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Jääskeläinen, Sirpa

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Impacts of the counter ions on 4,5-dicyano-1-methylimidazole silver coordination

Sirpa Jääskeläinen*, Nana Sakyibea Appiah, Igor Koshevoy and Pipsa Hirva

Department of Chemistry, University of Eastern Finland, P.O. Box 111, Fi-80101 Joensuu, Finland
E-mail: *sirpa.jaaskelainen@uef.fi

Abstract

Silver complexes \([\text{Ag}(4,5\text{-dicyano-1-methylimidazole})_2]_n[\text{CF}_3\text{SO}_3]_n\) (1), \([\text{Ag}_2(4,5\text{-dicyano-1-methylimidazole})_2][\text{NO}_3]_2\) (2) and \([\text{Ag}_2(4,5\text{-dicyano-1-methylimidazole})_2][\text{ClO}_3]_2n\) (3) were synthesized in reactions between 4,5-dicyano-1-methylimidazole and silver salts \(\text{AgCF}_3\text{SO}_3\), \(\text{AgNO}_3\) and \(\text{AgClO}_3\). The compounds were characterized via crystallographic and spectroscopic methods. Due to the different counter ions, variation in the ligand coordination modes and as a consequence, different types of solid state structures were generated.

The absorption characteristics were explained by simulation of the UV-Vis spectra using the TD-DFT method. Additionally, computational studies were performed in order to discover the effect of the counter ions via various weak intra- and intermolecular interactions present in the solid state structures. The nature of the interactions was further investigated by topological charge density analysis using the QTAIM method.
Introduction

Inorganic cyanides are known by their extreme toxicity derived from the high coordination ability with metal centers, which disturbs the electron transfer chains in cells. However, due to this feature they are fertile in respect to their chemistry with various metals and have a large variety of applications, e.g. in mining, pigments and electroplating. Nitriles, the organo compounds with CN groups, usually do not release cyanides and are thus less toxic. Nitriles are utilized in pharmaceutics and industry, e.g. as glues and precursors of polymers.

The behavior of the cyano groups, either in inorganic or organic form, has led to diverse sets of assemblies in their metal compounds\(^1\) and consequent magnetic\(^2\), luminescent\(^3\) and catalytic\(^4\) properties. Typically, cyanides act as N-donors, but their coordination through carbon, thus acting as isocyanides or isonitriles, is also possible. In most cases, linear arrangement of C-N-M moiety is present, but incidental examples of side-on or bridging modes have been reported.\(^5\)

Cyano derivatized aromatic N-heterocycles, such as cyanopyridines, cyanobi-imidazoles\(^6,7,8,9\) and cyanoimidazoles, are interesting candidates for the engineering of metal-organic frameworks. In these, the two types of nitrogen donors allow diverse reactivity and tailoring of the supramolecular structures. Mono- and dicyanopyridines predominantly act as monodentate pyridine bound ligands in transition metal complexes. Utilization of the cyano group in addition, thus acting also as a nitrile ligand, is significantly less common\(^10,11\)

Catena or network complexes with bridging multidentate cyanopyridyls are found e.g. for cadmium\(^12,13\), ruthenium,\(^14\) rhodium\(^15\), and more typically for silver and copper\(^16,17,18\).

The more systematic studies on the coordination modes of cyanopyridines to silver have revealed that the counter ion and the crystallization conditions exert solid state architectures. For example, 2-cyanopyridine gave Ag\(_2\)L\(_2\)^{2+} dimers with bridging bidentate ligands, which formed a two dimensional solid state network with bridging NO\(_3^-\) anions.\(^19\)

When BF\(_4^-\) anions
were introduced to 2-cyanopyridine/Ag reaction, Ag$_2$L$_4^{2+}$ building blocks containing two terminal pyridine bound ligands in addition to two bridging ligands, were again linked by the counter ions in solid state.$^{20}$ On the other hand, 4-cyanopyridine has produced a ligand bridged catena compound with nonbonding BF$_4^-$ anions.$^{21}$ 3-cyanopyridine with AgSiF$_6$ formed AgL$_2^+$ building blocks with pyridine bound ligands, while the nitrile groups remained uncoordinated. The tetranuclear units [AgL$_2^+$]$_4$ were connected by Ag-Ag interactions and $\pi-\pi$ contacts between adjacent pyridines. 3-cyanopyridine and 3,4-dicyanopyridine, gave AgL$_2$ units with pyridine nitrogen coordinated ligands in reactions with AgNO$_3$. The nitrate anion again displayed a bridging character in composition of the supramolecular architecture. Simultaneously, cyanopyridines in the bridging mode have been used as terminal stoppers in order to control structure diversity, and to stabilize discrete silver acetylide clusters, to prevent them from yielding polymeric molecules.$^{22,23}$

Cyano derivatives of imidazole and their metal complexes are less explored. Common to these compounds is the more acidic character of the ligands rather than the imidazole itself, and formation of complexes as anions after deprotonation. In the catena-Zn-dicyanoimidazolato complex the chain is built up by only utilizing the two imidazole nitrogens, the cyano groups remain unbound.$^{24}$ 4,5-dicyanoimidazole was demonstrated to be a good template in the assembly of Cd-alkali metal-organic frameworks and a series of coordination polymers were obtained by altering halides and alkali metals. The ligands purely utilized the imidazole nitrogens for coordination at Cd centers and the cyano groups coordinated at alkali centers.$^{25,26}$

The use of 4,5-dicyanoimidazole with copper has always led to deprotonation of the ligand and direct attachment by the imidazole nitrogen$^{27}$, or bidentate coordination via carbonyl assisted alcoholysis reaction$^{28}$. Likewise, a deprotonated dicyanoimidazole is present in a chiral 3D porous framework [Cu(dicyanoimidazolate)]$_n$. Gas absorption was studied after guest solvent molecules were removed from the material.$^{29}$
Among silver complexes, catena-Ag(2-amino-4,5-dicyanoimidazole), where the ligand utilizes both the two imidazole and one cyano nitrogen for coordination, the imidazole ring again exists in deprotonated form. The cooperative coordination of two types of nitrogens led to the formation of impressive SHG (second-harmonic generation) activity in the complex.\(^\text{30}\)

The variable role of the counter ions was recently studied in silver supramolecular complexes generated from polydentate ligands containing cyano and pyridyl groups. In the solid state structures, the NO\(_3^−\) counter ions behaved as coordinating ligands, while ClO\(_4^−\), BF\(_4^−\), and SO\(_4^{2−}\) were considered to be non-coordinating.\(^\text{31}\) Therefore, modification of counter ions could be shown to considerably affect the structural features, thus providing a means for crystal engineering.

In the present study, we investigated the contribution of the counter ions in the solid state architectures developed in the reactions between 4,5-dicyano-1-methylimidazole and silver triluoromethanesulfonate (triflate), nitrate and chlorate (AgCF\(_3\)SO\(_3\), AgNO\(_3\) and AgClO\(_3\)). X-ray crystallography, IR and UV-Vis spectroscopy as well as computational methods, were used to analyze the solid state structures and the electronic properties of the materials.
Experimental

Materials and Methods.

All manipulations were performed at room temperature and in aerobic conditions protected from light. AgCF₃SO₃ (Alfa Aesar, 98+%), AgNO₃ (Sigma-Aldrich, 99+%), AgClO₃ (Aldrich, 99.9+%) and 4,5-dicyano-1-methylimidazole (Alfa Aesar, 97%) were commercially available and used as received. The solvents were dried using molecular sieves. The elemental analysis was determined by varioMICRO V1.7, Bruker Avance 400 MHz was used for the ¹H NMR. IR were measured in KBr with Shimadzu FTIR-8400S and UV-VIS spectra with a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer.

All the products (1-3) were analysed in solution by using ¹H NMR. In all cases identical spectra (δ 3.85(CH₃, 3H) and 8.29 (CH) ppm in DMSO-d₆) were obtained showing that the structures found in solid state are not present in solution, but the compounds exist rather in variable Ag-ligand fragments. Contrary to NMR, UV-Vis is sensitive to the coordination mode in the fragments, therefore we used the results from fragments in solution to compare with computationally simulated spectra.

Synthesis of Complexes 1-3.

[Ag(4,5-dicyano-1-methylimidazole)₂]ₙ[CF₃SO₃]ₙ (1). A solution of 4,5-dicyano-1-methylimidazole (11.4mg, 0.086 mmol) in ethanol (0.5 ml) was combined with a solution of AgCF₃SO₃ (26.3mg, 0.102 mmol) in ethanol (0.5 ml). The mixture was stirred for an hour at room temperature. Crystallization at 2 C° gave colorless crystals. Yield 14.3 mg, 64%. 
IR(KBr): ν(CN): 2245, 2255 cm\(^{-1}\). UV-Vis (DMSO): 255 nm. Calc. for Ag\(_{13}\)H\(_8\)N\(_8\)O\(_3\)SF\(_3\) C% 29.96; H% 1.55; N% 21.50; S 6.15%. Found. C% 29.90; H% 1.74; N% 21.53; S% 6.20.

\[ \text{[Ag}_2(4,5\text{-dicyano-1-methylimidazole})_2][\text{NO}_3]_2 \text{ (2).} \] A solution of 4,5-dicyano-1-methylimidazole (30.0 mg, 0.176 mmol) in methanol (1.5 ml) was combined with a solution of AgNO\(_3\) (23.4mg, 0.177 mmol) in methanol (1.0 ml). Crystallization at 2 C° gave colorless crystals. Yield 15.8 mg, 30%. IR(KBr): ν(CN): 2241, 2257 cm\(^{-1}\). UV-Vis (DMSO): 271 nm. Calc. for Ag\(_2\)C\(_{12}\)H\(_8\)N\(_{10}\)O\(_6\) C% 23.86; H% 1.34; N% 23.19. Found. C% 23.57; H% 1.44; N% 22.77.

\[ \text{[Ag}_2(4,5\text{-dicyano-1-methylimidazole})_2]_n[\text{ClO}_3]_2_n \text{ (3).} \] A solution of 4,5-dicyano-1-methylimidazole (36.0 mg, 0.272 mmol) in methanol (3.0 ml) was combined with a solution of AgClO\(_3\) (54.5 mg, 0.284 mmol) in acetonitrile (1.5 ml). Crystallization at 2 C° gave colorless crystals. Yield 29.1 mg, 33%. IR (KBr): ν(CN): 2247 (br) cm\(^{-1}\). UV-Vis (DMSO): 266 nm. Calc. for Ag\(_2\)C\(_{12}\)H\(_8\)N\(_8\)O\(_6\)Cl\(_2\) C% 22.28; H% 1.25; N% 17.32 Found. C% 22.50; H% 1.32; N% 17.14.

**Crystal Structure Determinations**

The crystals of 1–3 were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 120K. The X-ray diffraction data were collected on a Bruker Kappa Apex II Duo diffractometer using Mo Kα radiation (\(λ = 0.71073 \ \text{Å}\)). The APEX2\(^{32}\) program package was used for cell refinements and data reductions. The structures were solved by direct methods using the SHELXS-2014\(^{33}\) program with the WinGX\(^{34}\) graphical user interface. A semi-empirical absorption correction (SADABS)\(^{35}\) was applied to all data. Structural refinements were carried out using SHELXL-2014.\(^{33}\) The triflate counterion in 1 was found close to the special position and was refined with 0.5 occupancy. Hydrogen atoms were positioned
geometrically and constrained to ride on their parent atoms, with C-H = 0.95-0.98 Å and U_{iso} = 1.2-1.5 U_{eq} (parent atom). The crystallographic details are summarized in Table 1.

Table 1. Crystallographic data for 1 - 3

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Computational Details

All models were calculated with the Gaussian 09 program package\textsuperscript{36} at the DFT level of theory. The hybrid density functional PBE0\textsuperscript{37} was utilized together with the basis set consisting of the def2-TZVPPD\textsuperscript{38} effective core potential basis set with triple-zeta-valence basis set with two sets of polarization and diffuse basis functions for Ag atoms, the standard all-electron basis sets 6-311+G(d) for N and O atoms, and 6-31G(d,p) for other ligand/counter ion atoms. The extended models of the solid state structures were directly cut from the corresponding experimental crystal structures and analyzed without geometry optimization.

In order to study the electronic and coordination properties of the complexes in the solid state, we performed topological charge density analysis by using the QTAIM (Quantum Theory of Atoms in Molecules) method.\textsuperscript{39} This analysis was conducted with the AIMAll program\textsuperscript{40}, which uses the wave functions obtained from the DFT calculations. The selected properties were: \( \rho = \) local electron density at the BCP; \( |V|/G = \) ratio of potential energy density (V) and kinetic energy density (G); \( E_{\text{INT}} = \) interaction energy between two interacting atoms = \( 1/2 \times V(BCP) \) as stated by Espinosa et. al.\textsuperscript{41} \( q(A) = \) total atomic charge of atom A according to AIM analysis.

Absorption characteristics were studied for single molecular models (Figure S4) with the TD-DFT method at the same level of theory as the more extended models.
Results and discussion

All the reactions were conducted in a 1:1 molar ratio of the silver salt and the ligand to exclude the effect of reaction conditions and to reveal the sole effect of the counter ions. In addition, the solvents, as far as possible within the limits of solubility, were the same in each reaction. The methyl group substituent in imidazole nitrogen detracts deprotonation and simplifies the study of the counter ion by limiting the possibilities for side reactions.

Synthesis and structure of [Ag(4,5-dicyano-1-methylimidazole)₂][CF₃SO₃]ₙ (1).

The reaction between 4,5-dicyano-1-methylimidazole and AgCF₃SO₃ yielded [Ag(4,5-dicyano-1-methylimidazole)₂][CF₃SO₃]ₙ (1). Single crystal X-ray diffraction analysis showed the formation of a asymmetric unit with two ligands bound through imidazole nitrogen atoms by N-Ag 2.195(1) Å with an approximately linear arrangement N-Ag-N 168.85(8)°. The cyano groups of the two imidazoles lie in cis position. (Figure 1)

![Figure 1. Structure of [Ag(4,5-dicyano-1-methylimidazole)₂][CF₃SO₃] (1)](image)

Selected bond lengths and angles: Ag-N1 2.195(1) Å, Ag-N3 2.686(2) Å, C3-N2 1.143(2) Å, C5-N3 1.140(2) Å, Ag-O3 2.774(3) Å, N1-Ag1-N1 168.85(8)°.
The bidentate character of the ligand induces intermolecular interactions with a distance of 2.686(2) Å between the nitrogen of the cyano groups and adjacent silver atoms and gives rise to three dimensional solid state structures, as presented in Figure 2, where each d^{10} silver atom has four attached nitrogens. The ligand utilizes its N1 and N3 coordination sites and the second cyano group remains uncoordinated. The coordinated cyano group has a nearly linear C-N-Ag angle of 169.3(2)°.

The disordered counter ion CF_3SO_3^- fills the coordination sphere to complete the distorted tbp environment at the metal center with a Ag–O distance of 2.774(3) Å, which is clearly shorter than the corresponding sum of the van der Waals radii (3.24 Å). The O(1)–H(1) and O(2)–H(1) distances to imidazole hydrogen atoms are 2.423(4) and 2.505(4) Å, respectively, while the sum for the van der Waals radii is 2.72Å, indicating the existence of supporting intermolecular hydrogen bonding in the stabilization of the 3D structure. The other end of the counter ion has F(3)–C(6) and F(2)–C(3) contacts of 2.983(5) and 3.101(3) Å with methyl and cyano carbon atoms and a F-H contact of 2.460(5) Å to methyl hydrogens (sums of vdW radii CF 3.17Å and FH 2.67Å). Despite the short contacts between the triflate fluorines and the adjacent ligands, the major intermolecular interactions are formed via stronger Ag-N coordination, as can be seen in Figure 2, where the counter ions are omitted.

In the IR spectrum, the C-N stretching vibrations appeared at 2245 and 2255 cm\(^{-1}\), shifted from the 2237 cm\(^{-1}\) of the free ligand. The shifts to higher frequencies are characteristic for end-on coordination of nitrile to the metal center, but systematic information that links the coordination mode and the shift is lacking. The shift to lower frequencies is usually attributed to side-on coordination of the cyano group.\(^{42}\) In order to compare the side-on and end-on coordination, we calculated the C-N frequencies with the DFT method in limited molecular AgL models. The results showed a similar shift in the C-N stretching frequencies to that of the experimental frequencies, which agrees well with the end-on coordination of the cyano group.
In the solid state structure of 1 the metal:ligand ratio is 1:2 even though the synthesis was done with equal amounts of starting materials. To test the effect of the ratio, the reaction was repeated with Ag:L = 1:2. Clear crystals were formed and the determination of the unit cell confirmed the same product to that in the original synthesis.

**Figure 2.** View along b axis of [Ag(4,5-dicyano-1-methylimidazole)₂][CF₃SO₃]ₙ (1) showing the 3D structure. The counter ions are omitted for clarity.
Synthesis and structure of [Ag₂(4,5-dicyano-1-methylimidazole)₂][NO₃]₂ (2).

When the CF₃SO₃⁻ was changed to NO₃⁻, the complex [Ag₂(4,5-dicyano-1-methylimidazole)₂][NO₃]₂ (2) was formed (Figure 3). Unlike in the previous case, a dimer with two bidentate bridging ligands in a head-to-tail conformation was obtained. The ligand also utilizes, in addition to the imidazole nitrogen, one of the cyano groups with N² coordination to give a planar structure. The Ag-N distances are 2.265(1) and 2.323(2) Å, respectively, and the C-N-Ag angle for the coordinating cyano group is 161.8(2)°. The coordination sphere of the metal center is completed to a distorted tetrahedral geometry by two NO₃⁻ counter ions with the Ag-O(1) bond of 2.392(1), the Ag-O(2) bond of 2.465(1) Å and the Ag-O(3) bond of 2.818(1) Å and a network structure is built-up (Figure 4). The Ag-O distances are clearly shorter than the sum of the van der Waals radii of 3.24Å. Simultaneous coordination via the imidazole nitrogen and the neighboring cyano group results in a much tighter network compared to 1, with considerably shorter separation between the metal centers (Ag···Ag distances are 5.659 Å and 8.848 Å in 2 and 1, respectively) and a substantially larger density of the material (2.280 g/cm³ for 2 vs 1.887 g/cm³ for 1). In the IR spectrum the C-N stretching vibrations appeared at 2241 and 2257 cm⁻¹, again supporting an end-on coordination of the cyano groups.
**Figure 3.** Structure of $[\text{Ag}_2(4,5\text{-dicyano-1-methylimidazole})_2][\text{NO}_3]_2$ (2).

Selected bond lengths and angles: Ag-N1 2.265(1) Å, Ag-N2 2.323(2) Å, Ag-N2-C3 161.8(2)$^\circ$.

**Figure 4.** Packing of $[\text{Ag}_2(4,5\text{-dicyano-1-methylimidazole})_2][\text{NO}_3]_2$ (2).

Ag-O1 2.392(1) Å, Ag-O2 2.465(1) Å, Ag-O3 2.818(1) Å.
Synthesis and structure of [Ag₂(4,5-dicyano-1-methylimidazole)₂][ClO₃]₂ (3).

When the counter ion of the silver salt was further changed to ClO₃⁻, a dimeric unit [Ag₂(4,5-dicyano-1-methylimidazole)₂][ClO₃]₂ (3) was formed similarly to 2 (Figure 5). The Ag-N distances are 2.277(1) Å for the imidazole and 2.257(1) Å for the cyano group. Thus, in 3, the Ag-N for the cyano group is shorter than for the imidazole, contrary to 2. Furthermore, unlike in 2, where the second cyano group remained uncoordinated, in 3 the cyano group at 4-position interacted with silver ions with only a slightly larger Ag-N(3) distance of 2.460(1) Å, and an extended coordination polymer was formed (Figure 6). The C-N-Ag angle is 165.6(1)° inside the dimer, but the dimers’ bridging group is clearly bent with C-N-Ag 139.2(1)°. Another difference between 2 and 3 is, that in 2 the NO₃⁻ ions participate in connecting the dimeric units together, but in 3 the role of the ClO₃⁻ ions is merely to complete the coordination sphere of the metal centers, and the dimensionality is expanded directly by the bridging ligands. The Ag-Ag distance inside the dimeric unit is 5.590 Å, which is similar to the one obtained in 2 (5.659 Å). The counter ion forms contacts to the metal atoms via two oxygens with distances Ag-O of 2.413(1) and 2.645(2) Å, which are longer than in the case of nitrate ions, indicating weaker interaction between the metal and the counter ions in 3 than in 2. The IR spectrum shows a broad C-N stretching at 2247 cm⁻¹, supporting end-on coordination of both cyano groups with silver.
Figure 5. Structure of the dimeric unit $\text{[Ag}_2(4,5\text{-dicyano-1-methylimidazole})_2][\text{ClO}_3]_2$ in 3. Selected bond lengths and angles: Ag-N1 2.277(1) Å, Ag-N2 2.257(1) Å, Ag-N3 2.460(1) Å, Ag-O1 2.413(1), Ag-O2 2.642(2) Å, C3-N2-Ag 165.6(1)°, C5-N3-Ag 139.2(1)°.

Figure 6. 3D structure of $\text{[Ag}_2(4,5\text{-dicyano-1-methylimidazole})_2]_n[\text{ClO}_3]_{2n}$ (3). The counter ions are omitted.
In the solid state structures, the number of coordinated ligand atoms to the metal center is 4, 2 and 3 for 1-3, which indicates that the nature of the counter ion has a crucial effect on the self-assembly of silver coordination polymers.

Santillan et al. have experimentally studied the effect of the charge density localization and the shape of the counter ion on the crystal packing schemes in silver coordination polymers with oxygen containing ligands. They concluded that differences were formed through different hydrogen bonding patterns. They also suggested, that ligands with a less delocalized charge density have a greater tendency to act as bridging counter ions. In our study, the structures of the counter ions were of a similar type and therefore their delocalization properties did not differ enough to explain the different behavior.

**Computational Charge Density Analysis**

We performed a topological charge density analysis according to QTAIM in order to obtain information on the relative nature of the coordinative interactions between the silver ion and the ligand and the counter anions. Figure 7. lists the most important bond critical points in a simplified presentation of the solid state structures and Table 2. shows the selected properties of the electron density at these BCPs. It should be noted, that the actual calculations were performed with more extended models shown as supplementary material (Figures S1-S3).
Figure 7. Simplified presentation of the main interactions in the crystal structures of compounds 1-3, (a) structure 1, (b) structure 2, (c) structure 3. The orange balls represent corresponding bond critical points. The numbering of the BCPs is followed in Table 2.
Table 2. Selected properties of the Ag-N and Ag-O interactions in compounds 1-3. The properties are calculated according to the QTAIM analysis at the corresponding bond critical points. The numbering of the BCPs is shown in Figure 7. The properties are: bond distance (d, Å), electron density at the BCP (ρ, eÅ⁻³), ratio of the potential energy density and the kinetic energy density (|V|/G), and interaction energy (E_{INT}, kJmol⁻¹).

| BCP # | type       | d (Å) | ρ (eÅ⁻³) | |V|/G | E_{INT} (kJmol⁻¹) |
|-------|------------|-------|----------|------|------------------|
| (1) Triflate |
| 1     | Ag – N(1)  | 2.195 | 0.501    | 1.13 | -135             |
| 2     | Ag – N(3)  | 2.686 | 0.167    | 0.98 | -30              |
| 3     | Ag – O(2)  | 2.774 | 0.131    | 0.98 | -23              |
| (2) Nitrate |
| 1     | Ag – N(1)  | 2.265 | 0.424    | 1.10 | -109             |
| 2     | Ag – N(2)  | 2.323 | 0.351    | 1.06 | -86              |
| 3’    | Ag – O(2)  | 2.465 | 0.259    | 1.03 | -55              |
| 3”    | Ag – O(3)  | 2.818 | 0.131    | 1.02 | -22              |
| (3) Chlorate |
| 1     | Ag – N(1)  | 2.277 | 0.434    | 1.11 | -112             |
| 2’    | Ag – N(2)  | 2.257 | 0.392    | 1.07 | -100             |
| 2’’   | Ag – N(3)  | 2.460 | 0.261    | 1.04 | -55              |
| 3     | Ag – O(1)  | 2.413 | 0.281    | 1.03 | -64              |
| 3’’   | Ag – O(2)  | 2.642 | 0.180    | 1.04 | -34              |

In all structures, there is a clear preference for coordination via the imidazole nitrogen, as can be expected from the previous studies on substituted imidazole complexes. However, the cyano groups are also able to form strong coordination bonds with silver ions, so that the strength of the Ag-N interaction grows in the order of N(3) < N(2) < N(1). Interestingly, the oxygens of the counter anions also coordinate fairly strongly, even more strongly in the case of NO₃⁻ and ClO₃⁻ than N(3). Therefore, there is a competition between the ligand and the counter ions on the coordination sites of the metal. Furthermore, coordination of the counter ions also affects the interaction strength of the ligands – the interaction energy of the imidazole nitrogen decreases in the order triflate > chlorate > nitrate, showing that the preference on the N1
coordination is most profound with the triflate counter ion, which on the other hand coordinates less strongly than the other two anions. The opposite is true in the coordination of the nitrogens of the cyano groups, the interaction energy increases with triflate < nitrate < chlorate counter anions.

The strong coordination of the counter ions can be seen in the UV-Vis spectra of the complexes. The spectra were simulated with molecular models [Ag(L)₂][CF₃SO₃] (1), [Ag(L)₂][NO₃]₂ (2), and [Ag(L)₂][ClO₃]₂ (3), which are shown as supporting information in Figure S4. The molecules with nitrate or perchlorate anions showed their maximum absorbances at higher wavelengths (Figures S5 and S6), in agreement with the experimental values, which resulted from the presence of low energy excitations between the silver d-orbitals and the p-orbitals of the counter anions. In complex 1 these low energy excitations were missing, because the HOMO concentrated completely on the triflate counter anion without any contribution from the metal orbitals. The appearance of the FMOs involved in the lowest energy excitations is presented in Figure S7.

In summary, the counter ions were found to have a major effect on the coordination of the 4,5-dicyano-1-methylimidazole ligand with Ag⁺ ions. Triflate ions were found to coordinate through only one oxygen with purely electrostatic interaction, and the other two oxygens formed stabilizing hydrogen-bonding interactions within the monomeric complexes. Additionally, the fluorines at the other end of the triflates formed supporting hydrogen bonding with adjacent complexes. Therefore, the 3D network is formed via Ag-N coordination, and the counter anions lie at the center of the network.

The nitrate ions are able to truly participate in forming the network in the solid state structure of 2 by acting as bridging ligands between dimeric units formed via Ag-N coordination. All oxygens are involved in Ag-O coordination, which is not entirely electrostatic in nature, but shows some electron sharing at the corresponding BCP (|V|/G > 1). A similar kind of bridging
interaction of the NO$_3^-$ ions was previously found in silver imidazole oxime complex [Ag(1$H$-
5-methylimidazole-4-carbaldehyde oxime)]$_2$[NO$_3$]$_2$.\textsuperscript{44}

The chlorate anions do not participate in forming the network, they merely support the adjacent
rows of dimers via hydrogen bonding interactions between the uncoordinated oxygen and
hydrogens of the neighboring imidazole ligands. The coordinative Ag-O interactions are
somewhat weaker than in the case of nitrate, but otherwise their nature is very similar.
Interestingly, the N3 nitrogen of the ligand coordinates with a similar strength as the bridging
O3 in the structure of 2, indicating the similar natures of Ag-O and Ag-N of the cyano
substituents, supporting the idea of competition between these two interactions. Obviously,
steric effects will also have some influence on the final 3D structure in the solid state.
Conclusions

The counter ion was found to have a crucial effect on the solid state structure of the dicyano substituted methyl imidazole silver complexes. The dicyanoimidazole ligand preferably coordinates through the imidazole nitrogen, but also one or both of the cyano groups may be reactive, therefore the dicyano substituted methyl imidazole can act as a two or three dentate ligand. The number of coordinated nitrogens at the metal center was 4, 2 or 3, depending on the coordination of the counter ions. The detailed QTAIM analysis of the coordinative interactions of silver ions with either the ligands or the counter ions revealed the similarity of the Ag-N and Ag-O interactions. One might suggest, that there is competition between the different types of coordination, and the electronic and steric nature of the counter ions influences the coordination of the ligand. No argentophilic interactions were found in the dimeric units in contrast to the bridging coordination of the oxime substituted ligand in [Ag(1H-5-methylimidazole-4-carbaldehyde oxime)]$_2$[NO$_3$]$_2$ complex, which was also found to form chains of dimeric units linked via nitrate ions.$^{21}$
Supplementary material

The crystallographic data for compounds [Ag(4,5-dicyano-1-methylimidazole)₂][CF₃SO₃]ₐ (1), [Ag₂(4,5-dicyano-1-methylimidazole)₂][NO₃]₂ (2) and [Ag₂(4,5-dicyano-1-methylimidazole)₂][ClO₃]₂ (3) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1576775-1576777. Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary material includes also figures of simulated UV-Vis spectra and the interpretation of the selected excitations, as well as bond paths and bond critical points of extended models of 1 - 3. Supplementary data associated with this article can be found in the online version.

Conflicts of interest

There are no conflicts to declare

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