

Synthesis and crystal structure of an Ag(I) complex of composition $(C_9H_7N(C_3H_5))_2[AgBr_2]Br(H_2O)_2$

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The crystalline complex $(C_9H_7N(C_3H_5))_2[AgBr_2]Br(H_2O)_2$ has been obtained and structurally investigated by X-ray diffraction: space group *I*-42*d*, *Z* = 8, *a* = 26.903(6), *c* = 7.090(2) Å, *V* = 5132(2) Å³, *D*_x = 1.784 g·cm⁻³, number of independent reflection 6295, reliability factors *R* = 0.022, *wR* = 0.039. The coordination mode of the Ag(I) atom includes four bromine atoms. The crystal structure contains distinct polymeric anionic chains $\{AgBr_2\}_n^{n+}$ and isolated Br⁻ anion, which are connected to the N-allylquinolinium cations and water molecules through electrostatic forces and hydrogen bonds.

Silver(I) / σ-Complexes / N-Allyl derivatives / Quinoline / Crystal structure

Introduction

Copper(I) and silver(I) are suitable coordination centers for industrial catalytic systems [1,2] and attractive objects for scientific investigations, due to their unique properties [3-5].

Previous studies of the first copper(I) compounds with N-allyl derivatives of quinoline [6,7] and isoquinoline [8,9] showed the absence of π-coordination of the allylic C=C bond of the allyl group in halide complexes with N-allylquinolinium cations, contrary to what is observed for N-allylisoquinolinium cations.

In order to study the coordination behavior of Ag(I) with N-allylquinolinium cations, we prepared $(C_9H_7N(C_3H_5))_2[AgBr_2]Br(H_2O)_2$ and determined its crystal structure.

Experimental section

Synthesis of N-allylquinolinium bromide $(C_9H_9NC_3H_5Br)$

N-allylquinolinium bromide was obtained from quinoline (preliminarily purified by distillation) and excess of freshly distilled allyl bromide in chloroform. After 10 h of reflux boiling and stirring, the mixture

was filtered and most of the solvent was distilled off. Crystalline N-allylquinolinium bromide was isolated with a yield of ~88 %.

Preparation of $(C_9H_7N(C_3H_5))_2[AgBr_2]Br(H_2O)$ (I)

Good quality crystals of complex **I** were obtained by direct reaction between AgSCN and the corresponding N-allylquinolinium bromide: AgSCN (0.092 g, 0.7 mmol) was added to a methanol solution of N-allylquinolinium bromide (0.20 g, 0.7 mmol). The mixture was placed in a small test tube, heated until boiling of the solvent and then a rubber cork was inserted. After 10 days, red plates were formed on the walls of the tube with a yield of 60 %.

X-ray crystal structure determination

The crystallographic parameters and a summary of the data collection for **I** are presented in Table 1. Single crystals of **I** were preliminarily studied by the photographic method and then diffraction data were collected on a KUMA-KM4/CCD (graphite monochromated Mo K_α radiation) diffractometer. Lorentz and polarization corrections were applied to the intensities.

The X-ray diffraction data were processed using the CrysAlisRED program [10]. An absorption correction was applied by the analytical method [11].

Table 1 Crystallographic data and experimental details for **I**.

	I
Empirical formula	(C ₁₂ H ₁₄ N) ₂ ·(AgBr ₂)·Br·(H ₂ O) ₂
Formula weight	724.07
Temperature, K	100
Wavelength, Å	0.71073 (Mo K _α)
Crystal system, space group	Tetragonal, <i>I</i> -42 <i>d</i>
Diffractometer	KM4 CCD
Unit cell dimensions	
<i>a</i> , Å	26.903(6)
<i>b</i> , Å	26.903(6)
<i>c</i> , Å	7.090(2)
<i>α</i> , °	90
<i>β</i> , °	90
<i>γ</i> , °	90
Volume, Å ³	5132(2)
<i>Z</i>	8
Calculated density, g·cm ⁻³	1.874
Absorption coefficient, mm ⁻¹	5.48
<i>F</i> (000)	2832
Crystal size, mm	0.3 × 0.14 × 0.05
Color, shape	Red, plate
Theta range for data collection, °	3-37
Limiting indices	-45 ≤ <i>h</i> ≤ 44, -43 ≤ <i>k</i> ≤ 45, -11 ≤ <i>l</i> ≤ 9
Refinement method	Full-matrix least-squares on <i>F</i> ²
Measured reflections	37444
Independent reflections	6295
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	5072
Free parameters	154
Weight scheme ^a	[σ ² (<i>F</i> _o ²) + (0.0209 <i>P</i>) ²] ⁻¹
Goodness-of-fit on <i>F</i> ²	0.91
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.022, w <i>R</i> ₁ = 0.039
Largest difference peak and hole, e·Å ⁻³	1.10 and -0.36

^a $P = (F_o^2 + 2F_c^2)/3$

The structure of **I** was solved by direct methods, and the light atoms were revealed from difference Fourier syntheses, using the SHELX program package [12]. Full-matrix least-squares refinements based on *F*² were carried out for the positional and thermal parameters of all non-hydrogen atoms. The hydrogen atoms were revealed from the difference Fourier syntheses and refined in the riding mode along with the non-hydrogen atoms (fixed C–H distances and *U*_{iso}(H) equal to 1.2*U*_{eq}(C), restrained O–H distances and *U*_{iso}(H) equal to 1.5*U*_{eq}(O)).

Atomic positional and displacement parameters for **I** are given in Table 2.

Results and discussion

In the crystal structure of **I**, two crystallographically independent metal atoms are tetrahedrally coordinated by four symmetry-equivalent bromine

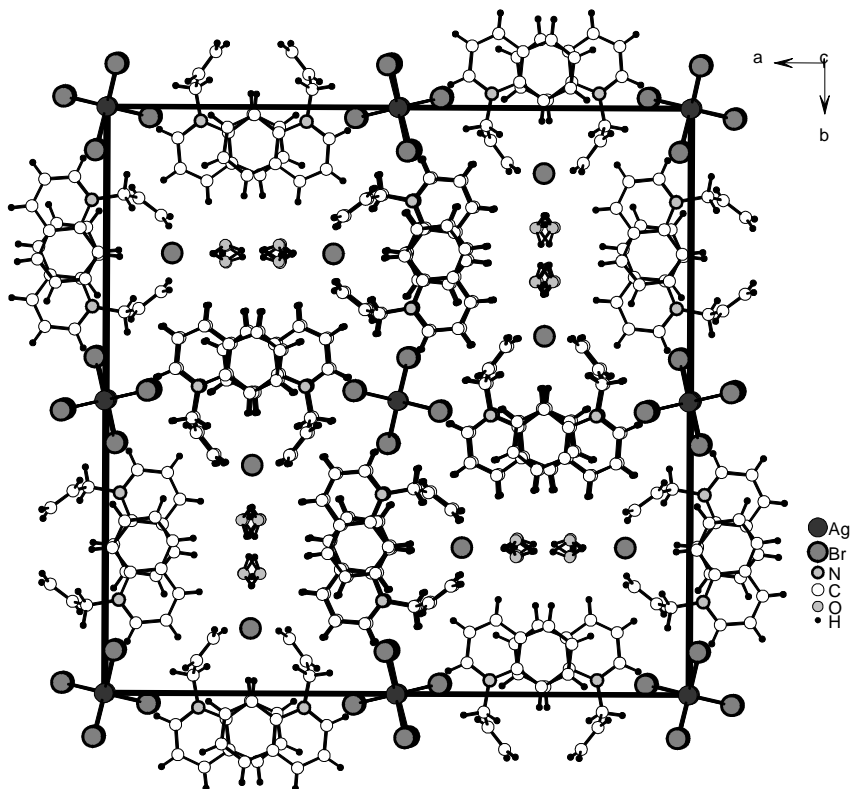
atoms (Table 3). Due to the bridging function of the halogens (Br(1) atoms connect Ag(1) and Ag(2) atoms), the coordination polyhedra are joined through opposite edges and the structure consists of chain-like {[AgBr₂]⁺]_n topological units with -4 symmetry (Fig. 1). Bromine ions of the second crystallographic type are placed around the inorganic chains with formation of {[AgBr₂]Br}_n²ⁿ⁻ polyanions, preserving the symmetry. The compound (C₉H₇N(C₃H₅))₂[AgBr₂]Br(H₂O)₂ (**I**) is isostructural with the previously studied copper(I) bromide complex (C₉H₇N(C₃H₅))₂[CuBr₂]Br(H₂O)₂ (**II**) [13]. Similar inorganic fragments are also observed in (C₃H₉S)[AgBr₂] (**III**) [14], but the coordination polyhedra of the metal atoms form zigzag polyanions {[AgBr₂]}_nⁿ⁻. Analogous zigzag units are observed in the Cu complexes [C₉H₇N(C₃H₅)]CuBr₂ and [CHOOCH(CH₂=CH-CH₂-NH₃)]CuX₂ (X = Cl, Br) [7,15].

Table 2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for **I**, space group $I-42d$.

Atom	x	y	z	$U_{\text{iso}}/U_{\text{eq}}^{\text{a}}$	Atom	x	y	z	$U_{\text{iso}}/U_{\text{eq}}^{\text{a}}$
Ag(1)	0	0	0	0.01814(4)	C(8)	0.48678(6)	0.25216(5)	0.3779(2)	0.0205(3)
Ag(2)	0	0	$-\frac{1}{2}$	0.02257(4)	H(8)	0.5219	0.2556	0.3760	0.025
Br(1)	0.073560(5)	-0.017410(5)	-0.24988(2)	0.01761(3)	C(9)	0.45592(5)	0.29371(5)	0.3511(2)	0.0174(3)
Br(2)	0.888837(8)	$\frac{1}{4}$	$\frac{1}{8}$	0.01942(4)	C(10)	0.40341(6)	0.28799(6)	0.3482(2)	0.0230(3)
N(1)	0.47560(5)	0.34108(4)	0.32965(17)	0.0183(2)	C(11)	0.53011(6)	0.35056(6)	0.3430(2)	0.0214(3)
C(2)	0.44596(7)	0.37999(6)	0.2988(2)	0.0260(3)	H(11a)	0.5449	0.3273	0.4357	0.026
H(2)	0.4605	0.4118	0.2815	0.031	H(11b)	0.5357	0.3848	0.3891	0.026
C(3)	0.39443(7)	0.37552(7)	0.2910(2)	0.0333(4)	C(12)	0.55558(6)	0.34410(6)	0.1557(2)	0.0231(3)
H(3)	0.3743	0.4038	0.2671	0.040	H(12)	0.5432	0.3620	0.0503	0.028
C(4)	0.37336(6)	0.33033(8)	0.3181(3)	0.0317(4)	C(13)	0.59367(6)	0.31520(6)	0.1310(3)	0.0289(3)
H(4)	0.3382	0.3271	0.3168	0.038	H(13a)	0.6068	0.2969	0.2342	0.035
C(5)	0.38348(7)	0.23995(7)	0.3772(2)	0.0324(4)	H(13b)	0.6084	0.3124	0.0098	0.035
H(5)	0.3485	0.2354	0.3765	0.039	O(1w)	0.79594(11)	0.23678(14)	0.4396(4)	0.0357(10) ^b
C(6)	0.41379(7)	0.20023(7)	0.4062(2)	0.0322(4)	O(2w)	0.79582(14)	0.26547(19)	0.4375(5)	0.0457(13) ^b
H(6)	0.3999	0.1682	0.4261	0.039	H(0w)	0.8167(6)	0.2508(3)	0.364(3)	0.068
C(7)	0.46530(7)	0.20653(6)	0.4068(2)	0.0272(4)	H(1w)	0.8012(16)	0.248(2)	0.551(3)	0.068 ^c
H(7)	0.4860	0.1785	0.4277	0.033	H(2w)	0.7678(6)	0.2561(17)	0.391(6)	0.068 ^c

^a For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\bar{a}_i \bar{a}_j)$, for hydrogen U_{iso} was set equal to 1.2 $U_{\text{eq}}(\text{C})$ or 1.5 $U_{\text{eq}}(\text{O})$.

^b For O(1w) and O(2w) the occupation factors are 0.54 and 0.46, respectively; for H(1w) and H(2w) they are equal to 0.5.

**Fig. 1** Projection of the structure of $(\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5))_2[\text{AgBr}_2]\text{Br}(\text{H}_2\text{O})$ (**I**).

The N-allylquinolinium cations in the structure of **I** are situated around the inorganic polyanions and remain in position due to electrostatic forces and weak hydrogen bonds (Table 4), like the rest of the bromine atoms and the water molecules. The latter are disordered between two positions with occupations 0.54 and 0.46.

An interesting feature of the structure is the π - π stacking of the quinolinium cores [16]. The organic cations build up columns in the direction of the *c*-axis (the benzene rings are situated one below the other and the pyridine moieties are shifted to the left and to the right). The distance between core planes and centers of phenyl rings is approximately 3.5 Å, the angle between core planes is equal to 4°.

The coordination behavior of the Ag(I) ion in (C₉H₇N(C₃H₅))₂[AgBr₂]Br(H₂O)₂ is similar to that of Cu(I) in the halide compounds with N-allylquinolinium cations [6], and pi-coordination M(I)-(C=C) is not observed here either. Energy-preferable Ag(I) or Cu(I) pi-complex formation

involving the C=C bond of the allylic functional group is predicted on the basis of Pearson's HSAB conception [17], since silver(I) (copper(I)) and the C=C bond are a soft acid and base, respectively, in contrast to the bromide anion, which is an intermediate base. However, in the case of the Cu(I) halide complex with N-allylquinolinium cations, this assumption fails, due to the influence of the electronic structure of the ligand, which can be evaluated through the pK_a value of the heterocyclic core of the ligand [18]. The corresponding pK_a values of quinoline-core-containing N-allyl derivatives are too low to produce CuHal π -compounds. But the presence of a hard base, such as a nitrate anion, changes the situation and copper(I) forms pi-complexes with N-allylquinolinium cations [19]. Since only Ag-Br interactions exist in the crystal structure of (C₉H₇N(C₃H₅))₂[AgBr₂]Br(H₂O)₂, we can assume similar influence of the pK_a value on silver(I) complexation and outline the object for our next investigation: silver nitrate compounds with C₉H₇N(C₃H₅)⁺ cations.

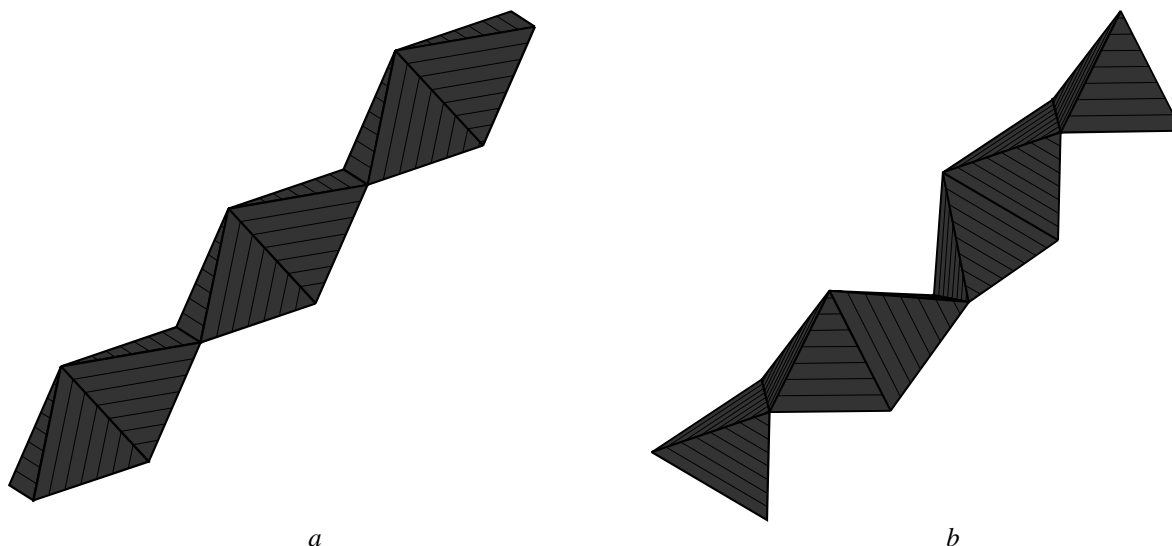
Table 3 Selected bond lengths and angles in the structure of **I**.

Bond ^a	<i>d</i> , Å	Angle	ω , deg	Bond	<i>d</i> , Å	Angle	ω , deg
Ag(1)-Br(1) ⁱ	2.6971(5)	Br(1) ⁱ -Ag(1)-Br(1) ⁱⁱ	115.56(1)	N(1)-C(2)	1.334(2)	C(2)-N(1)-C(9)	120.7(1)
Ag(1)-Br(1) ⁱⁱ	2.6971(5)	Br(1) ⁱ -Ag(1)-Br(1)	115.56(1)	N(1)-C(9)	1.389(2)	C(2)-N(1)-C(11)	117.6(1)
Ag(1)-Br(1)	2.6971(5)	Br(1) ⁱⁱ -Ag(1)-Br(1)	97.88(2)	N(1)-C(11)	1.491(2)	C(9)-N(1)-C(11)	121.7(1)
Ag(1)-Br(1) ⁱⁱⁱ	2.6971(5)	Br(1) ⁱ -Ag(1)-Br(1) ⁱⁱⁱ	97.88(2)	C(2)-C(3)	1.393(3)	N(1)-C(2)-C(3)	122.3(2)
Ag(2)-Br(1) ^{iv}	2.6983(5)	Br(1) ⁱⁱ -Ag(1)-Br(1) ⁱⁱⁱ	115.56(1)	C(3)-C(4)	1.355(3)	C(4)-C(3)-C(2)	119.2(2)
Ag(2)-Br(1)	2.6983(5)	Br(1)-Ag(1)-Br(1) ⁱⁱⁱ	115.56(1)	C(4)-C(10)	1.413(2)	C(3)-C(4)-C(10)	120.3(2)
Ag(2)-Br(1) ⁱⁱ	2.6983(5)	Br(1) ^{iv} -Ag(2)-Br(1)	115.59(1)	C(5)-C(6)	1.360(3)	C(6)-C(5)-C(10)	120.8(2)
Ag(2)-Br(1) ^v	2.6983(5)	Br(1) ^{iv} -Ag(2)-Br(1) ⁱⁱ	115.59(1)	C(5)-C(10)	1.415(2)	C(5)-C(6)-C(7)	120.0(2)
		Br(1)-Ag(2)-Br(1) ⁱⁱ	97.82(2)	C(6)-C(7)	1.396(3)	C(8)-C(7)-C(6)	121.8(2)
		Br(1) ^{iv} -Ag(2)-Br(1) ^v	97.82(2)	C(7)-C(8)	1.372(2)	C(7)-C(8)-C(9)	118.9(2)
		Br(1)-Ag(2)-Br(1) ^v	115.59(1)	C(8)-C(9)	1.405(2)	N(1)-C(9)-C(8)	121.3(1)
		Br(1) ⁱⁱ -Ag(2)-Br(1) ^v	115.59(1)	C(9)-C(10)	1.421(2)	N(1)-C(9)-C(10)	118.5(1)
		Ag(1)-Br(1)-Ag(2)	82.15(2)	C(11)-C(12)	1.505(2)	C(8)-C(9)-C(10)	120.2(1)
				C(12)-C(13)	1.298(2)	C(4)-C(10)-C(5)	122.8(2)
				O(1w)-H(0w)	0.861(3)	C(4)-C(10)-C(9)	118.9(2)
				O(1w)-H(1w)	0.860(3)	C(5)-C(10)-C(9)	118.3(2)
				O(1w)-H(2w)	0.98(4)	N(1)-C(11)-C(12)	111.8(2)
				O(2w)-H(0w)	0.862(3)	C(13)-C(12)-C(11)	123.2(2)
				O(2w)-H(1w)	0.93(4)	H(0w)-O(1w)-H(1w)	108(2)
				O(2w)-H(2w)	0.861(3)	H(0w)-O(2w)-H(1w)	101(3)

^a symmetry codes: (i) -y, x, -z; (ii) -x, -y, z; (iii) y, -x, -z; (iv) -y, x, -z-1; (v) y, -x, -z-1.

Table 4 Geometry of selected H-contacts in the structure of **I**.

Contact D–H...A	Bond length, Å			Angle D–H...A, deg	Atom coordinates of A
	D–H	H...A	D...A		
O(1w)–H(0w)...Br(2)	0.86	2.58	3.369(3)	153	x, y, -1+z
C(4)–H(4)...Br(2)	0.95	2.93	3.695(2)	139	
C(7)–H(7)...Br(1)	0.95	2.57	3.668(2)	142	x, 1/2-y, 5/4-z

**Fig. 2** Inorganic fragment $\{[AgBr_2]^+\}_n$ in the structures of $(C_9H_7N(C_3H_5))_2[AgBr_2]Br(H_2O)$ (**I**) (a) and $(C_3H_9S)[AgBr_2]$ (b).

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