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Syntheses, single-crystal structures, vibrational spectra and DSC/TG analyses of orthorhombic and trigonal $Ag[N(CN)_2]$

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Abstract: Colorless powders of orthorhombic $Ag[N(CN)_2]$ were synthesized by blending aqueous solutions $Ag[NO_3]$ with stoichiometric amounts of $Na[N(CN)_2]$ equally dissolved in water. Single crystals of both modifications of $Ag[N(CN)_2]$ could be obtained by recrystallizing the powder with aqueous ammonia. Non-isothermal evaporation of the solvent at room temperature within a few hours yielded the orthorhombic modification as the main product crystallizing in the space group *Pnma* (no. 62) with the unit-cell parameters $a = 1612.45(12)$, $b = 361.58(3)$ and $c = 599.02(4)$ pm ($Z = 4$). Upon evaporating the solvent much more slowly, isothermally within a few days, mainly thin hexagonal platelets of the trigonal modification of $Ag[N(CN)_2]$ were obtained, crystallizing in the space group $P3_121$ (no. 152) with the lattice constants $a = 359.86(3)$ and $c = 2285.91(17)$ pm ($Z = 3$). Both results corroborate earlier structure determinations, but show higher precision. The vibrational spectra confirm the presence of the dicyanamide anion $[N(CN)_2]^-$, but exhibit slight differences to literature data. Differential scanning calorimetry/thermogravimetry (DSC/TG) analyses were performed to further characterize the two modifications.

Keywords: crystal structure; dicyanamide; DSC/TG analyses; Raman and IR spectra; silver.

1 Introduction

Silver shows a remarkably high affinity for nitrogen containing moieties. Next to anions such as cyanide, cyanamide, dicyanamide and tricyanomethanide solvents such as liquid ammonia or even aqueous ammonia can be named as examples. If the anion is redox-stable enough, the mostly amorphous precipitates of silver salts can often be recrystallized from liquid ammonia or ammonia–water mixtures in order to obtain crystals suitable for single-crystal diffraction experiments. Compounds such as $Ag[CN]$ [1], $Ag_2[CN]_2$ [2], $Ag[N(CN)_2]$ [3, 4] and $Ag[C(CN)_3]$ [5] have been structurally characterized in this way. $Ag[N(CN)_2]$ has a special position within this series, since it is the only one of these compounds to crystallize with more than one modification, as known so far. Being interested in compounds containing the $[N(CN)_2]^-$ anion (abbreviated as 'dca') as an easy-to-use building block and/or spacer for tailor-made compounds with potentially interesting structural or magnetic properties [6, 7], a closer look into the dimorphic nature of Ag[dca], the properties of both forms and a strategy to synthetize each modification separately seemed desirable. The results of these efforts to characterize orthorhombic and trigonal Ag[dca] are presented here.

2 Experimental section

2.1 Synthesis

All manipulations were performed under normal atmospheric conditions in air. Ag[dca] was obtained by mixing aqueous solutions of $Ag[NO_3]$ (≥99%, Sigma-Aldrich, St. Louis, MO, USA) with a solution containing stoichiometric amounts of Na[dca] (Alfa Aesar, Ward Hill, MA, USA, 96%) dissolved in water. The colorless X-ray amorphous material precipitated immediately as fine powder and was filtered off. Single crystals of Ag[dca] were obtained by recrystallizing some of this powder in a small petri dish (5 cm diameter) from a 25% aqueous solution of ammonia NH_3 (Fisher, Analytical Grade). The orthorhombic form occurs as the main product (>80% as estimated with the help of a polarizing microscope by the bare eye) when the warm solvent (50°C) is evaporated quickly within hours

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at room temperature, whereas the trigonal modification forms almost exclusively when the evaporation is isothermal, slow and hampered (e.g. by placing a not completely air-tight cover over the petri dish) thus taking place within days, but also at room temperature.

Both modifications of Ag[dca] are stable toward normal atmosphere (moist air), but become greyish after exposition to daylight for an extended time.

2.2 Crystallographic studies

Single crystals of both modifications of Ag[dca] were selected under a polarization microscope in normal atmosphere and sealed into thin-walled glass capillaries. A suitable crystal was mounted on a Bruker–Nonius Kappa-CCD diffractometer with graphite-monochromatized MoKα radiation (λ = 71.07 pm). The quality of the respective crystal was checked and a set of intensity data was collected on a specimen of sufficient quality at room temperature. The processing of the intensity data was performed with the software package that came with the diffractometer [8]. The intensity data were corrected for Lorentz and polarization effects as well as for absorption with the program HABITUS [9]. Systematic absences were analyzed and led to the space groups $Pna2_1$ (no. 33) or *Pnma* (no. 62) for the orthorhombic form of Ag[dca], but a reasonable refinement was only achieved in the latter centro-symmetric space group. For the trigonal form, several space groups were possible according to the reflection conditions, but the only solution that could be refined was achieved in $P3_121$ (no. 152). Both structure solutions were obtained by using Direct Methods with SHELXS-97 [10, 11], reliably delivering the positions of the silver atoms. The carbon and nitrogen sites became apparent from the positions of highest electron density on the difference Fourier map resulting from the first refinement cycles by full-matrix least-squares techniques with the use of SHELXL-97 [12, 13]. Doing further cycles of refinement, the respective calculations converged and resulted in stable models for both crystal structures. Additional crystallographic details can be found in Table 1. Atomic coordinates as well as the anisotropic and equivalent isotropic displacement coefficients are shown in Table 2. Table 3 displays selected interatomic distances and angles of both modifications of Ag[dca].

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-429835 for orthorhombic Ag[dca] and CSD-429836 for trigonal Ag[dca].

2.3 Raman and IR spectroscopy

The colorless single crystals of both Ag[dca] modifications used for the structure determinations sealed in thin-walled glass capillaries were also taken for the Raman-spectroscopic investigations, which were performed on a microscope laser Raman spectrometer (Jobin Yvon, Unterhaching, Germany, 4 mW, equipped with a HeNe laser with an excitation line at λ = 632.817 nm, 50× magnification, 8 × 240 s accumulation time).

The IR spectra were recorded with a Bruker AFS 66 FT-IR instrument (Karlsruhe, Germany) with the KBr pellet technique (2 mg Ag[dca] being ground together with 400 mg desiccator-dried KBr).

The IR and Raman spectra of the orthorhombic and the trigonal form of Ag[dca] are displayed in Figs. 1 and 2, respectively; the exact frequencies and their assigned modes might be taken from Table 4 juxtaposed to related IR data from literature data [3, 16].

2.4 DSC/TG measurements

Orthorhombic Ag[dca] (24.04 mg) and trigonal Ag[dca] (21.52 mg), respectively, were placed on a DSC/TG pan made of aluminum oxide for separate experiments. This setup was inserted into a Netzsch STA 449C Jupiter instrument (Selb, Germany) under a constant stream of pure argon (Messer Griesheim). After flushing the material at room temperature for 10 min, each sample was heated at a rate of 10 K min^{-1} up to 800°C (Figs. 3 and 4).

3 Results and discussion

3.1 Vibrational spectra

The frequencies obtained from the IR and Raman spectra of the title compounds confirm the presence of the dicyanamide anion ([NCNCN]$^-$). Judging by these numbers, the frequencies obtained by IR techniques reported in the literature were most probably obtained on orthorhombic Ag[dca] [3, 16]. The reported modes with frequencies below 1000 cm^{-1} agree with our measurements on orthorhombic Ag[dca]; the modes above this region are systematically smaller than the reported numbers except for the ν_s(C≡N)

Table 1: Summary of single-crystal X-ray diffraction structure determination data of Ag[dca].

Compound	**o-Ag[N(CN)$_2$]**	**t-Ag[N(CN)$_2$]**
M_r	173.92	173.92
Crystal color	Transparent colorless	Transparent colorless
Crystal shape	Rectangular plate	Hexagonal plate
Crystal size, mm^3	0.18 × 0.15 × 0.04	0.12 × 0.12 × 0.02
Crystal system	Orthorhombic	Trigonal
Space group (no.)	*Pnma* (62)	$P3_121$ (152)
Z	4	3
Lattice parameters		
a, pm	1612.45(12)	359.86(3)
b, pm	361.58(3)	*a*
c, pm	599.02(4)	2285.91(17)
V, Å^3	349.25(5)	256.36(4)
D_{calcd}, g cm^{-3}	3.31	3.38
F(000), *e*	320	240
μ, mm^{-1}	5.6	5.7
Diffractometer	Nonius KappaCCD (Bruker AXS)	
Radiation; λ, pm; monochromator	MoKα; 71.07; graphite	
T, K	293(2)	
Ranges $2\theta_{max}$, deg	54.18	55.64
hkl range	±20; ±4; ±7	±4; ±4; ±30
Data correction	Numerically (X-SHAPE [9])	
Reflections: measured; unique	2491; 412	4351; 414
Unique reflections with $F_o > 4\sigma(F_o)$	346	358
R_{int}; R_σ	0.055; 0.030	0.048; 0.019
Refined parameters	38	31
Flack parameter [14, 15]	–	0.19(13)
$R1^a$; $wR2^b$; GoF^c (all refl.)	0.038; 0.069; 1.046	0.025; 0.055; 1.069
Max. shift/esd, last refinement cycle	<0.00005	<0.00005
$\Delta\rho_{fin}$ (max; min), *e* Å^{-3}	0.57; −0.74	0.36; −0.39
CSD number	429835	429836

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = [(F_o^2) + 2F_c^2]/3$ and *x* and *y* are constants adjusted by the program.

[c] GoF (S) $= [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, with *n* being the number of reflections and *p* being the number of refined parameters.

Table 2: Atomic coordinates and equivalent isotropic displacement parameter[a] of orthorhombic and trigonal Ag[dca].

Atom	**Wyckoff site**	***x/a***	***y/b***	***z/c***	**U_{eq}/pm^2**
Ag	4*c*	0.08662(2)	¼	0.11177(3)	620(3)
N1	4*c*	0.3600(3)	¼	0.9575(9)	681(15)
N2	4*c*	0.2104(3)	¼	0.9889(9)	584(14)
N3	4*c*	0.4657(3)	¼	0.2447(9)	519(14)
C1	4*c*	0.2795(3)	¼	0.9872(9)	472(14)
C2	4*c*	0.4126(3)	¼	0.1192(9)	467(14)
Ag	3*a*	0.34493(7)	*x*	0	526(2)
N1	3*b*	0	0.7636(9)	1/6	473(8)
N2	6*c*	0.1115(6)	0.5411(6)	0.07101(8)	429(6)
C	6*c*	0.0615(7)	0.6272(7)	0.11738(9)	336(5)

[a] U_{eq} is defined as a third of the orthogonalized U_{ij} tensors.

modes at around 2285 cm^{-1} showing good agreement again (Table 4). No satisfying explanation for the deviation can be offered. The Raman spectra taken on single crystals of both polymorphs are quite similar, but their IR spectra are obviously different from each other mirroring their different crystal structures.

3.2 DSC/TG measurements

Two exothermic effects can be observed during the thermal treatment of orthorhombic Ag[dca]. There is a sharp peak at 278°C and a broad peak at higher temperatures with its maximum at around 680°C (Fig. 3). Exothermic effects of [dca]-containing compounds around 300°C are usually attributed to a trimerization reaction of $[N(CN)_2]^-$ forming the cyclic $[C_6N_9]^{3-}$ anion with a six-membered (C_3N_3) ring with alternating carbon and nitrogen atoms and NCN groups attached to carbon [17]. A mass loss of about 3% accompanies the onset of the cyclization, which might be an indication of a partial

Table 3: Selected bond lengths (pm) and angles (deg) of orthorhombic and trigonal Ag[dca] compared with literature data [3, 4].

Orthorhombic Ag[dca]		**This work**	**[4]**
Ag–	N2	212.7(4)	208(2)
	N3	213.1(4)	214(2)
Ag–	*N1 (2×)*	*288.1(4)*	*Not given*
Ag–	*N3′ (2×)*	*296.9(4)*	*Not given*
N1–	C2	128.8(7)	128(3)
	C1	131.0(6)	129(3)
C1–	N2	111.4(7)	116(3)
C2–	N3	113.9(6)	117(3)
∡(N2–Ag–N3)		176.5(2)	177(1)
∡(N2–C1–N1)		172.7(7)	172(3)
∡(C2–N1–C1)		123.4(5)	123(2)
∡(N3–C2–N1)		172.5(5)	170(2)
Trigonal Ag[dca]		**This work**	**[3, 4]**
Ag–	N2 (2×)	210.5(4)	211(1)
	N2′ (2×)	*296.6(4)*	*Not given*
	N2″(2×)	*304.6(2)*	*Not given*
N1–	C (2×)	129.2(3)	129(1)
C–	N2	114.3(3)	115(1)
∡(N2–Ag–N2)		176.4(1)	173(1)
∡(N2–C–N1)		172.6(3)	170(2)
∡(C–N1–C)		124.5(3)	127(2)

The italic numbers are of significance for the complete coordination spheres and for pointing out the difference between these spheres in the different polymorphs.

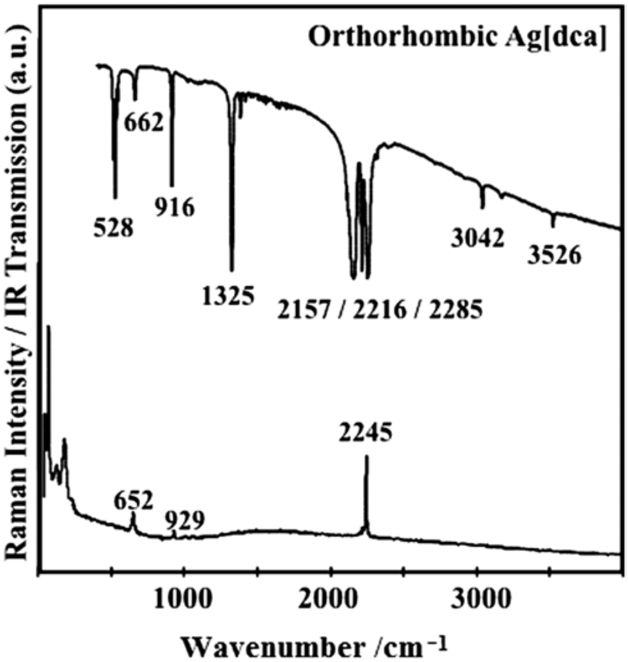

Fig. 1: Vibrational spectra of orthorhombic Ag[dca].

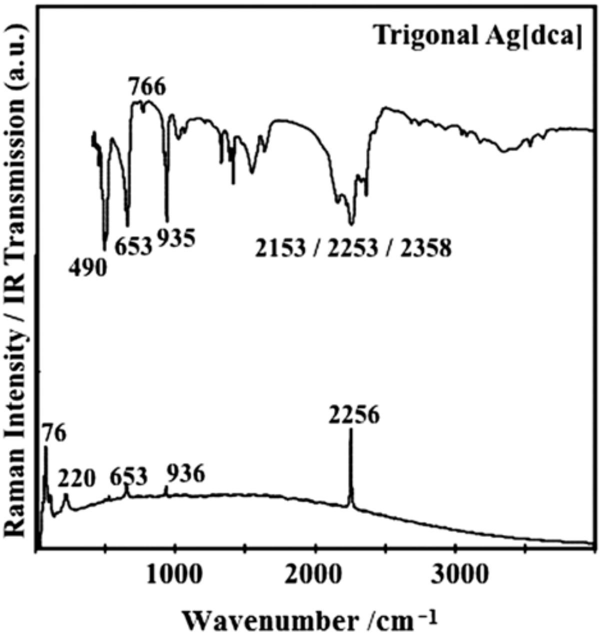

Fig. 2: Vibrational spectra of trigonal Ag[dca].

Table 4: Vibrational data from the literature with data for the orthorhombic and the trigonal Ag[dca] modifications with the assigned vibrational modes.

Assigned modes [3, 16]	**Ag[dca] [3]**	**Ag[dca] [16]**	**Ag[dca] (orthorhombic)**	**Ag[dca] (trigonal)**
γ_{as}(N–C≡N)	–	493/527	513/528	490/**523**
δ_{s}(N–C≡N)	–	654	662/**652**	653/**653**
ν_{s}(N–C)	–	930	916/**929**	935/**936**
ν_{s}(N–C)	1344	1346	1325	1324
ν_{as}(C≡N)	2180	2183	2157	2153
ν_{as}(N–C) + ν_{s}(N–C)	2230	2227	2216/**2245**	2253/**2256**
ν_{s}(C≡N)	2288	2283	2285	2358

Bold values indicate Raman results; other frequencies were obtained by IR spectroscopy. All numbers are given in cm^{-1}.

decomposition of the material setting free some nitrogen (Fig. 4). The broad, exothermic effect is accompanied by a considerable decrease of mass starting at about 560°C. The overall loss in mass of about 38% (theoretically expected loss: 38.0%) can be attributed to the loss of carbon and nitrogen. This is in accordance with the silver flakes found as a residue.

For trigonal Ag[dca], the situation is similar in some respect, but three exothermic peaks and one endothermic signal are observed. The small, sharp peak at 279°C can be attributed to some orthorhombic Ag[dca] impurity undergoing the trimerization. The large sharp signal at 288°C indicates the trimerization of the trigonal phase. Once more, the broad, exothermic effect is accompanied by a considerable decrease of mass starting at about 560°C. The overall loss in mass of about 37.9% (theoretically

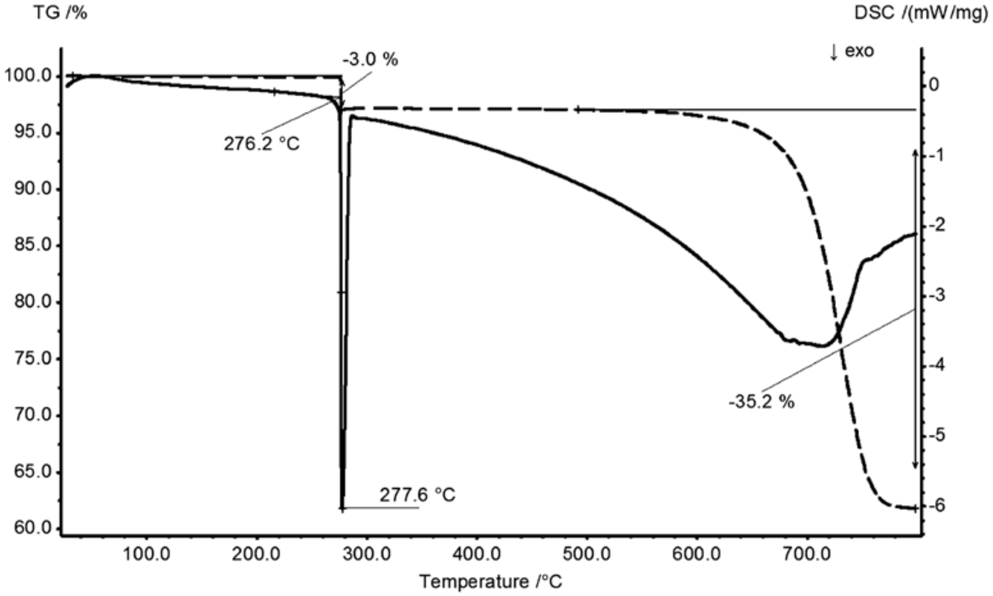

Fig. 3: DSC/TG analysis of orthorhombic Ag[dca].

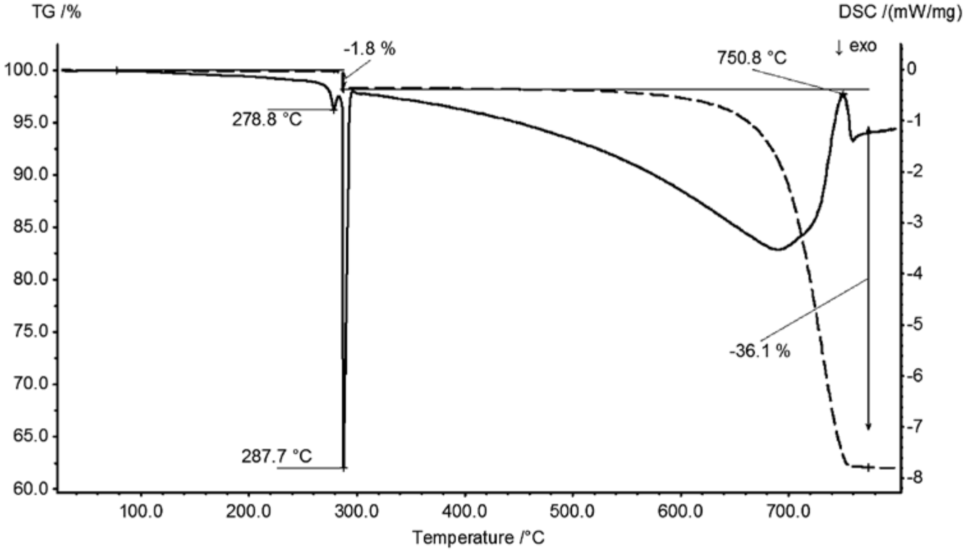

Fig. 4: DSC/TG analysis of trigonal Ag[dca].

expected loss: 38.0%) can be attributed to the loss of carbon and nitrogen. The endothermic peak at 751°C could be due to the melting of the silver particles. This as well as the mass loss is in accordance with the silver flakes found as a residue.

3.3 Crystal structure

For both modifications of Ag[dca], Fig. 5 shows a planar boomerang-shaped dicyanamide anion ([NCNCN]$^-$) already well investigated and characterized in the crystal structure of Li[N(CN)$_2$] [18]. The relevant angle (C2–N1–C1) of the [N(CN)$_2$]$^-$ anion of orthorhombic Ag[dca] amounts to 123° in slightly differing from the corresponding (C–N1–C) angle in trigonal Ag[dca], where a value of 125° is observed. The short distances C2–N3 and C1–N2 of 114 and 111 pm (orthorhombic Ag[dca]) as well as C–N2 of twice 114 pm (trigonal Ag[dca]) emphasize the triple bond of a cyanide group as reported for the formally analogous lithium compound [18]. The distances N1–C2 and N1–C1 or N1–C, respectively, show markedly larger values (129–131

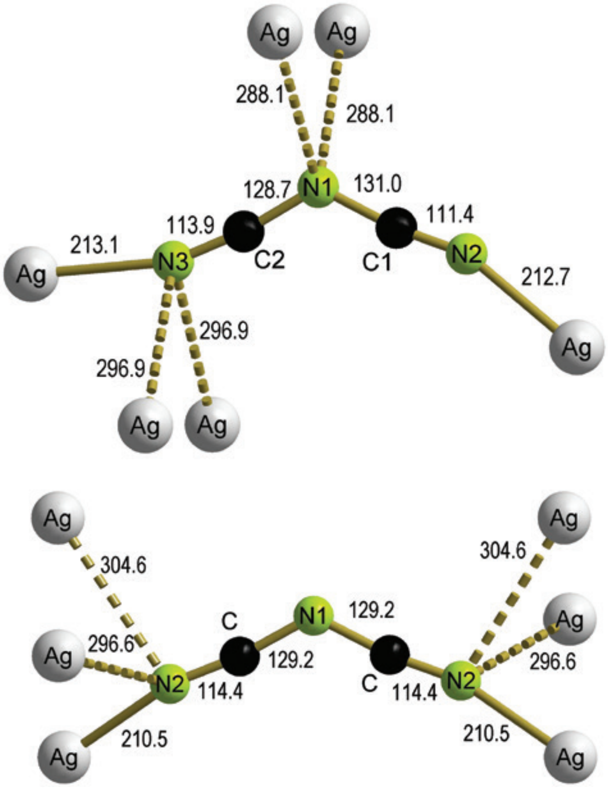

Fig. 5: Coordination of the [dca]$^-$ anion in orthorhombic Ag[dca] (top) and trigonal Ag[dca] (bottom).

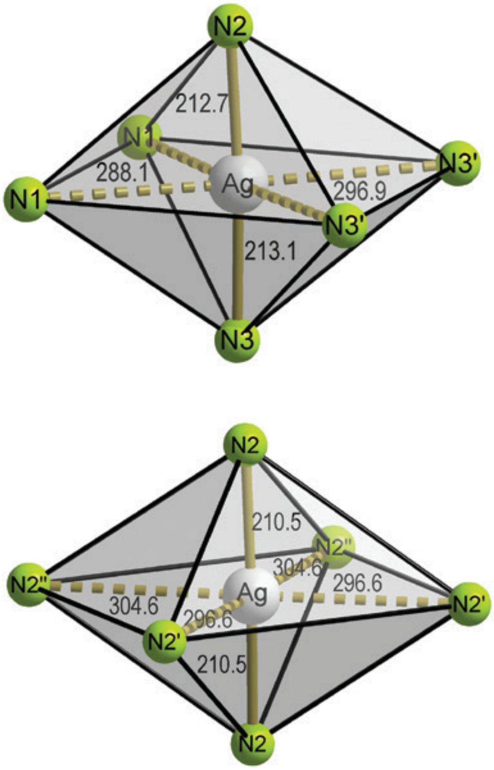

Fig. 6: Coordination of Ag$^+$ in orthorhombic Ag[dca] (top) and orthorhombic Ag[dca] (bottom).

pm) suggesting single-bond character (see Table 3 and Fig. 5). According to Fig. 6, in both forms of Ag[dca], each silver cation is coordinated in an octahedral fashion by four nitrogen atoms of [dca]$^-$ anions with rather long distances (288–305 pm) and two *trans*-bonded [dca]$^-$ moieties with short bond length (211–213 pm). All bond lengths and bond angles are in familiar ranges (Table 3), considering their respective (2 + 4) coordination. Regarding only the shorter distances Ag–N, which leaves the common coordination number of two (CN = 2) for Ag$^+$ behind, and correlating this with the connectivity Ag[dca]$_{2/2}$, there is at first glance no striking difference between the orthorhombic and the trigonal crystal structure of Ag[dca]. However, including the (2 + 4) coordination sphere of Ag$^+$, Fig. 5 shows that the bridging nitrogen atom (N1) of the dicyanamide anion in the orthorhombic modification of Ag[dca] exhibits distant contacts to two Ag$^+$ cations (288 pm), while there is nothing of this kind observed for N1 in the trigonal crystals. In the orthorhombic crystals N2 is only surrounded by one Ag$^+$ cation with short distance (213 pm), while N3 in the same [dca]$^-$ unit and both N2 atoms in trigonal Ag[dca] show three Ag$^+$ neighbors (213 and 2 × 297 pm (orthorhombic) versus 211, 297 and 305 pm (trigonal)).

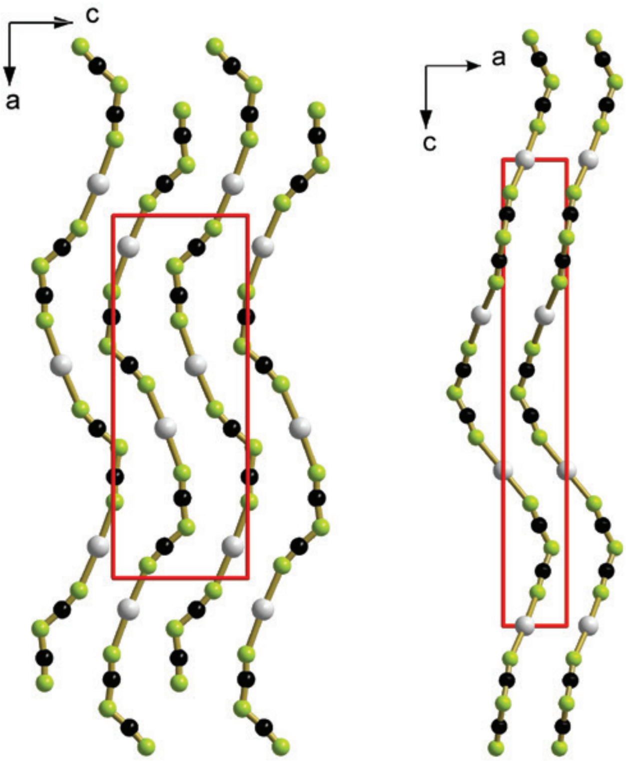

Fig. 7: Infinite $^1_\infty\{\mathrm{Ag[N(CN)_2]_{2/2}}\}$ chains running along [100] in orthorhombic Ag[dca] (left) and along [001] in trigonal Ag[dca] (right).

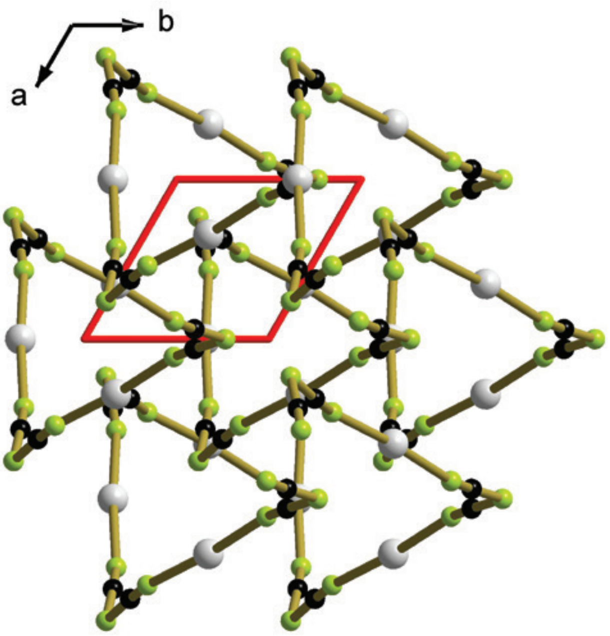

Fig. 9: View along [001] of the interpenetrating ${}^{1}_{\infty}\{Ag[N(CN)_2]_{2/2}\}$ helices in trigonal Ag[dca].

Considering only the short Ag–N contacts (<220 pm), the crystal structures of both forms can be described with infinite chains ${}^{1}_{\infty}\{Ag[N(CN)_2]_{2/2}\}$, which are running along [100] for orthorhombic Ag[dca] (Fig. 7, left) and along [001] for the trigonal modification (Fig. 7, right). Just like in the crystal structure of trigonal HgS [19] and elemental selenium (gray Se or γ-Se) [20] as well as in trigonal Ag[dca] (all are crystallizing in the space group $P3_121$ or its $P3_221$ enantiomorph), infinite chains ${}^{1}_{\infty}\{HgS_{2/2}\}$, ${}^{1}_{\infty}\{SeSe_{2/2}\}$ and ${}^{1}_{\infty}\{Ag[N(CN)_2]_{2/2}\}$ occur, which are winding in a helical manner. By contrast, in orthorhombic Ag[dca] these chains are corrugated in a planar fashion as shown in Fig. 8 (left and right). This fact is illustrated nicely in a projection of these strands along [100] for orthorhombic Ag[dca] (Fig. 8, right) and along [001] for trigonal Ag[dca] (Fig. 9). In the latter case, the helices interpenetrate each other (Fig. 9), explaining the significantly higher space-filling, calculated with the help of the program MAPLE [21–26] and the higher density (15.1% and 3.38 g cm^{-3} for trigonal Ag[dca] versus 15.0% and 3.31 g cm^{-3} for orthorhombic Ag[dca]).

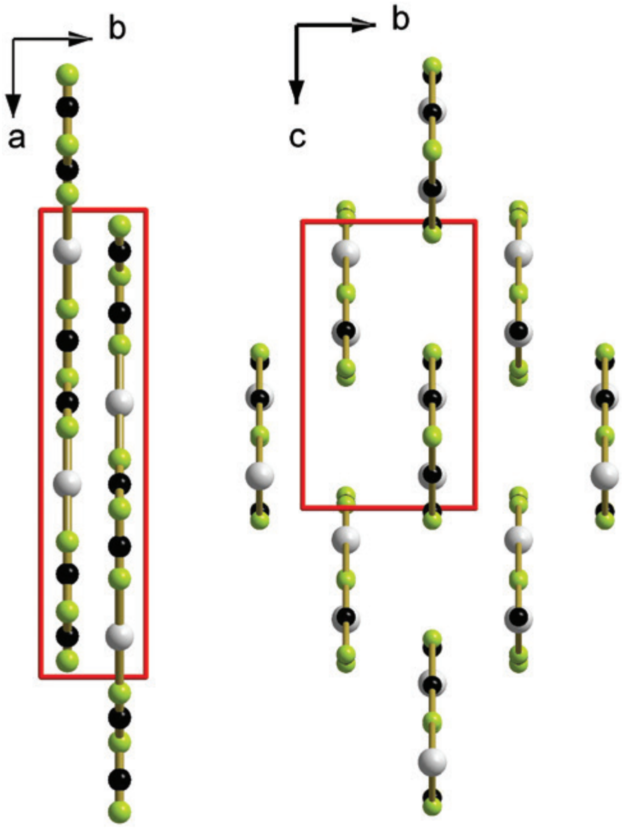

Fig. 8: Different views on the corrugated, but plain ${}^{1}_{\infty}\{Ag[N(CN)_2]_{2/2}\}$ chains running along [100] in orthorhombic Ag[dca].

4 Conclusion

A protocol has been reported to synthesize the orthorhombic and the trigonal polymorph of Ag[dca]. Single-crystal structure analyses corroborate earlier results [3, 4] and deliver more precise structural information. The polymorphic forms of the title compounds can be distinguished by vibrational spectroscopy and by their different thermal behavior. The IR spectrum of the orthorhombic form deviates in some parts to literature data. As stated before [4], crystallization experiments show that orthorhombic Ag[dca] with the lower density forms first according to the Ostwald step rule and later transforms into the trigonal modification, which seems to be the thermodynamically stable one with higher density. This behavior resembles the situation of HgS precipitates, where metacinnabarite (black cubic, sphalerite-type HgS with CN = 4) appears first, but transforms to the more dense and thermodynamically stable cinnabar (orange-red HgS, CN = 2 + 4) [19].

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