Imidazolium Dicyanoargentates

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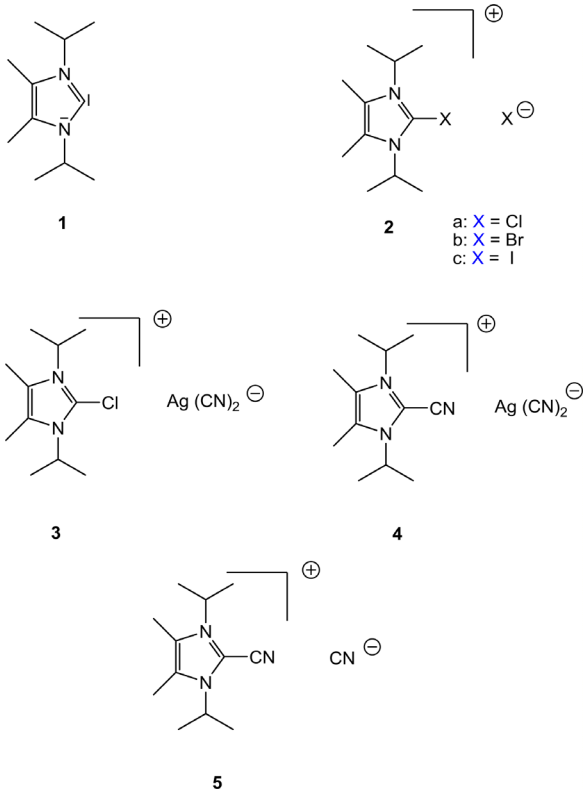
New imidazolium dicyanoargentate salts were synthesized by treatment of 2-chloro-1,3-diisopropyl-4,5-dimethylimidazolium chloride (**2a**) with an excess of silver cyanide in acetonitrile to afford 2-chloro-1,3-diisopropyl-4,5-dimethylimidazolium dicyanoargentate (**3**) and its conversion into the corresponding 2-cyano-1,3-diisopropyl-4,5-dimethylimidazolium dicyanoargentate (**4**) by reaction with an excess amount of potassium cyanide. The crystal structures of **3** and **4** are reported.

Key words: Imidazoles, Heterocycles, Dicyanoargentate, Crystal Structure

Introduction

Transition metal cyanide chemistry has undergone remarkable advances over the past decade, and a variety of cyanide-bridged compounds exhibiting polymeric and oligomeric structures have been prepared [1]. The possibility for the dicyanoargentate anion $[Ag(CN)_2]^-$ to form additional coordination bonds through the nitrogen atoms of the cyano groups leads them to play different roles in crystal structures [2]. The $[Ag(CN)_2]^-$ moiety is a versatile rod-shaped building block for the construction of coordination polymers [1].

Using the strongly basic character of *N*-heterocyclic carbenes [3, 4], we were recently able to detect weak interionic halogen contacts between 2-haloimidazolium cations and halogen containing counter ions



[5, 6]. The nucleophilic attack of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) at hexachloroethane led to the formation of the charge–transfer adduct **2a** in almost quantitative yield [6, 7].

Expanding our systematic study on heterocyclic carbenes and continuing our investigations on the structural chemistry of imidazolium salts [8, 9], we decided to explore their coordination with the $[Ag(CN)_2]^-$ moiety. The literature concerning imidazolium salts incorporating metalloanions is very limited [10]. In this work we have synthesized and characterized two new imidazolium dicyanoargentate salts. The molecular structures of **3** and **4** have been elucidated by single-crystal X-ray crystallography. To the best of our knowledge, we present the first structural report on imidazolium dicyanoargentate salts.

Results and Discussion

Using the strongly basic character of heterocyclic carbenes, Kuhn *et al.* have shown that the reaction of hexachloroethane with 2,3-dihydroimidazole-2-

Table 1. Crystal data and structure refinement for $C_{13}H_{20}N_4AgCl$ (**3**) and $C_{14}H_{20}N_5Ag$ (**4**).

	3	**4**
Empirical formula	$C_{13}H_{20}N_4AgCl$	$C_{14}H_{20}N_5Ag$
Formula weight	375.65	366.22
Temperature, K	210(2)	173(2)
λ, Å	0.71073	
Crystal system	orthorhombic	orthorhombic
Space group	$Pmn2_1$	$Pmcn$
a, Å	11.0571(9)	6.7686(5)
b, Å	11.0222(7)	12.0602(14)
c, Å	6.6712(4)	41.861(4)
Volume, Å^3	813.0(1)	3417.2(6)
Z	2	8
D_{calcd}, g cm^{-3}	1.53	1.42
μ (MoK_α), mm^{-1}	1.4	1.2
F(000), e	380	1488
θ range, deg	3.57 – 25.30	2.92 – 27.64
Refls. coll.	7192	16338
Refls. indep.	1566	3936
Refinement method	Full-matrix least-squares on F^2	
Param. refined	137	232
Final R_1 / $wR2$ [$I \geq 2\sigma(I)$]	0.0341 / 0.0772	0.0640 / 0.1275
Goodness-of-fit on F^2	0.987	1.109
Flack parameter x	−0.02(4)	–
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	+0.87/−0.47	+1.60/−0.56

Table 2. Selected bond lengths (Å) and angles (deg) for $C_{13}H_{20}N_4AgCl$ (**3**).

Ag(1)–C(1)	2.021(8)	Ag(1)–N(2)	2.131(9)
C(1)–N(1)	1.127(9)	C(2)–N(2)	1.080(10)
C(3)–N(6)	1.329(4)	C(3)–N(6A)	1.329(4)
C(3)–Cl(1)	1.677(5)	C(4)–C(4A)	1.358(8)
C(1)–Ag(1)–N(2)	178.0(3)	N(1)–C(1)–Ag(1)	179.4(7)
C(2)–N(2)–Ag(1)	173.4(7)	N(6A)–C(3)–N(6)	110.6(4)
N(6A)–C(3)–Cl(1)	124.7(2)	N(6)–C(3)–Cl(1)	124.7(2)
C(4A)–C(4)–N(6)	107.4(2)	C(4A)–C(4)–C(5)	128.4(3)

ylidene (**1**) is a high yield route to 2-chloro-1,3-diisopropyl-4,5-dimethylimidazolium chloride (**2a**) [6, 7]. The imidazolium chloride (**2a**) reacts readily with silver cyanide in refluxing acetonitrile, and the imidazolium salt **3** is obtained as stable colorless crystals in high yield. In addition, the reaction of **3** with potassium cyanide at room temperature in 1:10 molar ratios gives the salt **4** in good yield.

The formation of these new compounds is supported by their NMR and FT-IR spectra, FAB mass spectrometry, elemental analysis, and single-crystal X-ray diffraction. The NMR data of the solutions (see Experimental Section) imply the presence of separated ions. The ^{13}C NMR spectra of **3** and **4** showed distinctive signals assigned to the C–Cl and C–CN groups at the 2-position of the imidazolium rings at δ = 126.23 and 113.70, respectively, the chemical shift values for the dicyanoargentate anions being δ = 142.07 and 143.63, respectively. The FAB experiments displayed intense peaks for the imidazolium cations of **3** and **4**, observed at *m/z* (100 %) = 215.1 and 206.2, respectively. The presence of dicyanoargentate anions in the prepared salts has also been proven by IR spectra which showed typical cyanometallate vibrations. Strong bands are assigned at ν(CN) = 2136 and 2137 cm^{-1} for **3** and **4**, respectively [9].

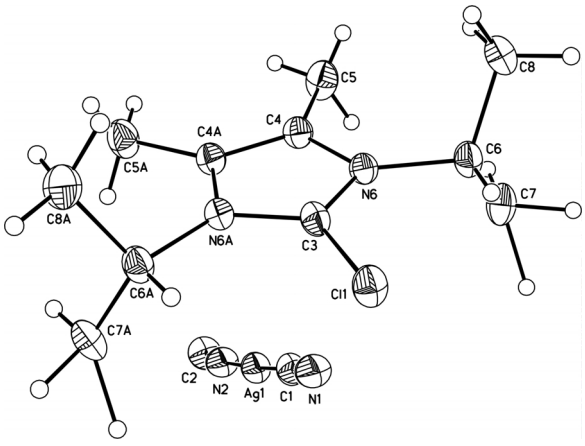


Fig. 1. View of the ion pair of $C_{13}H_{20}N_4AgCl$ (**3**) in the crystal.

Crystal structure determinations

Suitable crystals for crystallographic investigations of **3** and **4** were obtained by slow diffusion of ether into dichloromethane and acetonitrile solutions, respectively. Both imidazolium salts are obtained as stable colorless crystals in good yield. Numerical data of the crystal structures, data collections and structure refinements are given in Table 1.

The crystal structure of **3** which is shown in Fig. 1 reveals the presence of "symmetrical" imidazolium cations perpendicular to a crystallographic mirror plane [C(3)–N(6) 1.329(4) Å]. The packing of the molecules of **3** shows no interactions between the dicyanoargentate anions and neighboring imidazolium cations. The dicyanoargentate anions are almost linear, and the Ag–C and C–N bond lengths are in the expected range [11]. For individual bond lengths and angles see Table 2.

The crystallographic data for salt **4** are given in Table 1. The unit cell contains two crystallographically independent imidazolium cations and $[Ag(CN)_2]^-$ anions (Fig. 2). The bond lengths and angles of the two ion pairs are very close together (Table 3).

Table 3. Selected bond lengths (Å) and angles (deg) for $C_{14}H_{20}N_5Ag$ (**4**).

C(1)–N(2)	1.342(9)	C(21)–N(25)	1.343(10)
C(1)–N(5)	1.366(9)	C(21)–N(22)	1.359(10)
C(1)–C(6)	1.404(11)	C(21)–C(32)	1.377(14)
C(3)–N(2)	1.343(9)	C(24)–N(25)	1.358(11)
C(4)–N(5)	1.374(10)	C(23)–N(22)	1.350(11)
C(6)–N(7)	1.157(11)	C(32)–N(33)	1.146(12)
Ag(40)–C(43)	1.999(10)	Ag(50)–C(53)	1.985(14)
Ag(40)–C(41)	2.055(12)	Ag(50)–C(51)	2.081(11)
C(41)–N(42)	1.115(13)	C(51)–N(52)	1.103(11)
C(43)–N(44)	1.162(12)	C(53)–N(54)	1.208(14)
N(2)–C(1)–N(5)	108.7(6)	N(25)–C(21)–N(22)	107.6(8)
N(2)–C(1)–C(6)	126.3(7)	N(25)–C(21)–C(32)	126.6(8)
N(5)–C(1)–C(6)	125.0(7)	N(22)–C(21)–C(32)	125.8(8)
C(1)–N(2)–C(3)	109.0(6)	C(21)–N(25)–C(24)	109.4(7)
C(1)–N(5)–C(4)	106.9(5)	C(23)–N(22)–C(21)	109.3(7)
N(7)–C(6)–C(1)	179.7(7)	N(33)–C(32)–C(21)	178.8(10)
C(43)–Ag(40)–C(41)	179.2(3)	C(53)–Ag(50)–C(51)	178.1(4)
N(42)–C(41)–Ag(40)	179.0(9)	N(52)–C(51)–Ag(50)	177.0(8)
N(44)–C(43)–Ag(40)	179.9(6)	N(54)–C(53)–Ag(50)	178.6(8)

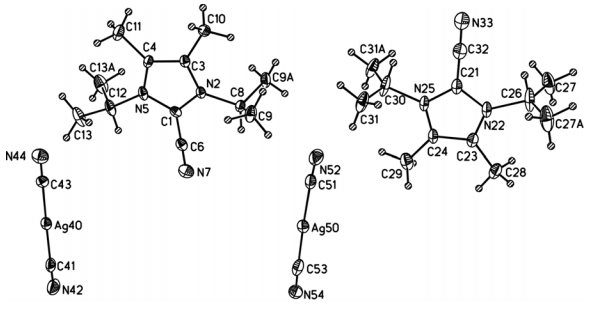


Fig. 2. View of the ion pairs of $C_{14}H_{20}N_5Ag$ (**4**) in the crystal.

$[Ag(CN)_2]^-$ can act as an isolated counterion in structures with ionic character or as a bridging spacer between atoms giving rise to polymeric structures [2]. The imidazolium cations in **4** form a two-dimensional layer in the *ab* plane, and the layers are separated from each other in the *c* direction by the $[Ag(CN)_2]^-$ anions. Within the layer, the cations are linked to each other by N–Ag interactions to form one-dimensional zigzag chains along the *a* axis. The Ag–N distances (3.730(4) Å) are considered to be longer than those observed for weak bonding [12]. The distance between the planes of two imidazolium rings is 6.77(2) Å [3].

Fig. 3 indicates the multidecker type structure of **4**. The Ag···Ag separation in Ag(40)–Ag(4A) is noticeably longer than the sum of van der Waals radii of two Ag atoms [3.40(3) Å] [14], indicating the absence of direct Ag···Ag interactions in the chains. The lack of this interaction between silver atoms is clearly a result of the presence of bulky imidazolium cations that deny access to silver atoms. A number of examples are known where these anions show self-association. Argentophilic interactions between $(Ag(CN)_2)^-$ ions unsupported by additional ligands occur, *e. g.*, in $Tl[Ag(CN)_2]$ [13].

All attempts to obtain 2-cyanoimidazolium cyanides (**5**) failed. On reacting **3** or **4** with cyanide salts under forced conditions we observed ring opening reactions resulting as a consequence of a nucleophilic attack of cyanide at the C2 carbon atom.

Experimental Section

All reactions were performed in purified solvents under argon. The reagents were purchased (Aldrich) and used as received. 2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) was obtained by a published procedure [15].

*$C_{13}H_{20}N_4AgCl$ (**3**)*

To a solution containing 1,3-diisopropyl-4,5-dimethylimidazolium chloride (0.70 g, 2.79 mmol) in acetonitrile (30 mL) was added silver cyanide (1.12 g, 8.37 mmol). The mixture was refluxed for 25 h. The filtered solution was evaporated to dryness, and the resulting solid was washed with Et_2O; yield: 0.83 g (79 %). This solid was recrystallized from CH_2Cl_2/ Et_2O. – ^1H NMR (CD_2Cl_2): δ = 1.58 (d, 12H, 1,3-CH*Me*$_2$, ^3J = 6.70 Hz), 2.30 (s, 6H,4,5-Me), 4.77 (sept, 2H, 1,3-C*H*Me$_2$). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 9.57 (4,5-Me), 19.83 (1,3-CH*Me*$_2$), 52.77 (1,3-CHMe$_2$), 142.07 {$Ag(CN)_2$} 126.23 (C_2), 127.59 ($C_{4,5}$). – Elemental analysis for $C_{13}H_{20}N_4AgC$ (375.64): calcd. C 41.57, H 5.37, N 14.90; found C 40.05, H 5.51, N 14.60. – MS ((+)-FAB): *m/z* (%) = 215.1 (100).

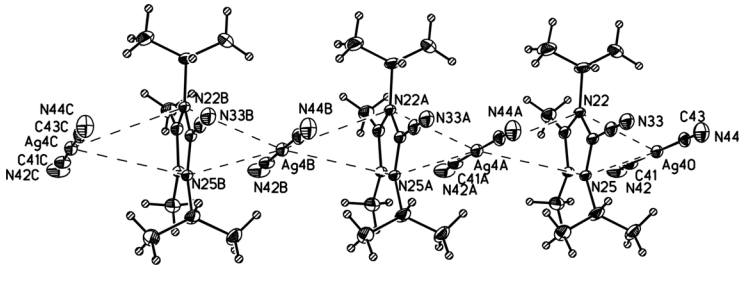


Fig. 3. View of the multidecker array of $C_{14}H_{20}N_5Ag$ (**4**) in the crystal.

*$C_{14}H_{20}N_5Ag$ (**4**)*

To a solution containing 1,3-diisopropyl-4,5-dimethyl-2-chloroimidazolium dicyanoargentate (0.561 g, 1.49 mmol) in acetonitrile (30 mL) was added potassium cyanide (0.972 g, 14.91 mmol) at r. t. After stirring for 3 d the filtered solution was evaporated to dryness, and the resulting solid was washed with Et_2O; yield: 0.37 g (69 %). This solid was recrystallized from CH_3CN/ Et_2O. – ^{1}H NMR (CD_2Cl_2): δ = 1.68 (d, 12H, 1,3-CH*Me*$_2$, ^3J = 6.70 Hz), 2.39 (s, 6H,4,5-Me), 4.80 (sept, 2H, 1,3-C*H*Me$_2$). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 10.86 (4,5-Me), 21.95 (1,3-CH*Me*$_2$), 55.03 (1,3-CHMe$_2$), 106.81 (CN), 143.63 {Ag(CN)$_2$} 113.70 (C_2), 133.34 ($C_{4,5}$). – Elemental analysis for $C_{14}H_{20}N_5Ag$ (366.20): calcd. C 45.92, H 5.50, N 19.12; found C 46.68, H 6.52, N 19.35. – MS ((+)-FAB): *m/z* (%) = 206.2 (100).

Further crystal structure data

CCDC 797232 (**3**) and CCDC 797233 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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