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Potassium melonate, $K_3[C_6N_7(NCN)_3] \cdot 5H_2O$, and its potential use for the synthesis of graphite-like C_3N_4 materials†

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Received (in Montpellier, France) 24th October 2004, Accepted 11th January 2005
First published as an Advance Article on the web 18th March 2005

Melonates, $M^{x}_{3/x}[C_6N_7(NCN)_3]$, contain the aromatic and planar tricyanamino-*s*-heptazine anion. Only one example, the potassium derivative, has been isolated in pure form so far, but it has never been characterised comprehensively. Potassium melonate is obtained from a reaction of the polymer melon, $[C_6N_9H_3]_n$, with KSCN. ^{13}C NMR, FTIR, Raman, UV-vis and luminescence spectroscopy support the proposed molecular structure. The crystal structure of the hydrate $K_3[C_6N_7(NCN)_3] \cdot 5H_2O$ was determined by single crystal X-ray analysis (MoK_α: *Pbca* (no. 161), $a = 6.538(2)$, $b = 24.033(6)$, $c = 23.684(6)$ Å and $Z = 8$). Thermogravimetric analysis shows that the dehydrated salt starts to decompose at temperatures above 500 °C. The $[C_6N_7(NCN)_3]$ unit is an ideal molecular building block for carbon(IV) nitrides, especially *s*-heptazine based graphite-like C_3N_4 networks.

Introduction

Carbon(IV) oxide (CO_2) and carbon(II) oxide (CO) are very stable and extremely well characterised compounds. Comparable carbon(IV) nitrides are not known.[1] Several 3D C_3N_4 crystalline phases have been predicted to be stable and are expected to show very interesting properties similar to diamond, that is, extreme hardness, inertness and wide band gaps.[1] Although some early reports discussed the possibility of synthesising stable CN_x materials,[2] the research in the field of carbon(IV) nitrides was initiated by predictions published by Cohen and Liu,[3] followed by numerous theoretical[4] and experimental[5] studies.[1] For the two monomolecular carbon(IV) nitrides, dicyanocarbodiimide NC–NCN–CN and tricyanamine $N(CN)_3$, the latter has only been calculated[6] while the former was recently photolytically generated in an inert matrix at 20 K.[7] In addition, about a dozen 3D C_3N_4 crystalline phases and about the same number of graphite-like 2D compounds have been predicted. A selection of the latter is depicted in Scheme 1. Most authors have examined the *s*-triazine based structure **A**, which was considered to be the thermodynamically most stable modification.[1c,8–10] We found that *s*-heptazine[11] based layered C_3N_4 structures like **B** should be significantly more stable.[12] Therefore, we are currently synthesising molecular, oligomeric and polymeric *s*-heptazine derivatives. Other *s*-triazine based carbon(IV) nitrides have been postulated, such as networks **C** and **D**, as well as two recently predicted 3D structures derived from $SrSi_2$ and $ThSi_2$.[1c,13] Replacing the *s*-triazine unit by the larger *s*-heptazine unit leads to **E**–**H**.

The *s*-heptazine unit is present in the polymer melon $[C_6N_9H_3]_n$, as well as in melem $C_6N_7(NH_2)_3$ (**1**), a compound that has been characterised recently by Schnick *et al.* (Scheme 2).[14] Only a very few other derivatives have been comprehensively characterised, such as the parent molecule $C_6N_7H_3$ (**2**),[15] trichloro-*s*-heptazine $C_6N_7Cl_3$,[12] the alkali cyamelurates $M_3[C_6N_7O_3]$,[16] and triazido-*s*-heptazine $C_6N_7(N_3)_3$ (**3**),[17] a molecule that was theoretically investigated along with other *s*-heptazine derivatives in 1937 by Pauling and Sturdivant.[18] In contrast to the corresponding *s*-triazine analogue, such as the explosive triazido-*s*-triazine (C_3N_{12}) (**5**), which was first synthesised in 1907 and whose various aspects, including crystal structure,[19] explosive properties,[20] and its use as a C_3N_4 precursor,[21,22] have since been investigated, the *s*-heptazine compound $C_6N_7(N_3)_3$ (**3**) and nearly all of the above-mentioned *s*-heptazine derivatives remained unexplored for over 60 years.[23]

The geometry, electronic structure, and properties of a number of *s*-heptazine derivatives were theoretically studied.[24,25] Komatsu first synthesised "prototype carbon nitrides" from *s*-heptazine derivatives.[26] He obtained mixtures of oligomeric and polymeric materials, which made it difficult to investigate the products.[26] The title compound potassium melonate $K_3[C_6N_7(NCN)_3]$ (**4**) was first mentioned by Gmelin in 1835, but he could not purify the product.[27] Later, potassium melonate was described by Liebig, who investigated several different synthetic routes, such as the reaction of melon with KSCN.[28] However, no reaction equations and structures were provided and product characterisation was solely performed by combustion analysis, solubility and chemical reactivity. Redemann and Lukas[29] in 1939 and, later, Finkel'shtein and Fedoruk[30] reinvestigated the synthesis of potassium melonate. Still, no structural studies and spectroscopic data, except for FTIR data, on any melonate have yet been published.

In this work, we report the first structural and spectroscopic characterisation of a melonate, namely, potassium melonate hydrate $K_3[C_6N_7(NCN)_3] \cdot 5H_2O$, including a single crystal X-ray analysis. We discuss its potential use as a building block for C_3N_4 networks.

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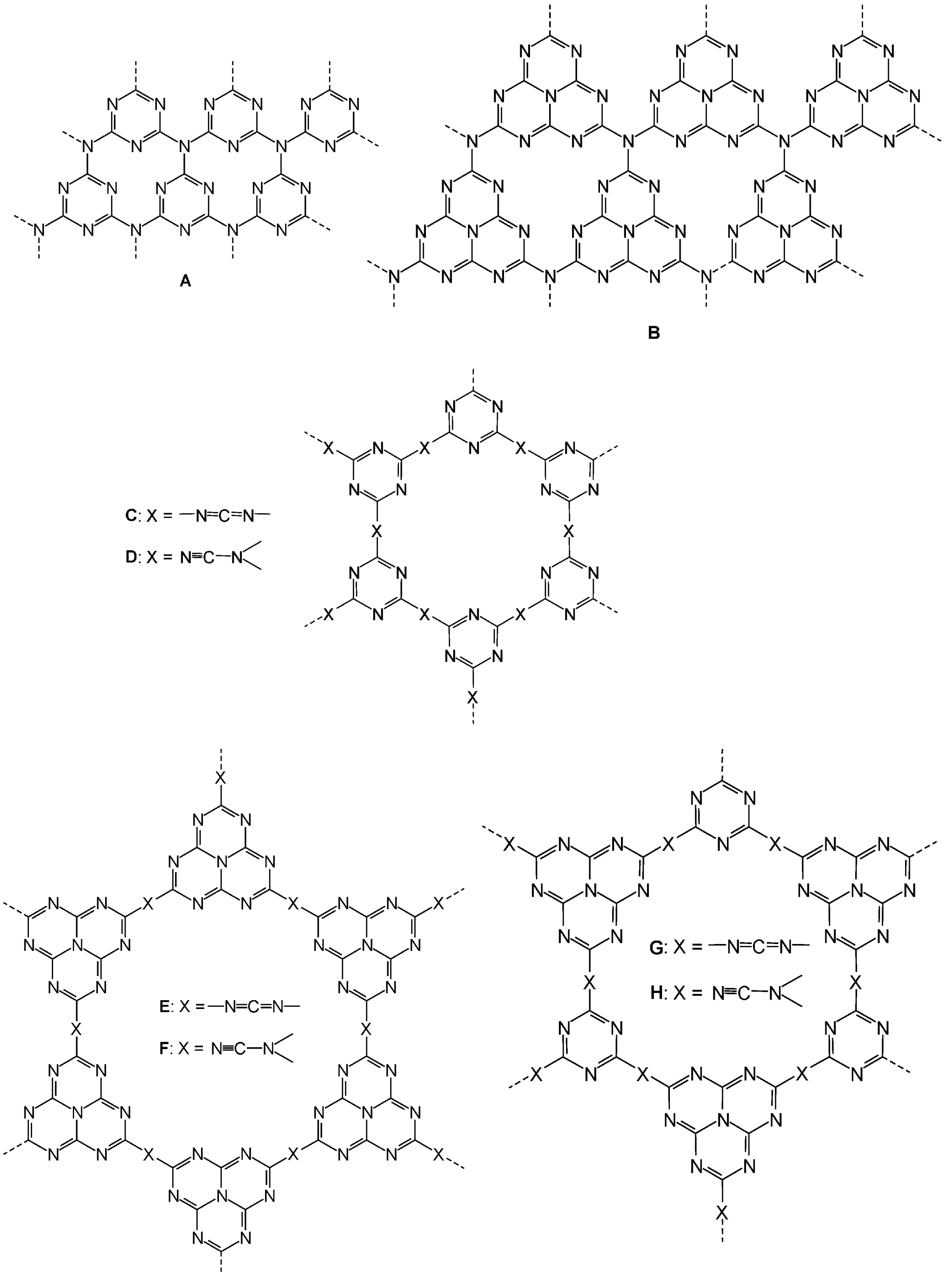
† Tri-*s*-triazine derivatives. Part III. For parts I and II see refs. 12 and 16.

DOI: 10.1039/b416390g

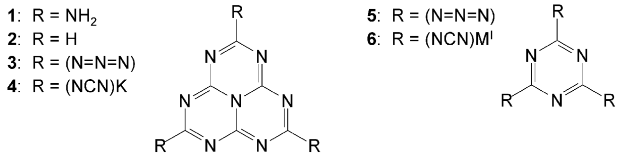


Scheme 1 Selected graphitic carbon(IV) nitride structures.

Experimental

Materials and instrumentation

The starting material melon was obtained from Dufferit GmbH (formerly Degussa). It is widely used for the regeneration of nitridation baths for steel hardening. Its composition has been analysed thoroughly in our lab: it corresponds to the idealised linear polymer structure $[(C_6N_7(NH_2)NH]_n$ $(= C_6N_9H_3)$.[17b] Potassium thiocyanate KSCN was purchased from Riedel-de Haen (99%).



Scheme 2 A selection of carbon(IV) nitride precursors based on the tri-*s*-triazine unit: melem (**1**), tri-*s*-triazine (or *s*-heptazine; **2**), triazido-*s*-heptazine (**3**), potassium melonate (**4**), and two of the corresponding *s*-triazine derivatives: triazido-*s*-triazine (**5**) and alkali tricyanomelaminates (**6**).

Elemental analyses were performed at the Pascher analytical laboratory in Remagen, Germany. The STA-MS (simultaneous thermal analysis coupled with mass spectrometry) investigations were performed using a Netzsch STA 429 equipped with a Balzers QMG 420 quadrupole mass spectrometer. Potassium melonate (82.54 mg) was heated in an alumina crucible up to 860 °C (heating rate 2.5 C° min^{-1}) under a helium (grade 5.0) atmosphere. ^{13}C NMR spectroscopy measurements were performed on a 300 MHz Bruker ARX300 spectrometer using D_2O as a solvent. FTIR spectra were recorded from KBr pellets of the dried sample using a Perkin-Elmer FT-IR 1750 spectrometer. Raman spectra were obtained on dried powder samples in glass capillaries of 0.5 mm diameter, using a Bruker IFS55 module with a Nd:YAG laser at λ = 1064 nm. Photoluminescence (PL) spectra were measured on a spectrofluorimeter Cary Eclipse/Varian. The employed light source was a xenon lamp and the detector was a Hamamatsu photomultiplier. UV absorption spectra were collected with a UV-vis-NR Perkin Elmer Lambda 900 spectrophotometer. For both PL and UV measurements, the spectra were collected from water solutions of the sample (c = 0.2 mol l^{-1}) at 290 K in the range 200–400 nm and a naphthalene solution in cyclohexane was used as reference (c = 0.2 mol l^{-1}).

Synthesis of $K_3[C_6N_7(NCN)_3] \cdot 5H_2O$

In order to isolate a pure sample of a melonate salt we carefully tried to reproduce the synthesis routes to potassium melonate described in the literature (see references above). After several attempts resulting in complex mixtures we obtained analytically pure materials by an optimised procedure based on the data provided in ref. 29. In a porcelain crucible, 20 g (99.5 mmol) of melon and 40 g (137.45 mmol) of KSCN were thoroughly mixed and carefully heated to ~400 °C in air (***CAUTION!*** this results in a very exothermic reaction!). After about 1 h, gas evolution had ceased and the solid was further heated to about 450–500 °C for 30 min. The reaction product was dissolved in distilled water and recrystallised twice from acetone–water. Colourless thin needles were isolated and dried at 100 °C under vacuum (73.4% yield). Anal. calcd for $C_6N_7(NCNK)_3 \cdot 4.5H_2O$: C: 22.13, N: 37.30, H: 1.84; found: C: 22.00, N: 37.50, H: 1.84; ^{13}C NMR (D_2O): δ 158.6 (CN_3), 174.3 [C(NKCN)N_2)]; 124.8 (C≡N); FTIR (cm^{-1}): 3405 (w), 2181 (m), 1649 (s), 1500 (m), 1432 (vs), 790 (m); Raman (cm^{-1}): 2183 (vs), 1638 (w), 1578 (s), 1483 (vw), 1423 (m), 1195 (vw), 756 (w), 450 (m), 421 (w), 303 (m), 274 (w), 148 (m); UV and PL maxima (nm): $\lambda_{\mathrm{max,abs}}$ 235, 253, 264; $\lambda_{\mathrm{max,em}}$ 362, 378, 396 (Φ_{f} = 0.20 ± 0.05).

X-Ray crystallography

Small crystals of the pentahydrate $K_3[C_6N_7(NCN)_3] \cdot 5H_2O$ suitable for single crystal X-ray diffraction were produced by slow diffusion of acetone vapour into an aqueous solution of potassium melonate. X-Ray diffraction data were collected on an Oxford Xcalibur CCD diffractometer with a Sapphire CCD detector using the ω-scan technique. The structure was solved using direct methods and refined by full-matrix least squares on $|F^2|$ with SHELXL97 and SHELXS97.[31]

Results and discussion

Synthesis

Although the synthesis of the title compound, potassium melonate, as described in the experimental part is simple and the obtained product is very pure, as shown by the elemental analysis and spectroscopic data, the involved reaction mechanism seems to be rather complex. Based on the idealised formula of melon $[C_6N_7(NH_2)NH]_n$ (supported by elemental analyses of the starting material), which corresponds to a chain-like polymer and/or cyclic oligomers, several different reaction equations may be formulated to describe the formation of potassium melonate as, for example:

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

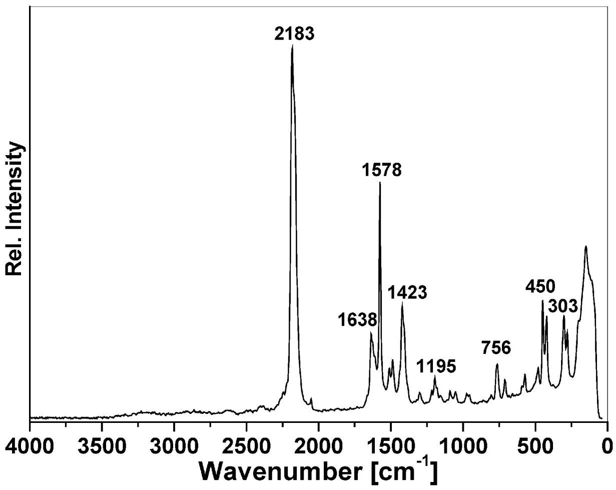


Fig. 1 Raman spectrum of potassium melonate.

The evolution of CS_2 is supported by the observation of blue flames during the synthesis. However, H_2S or other sulfur-containing by-products might also be formed. Interestingly, melon may be obtained by pyrolysis of ammonium thiocyanate,[32] but potassium melonate is not formed upon heating potassium thiocyanate without the addition of melon. Annealing KSCN at 400 °C results in 0.65% decomposition into sulfur and KCN, 4 h at red heat under vacuum results in only 2% transformation into the same products, and at higher temperatures a complete decomposition into sulfur and KCN is observed.[33] Further synthetic routes to potassium melonate, as described by Liebig, involve impure (sulfur-containing) melon, a mixture of copper and iron thiocyanate, or potassium ferrocyanide, as well as reactions of $SbCl_3$ and $BiCl_3$ with KSCN.[28] These routes are less straightforward than the reaction of melon with KSCN and are presumably based on related reaction mechanisms.

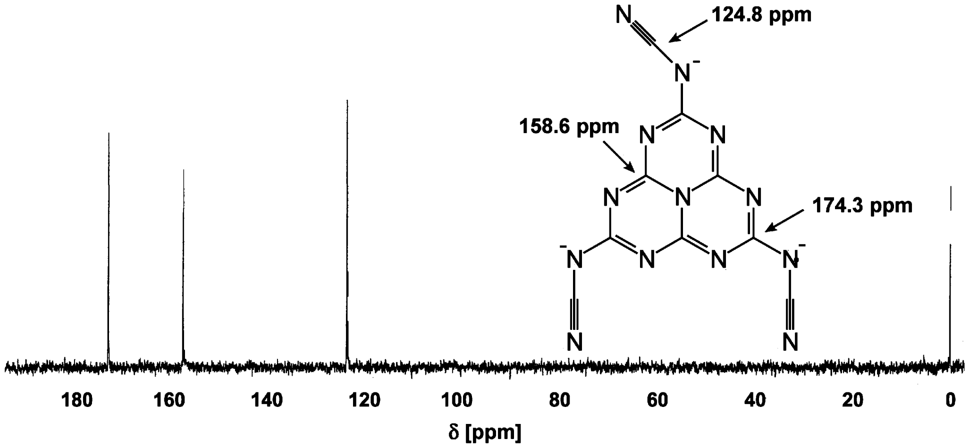


Fig. 2 ^{13}C NMR spectrum and signal assignment for potassium melonate.

Spectroscopic characterisation

The FTIR spectrum of the title compound was in good agreement with values reported by Finkel'shtein and Fedoruk.[30] Fig. 1 exhibits the Raman spectrum of potassium melonate. It shows a very strong symmetrical stretching vibration at 2183 cm^{-1} for $\nu(C{\equiv}N)$ and a weak symmetrical deformation vibration at 756 cm^{-1} for $\delta(C{\equiv}N)$ due to the three cyano groups. These observed frequencies are similar to those of alkali tricyanomelaminates, $M_3[C_3N_3(NCN)_3]$ (**6**), which were recently investigated by Schnick *et al.*[34] The tricyclic "cyameluric" nucleus (C_6N_7) is characterised by vibrational bands at 1638 (w), 1578 (s), 1423 (m) and 1195 (vw) cm^{-1}. A similar fingerprint was also found for the *s*-heptazine compounds melem,[14] trichloro-*s*-heptazine[12] and cyamelurates.[16]

The ^{13}C NMR spectrum (Fig. 2) of potassium melonate in D_2O shows resonances at 158.6 and 174.3 ppm. The other *s*-heptazine derivatives that have been analysed so far, that is, the molecular compounds $C_6N_7R_3$ with R = H,[15] Cl,[12] NH_2[14] and N_3,[17] as well as the alkali cyamelurates $M_3[C_6N_7O_3]$,[16] also show signals around 160 ppm for the central and around 170 ppm for the peripheral carbon atoms. The ^{13}C NMR chemical shift of the cyanamide carbon atoms in the N–C≡N unit is 124.8 ppm for potassium melonate, which is shifted only very slightly downfield by 4–8 ppm compared to organic cyanides like acetamide (116.8 ppm), propionitrile (120.8 ppm) or benzonitrile (118.7 ppm).[35]

The UV absorption and photoluminescence spectra of a potassium melonate solution in water are shown in Fig. 3. The absorption maximum at 264 nm and the extinction coefficient (ε) of 0.75×10^2 l mol^{-1} cm^{-1} indicate a $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition. The emission spectra at both c = 0.02 and 0.002 mol l^{-1} exhibit a maximum at ~380 nm, which is in the same range as observed for alkali cyamelurates $M_3[C_6N_7O_3]$ in solution (369 nm), as well as for melem in the solid state (366 nm).[36] The fluorescence quantum yield of potassium melonate ($\Phi_f = 0.20 \pm 0.05$) is similar to the quantum yield of naphthalene ($\Phi_{fs} = 0.23$), which was used as a standard.[37,38]

Crystal structure

Selected crystal data for potassium melonate hydrate $K_3[C_6N_7(NCN)_3]\cdot 5H_2O$ are listed in Table 1.‡ Potassium melonate crystallizes with five molecules of water in the orthorhombic space group *Pbca*. The tricyclic C_6N_7 core of the melonate ions is completely planar as indicated by the sum of bond angles of 360° around the C and N atoms. This was expected, based on the aromatic nature of the tricyclic 14-π-electron unit. Besides, the bent terminal cyanamido substituents share the same plane with the tricycle, giving rise to C_{3h} symmetry of the anion. An analogous molecular geometry was found for the triazido derivative $C_6N_7(N_3)_3$[17] and, similarly, in sodium tricyanomelaminate hydrate,[34a] $Na_3[C_3N_3(NCN)_3]\cdot 3H_2O$, which contains the *s*-triazine ring instead of the *s*-heptazine unit. Contrarily, in the tricyanomelaminate anion in the potassium salt, which crystallises as a monohydrate $K_3[C_3N_3(NCN)_3]\cdot H_2O$, one of the three cyanamide side arms is turned by 180°, reducing the molecular symmetry to C_s.[34b] The same situation was also found for the anhydrous alkali tricyanomelaminates $M_3[C_3N_3(NCN)_3]$ (M = Na, K, Rb).[34c,d] The latter observation indicates a very weak π interaction between the NCN group and the aromatic π system. This is supported by recent DFT calculations on $C_6N_7(N_3)_3$, which indicate a nodal plane for the delocalised occupied π orbitals between the tricyclic core and the three azide substituents, although the lowest energy conformation was predicted to be completely planar with C_{3h} symmetry.[24b]

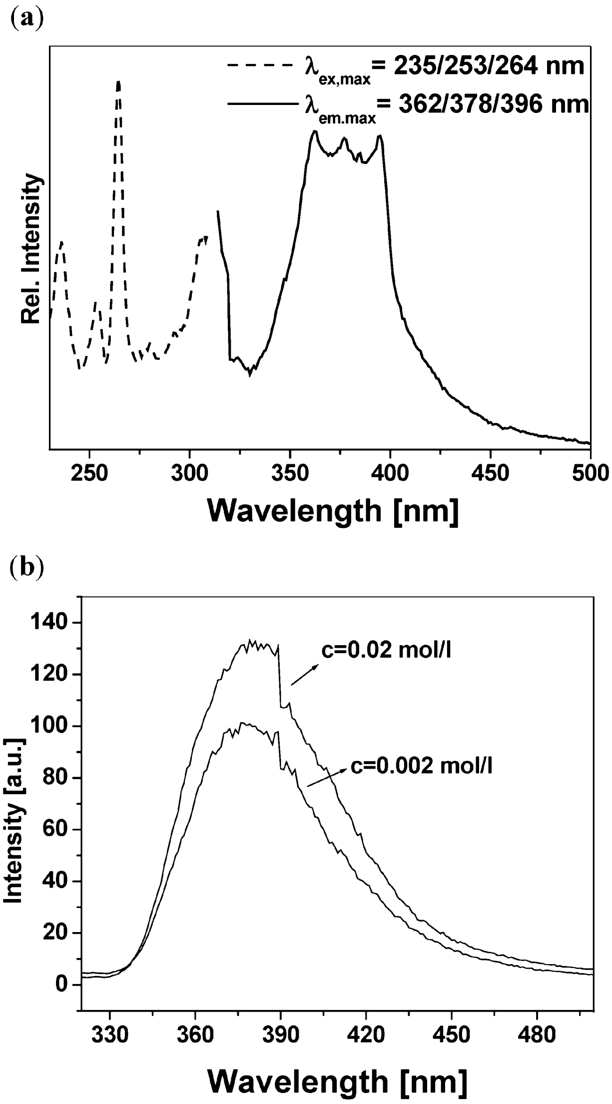


Fig. 3 (a) UV absorption (dashed line) and photoluminescence (PL; solid line) spectra of potassium melonate solution in water: c = 0.2 mol l^{-1}. (b) PL spectra of potassium melonate solution in water at 0.02 mol l^{-1} and 0.002 mol l^{-1}.

Table 1 Crystallographic data for potassium melonate

Parameter	$C_6N_7(NCNK)_3\cdot 5H_2O$
Molecular mass	497.60
Temperature/K	302(2)
Wavelength /Å	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	6.538(2)
b/Å	24.033(6)
c/Å	23.684(6)
U/Å^3	3721.4(17)
Z	8
μ/mm^{-1}	0.790
Calcd density/g cm^{-1}	1.776
Reflections collected	7159
Independent reflections	3799
R_{int}	0.1303
R_1	0.0395
wR_2 [$I > 2\sigma(I)$]	0.0387

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‡ CCDC reference number 260833. See http://www.rsc.org/suppdata/nj/b4/b416390g/ for crystallographic data in CIF or other electronic format.

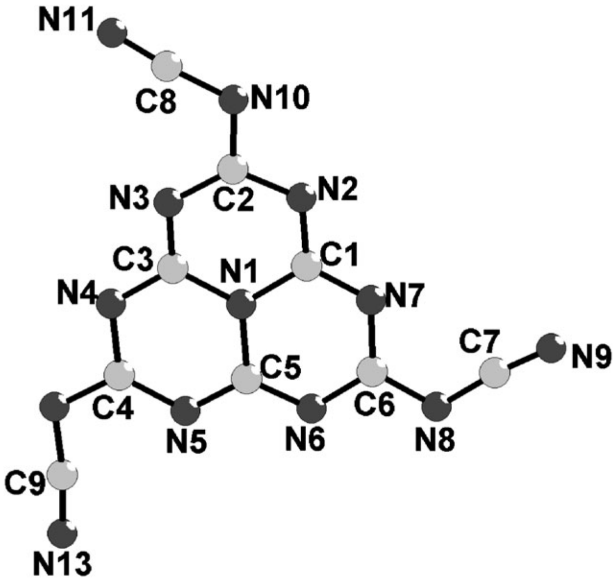

Fig. 4 View of the melonate anion $[C_6N_7(NCN)_3]^{3-}$ with atom labelling.

Fig. 4 shows the structure of the melonate anion while bond lengths and bond angles are summarised in Table 2. The C–N bond lengths in the cyanamide groups are 1.32 (C–N) and 1.14 (C≡N) Å, respectively. While estimations based on Hückel theory suggested slightly elongated C≡N bonds [1.32 Å (C–N), 1.20 Å (C≡N)],[18] very similar values were reported for tricyanomelaminates [1.34 Å (C–N), 1.15 Å (C≡N)] and organic cyanamides such as 2-cyanoguanidine [1.17 Å (C≡N), 1.30 Å (C–N)].[34,39] The N10–C8–N11 angle is slightly bent at 173.8°, which was also found for the cyanamide groups in $[C_3N_3(NCN)_3]^{3-}$ ions and reported for the isoelectronic azide groups in $C_6N_7(N_3)_3$.[17] The distortion of the *s*-heptazine unit, that is, the variations of the bond lengths and angles within the tricycle of 130.2–140.5 pm and 117.3–125.6°, is comparable to the data of 132.5–140.1 pm and 118.9–122.9° found for cyamelurate $[C_6N_7O_3]^{3-}$ ions[16] and similar to the triazide (132.5–140.0 pm and 115.5–128.4°).[17] As predicted by recent theoretical studies,[24b] the stronger the electron-donating capability of the substituent the larger the increase of the adjacent C–N bond length: *d*(C–N) = 132.6 pm for R = H, 134.0 pm for R = N_3 and 136.2 pm for R = NCN^-. The remaining C–N bond length are practically independent of the substituents.

Table 2 Bond lengths and angles of the melonate anion $[C_6N_7(NCN)_3]^{3-}$

N1–C1	1.43(13)	C1–N1–C3	118.6(11)
C1–N2	1.32(12)	N1–C1–N2	119.4(11)
C1–N7	1.31(12)	C1–N2–C2	116.8(10)
C2–N2	1.36(13)	N2–C2–N3	126.3(11)
C2–N10	1.35(13)	C2–N3–C3	117.4(11)
N10–C8	1.35(14)	N3–C3–N1	121.4(11)
C8–N11	1.15(14)	N7–C1–N2	121.7(12)
C2–N3	1.35(13)	N2–C2–N10	112.0(11)
C3–N3	1.28(13)	N3–C2–N10	121.6(12)
C3–N1	1.40(15)	C2–N10–C8	116.1(11)
		N10–C8–N11	174.7(18)

The K^+ cations in $K_3[C_6N_7(NCN)_3] \cdot 5H_2O$ do not share the same plane with the anions. The coordination number of the cations is six and the resulting polyhedra are nonregular distorted octahedra (Fig. 5). K(1) is coordinated by two oxygen atoms from water molecules, two peripheral nitrogen atoms from the *s*-heptazine nucleus and two nitrogen atoms from the cyanamide groups. The coordination polyhedron of K(2) contains one O atom and five N atoms, while three water molecules, two N atoms from the cyanamide group and one N atom of the heptazine nucleus form the distorted octahedron around K(3).

The layers in potassium melonate are π-stacked along the *a* axis, forming an ABA′B′AB pattern. Layers A and A′ consist of the disk-like $[C_6N_7(NCN)_3]^{3-}$ anions in a coplanar arrangement while the cations and water molecules are arranged around the anion columns in layers B and B′. Two successive anions in potassium melonate are rotated in the *bc* plane by 26.7° (Fig. 6). A similar π-stacking of the anions was observed for potassium tricyanomelaminate $K_3[C_3N_3(NCN)_3] \cdot H_2O$ and the cyamelurate $K_3[C_6N_7O_3] \cdot 3H_2O$.[16,34b] Face-to-face stacking has been frequently observed for aromatic, disk-like species such as the neutral molecules naphthalene and benzopyrene,[40] pyrene radical cations,[41] or the $[C_3N_3O_3]^{3-}$ anions in alkali cyanurates.[42] In contrast, a different arrangement was reported for triazido-*s*-heptazine $C_6N_7(N_3)_3$ and triazido-*s*-triazine $C_3N_3(N_3)_3$.[17,19] Although these molecules are also planar with C_{3h} symmetry and coplanar ordered in the crystals, an alternating stacking of the layers without π contacts is found (Fig. 7). The interlayer distance in $K_3[C_6N_7(NCN)_3] \cdot 5H_2O$ between two anions is approximately 3.26 Å. This distance is in the range observed for other compounds with typical π-π interactions such as melem (3.27 Å), graphite (3.34 Å) and h-BN (3.30 Å).

Thermal stability

The properties of potassium melonate hydrate were examined by STA-MS measurements. The TG curve shows weight losses in two steps at 86 and at 516 °C. The first weight loss is due to the evaporation of crystal water (*m*/*z* = 18, H_2O) and the second is caused by thermal decomposition of the anhydrous potassium melonate (*m*/*z* = 26, CN; *m*/*z* = 27, HCN; *m*/*z* = 52, C_2N_2). It is remarkable that the dehydrated melonate salt is stable up to >500 °C since most other nitrogen-rich CN heterocyclic compounds tend to decompose far below 500 °C. A high thermal stability was also found for other *s*-heptazine derivatives like melem, cyameluric acid and its alkali salts.[16]

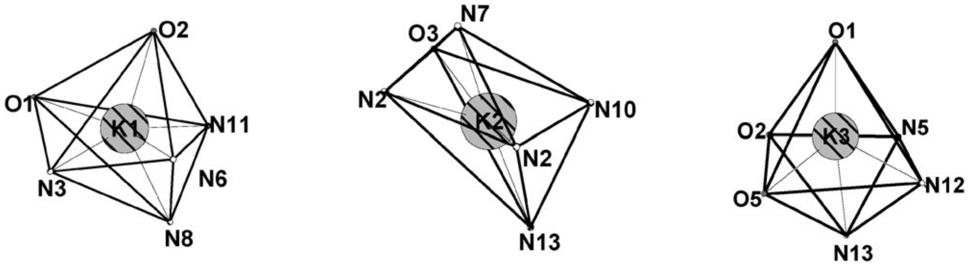

Fig. 5 Coordination polyhedra of the cations (K1, K2, K3) in potassium melonate [oxygens from crystal water: O1, O2, O3, O5; nitrogens from the cyameluric nucleus (C_6N_7): N2, N3, N5, N6, N7; nitrogens from cyanamide groups: N8, N10, N11, N12, N13].

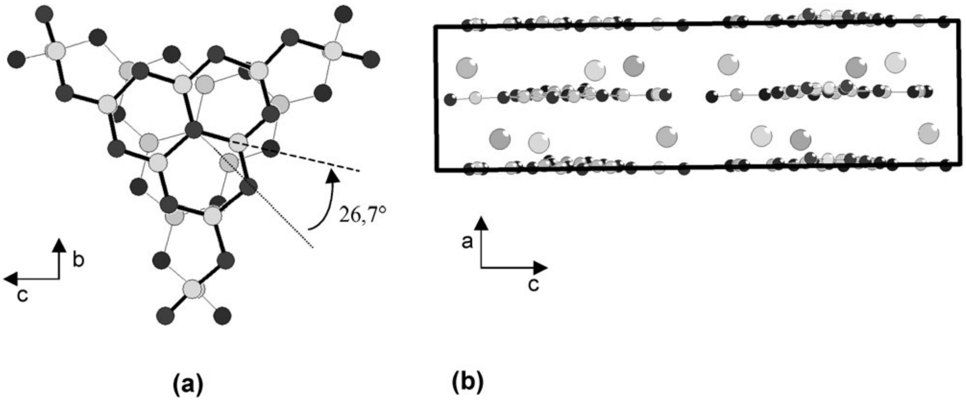

Fig. 6 View along the (a) *a* and (b) *b* axes of potassium melonate hydrate.

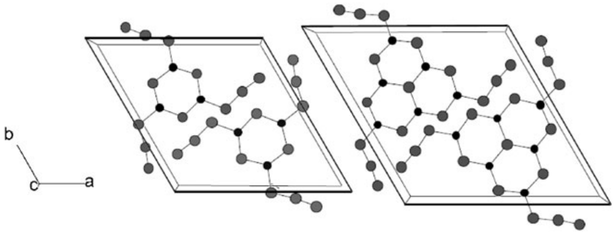

Fig. 7 View along the *c* axis of the unit cells of $C_3N_3(N_3)_3$ (left) and $C_6N_7(N_3)_3$ (right).

Suggested syntheses of C_3N_4 networks

Many synthetic approaches to CN_x materials—especially graphitic carbon(IV) nitrides such as **A**, **C** and **D** in Scheme 1—were based on *s*-triazine starting materials.[1] These studies include several reports on the successful syntheses of C_3N_4 phases, but none of the products were characterised comprehensively or reproduced by independent research groups. Due to the fact that the *s*-heptazine unit is more stable and may be formed upon pyrolysis of *s*-triazine derivatives, it is worthwhile to consider the possible synthesis of C_3N_4 phases starting with *s*-heptazine compounds. This strategy was followed in our laboratory[1c,12,17b,36] as well as by Komatsu and Nakamura,[26] Gillan *et al.*[17a] and Schnick *et al.*[14] One of the synthetic routes tested is based on reaction of potassium melonate with cyameluric chloride ($C_6N_7Cl_3$), which should give the C_3N_4 networks **E** or **F**. All attempts so far have given inhomogeneous and impure products, which usually contained hydrogen and/or oxygen as well as other heteroelements.[17b,26c,36] Nevertheless, modified synthesis conditions might lead to the desired product.

The networks **G** and/or **H** might be obtained by reaction of the title compound with cyanuric chloride or fluoride. However, the biggest challenge for this approach is similar to the above-mentioned attempts, as well as many other syntheses of strongly cross-linked, insoluble 2D or 3D polymers: the products should not be contaminated with significant amounts of heteroelements caused by the presence of by-products or end groups. Purification procedures, such as washing with water or extraction with an organic solvent, generally resulted in rather large amounts of hydrogen and/or oxygen in the "purified" materials.

Nevertheless, we believe that the high thermal stability of the melonate anion and the fact that this unit probably represents the largest known fragment with an alternating arrangement of carbon and nitrogen, which is a prerequisite for a carbon(IV) nitride network, make melonates promising building blocks for these C_3N_4 structures.

Conclusion

The present study reports the first comprehensive spectroscopic characterisation and the first crystal structure of a melonate. The colourless, air-stable and water-soluble title compound is easily obtained in good yields from cheap starting materials. It contains planar, π-stacked $[C_6N_7(NCN)_3]^{3-}$ anions in the crystal. Due to the high thermal stability of dehydrated potassium melonate, up to ~500 °C, and due to the unique alternating arrangement of C and N atoms, this material may be a promising precursor for the synthesis of graphite-like carbon(IV) nitrides, that is, C_3N_4 networks.

Acknowledgements

The authors are thankful to R. Schmechel and H. v. Seggern for their help with the UV-vis and luminescence spectroscopy analyses and S. Nahar-Borchert and M. Schwarz for useful discussions. We would like to thank C. Fasel for STA-MS measurements. U. Baudis (Durferrit GmbH, Hanau) is acknowledged for providing the melon. The Deutsche Forschungsgemeinschaft (Kr 1739/2-3 and Kr 1739/9-1), Bonn (Germany), supported the present work financially.

References

1 For reviews, see: (*a*) S. Muhl and J. M. Mendez, *Diamond Relat. Mater.*, 1999, **8**, 1809; (*b*) T. Malkow, *Mater. Sci. Eng., A*, 2001, **292**, 112; (*c*) E. Kroke and M. Schwarz, *Coord. Chem. Rev.*, 2004, **248**, 493.
2 See, for example: E. C. Franklin, *J. Am. Chem. Soc.*, 1922, **44**, 486.
3 (*a*) M. L. Cohen, *Phys. Rev. B*, 1985, **32**, 7988; (*b*) A. Y. Liu and M. L. Cohen, *Science*, 1989, **245**, 841; (*c*) A. Y. Liu and M. L. Cohen, *Phys. Rev. B*, 1990, **41**, 10727.
4 Dozens of reports have appeared; see, for example: (*a*) K. M. Yu, M. L. Cohen, E. E. Haller, W. L. Hansen, A. Y. Liu and I. C. Wu, *Phys. Rev. B*, 1994, **49**, 5034; (*b*) A. Y. Liu and R. M. Wentzcovich, *Phys. Rev. B*, 1994, **50**, 10362; (*c*) Y. Guo and W. A. Goddard III, *Chem. Phys. Lett.*, 1995, **237**, 72; (*d*) J. E. Lowther, *Phys. Rev. B*, 1999, **59**, 11683; (*e*) F. Weich, J. Widany and T. Fraunheim, *Carbon*, 1999, **37**, 545; (*f*) M. Mattesini, S. F. Matar and J. Etourneau, *J. Mater. Chem.*, 2000, **10**, 709; for a comprehensive discussion of the literature see the reviews in ref. 1.
5 Several hundred reports have appeared; see, for example: (*a*) C. Niu, Y. Z. Lu and C. M. Lieber, *Science*, 1993, **262**, 334; (*b*) J. Narayan, J. Reddy, N. Biunno, S. M. Kanetkar, P. Tiwari and N. Parikh, *Mater. Sci. Eng., B*, 1994, **26**, 49; (*c*) H. Sjoestroem, I. Ivanov, M. Johansson, L. Hultman, J.-E. Sundgren, S. V. Hainsworth, T. F. Page and L. R. Wallenberg, *Thin Solid Films*, 1994, **246**, 103; (*d*) S. Veprek, J. Weidmann and F. Glatz, *J. Vac. Sci. Technol., A*, 1995, **13**, 2914; (*e*) S. Kumar, K. S. A. Butcher and T. L. Tansley, *J. Vac. Sci. Technol., A*, 1996, **14**, 2687; (*f*) J. Bulir, M. P. Delplancke-Ogletree, J. Lancok, M. Jelinek, C. Popov,

A. Klett and W. Kulisch, *Diamond Relat. Mater.*, 2001, **10**, 1901; for a comprehensive discussion of the literature see the reviews in ref. 1.

6 (*a*) J. J. BelBruno, *Chem. Phys. Lett.*, 1997, **270**, 99; (*b*) J. J. BelBruno, Z.-C. Tang, R. Smith and S. Hobday, *Mol. Phys.*, 2001, **99**, 957.

7 T. Sato, A. Narazaki, Y. Kawaguchi, H. Niino and G. Bucher, *Angew. Chem, Int. Ed.*, 2003, **115**, 5364.

8 (*a*) D. M. Teter and R. J. Hemley, *Science*, 1996, **271**, 53; (*b*) P. Kroll and R. Hoffmann, *J. Am. Chem. Soc.*, 1999, **121**, 4698.

9 M. Mattesini, S. F. Matar, A. Snis, J. Etourneau and A. Mavromaras, *J. Mater. Chem.*, 1999, **9**, 3151.

10 I. Alves, G. Demazeau, B. Tanguy and F. Weill, *Solid State Commun.*, 1999, **109**, 697.

11 Synonyms: tri-*s*-triazine, 1,3,4,6,7,9,9*b*-heptaazaphenalene, 1,3,4,6,7,9-hexaazacycl[3.3.3]azine or cyamelurine.

12 E. Kroke, M. Schwarz, P. Kroll, E. Horvath-Bordon, B. Noll and A. Norman, *New J. Chem.*, 2002, **26**, 508.

13 D. T. Vodak, K. Kim, L. Iordanidis, P. G. Rasmussen, A. J. Matzger and O. M. Yaghi, *Chem.-Eur. J.*, 2003, **9**, 4197.

14 B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller and W. Schnick, *J. Am. Chem. Soc.*, 2003, **125**, 10288.

15 (*a*) M. A. Rossman, N. J. Leonard, S. Urano and P. R. LeBreton, *J. Am. Chem. Soc.*, 1985, **107**, 3884; (*b*) R. S. Hosmane, M. A. Rossman and N. J. Leonard, *J. Am. Chem. Soc.*, 1982, **104**, 5497; (*c*) M. Shahbaz, S. Urano, P. R. LeBreton, M. A. Rossman, R. S. Hosmane and N. J. Leonard, *J. Am. Chem. Soc.*, 1984, **106**, 2805; (*d*) M. A. Rossman, R. S. Hosmane and N. J. Leonard, *J. Phys. Chem.*, 1984, **88**, 4324.

16 E. Horvath-Bordon, E. Kroke, I. Svoboda, H. Fueß, R. Riedel, N. Sharma and A. K. Cheetham, *Dalton Trans.*, 2004, 3900.

17 (*a*) D. R. Miller, D. C. Swenson and E. G. Gillan, *J. Am. Chem. Soc.*, 2004, **126**, 5372; (*b*) E. Kroke, *Habilitation*, Darmstadt University of Technology, Tenea Verlag, Berlin, 2004.

18 L. Pauling and J. H. Sturdivant, *Proc. Natl. Acad. Sci. USA*, 1937, **23**, 615.

19 (*a*) E. Kessenich, T. M. Klapoetke, J. Knizek, H. Noeth and A. Schulz, *Eur. J. Inorg. Chem.*, 1998, **12**, 2013–2016; (*b*) E. Kessenich, K. Polborn and A. Schulz, *Inorg. Chem.*, 2001, **40**, 1102, and references therein.

20 (*a*) E. Ott and E. Ohse, *Chem. Ber.*, 1921, **54**, 179; (*b*) H. Murarour, *Bull. Soc. Chim. Fr.*, 1932, **51**, 1152; (*c*) F. P. Bowden and H. T. Williams, *Proc. R. Soc. London, Ser. A*, 1951, **208**, 176; (*d*) A. D. Yoffe, *Proc. R. Soc. London, Ser. A*, 1951, **208**, 188; (*e*) B. L. Evans and A. D. Yoffe, *Proc. R. Soc. London, Ser. A*, 1957, **238**, 325.

21 (*a*) E. G. Gillan, *Chem. Mater.*, 2000, **12**, 3906; (*b*) J. Wang and E. G. Gillan, *Thin Solid Films*, 2002, **422**, 62.

22 E. Kroke, M. Schwarz, V. Buschmann, G. Miehe, H. Fueß and R. Riedel, *Adv. Mater.*, 1999, **11**, 158.

23 Recent highlights on tri-*s*-triazine derivatives: (*a*) E. K. Wilson, *Chem. Eng. News*, 2004May 31), 34; (*b*) M. Epple, *Nachr. Chem.*, 2003, **51**, 1028; (*c*) U. Ruschewitz and M. Kilo, *Nachr. Chem.*, 2004, **52**, 260.

24 (*a*) W. Zheng, N.-B. Wong, G. Zhou, X. Liang, J. Li and A. Tian, *New J. Chem.*, 2004, **28**, 275; (*b*) W. Zheng, N.-B. Wong, W. Wang, G. Zhou and A. Tian, *J. Phys. Chem. A*, 2004, **108**, 97; (*c*) W. Zheng, N.-B. Wong, X. Liang, X. Long and A. Tian, *J. Phys. Chem. A*, 2004, **108**, 840; (*d*) X. Liang, W. Zheng, N.-B. Wong, J. Li and A. Tian, *THEOCHEM*, 2004, **672**, 151.

25 I. Alkorta, N. Jagerovic and J. Elguero, *ARKIVOC*, 2004, **4**, 130.

26 (*a*) T. Komatsu, *Phys. Chem. Chem. Phys.*, 2004, **6**, 878; (*b*) T. Komatsu, *J. Mater. Chem.*, 2001, **11**, 799; (*c*) T. Komatsu, *J. Mater. Chem.*, 2001, **11**, 802; (*d*) T. Komatsu and T. Nakamura, *J. Mater. Chem.*, 2001, **11**, 474.

27 L. Gmelin, *Ann. Pharm.*, 1835, **15**, 252.

28 (*a*) J. Liebig, *Ann. Chem. Pharm.*, 1844, **50**, 337; (*b*) J. Liebig, *Ann. Chem. Pharm.*, 1850, **73**, 257.

29 C. F. Redemann and H. J. Lucas, *J. Am. Chem. Soc.*, 1939, **61**, 3420.

30 (*a*) A. I. Finkel'shtein and S. G. Fedoruk, *Chem. Heteroorg. Compd.*, 1980, **8**, 67; (*b*) A. I. Finkel'shtein and S. G. Fedoruk, *Zh. Prikl. Spektrosk.*, 1983, **4**, 606.

31 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.

32 J. Liebig, *Ann. Pharm.*, 1834, **10**, 1.

33 *Gmelins Handbuch der anorganischen Chemie*, 8th edn., Kalium (sytem number 22), Verlag Chemie, Weinheim 1938, p. 899.

34 (*a*) B. Jürgens, W. Milius, P. Morys and W. Schnick, *Z. Anorg. Allg. Chem.*, 1998, **624**, 91; (*b*) E. Irran, B. Jürgens and W. Schnick, *Solid State Sci.*, 2002, **4**, 1305; (*c*) E. Irran, B. Jürgens and W. Schnick, *Chem.-Eur. J.*, 2001, **7**, 5372; (*d*) E. Irran, B. Jürgens, J. Schneider and W. Schnick, *Inorg. Chem.*, 2000, **39**, 665.

35 M. Hesse, H. Meier and B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1995.

36 E. Horvath-Bordon, *Ph.D. Dissertation*, Darmstadt, University of Technology, Darmstadt, Germany, 2004, in German.

37 I. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, London, 1965.

38 I. Klessinger and J. Michl, *Lichtabsorption und Photochemie organischer Moleküle*, VCH–Verlag, Weinheim, 1989.

39 (*a*) F. L. Hirshfeld and H. Hope, *Acta Crystallogr., Sect.. B*, 1980, **36**, 406; (*b*) E. W. Hughes, *J. Am. Chem. Soc.*, 1940, **62**, 1258; (*c*) P. Rademacher, *Strukturen organischer Moleküle*, VCH–Verlag, Weinheim, 1987.

40 (*a*) H.-G. Franck and J. W. Stadelhofer, *Industrial Aromatic Chemistry*, Springer Verlag, Berlin, 1988; (*b*) D. Viterbo, J. Hodder and K. Prout, *Acta Crystallogr., Sect. A*, 1969, **25**, 144.

41 S. Lee, B. Chen, D. C. Fredricksen, F. J. DiSalvo, E. lobkovsky and J. A. Adams, *Chem. Mater.*, 2003, **15**, 1420.

42 T. F. Sysoeva, M. Z. Branzburg, M. Z. Gurevich and Z. A. Starikova, *Zh. Strukt. Khim.*, 1990, **31**, 90.