the synthesis of melonates from salt melts. The applicability of this reaction has been broadened, as we were able to show that apart from potassium thiocyanate melts potassium cyanate and sodium thiocyanate are applicable for yielding melonates. Thus, we were able to describe new and to our belief more convenient reaction routes. The crystal structure of anhydrous potassium melonate, solved during our investigations, is one of few structural analyses conducted for a melonate salt so far. The XRD data also prove that melonates are already yielded in the melt as such and are not affected or generated by further treatment of the melt (like contact with water).

Offering a conclusive mechanism to explain the observed reactivity is still a major concern in understanding the formation of the melonate ion. It is quite astonishing that a large variety of different conditions are suitable to yield melonates and that compounds like melon, melem, or melamine are not essentially necessary as starting materials. As can be shown by our work on cyanate melts, the cyameluric nucleus is prone to decomposition under certain reaction conditions. All this shows that the formation of melonate salts from melem or melon is probably much more complex than a single derivatization reaction of the amino groups or a substitution reaction at the heptazine core alone. Additional efforts are certainly necessary to understand details of the reactivity.

Apart from their possible use as precursors for carbon nitride materials, melonates or tricyanomelaminates certainly are valuable starting compounds for covalent organic frameworks or coordination polymers. Although we were able to gain some additional insight, a lot of research needs to be done to fully understand the synthesis of these compounds in salt melts.

The aim in this respect must be the gathering of mechanistic information to establish a well-grounded reaction equation for the formation of melonate ions.

Experimental Section

General Methods: ^{13}C NMR spectra were recorded in D_2O with a JEOL Eclipse 270 (270 MHz) spectrometer at room temperature. Chemical shifts are referenced in respect to TMS. FTIR spectra were recorded with a Spektrum BX II FTIR spectrometer (Perkin–Elmer) equipped with a DuraSampler diamond-ATR. The measurements were conducted at room temperature. Elemental analyses (C/N/H) were conducted by "Mikroanalytisches Labor der LMU" by using a vario EL analyzer (Elementar Analysensysteme GmbH). Analyses for alkali metal contents were conducted with a VISTA RL CCD simultaneous ICP-AES analyzer system (Varian). The wavelengths 766.491 (K) and 588.995 nm (Na) were used. X-ray powder diffraction patterns (XRPD) were recorded with a Huber G670 Gunier Imaging Plate or a Stoe STADI P (transmission geometry) diffractometer. Measurements were conducted by using Cu-$K_{\alpha 1}$ radiation at room temperature. Theoretical powder diffraction patterns were simulated from single-crystal data by using the Win XPOW software package.[30]

Single-Crystal X-ray Diffraction: The crystal data of potassium melonate was measured with a Nonius Kappa-CCD diffractometer. The measurement was conducted at a temperature of 200 K. The diffraction intensities were scaled by using the SCALEPACK software package.[31] No additional absorption correction was applied. The crystal structure was solved by direct methods (SHELXS-97) and refined against F^2 on all data by full-matrix-least-squares (SHELXL-97).[32] Crystallographic data is summarized in Table 3. Selected distances and angles are presented in Table 2.

Table 3. Crystallographic data and details of the refinement procedures for $K_3[C_6N_7(NCN)_3]$.

Empirical formula	$K_3C_9N_{13}$
Formula weight / g mol^{-1}	407.52
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	1321.3(3)
b / Å	755.6(4)
c / Å	1311.4(3)
β / °	114.17(3)
Crystal size / mm^3	$0.03 \times 0.08 \times 0.31$
Volume / Å^3	2775.4(13)
Formula units per unit cell	8
μ / mm^{-1}	1.011
F(000)	1616
Radiation	Mo-K_α (λ = 71.073 pm), graphite monochromated
Temperature / K	200
θ range / °	3.31 to 27.49
Corrections	Lorentz, polarization, SCALEPACK
Data, restraints, parameters	6355, 0, 451
R_1	0.0384 [$F_0 > 4\sigma(F_0)$] (4756 reflections)
R_1	0.0612 (all data)
wR_2	0.0890 [$F_0 > 4\sigma(F_0)$]
wR_2	0.0985 (all data)
GooF	1.047
Largest peak, deepest hole / e Å^{-3}	0.714, –0.610

Thermal Analysis: The thermal analysis experiments were conducted by using a Setaram TG92 thermal analyzer equipped with a protected S-type DTA/TG rod. Measurements were made in 100 µL alumina crucibles under a streaming helium atmosphere between room temperature and 750 °C (for cyanate melts) or 600 °C (for thiocyanate melts) with a scanning rate of 10 °C min^{-1}. Thermograms of the pure compounds were used to distinguish reaction steps from melting or decomposition steps and to check for possible impurities.

Synthesis of Melon: A polymeric compound that can be assigned the idealized formula $(C_6H_3N_9)_n$ was synthesized by heating melamine (Fluka, purum) to 490 °C for 4 d in a porcelain crucible loosely covered with a porcelain cap. The resulting yellow solid was ground into a powder.

CAUTION: Thiocyanate melts are highly corrosive towards metals; therefore, especially the use of steel or nickel equipment should be strictly avoided when conducting these reactions. Reactions can by very vigorous and the ones described for thiocyanate melts result in the appearance of open flames if carried out in air. Therefore, appropriate precaution is advisable. Commercially available cyanate salts are usually not available at higher purities than 96–97%. We were, however, not able to increase the purity by application of common literature procedures.[33]

Synthesis of Potassium Melonate from a Thiocyanate Melt: Potassium thiocyanate (14 g, 144 mmol, Acros, p.a.) was molten in a

ceramic evaporation dish by using a Bunsen burner. Once the bottom of the dish had reached red heat, melon (6.9 g, 34 mmol) was added to the melt in small portions. The carbon disulfide liberated during the vigorous reaction was allowed to burn. After the reaction had ceased to evolve gases the temperature was maintained for approximately 10 min after which the melt was slowly cooled until it had completely solidified. Then, the evaporation dish was quickly transferred into a glove box under an argon atmosphere where the crystals were collected from the melt.

For yielding bulk material, potassium thiocyanate (4.0 g, 41 mmol, Acros, p.a.) was molten in a ceramic evaporation dish by using a Bunsen burner. Melon (1.66 g, 8.2 mmol) was added to the melt. After the vigorous reaction had ceased, the product was dissolved in water (about 100 mL). A small amount of active carbon was added, and the solution was boiled until it lost its slightly yellow color. After cooling to room temperature a small amount of ethanol was added and all insoluble parts were removed by filtration. The solution was completely precipitated by using ethanol (about 200 mL were required). The product was collected by filtration and thoroughly washed with acetone. After drying in air at room temperature overnight a white solid (1.04 g, 2.1 mmol, 32%)[34] was collected. Further purification was possible by recrystallization from water. FTIR (reflection, 25 °C): $\tilde{\nu}$ = 3392 (s, br.), 2171 (s), 2142 (m), 1641 (s), 1493 (m), 1433 (s), 1300 (w), 1190 (w), 1093 (w), 793 (m) cm^{-1}. ^{13}C NMR (270 MHz, D_2O, 25 °C): δ = 122.3, 156.1, 171.8 ppm. $K_3C_9N_{13}{\cdot}5H_2O$ (497.55): calcd. C 21.73, H 2.03, K 23.57, N 36.60; found C 21.81, H 2.04, K 23.55, N 37.04.

Synthesis of Potassium Melonate from a Cyanate Melt: Melon (500 mg, 2.47 mmol) and (1000 mg, 12.3 mmol) potassium cyanate were ground together and heated at 400 °C for about 30 min. The reaction mixture was cooled to room temperature and dissolved in water (50 mL). After boiling with a small amount of active carbon, insoluble components were removed by filtration. After cooling to room temperature, the product was precipitated by addition of at least three volume equivalents of ethanol. The precipitate was collected by filtration, washed with acetone, and dried under steaming air. The product was yielded as a white solid (515 mg, 1.04 mmol, 53%).[34] Recrystallization from water followed by drying at 40 °C was used for purification purposes. FTIR (reflection, 25 °C): $\tilde{\nu}$ = 3377 (s, br.), 2166 (s), 2137 (m), 1636 (s), 1491 (m), 1427 (s), 1301 (w), 1187 (w), 1090 (w), 1045 (w), 792 (m) cm^{-1}. ^{13}C NMR (270 MHz, D_2O, 25 °C): δ = 122.3 (N–C≡N), 156.1, 171.7 (C–NCN) ppm. $K_3C_9N_{13}{\cdot}5H_2O$ (497.55): calcd. C 21.73, H 2.03, N 36.60; found C 21.57, H 2.10, N 36.12.

Synthesis of Potassium Tricyanomelaminate from a Cyanate Melt: Melon (500 mg, 2.47 mmol) and potassium cyanate (1000 mg, 12.3 mmol) were ground together and heated at 500 °C for about 60 min. The reaction mixture was cooled to room temperature and dissolved in water (50 mL). After heating to about 80 °C for a short time a small amount of active carbon was added, and the solution was allowed to cool to room temperature. After filtration, the product was precipitated by the addition of at least three volume equivalents of ethanol. The precipitate was collected by filtration and recrystallized from water. White solid (408 mg, 1.22 mmol, 37%).[34] FTIR (reflection, 25 °C): $\tilde{\nu}$ = 3534 (w), 3014 (w, br.), 2228 (w), 2154 (s), 1644 (w), 1592 (w), 1507 (s), 1391 (s), 1244 (w), 1136 (w), 1027 (w), 982 (w), 808 (w) cm^{-1}. ^{13}C NMR (270 MHz, D_2O, 25 °C): δ = 124.8 (N–C≡N), 172.9 ppm. $K_3C_6N_9{\cdot}H_2O$ (333.43): calcd. C 21.61, H 0.60, K 35.2, N 37.81; found C 20.79, H 0.83, K 34.5, N 35.55.

Synthesis of Sodium Tricyanomelaminate from a Cyanate Melt: Melon (500 mg, 2.47 mmol) and NaOCN (800 mg, 9.88 mmol) were ground together and heated at 500 °C for about 90 min. After initial melting, the reaction mixture completely solidified again. The product was dissolved in water (20 mL). After the addition of a small amount of active carbon and short boiling all insoluble impurities were removed by filtration. The product was precipitated from the solution after cooling to room temperature by the addition of ethanol, collected by filtration, and washed with acetone. White solid (543 mg, 1.7 mmol, 52%).[34] FTIR (reflection, 25 °C): $\tilde{\nu}$ = 3615 (m), 2930 (m, br.), 2377 (w), 2240 (w), 2176 (s), 1662 (m), 1511 (s), 1396 (s), 1384 (s), 1235 (m), 1000 (w), 802 (m), 773 (w), 713 (w) cm^{-1}. ^{13}C NMR (270 MHz, D_2O, 25 °C): δ = 124.9 (N–C≡N), 173.0 ppm. $Na_3C_6N_9{\cdot}3H_2O$ (321.14): calcd. C 22.44, H 1.88, N 39.25, Na 22.4; found C 22.08, H 1.94, N 38.48, Na 21.2.

Synthesis of Sodium Melonate from a Thiocyanate Melt: Sodium thiocyanate (4.0 g, 50 mmol, Riedel-de Haën, purum) was molten in a ceramic evaporation dish by using a Bunsen burner. Melon (2.00 g, 10 mmol) was added to the melt. After the vigorous reaction had ceased the product was dissolved in water (100 mL). A small amount of active carbon was added, and the solution was boiled until it lost its slightly yellow color. After cooling to room temperature a small amount of ethanol was added and all insoluble parts were removed by filtration. The solution was completely precipitated by using ethanol (about 200 mL were required). The product was collected by filtration and thoroughly washed with acetone. After drying in air at room temperature overnight a white solid (0.82 g, 1.8 mmol, 23%)[34] was collected. Further purification was possible by recrystallization from dilute aqueous ammonia. FTIR (reflection, 25 °C): $\tilde{\nu}$ = 3366 (m, br.), 2173 (s), 2152 (m), 1641 (s), 1491 (m), 1432 (s), 1301 (w), 1194 (w), 1054 (w), 794 (m) cm^{-1}. ^{13}C NMR (270 MHz, D_2O, 25 °C): δ = 122.3, 156.1, 171.7 ppm. $Na_3C_9N_{13}{\cdot}6H_2O$ (449.55): calcd. C 23.13, H 2.59, N 38.97, Na 14.76; found C 22.70, H 2.75, N 38.69, Na 14.36.

Supporting Information (see footnote on the first page of this article): Selected graphical representations of the analytic data (thermal analysis, NMR, XRD, IR) and an overview of the experiments on the stability of certain compounds in KSCN melts.

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