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Solvent effects on the crystal structure of silver pentacyanocyclopentadienide: supramolecular isomerism and solvent coordination†

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Several coordination polymers of silver(I)–pentacyanocyclopentadienide (PCC) were studied by X-ray diffraction to examine the effects of different solvents on supramolecular isomerism of the PCC-ligand. While alcohols yield supramolecular isomers of [Ag(PCC)] without coordination of solvent molecules, less polar solvents show coordinate binding. The influence of solvent polarity can be observed by a gradual change in the lattice structure featuring distinct motifs.

Introduction

Over the last two decades, a large number of coordination polymers has been synthesized and characterized. While the amount of structures and potential applications is staggering, underlying issues still need to be addressed to advance the field. Despite the growth of respective databases, the prediction of resulting lattice structures has been a constant challenge. While prediction algorithms are common in the calculation of monomeric structures, the parameters to consider for the calculation of polymeric compounds have pushed computational approaches to their limits.[1,2] Not only do the effects of coordinating solvent during the preparation of coordination polymers influence the resulting topology, isomerisms and polymorphisms of the compounds are known to be created by changes in temperature, pressure, and solvent choice.[3] Understanding the effects that lead to supramolecular isomerism has been a goal since the foundation of this field of research[4] and is of great interest in biological[5] and pharmaceutical applications[6] that rely on structural properties of the polymeric lattice to induce or enhance certain attributes in a compound. While often sought after in the pursuit to create chiral templates, the control of the resulting structure can also be helpful in designing magnetic materials.[7]

Among the metal ions used for the construction of coordination networks, Ag^+ has gained a central role. This is based mainly on the fact that this d^{10} ion lacks any crystal field stabilization effects and therefore can assume variable coordination numbers from two to six and sometimes even higher, and also very different geometries.[8,9] While most of these polymers are based on neutral N-donor ligands which need additional non-coordinating anions which also can have a directing effect on the molecular architecture, there are also quite a few reports with coordinating polydentate anions that give rise to interesting structures. Thus, tricyanomethanide[10] and tetracyanidoborate[11] have been employed for a series of interesting coordination polymers. As a structurally related ligand to tricyanomethanide, the largely unexplored compounds of pentacyanocyclopentadienide $[C_5(CN)_5]^-$ (ref. 12) are likely to share properties observed in the $[C(CN)_3]^-$ anion[13] and offer the advantage to act as a planar, pentadentate ligand, able to link central ions into dense 3D framework structures. Since no corresponding crystal symmetry to this ligand symmetry exists,[14] they could be used in the creation of aperiodic lattice structures.[15] From a preparative view, the apparent high thermal and oxidative as well as hydrolytic stability of this anion allows for a wide choice of solvents and crystallization conditions.[16,17] As the negative charge is delocalized over the cylopentadienyl ring as well as five cyano group, the anion was regarded as "weakly coordinating",[18] which allows for multiple structural rearrangements during the crystallization process. The combination of Ag(I) cation and $[C_5(CN)_5]$ anion was expected to produce a fullerene-like spheroidal structure, based on computational studies.[14] A synthesis of $Ag[C_5(CN)_5]$ from $NEt_4[C_5(CN)_5]$ and $AgNO_3$, using acetonitrile as solvent, was reported first in two patents by *Webster* over 45 years ago,[16] and a report on "pentacyanocyclopentadienyl complexes of manganese(I), rhenium(I) and iron(II)" by *Venanzi* published in 1972,[19] however, no analytical data were given. Later on, a preparation from the same starting materials, however, with acetone as solvent, was reported by Reed.[18] Apparently, recrys-

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tallization from acetonitrile/toluene yielded crystals of composition "Ag[$C_5(CN)_5$] × $\frac{1}{2}$ MeCN". Then, a study directed towards the "self-assembly of spheroidal structures" reported another synthesis, using the same starting materials, however using methanol as solvent, yielding a brown powder of composition "Ag[$C_5(CN)_5$] × 2.5 H_2O".[14] Recrystallization from acetonitrile was reported to yield crystals of [Ag(MeCN)$_3$][$C_5(CN)_5$]. Finally, we ourselves reported the crystal structure of [Ag(DMF)[$C_5(CN)_5$]] obtained from the same starting materials after recrystallization from dimethylformamide.[20] In continuation of our studies on the coordination chemistry of polynitriles[19,21,22] we decided to have a closer look at the influence of solvents on the crystal structures of silver pentacyanocyclopentadienide. In this article, we show the extensive effect of solvent choice on binding modes of silver(I)-compounds of this ligand, as well as present a number of unusual motifs exhibited by this ligand class that will be helpful in understanding the coordination chemistry of the pentacyanocyclopentadienide anion.

Results and discussion

Ag[$C_5(CN)_5$] was prepared according to the literature, using methanol as solvent for the reaction, and a first purification step using a toluene–acetonitrile mixture (Scheme 1).[14,18]

X-ray crystallographic studies

Molecular and crystal structure of [Ag(PCC)] from methanol (1). Repeated recrystallization from methanol yields compound **1**, which crystallizes in the monoclinic space group $P2_1/n$.[23] PLATON analysis[24] shows no solvent accessible voids (*vide infra*). The silver(I)-center is coordinated by five PCC-ligands *via* all nitrile functions in a square pyramid (Fig. 1). With one short Ag–N bond of 2.25 Å and four longer ones of 2.48 ± 0.08 Å and N–Ag–N bond angles between 81.16° and 111.8°, the coordination polyhedron is heavily distorted. With C–N–Ag bond angles between 128.9° and 167.0°, only the N1-nitrile function is close to the ideal angle of 180° of a directional nitrile bond (Table 1). Moreover, cation–π-interactions can be formulated between the silver(I)-ion and the cyclopentadienide ring of a further symmetry-related PCC-ligand whose center could potentially pose as the second apex of a square bipyramidal coordination polyhedron (Fig. 2). The silver-centroid distance of 3.358 Å suggests a weak penta-hapto interaction.[9b,25] For comparison, the only crystallographically characterized silver pentahapto-cyclopentadienide, Ag[$C_5H_2(SiMe_3)_3$], shows a Ag–Ct distance of only 2.256 Å.[26]

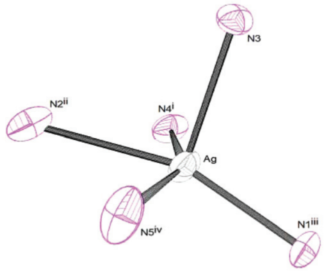

Fig. 1 ORTEP-presentation of the coordination sphere of the silver(I)-ion in compound **1** including atom labelling: i: $-x, 1 - y, 1 - z$; ii: $x - 1, y, z$; iii: $3/2 - x, y - \frac{1}{2}, 3/2 - z$; iv: $x - 1/2, 3/2 - y; z + \frac{1}{2}$.

Table 1 Selected bond lengths [Å] and angles [°] of compounds **1–3**

Compound **1**		Compound 2^a		Compound 3
Ag–N	2.250(6)	2.303(5)	2.322(5)	2.271(2)
	2.450(7)	2.252(5)	2.378(6)	2.337(2)
	2.400(6)	2.279(5)	2.259(5)	2.344(2)
	2.507(6)	2.345(6)	2.236(5)	
	2.566(7)			2.240(2)
Ag–Ct	3.359(6)	3.693(6)		
C–N–Ag	168.1(6)	168.0(5)	164.8(5)	169.7(2)
	129.0(6)	169.9(5)	152.6(6)	153.8(2)
	140.0(6)	166.3(5)	169.0(6)	168.3(2)
	134.4(6)	149.7(6)	164.4(5)	
	154.2(6)			172.2(2)
N–Ag–N′	158.9(2)	127.3(2)	88.0(2)	98.0(1)
	103.2(2)	105.4(2)	105.9(2)	100.1(1)
	111.9(2)	95.7(2)	110.9(2)	141.2(1)
	89.0(2)	111.5(2)	101.0(2)	115.9(1)
	92.5(2)	107.3(2)	113.1(2)	98.9(1)
	81.2(2)	107.4(2)	129.7(2)	103.4(1)
	75.3(2)			
	92.1(6)			
	95.5(2)			
	155.5(2)			

[a] The left column refers to distances and angles with Ag01, the right with Ag(02).

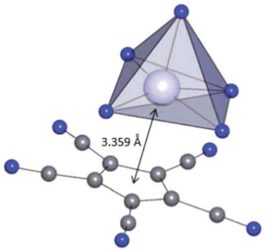

Fig. 2 The extended coordination environment of the silver(I)-center in compound **1** including cation–π-interactions.

Due to the 1 : 1 stoichiometry, the PCC ligand has also to coordinate to five Ag^+ ions. First of all, a point reflection at (0, 1/2, 1/2) generates a second AgPCC unit, creating a 14-membered ring, involving nitrile nitrogen atoms N3 and N4 and their symmetry equivalents (Fig. 3).

$$(NEt_4)[C_5(CN)_5] + AgNO_3 \xrightarrow[\text{RT, 3h}]{\text{MeOH}} Ag[C_5(CN)_5] + (NEt_4)NO_3$$

Scheme 1 Preparation of silver(I)–PCC.

These 14-membered rings stack along the *a*-axis, using nitrile nitrogen atom N2 and its inversion related counterpart. Viewed along the crystallographic *a*-axis, ribbons of the exhibi-

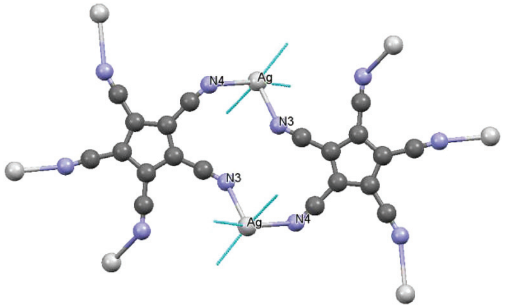

Fig. 3 Point reflection of PCC-rings in compound **1**.

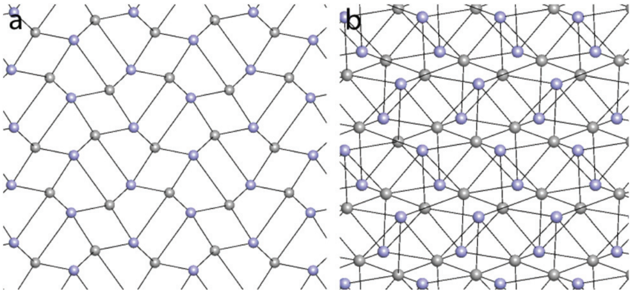

Fig. 5 (a) A simplified net of compound **1**, viewed along the crystallographic *a*-axis. (b) The same simplified net, viewed along the *c*-axis.

ted 14-membered rings can be observed that run along the *b*-axis. Created by the 2_1 screw axis, PCC ligands of neighboring ribbons take up an orthogonal orientation and exhibit a wavy 2D-sheet (Fig. 4a).

Several ribbons are interconnected *via* 16-membered rings using the 1,3-nitrile functions of the PCC ligand, creating sheets that run along the crystallographic *a*- and *b*-axis (Fig. 4b).

The topological structure of **1** can be analyzed by using TOPOS.[27] By simplifying the PCC-ligand and the silver(I)-center as five-connecting nodes, the 3D-network can be depicted as a complex and dense 2-nodal (5-c) (5-c) net-type framework structure (Fig. 5) with the point symbol $\{4^3{\cdot}6^6{\cdot}6^8\}$ that shows no solvent accessible spaces.

Molecular and crystal structure of [Ag(PCC)] from ethanol (2). Recrystallization from ethanol yields compound **2**, crystallizing in the chiral orthorhombic space group $P2_12_12$. When taken out of the mother liquor, the crystals quickly turn opaque, probably due to the loss of included solvent. PLATON analysis of the structure shows large solvent accessible voids, making up for 1171.7 Å^3 corresponding to *ca.* 40% of the crystal unit-cell volume. Assuming ethanol to be included in the voids, this corresponds to the van der Waals volume of *ca.* 22 EtOH molecules.[28] For the refinement, the SQUEEZE routine of PLATON was used. There are two symmetry-independent AgPCC molecules in the asymmetric unit, with each Ag$^+$ ion coordinating two nitrile nitrogen of its "own" PCC anion and two of the other (Fig. 6).

Ag01 exhibits a rather regular tetrahedral coordination environment, with only the angles involving N11 deviating substantially from the ideal values, and shares with compound **1** the tendency to form (very) weak cation–π-interactions, (Fig. 7). If the centroid of ring C21–C25 is included, the geometry could also be regarded as a distorted trigonal bipyramid (angle N24–Ag01–Ct2 = 168.6°). The geometry around Ag02 can be described as a very distorted tetrahedron, with only two angles close to the "ideal" ones. All Ag–N bonds are in the range from 2.236–2.377 Å, with C–N–Ag angles ranging from 150.1–170.4°.

For comparison, silver tricyanomethanide shows a distorted trigonal–pyramidal geometry with Ag–N bonds of 2.156 and 2.270 Å and two long contacts of 2.979 Å and C–N–Ag angles of 153.7 and 172.8°,[10b] and in silver tetracyanidoborate an "ideal" tetrahedron is formed with Ag–N bonds of 2.244 Å.[11]

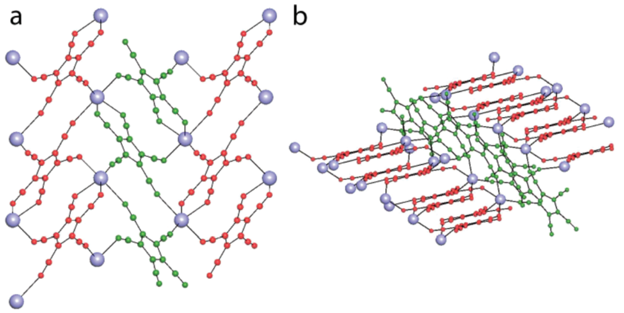

Fig. 4 (a) A view along the crystallographic *a*-axis, showing orthogonal sheets of 14-membered rings (green and red). (b) The 14-membered rings of [Ag$_2$(PCC)$_2$] viewed along (1/2, 1/2, 0), showing stacks of PCC-ligands.

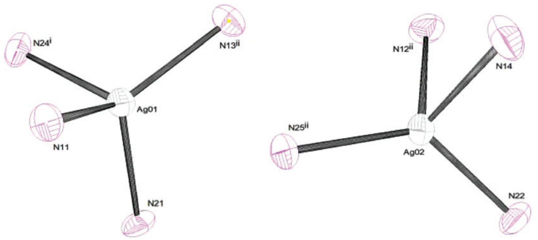

Fig. 6 ORTEP-presentation of the two silver(I)-ions of compound **2** including atom labelling: i: $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; ii: $x, y, z - 1$.

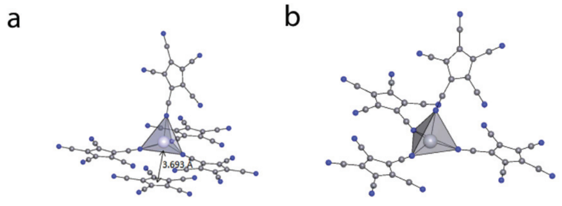

Fig. 7 The extended coordination environment of both silver centres (Ag01 in a, Ag02 in b) in compound **2** including cation–π-interactions.

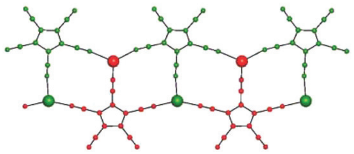

Fig. 8 A view along the *a*-axis, showing a ribbon of non-equivalent units of PCC and silver-ions (green and red).

Looking at the PCC ligands, both coordinate the metal centers *via* four nitrile functions. Three of the nitrile functions on each ring (N11, N12, N13; N21, N22, N25) are used to build a one-dimensional ladder structure running along the *c*-direction (Fig. 8), reminiscent of the situation found in the Ag(PCC)(DMF) compound reported by us earlier.[19] All the cyclopentadienyl rings in this ribbon are coplanar, with the Ag^+ ions only slightly shifted out of this plane.

The fourth nitrile functions are then used to interconnect orthogonal ribbons into an interwoven 3D framework, (Fig. 9). A topology analysis by simplifying the PCC-ligand, as well as the two silver-ions to 4-coordinating nodes, leads to a loss in symmetry information and shows a uninodal 4-c net representing the RCSR umx-type net with the point symbol $\{4^2 \cdot 6^3 \cdot 8\}$.

As can be seen, there are two different kinds of channels formed. Long narrow ones, which are formed *via* the above-mentioned cation–π-interactions, and rhomboid ones with diagonals of approximately 9 and 12 Å, both of them running along the *c*-direction. While the former ones do not allow any access to solvent, the latter ones make up for most of the 40% solvent accessible space mentioned above (Fig. 10). The SQUEEZE analysis yields an electron count of *ca.* 255 electrons in the voids of one unit cell. This corresponds to *ca.* 10 ethanol molecules.

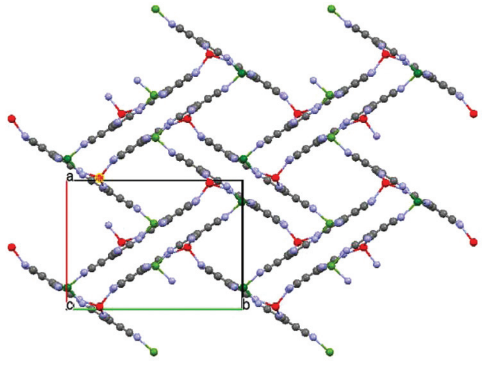

Fig. 9 A view along the crystallographic *c*-axis showing the different silver(I)-centers (red: Ag01 and green: Ag02).

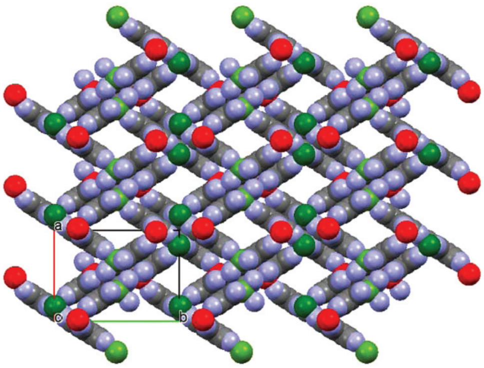

Fig. 10 Spacefilling diagram of compound **2** showing the large channels along *c*.

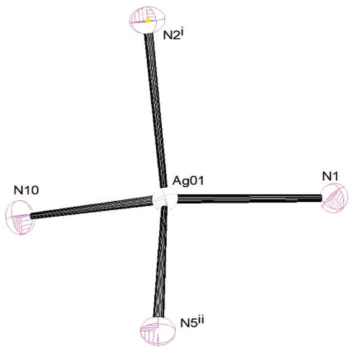

Fig. 11 ORTEP-presentation of the coordination sphere of the silver(I)-ion in compound **3** including atom labeling. I: $1 - x, 1 + y, \frac{1}{2} - z$; ii: $1 - x, 2 - y, 1 - z$.

Crystal structure of [Ag(PCC)(MeCN)] (3). [Ag(PCC)(MeCN)] crystallizes from acetonitrile/toluene in the monoclinic space group *C*2/*c*. The silver ion is coordinated by three different PCC anions and an acetonitrile molecule (Fig. 11). This is similar to $[Ag[C(CN)_3](MeCN)]$.[10a] However, the Ag–N bond to the acetonitrile is in **3** the shortest (2.24 Å *vs.* 2.27–2.34 Å), while in the tricyanomethanide complex it is the longest bond (2.40 Å *vs.* 2.22 Å). With bond angles at Ag^+ from 97.9 to 141.2° the AgN_4 unit can be described as a severely deformed tetrahedron.

The pentacyanocyclopentadienide anion coordinates to three different Ag^+ ions, using three nitrile functions in 1,2,3-position. Similar to the structures of **1** and **2** and also the earlier reported [Ag(PCC)(DMF)][19] two inversion related molecules form a 14-membered ring, using nitrogen atoms N1 and N5. These 14-membered rings are interconnected in *c*-direction *via* two nearly orthogonal 14-membered rings *via* nitrile nitrogen atoms N2. Additionally, further 14-membered ring systems related to the first one by a double translation in *b*-direction are also connected by the same token, giving rise to a system of corrugated sheets almost parallel to the *bc*-plane (Fig. 12).

Another sheet system related to the first one by a unit translation in *b* direction, but not connected to it leads to an interpenetrating network, as shown in Fig. 13.

The MeCN ligand exhibits a capping function, restricting the network to a 2D-coordination polymer (Fig. 14). As can be seen, the methyl group of the acetonitrile ligand fits nicely in the groove formed by the two non-coordinating nitrile nitro-

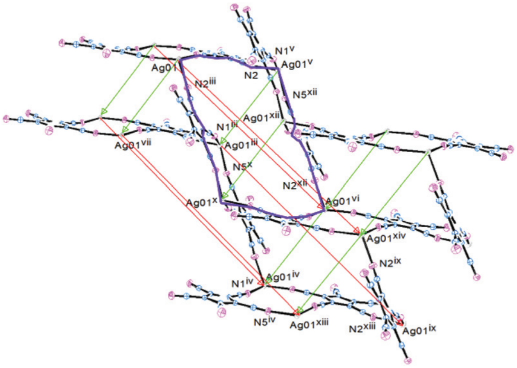

Fig. 12 Two stacked corrugated sheets in compound **3**. Green arrows connect Ag ions related by $y' = y + 2$, and red arrows connect Ag ions related by $z' = z - 1$. The purple line shows the connecting path between two 14-membered rings related by one translation in *c*-direction. Acetonitrile ligands omitted for clarity.

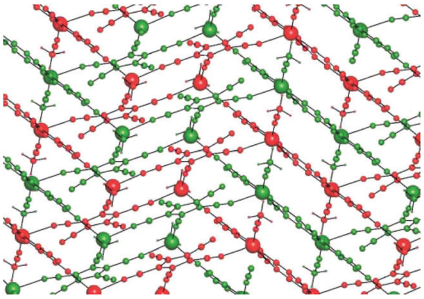

Fig. 13 The twofold interpenetrating network of **3** with interwoven sheets painted in green and red.

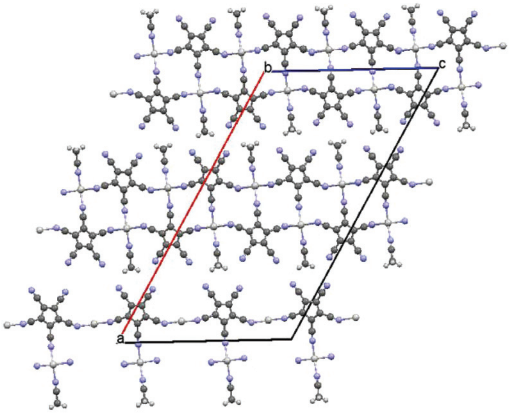

Fig. 14 A view of the crystal structure of **3** down the *b*-axis.

gens N3 and N4. A topological analysis can be carried out by reducing the PCC-ligand, as well as the silver(I)-center, to a 3-coordinating node with successive removal of 1-coordinating MeCN. Characterization of the resulting simplified net shows a uninodal 3-c net matching with the RCSR fes shubnikov plane net and a point symbol of $\{4{\cdot}8^2\}$.

Thermal analyses

All three compounds were examined for their thermal stability in the temperature region from 25 °C to 150 °C, using TG and DTA measurements (see Fig. SI_1–SI_3†). While **1** and **3** showed no mass change in the observed range, compound **2** exhibited a two-step mass gain of 10.58% in the range 84–87 °C. Since neither **1** nor **3** showed the presence of uncoordinated solvent(s) in the crystal structure determinations, the absence of any mass change is not surprising. The acetonitrile of **3** remains coordinated at least up to 150 °C. However, the observation that crystals of **2** lost solvent EtOH upon standing at r.t. would have suggested that heating would give rise to mass loss, corresponding to the evaporative loss of the adsorbed molecules. Thus, the observed mass gain at 84–87°, *i.e.* at the boiling point of ethanol, comes unexpected and is very unusual. Since the squeeze analysis hinted at incomplete filling of the voids (10 EtOH molecules delocalized in voids that could take up to 22 EtOH molecules, *vide supra*), it seems possible that the confined EtOH molecules exert a "bottle-neck" effect similar to the observations made with "InOF-1".[29] But the role of CO_2 in this compound must be played by the argon atoms of the TG apparatus, and it has to be postulated that at the same time the EtOH molecules evaporate they are immediately replaced by Ar. This interpretation has to remain speculative, since no single crystals were left after heating in order to repeat the crystal structure determination.

Conclusions

We prepared three crystal forms of AgPCC from different solvents. With methanol a dense 3D-coordination polymer with a five-fold coordinating ligand and cation–π interactions is formed, while crystallization from ethanol yields a porous structure with large voids, and one nitrile group left uncoordinated. On the other hand, recrystallization from a toluene–acetonitrile mixture gives a sheet structure with one solvent molecule acting as a ligand to the metal, which also coordinates only to three of the nitrile groups of the anionic ligand. The fact that acetonitrile acts as a ligand to silver, while the alcohols do not, can be attributed to the "soft" nature of Ag(I) cation in the sense of the HSAB principle,[30] and the softer nature of the MeCN solvent in comparison to alcoholic solvents (the "μ-parameter" for MeCN is 0.34, compared to 0.02 for MeOH and 0.08 for EtOH)[31] As there are several reported crystal structures of Ag(I) with coordinated MeOH or EtOH,[32] however, with O-donor anions like trifluoromethanesulfonate, the pentacyanocyclopentadienide anion must be of comparable softness to acetonitrile. The fact that we observed a porous structure with EtOH, while with MeOH a dense three-dimensional network was formed, may be due to the higher boiling point of EtOH together with its larger size, which makes the evaporative loss of the solvent kinetically hindered.

Experimental section

The starting material ($(Et_4N)PCC$) was obtained using literature routes.[33]

Synthesis of AgPCC

To a solution of the $(Et_4N)PCC$ (40.4 mmol, 1.00 eq.) in methanol (200.0 mL) was added silver nitrate (14.46 g, 80.8 mmol, 2.00 eq.) in one portion and the mixture was stirred for 3 h at room temperature. The solution was evaporated and the solid was subjected to column chromatography (Silica, MeCN/toluene: 20/80). The product was isolated as a white solid and recrystallized from methanol, ethanol or an acetonitrile/toluene mixture (90/10). Yield 8.8 g (73%). $^{13}C\ \{^1H\}$ NMR (100.16 MHz, +25 °C, d_6-DMSO), δ = 113.01 (s, C-CN), 101.78 (s, Cp). Elemental analysis, calcd for [AgPCC], C 40.30, N 23.50, H 0.00, found C 40.02, N 23.18, H 0.00. IR (cm^{-1}): ν = 3695(w), 3598(w), 2840(w), 2767(s), 2633(w), 2349(w), 2297(m), 2245(vs), 2214(vs), 1726(w), 1629(m), 1584(w), 1463(vs), 1266(m), 1120(m), 1030(m), 958(m), 913(w), 871(m), 778(m), 736(m), 684(m). Mass Spectrometry *m*/*z* (DEI$^+$): 107.0 [Ag^+], 190.1 [$C_{10}N_5^+$], 297.0 [M^+].

Crystal structure determinations

The structures of **1** and **2** were determined on a SYNTEX R3 diffractometer operating in $\omega/2\theta$ mode; the structure of **3** was determined on a BRUKER D8-Venture diffractometer TXS system equipped with a multilayer mirror optics monochromator and a Mo Kα rotating-anode X-ray tube. A total of 688 frames were collected. The structures of **1** and **2** were solved with SHELXS as included in the SHELXTL PLUS release 4.11/V, the structure of **3** with SHELXT as included in the WINGX program package.[34] All structures were refined with SHELXL version 2014/7. As compound **2** showed in the PLATON analysis large solvent accessible voids, the data were treated with the SQUEEZE routine of PLATON and refined correspondingly. More experimental details of the data collections and refinements are collected in Table SI1 in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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