Argentophilic Interactions in Two Ag^{I} Complexes of 3-(2-(Pyridin-4-yl)ethyl)pentane-2,4-dione, a Promising Ditopic Ligand

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Abstract: Reactions of 3-(2-(pyridin-4-yl)ethyl)pentane-2,4-dione (HacacPyen) with AgPF$_6$ and AgBF$_4$ afforded cationic silver complexes [Ag(HacacPyen)$_2$]$^+$ with essentially linear coordination of the Ag^{I} cation by two pyridine N atoms. Rather unexpectedly, the HacacPyen ligands in the PF$_6^-$ salt **1** adopt the diketo form, in contrast to the uncoordinated HacacPyen molecule, whereas the corresponding BF$_4^-$ salt **2** and the majority of 3-substituted acetylacetones crystallizes as the enol tautomer. In both compounds **1** and **2**, complex cations aggregate *via* short Ag···Ag interactions to pairs. These contacts amount to 3.21 Å in **1** and 3.26 Å or 3.31 Å in **2**. As they are unsupported by any additional bridging ligands and correspond to the closest interionic interactions between neighbouring complex cations, they may be addressed as argentophilic interactions. The PF$_6^-$ anions in **1** and the BF$_4^-$ counter ions in **2** are involved in long and presumably electrostatic Ag···F contacts of ca. 2.9 Å. Additional coordination between Ag^{I} and keto O atoms of symmetry-equivalent ligands occurs in **1** and leads to an extended two-periodic supramolecular structure.

Keywords: ditopic ligands; argentophilic interactions; keto-enol tautomrism; coordination chemistry; metal-organic frameworks

1. Introduction

The increasing interest in metal-organic frameworks (MOFs) is not only due to the structural diversity and inherent beauty of this class of compounds but also to their physical properties. The organic linkers may connect nodes with attractive magnetic [1,2] or optical [3] features, and often a large inner surface area enables a variety of applications such as gas storage [4] or catalysis [5–8]. The incorporation of more than a single cation type as nodes can obviously increase the range of accessible coordination polymers and in principle enable more potential applications. The resulting higher complexity will, however, also lead to synthetic challenges: well-ordered bimetallic systems will usually be easier to interpret and study with applications in mind but require selectivity. Substituted acetylacetone derivatives represent ditopic linkers with coordination sites of different Pearson hardness [9,10] and have been successfully employed to assemble well-ordered bimetallic extended structures. Scheme 1 compiles two widely used examples and our candidate from this class of compounds.
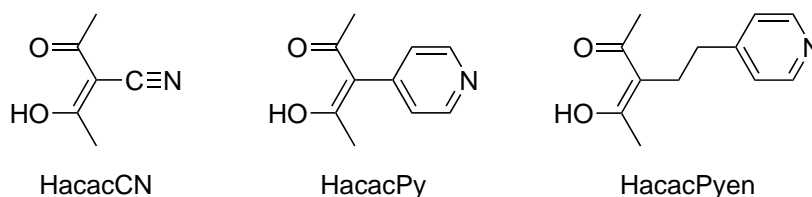
Scheme 1. Structures of two common N donor substituted acetylacetones and our candidate: 3-cyanopentane-2,4-dione (HacacCN), 3-(pyridin-4-yl)pentane-2,4-dione (HacacPy) and 3-(2-(pyridin-4-yl)ethyl)pentane-2,4-dione (HacacPyen), respectively.

HacacPy was introduced in 1995 by Sanders and coworkers [11]. Following that report, first the groups of Domasevitch [12–14] and Maverick [15–17], later others [18], including our group [19], have used the compound in coordination chemistry. The structure of the uncoordinated ligand was established in 2017 by temperature-dependent neutron diffraction [20]. The nitrile-substituted acetylacetone HacacCN [21,22] is more restricted with respect to its N donor capabilities [23–33]. Many other combinations of the chelating acetylacetonato and N donor sites may be envisaged; the subject has been recently reviewed [34]. We here address the less popular ditopic acetylacetone 3-(2-(pyridin-4-yl)ethyl)pentane-2,4-dione (HacacPyen, Scheme 1). HacacPyen was synthesized by Domasevitch and coworkers [14] and used as O,O′ chelating ligand for Be^{II}; the original authors also communicated the structure of a bimetallic chain polymer obtained by N coordination of the pyridyl rings in the Be^{II} complex to CdCl$_2$. We recently investigated the crystal structure of HacacPyen by temperature-dependent neutron diffraction and confirmed that the uncoordinated organic molecule exists as the enol tautomer [35]. In this study, we report the syntheses and structural characterizations of two bis adducts of HacacPyen to Ag^I and put the resulting hexafluorophosphate and tetrafluoroborate salts in the scientific context of argentophilic interactions.

2. Experimental Section

2.1. Methods and Materials

Pentane-2,4-dione (Alfa Aesar, Kandel, Germany, 99%), sodium (Sigma Aldrich, Munich, Germany, n. a.), AgPF$_6$ (Acros Organics, Darmstadt, Germany, 98%) and AgBF$_4$ (Merck, Darmstadt, Germany, n. a.) were used without further purification. 4-Vinylpyridine (Alfa Aesar, 95%) was purified by vacuum distillation prior to use. Magnetic resonance spectra were recorded with a Bruker Avance II UltrashieldT11 plus 400 instrument (400 MHz, referenced to tetramethylsilane). Infrared spectra were measured using a Nicolet Avatar 360 E.S.P. spectrometer in potassium bromide windows. Elemental analyses were performed using a Heraeus CHNO-Rapid VarioEL.

2.2. Synthesis of 3-(2-(Pyridin-4-yl)ethyl)pentane-2,4-dione (HacacPyen)

3-(2-(Pyridin-4-yl)ethyl)pentane-2,4-dione (HacacPyen) was prepared according to a slightly modified method by Vreshch et al. [14]. Using standard Schlenk techniques, a solution of freshly distilled 4-vinylpyridine (39.0 mL, 362 mmol) in dry ethanol (2.5 mL) was added to a boiling solution of sodium (2.725 g, 118.5 mmol) and acetylacetone (73.5 mL, 712 mmol) in dry ethanol (47.5 mL) over 15 min. The solution was kept at reflux for 2 h. After cooling to room temperature, the solvent was removed under reduced pressure and water (500 mL) was added. The aqueous phase was extracted with CHCl$_3$ (3 × 150 mL) and the combined organic phases were dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure and the residue was purified by vacuum distillation (15 mbar, 115 °C) to remove starting material. The residue was dissolved in a small amount of hot CH$_2$Cl$_2$ and stored at −25 °C overnight. The crystals were filtered off, washed with a small amount of cold diethyl ether and dried in air. The product was received as a pale orange crystalline solid. Yield: 12.325 g (60.05 mmol, 16.6%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 16.79 (s, 1H), 8.56 (d, ^3J = 6.0 Hz, 2H), 7.21 (d, ^3J = 6.0 Hz, 2H), 2.75 (d, ^3J = 8.0 Hz, 2H), 2.57 (d, ^3J = 8.0 Hz, 2H), 2.08 (s, 6H). ^{13}C{^{1}H} NMR

(100 MHz, CDCl$_3$) δ 203.48, 191.28, 150.04, 149.77, 123.88, 108.84, 32.71, 28.73, 28.35, 22.82. CHN: Anal. Calcd for C$_{12}$H$_{15}$NO$_2$: C, 70.22%; H, 7.37%; N, 6.82%. Found: C, 70.24%; H, 7.23%; N, 6.85%.

2.3. Synthesis and Crystallization of [Ag(HacacPyen)$_2$]PF$_6$, 1

HacacPyen (41.1 mg, 0.2 mmol) and AgPF$_6$ (25.3 mg, 0.1 mmol) were dissolved in acetone (2 mL each). The two solutions were mixed and stirred for 15 min. The solvent was slowly evaporated at room temperature. The crude product was received as a yellow oil. Yield: 30.3 mg (0.046 mmol, 46%). Recrystallization from benzene at room temperature afforded single crystals as colorless needles suitable for single crystal X-ray diffraction. Although the synthesis of the crude oil may be reliably reproduced, several recrystallization experiments failed to give a crystalline solid. When crystalline **1** is obtained, it corresponds to an essentially phase pure solid as shown by X-ray powder diffraction (Figure S1 in the supplementary materials). We also note **1** readily reacts with redox active substances; even manipulation with metallic laboratory equipment may result in formation of Ag^0. IR (KBr): $\tilde{v}$/cm^{-1} = 3431(s), 2930(w), 2860(w), 1724(m), 1699(s), 1604(s), 1560(w), 1418(m), 1361(m), 1153(w), 992(w), 844(s), 559(m) (Figure S2). CHN: Anal. Calcd for [Ag(HacacPyen)$_2$]PF$_6$, including a minor contamination of the oily residue: C, 43.46%; H, 4.56%; N, 4.22%. Found: C, 45.27%; H, 4.68%; N, 4.38%.

2.4. Synthesis and Crystallization of [Ag(HacacPyen)$_2$]BF$_4 \cdot$ C$_4$H$_8$O$_2$, 2

HacacPyen (41.1 mg, 0.2 mmol) and AgBF$_4$ (19.5 mg, 0.1 mmol) were dissolved in ethylacetate (2 mL each). The two solutions were mixed and stirred for 5 min and the solution was kept at $-25\,^{\circ}$C overnight. The product was received as a colorless crystalline solid. Yield: 37.5 mg (0.054 mmol, 54 %). Single crystals suitable for single crystal X-ray diffraction were received after storing a solution of lower concentration after 1 d at $-25\,^{\circ}$C. IR (KBr): $\tilde{v}$/cm^{-1} = 3424(s), 2961(m), 2930(m), 2867(w), 1692(s), 1618(s), 1564(w), 1435(m), 1365(m), 1147(m), 1054(s), 816(m), 525(m) (Figure S2). CHN: Anal. Calcd for the dry solid [Ag(HacacPyen)$_2$]BF$_4$: C, 47.63%; H, 5.00%; N, 4.63%. Found: C, 46.07%; H, 4.72%; N, 4.19%.

2.5. Structure Determinations

Intensity data were collected with a Bruker D8 goniometer equipped with an APEX CCD area detector and an Incoatec microsource (Mo-K$_\alpha$ radiation, λ = 0.710 73 Å, multilayer optics) at 100(2) K (Oxford Cryostream 700 instrument, Oxfordshire, UK). Crystal data for **1**: C$_{24}$H$_{30}$AgF$_6$N$_2$O$_4$P, 663.34 g mol^{-1}. Monoclinic, $P2_1/c$ (No. 14); a = 10.8000(16) Å, b = 16.310(2) Å, c = 16.006(2) Å; β = 107.103(4)$^{\circ}$; V = 2694.7(7) Å^3; Z = 4; 30097 reflections, of which 4940 were independent; R_{int} = 0.1103; $F(000)$ = 1344; μ = 0.882 mm^{-1}; ρ_{calc} = 1.635 g cm^{-3}. Crystal data for **2**: C$_{28}$H$_{38}$AgBF$_4$N$_2$O$_6$, 693.28 g mol^{-1}. Triclinic, $P\bar{1}$ (No. 2); a = 11.1270(11) Å, b = 14.8723(14) Å, c = 20.5106(19) Å; α = 77.897(2)$^{\circ}$; β = 74.931(2)$^{\circ}$; γ = 75.966(2)$^{\circ}$; V = 3140.5(5) Å^3; Z = 4; 42177 reflections, of which 14589 were independent; R_{int} = 0.0405; $F(000)$ = 1424; μ = 0.707 mm^{-1}; ρ_{calc} = 1.466 g cm^{-3}. Data were integrated with SAINT [36] and corrected for absorption by multi-scan methods [37]. The structure was solved by intrinsic phasing [38] and refined by full matrix least squares procedures based on F^2, as implemented in SHELXL-13 [38]. Hydrogen atoms were treated as riding with C–H = 0.98 Å for CH$_3$, C–H = 0.95 Å for aryl-CH and C–H = 1.00 Å for alkyl-CH groups and assigned isotropic displacement parameters constrained to $U_{\text{iso}}(H)$ = 1.5 $U_{\text{eq}}(C)$ for methyl groups or $U_{\text{iso}}(H)$ = 1.2 $U_{\text{eq}}(C,N)$ otherwise. The unit cell of **2** features two large voids, each characterized by a volume of ca. 300 Å^3 and an electron content of ca. 100 electrons, in good agreement with the requirements for two molecules of disordered ethylacetate per void. As no model with atomic resolution for the co-crystallized solvent molecules could be derived, their contribution of the structure factors was taken into account with the SQUEEZE procedure [39]. Convergence results for **1**: 347 refined parameters. R_1(all) = 0.0476; wR_2 = 0.1077; GOF = 1.026; ρ(min/max): $-0.45/0.49\,e$ Å^{-3} (Full information: Table S1). CCDC reference number: 1936466 [40]. Convergence results for **2**: 658 refined parameters. R_1(all) =

0.0385; wR_2 = 0.1079; *GOF* = 1.080; ρ(min/max): $-0.63/1.81\,e\,\text{Å}^{-3}$ (Full information: Table S1). CCDC reference number: 1944686 [41]. Figure 1 shows displacement ellipsoid plots of the asymmetric units in **1** and **2**.
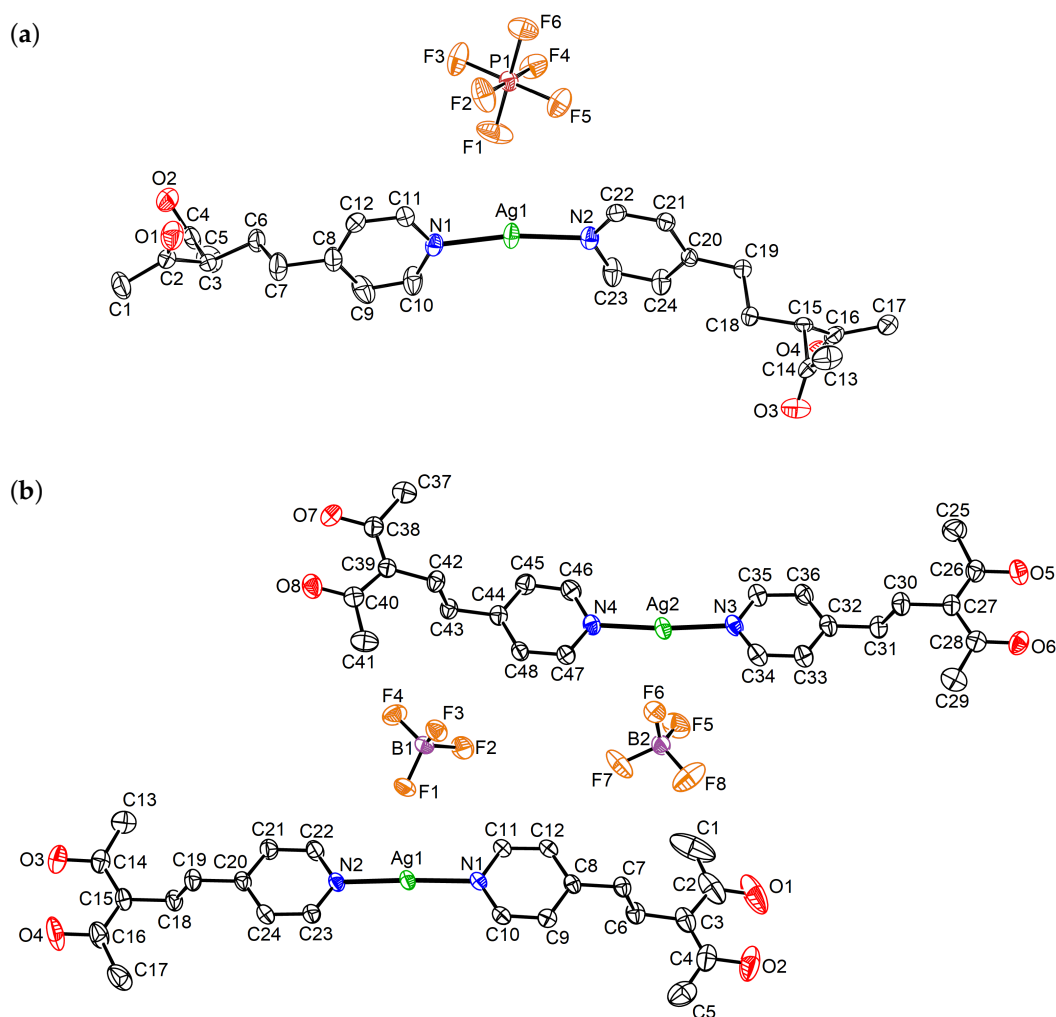

Figure 1. Displacement ellipsoid plots [42] of the asymmetric units (**a**) in **1** and (**b**) in **2**; ellipsoids are drawn at 50 % probability, H atoms have been omitted.

3. Results and Discussion

Reactions of HacacPyen with AgPF$_6$ in acetone and recrystallization from benzene and AgBF$_4$ in ethylacetate resulted in the formation of crystalline **1** and **2** (Scheme 2).

In the crystal of **1**, each Ag$^{\text{I}}$ cation is N coordinated by two symmetrically independent HacacPyen molecules. These ligands adopt slightly different conformations: the torsion angles between the central C of the acetylacetone moieties, the C atoms of the ethylene bridge and the *para* C in the pyridine ring amount to 155.3(4)° (C3–C6–C7–C8) and −173.6(4)° (C15–C18–C19–C20). In contrast to uncoordinated HacacPyen [35] both ligands exist as diketo tautomers, with short C=O double and long C−C single bonds (Table 1) in the non-planar acetylacetone moieties.
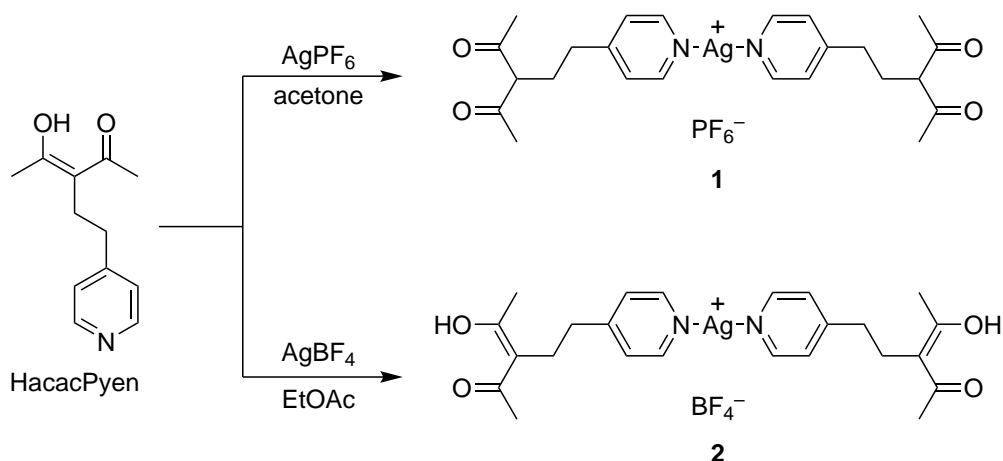
Scheme 2. Synthesis of **1** and **2** starting from HacacPyen.

Table 1. Selected bond distances and angles in the two symmetrically independent acetylacetone moieties of **1**.

O1–C2 / Å	1.221(6)	O3–C14 / Å	1.201(5)
O2–C4 / Å	1.233(6)	O4–C16 / Å	1.221(6)
C2–C3 / Å	1.508(6)	C14–C15 / Å	1.528(6)
C3–C4 / Å	1.525(7)	C15–C16 / Å	1.512(6)
∠(C2–C3–C4) / °	109.1(4)	∠(C14–C15–C16) / °	108.7(4)

We note that the enol tautomer is more popular for acetylacetones with N donor substitutents in 3-position ([34] and references cited therein.). In addition to the almost linear coordination by the two symmetrically independent pyridine N donor atoms, each Ag^I cation is engaged in short contacts to the keto oxygen atoms of a neighboring HacacPyen and to a Ag^I cation of an inversion-related bis(HacacPyen) silver complex (Figure 2).
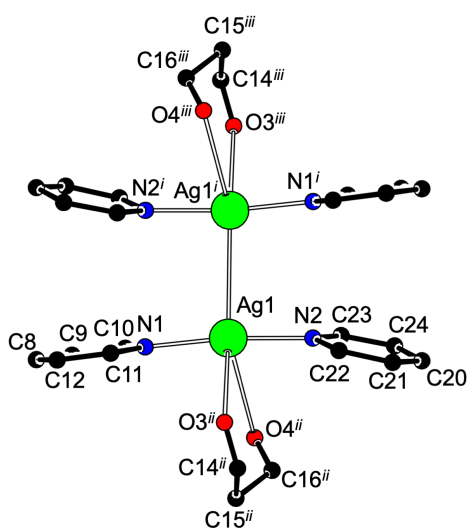

Figure 2. Cationic dinuclear aggregate of **1** [42], showing the coordination environment around Ag^I. Selected interatomic distances and angles: Ag1···Ag1^i 3.2129(8) Å, Ag1···N1 2.127(4) Å, Ag1···N2 2.130(4) Å, Ag1···O3^{ii} 2.806(3) Å, Ag1···O4^{ii} 2.915(3) Å, N1···Ag1···N2 171.48(15)°, O3^{ii}···Ag1···O4^{ii} 69.7(2)°. Symmetry operators: $i = 1 - x, 1 - y, 1 - z$; $ii = x, 0.5 - y, 0.5 + z$; $iii = 1 - x, 0.5 + y, 0.5 - z$.

This short Ag···Ag distance amounts to 3.2129(8) Å and deserves a closer inspection. Values of 1.7 [43] and 1.72 Å [44] are commonly accepted for the van der Waals radius of Ag, although

Batsanov [45] has suggested a significantly larger radius of 2.0 Å. Contacts between neighboring d^{10}-configured Ag^I cations are referred to as *argentophilic interactions* [26,43,46–54]; a review has been compiled a few years ago [55]. The relevance of such closed-shell interactions for the overall lattice energy of solids has been addressed by Pyykkö [56]. The Ag···Ag contact in **1** is not promoted by any bridging moiety. On the very contrary: the d^{10} cations approach closer than any other non-hydrogen atom pair in the $\{[Ag(HacacPyen)_2]^+\}_2$ aggregate. Figure 2 shows that the N donor ligands bend away from the contact region, with N1···N2^i contacts of 3.435(5) Å. The relevance of the argentophilic interaction is further corroborated by the arrangement of the N and O coordination partners about the Ag^I which all reside within the same hemisphere. Taking the short contacts into account, the HacacPyen ligands bridge neighboring Ag^I to chains in [0 0 1], and the argentophilic interactions crosslink these strands in [0 1 0] direction to a two-periodic supramolecular network in the (1 0 0) plane (Figure 3).
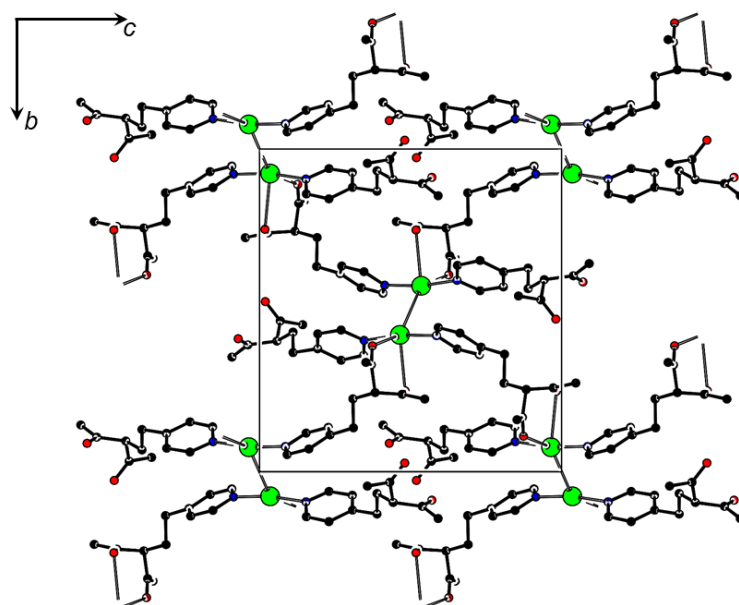

Figure 3. Two-periodic supramolecular network of complex cations in **1** [42]; H atoms and PF_6^- counter anions have been omitted for clarity.

Hexafluorophosphate counter anions are often non-coordinating [57,58]. In the case of **1**, they approach the silver centers in the extended cationic structure at a distance Ag1···F1 = 2.927(2) Å which can be interpreted as a very weak coordinative bond or simply as an electrostatically favorable contact. In the crystal of **2**, the HacacPyen moieties do not exhibit the diketo structure; rather, all four symmetrically independent acetylacetone moieties adopt the more common enol form with intramolecular hydrogen bonds and do not coordinate the Ag^I ions. All intra-ligand HacacPyen torsion angles between the central C of the acetylacetone moieties, the ethylene bridge and the *para* pyridyl C correspond to the *anti* conformer; the largest deviation from 180° is 8.9° in C39–C42–C43–C44. In contrast to **1**, all Ag···O_{Hacac} contacts in **2** are longer than 3 Å. Therefore, **2** should not be interpreted as a supramolecular network. Instead, the tetrafluoroborate counterions form closer contacts to the Ag^I ions (Figure 4).
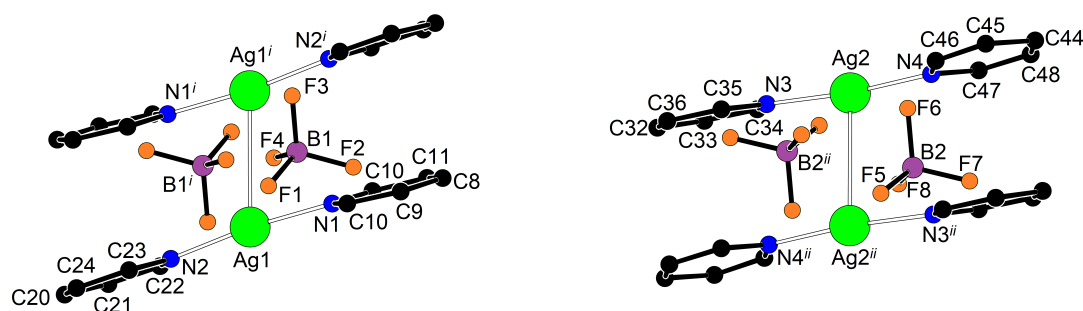
Figure 4. Coordination spheres of the two independent Ag^I ions in **2** [42]. Selected interatomic distances and angles: Ag1···Ag1^i 3.2605(4) Å, Ag1···N1 2.1222(19) Å, Ag1···N2 2.131(2) Å, Ag1···F1 2.8796(16) Å, Ag1···F3^i 2.9624(17) Å, N1···Ag1···N2 174.33(7)°; Ag2···Ag2^{ii} 3.3105(4) Å, Ag2···N3 2.132(2) Å, Ag2···N4 2.133(2) Å, Ag2···F5 2.998(2) Å, Ag2···F6 2.9129(17) Å, N3···Ag2···N4 174.30(8)°. Symmetry operators: $i = 1 - x, 1 - y, 1 - z$; $ii = 1 - x, 1 - y, 2 - z$.

In comparison with **1**, two instead of one F atom of the counter ions come close to each Ag^I. This is in accordance with the slightly higher coordinating ability of BF$_4^-$ compared to PF$_6^-$ [59]. However, this small difference has an impact on the acetylacetone moieties resulting in the more uncommon 1,3-diketo tautomer for **1**. Furthermore, the pyridine moieties in **2** are closer to each other than in **1**. This results in favorable π-interactions. Nevertheless, the Ag···Ag interactions remain the closest inter-residue contacts in both independent dinuclear {[Ag(HacacPyen)$_2$]$^+$}$_2$ moieties in **2**; e.g., the N1···N2^i is longer with 3.456(3) Å.

4. Conclusions

To conclude, **1** and **2** represent the first N coordinated derivatives of neutral HacacPyen; in addition, **1** is a rare example of a 3-substituted acetylacetone in the diketo tautomer. We are confident that O,O′ chelated complexes of this ligand not only with Be^{II} but for a broad range of main group, transition metal and lanthanide cations may be obtained. After crosslinking with Pearson-soft cations such as Ag^I, solids of variable composition and dimensionality and with tunable luminescence properties will be accessible.

Abbreviations

The following abbreviations are used in this manuscript:

HacacCN	3-cyanopentane-2,4-dione
HacacPy	3-(pyridin-4-yl)pentane-2,4-dione
HacacPyen	3-(2-(pyridin-4-yl)ethyl)pentane-2,4-dione

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