Synthesis, Crystal Structure and Thermal Properties of Silver(I) Bromide Ethylenediamine Coordination Polymers

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Dedicated to Professor Kurt O. Klepp on the occasion of his 60th birthday

Reaction of silver(I) bromide with ethylenediamine (en) leads to the formation of the 1:1 compound poly[AgBr(μ_2-en-N,N')] (**I**). In the crystal structure the silver atoms of AgBr dimers are connected to two bridging bromine atoms and two nitrogen atoms of different en ligands. The dimers are thus connected by the ligands into layers *via* μ-N,N' coordination. In the 2:1 coordination polymer poly[(AgBr)$_2$(μ_2-en-N,N')] (**II**) a three-dimensional AgBr substructure occur which consists of helical AgBr chains that are connected *via* peripheral Ag-Br contacts into a three-dimensional network that contains large channels. The en ligands are situated in these channels bridging the Ag atoms. From solution this compound cannot be obtained as a pure phase, since compound **I** is always formed as the major phase. On heating the 1:1 compound **I** in a thermobalance the sample mass decreases slowly and several mass steps are observed, which are not fully resolved. If the reaction is stopped at 230 °C, pure AgBr has formed. At 115 °C only traces of compound **II** are found. The major phase consists of an as yet unidentified ligand poor compound.

Key words: Silver(I) Bromide, Ethylenediamine, Coordination Polymers, Crystal Structures, Thermal Properties

Introduction

We are interested in the synthesis, crystal structures and properties of inorganic organic coordination polymers based on copper(I) halides or pseudo halides and nitrogen donor ligands. Several of these compounds are known and were structurally characterised [1 – 38]. The compounds consist of typical CuX substructures which are connected by the nitrogen donor ligands to 1-, 2- or 3-dimensional coordination polymers. The dimensionality of these compounds depends predominantly on the coordination behaviour of the ligand and the nature of the halide anion. For a certain copper(I) halide or pseudohalide and a specific nitrogen donor ligand frequently several compounds are found, which contain a different content of the organic ligand. Therefore, ligand richer and ligand poorer compounds are found. We have observed that most of the ligand richer compounds loose their ligands stepwise on heating forming ligand poorer compounds as intermediates [26 – 38]. In most cases these intermediates can be isolated in almost 100% yield. Hence, the thermal decomposition of suitable CuX precursor compounds is an alternative route for the preparation of new CuX coordination polymers which cannot be prepared in solution or which are only obtained as components of mixtures. In further investigations we found no simple relationship between the structures of the starting compound and their properties [26 – 38]. We were able to show, that the product formation depends on the kinetics of the reactions [31]. In some cases several ligand poorer intermediates or polymorphs can be isolated [32 – 34].

From these investigations the question araises if this method of preparation can be employed for other coordination compounds or if it is limited to the copper(I) halide coordination polymers. Therefore, we have started investigations on silver(I) halide coordination polymers. Compared to the copper(I) halide compounds only a few silver(I) compounds were synthesized and structurally characterized possibly due to the low solubility and the low reactivity of the pure silver(I) halides and the light sensitivity of the coordination compounds [39 – 48]. Most of the silver(I) halide coordination polymers reported in literature contain
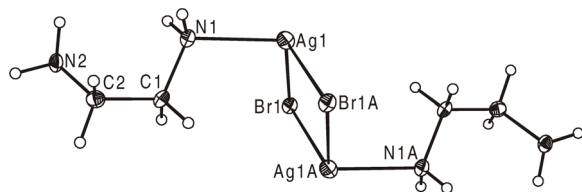
Fig. 1. Crystal structure of poly[AgBr(μ_2-en-N,N')] (**I**) with labelling and displacement ellipsoids drawn at the 50% probability level.
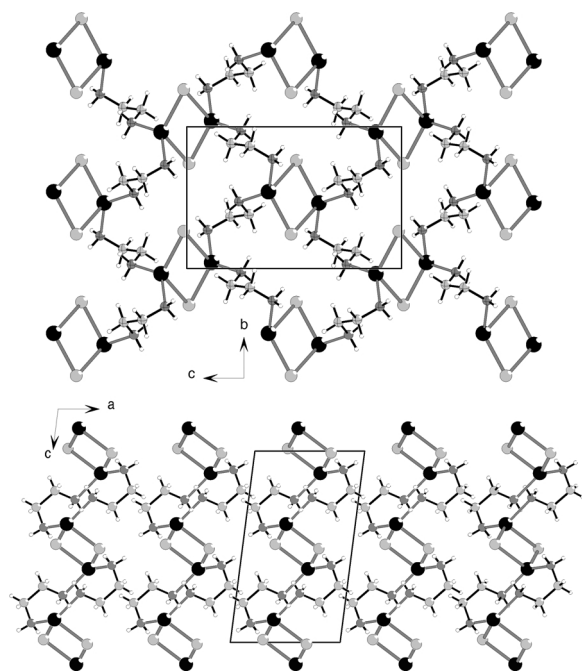

Fig. 2. Crystal structure of poly[AgBr(μ_2-en-N,N')] (**I**) with view in the direction of the *a*-axis (top) and of the *b*-axis (bottom).

monodentate N-donor ligands like *e. g.* quinoline [39] or methylpyridine [41]. Most of these amines exhibit a high vapor pressure and the corresponding coordination polymers decompose at relatively low temperatures to leave pure silver(I) halides.

The structures of the silver(I) halide coordination polymers with N-donor ligands are similar to those of the corresponding copper(I) halide counter parts. Most of the characteristic AgX substructures are known from the copper(I) halide compounds. Owing to the nature of the ligands mostly coordination networks of low dimensionality are found. Their thermal properties have not been investigated.

In the present work we report on the synthesis, crystal structure and thermal properties of two new

Table 1. Selected bond lengths (Å) and angles (°) for poly[AgBr(μ_2-en-N,N'] (**I**).

Ag(1)-N(2A)	2.271(3)	Ag(1)-N(1)	2.298(3)
Ag(1)-Br(1)	2.6870(5)	Ag(1)-Br(1A)	3.0055(5)
N(2A)-Ag(1)-N(1)	131.59(10)	N(2A)-Ag(1)-Br(1)	118.43(7)
N(1)-Ag(1)-Br(1)	106.71(8)	N(2A)-Ag(1)-Br(1A)	85.27(7)
N(1)-Ag(1)-Br(1A)	91.69(7)	Br(1)-Ag(1)-Br(1A)	114.48(1)

AgBr coordination polymers with the bidentate ligand ethylenediamine.

Results and Discussion

Crystal structures

The 1:1 compound poly[AgBr(μ_2-en-N,N')] (**I**) crystallizes in the monoclinic primitive space group P2$_1$/c with four formula units in the unit cell (Table 3). The asymmetric unit consists of one silver and one bromine atom as well as one en ligand all of them located in general positions. Each silver atom is coordinated by two bromine atoms and two nitrogen atoms of two symmetry related en ligands within a strongly distorted tetrahedron (Fig. 1).

The Ag and Br atom forms coplanar (AgBr)$_2$ dimers that are located around a centre of inversion (Fig. 1). The AgBr bond lengths amount to 2.6870 and 3.0055 Å and the Ag-N bond lengths to 2.271 and 2.298 Å (Table 1). The angles around the Ag atom scatter between 85.3 and 131.6° (Table 1). Within the dimers Ag···Ag contacts of 3.0920 Å are observed. This motive is well known from the CuX coordination polymers.

The (AgBr)$_2$ dimers are connected by the en ligands *via* μ-N,N'-coordination into corrugated layers that are oriented in the *b/c* plane (Fig. 2). These layers are stacked in the direction of the crystallographic *a*-axis (Fig. 2).

The 2:1 compound poly[(AgBr)$_2$(μ_2-en-N,N')] (**II**) crystallizes in the chiral tetragonal space group P4$_1$2$_1$2 with four formula units in the unit cell (Table 3). The asymmetric unit consists of one silver and one bromine atom in general positions as well as one en ligand in a special position. Each silver atom is coordinated by three bromine atoms and one nitrogen atom of the en ligand within an irregular polyhedron (Fig. 3 and Table 2). The angles around the silver atom scatter between 92.2 and 136.3°. The Ag···Ag contacts amount to 3.0489 Å and are comparable to those in compound **I**.

Table 2. Selected bond lengths (Å) and angles (°) for poly[(AgBr)$_2$(μ_2-en-N,N')] (**II**).

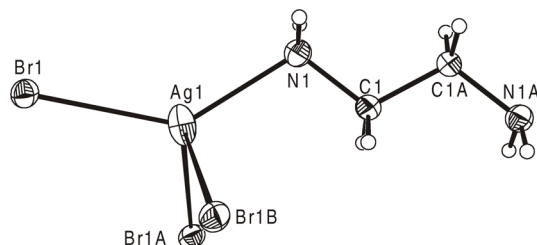| Ag(1)-N(1) | 2.275(5) | Ag(1)-Br(1) | 2.6497(8) |
Ag(1)-Br(1A)	2.7937(9)	Ag(1)-Br(1B)	2.9363(8)
N(1)-Ag(1)-Br(1)	136.31(13)	N(1)-Ag(1)-Br(1A)	112.26(14)
Br(1)-Ag(1)-Br(1A)	103.40(2)	N(1)-Ag(1)-Br(1B)	92.22(13)
Br(1)-Ag(1)-Br(1B)	102.66(2)	Br(1A)-Ag(1)-Br(1B)	104.55(2)

Fig. 3. Crystal structure of poly[(AgBr)$_2$(μ_2-en-N,N')] (**II**) with view of the coordination sphere of the silver atoms with labelling and displacement ellipsoids drawn at the 50% probability level.

Fig. 5. Crystal structure of poly[(AgBr)$_2$(μ_2-en-N,N')] (**II**) with view along the *c*-axis.

Thermal properties

In the crystal structure of compound **II** a unprecedented AgBr substructure is found. The Ag and Br atoms forms helical chains which elongate in the direction of the *c*-axis (Fig. 4: left). In these chains alternating short and long Ag-Br distances of 2.6497 and 2.7937 Å are observed, respectively (Table 2). These chains are linked by additional, relatively long Ag-Br contacts of 2.9363 Å into a three-dimensional AgBr network (Fig. 4: right). In this array channels are formed in the direction of the *c*-axis (Fig. 4: right). The en ligands are located in these channels and are connected to the Ag atoms (Fig. 5).
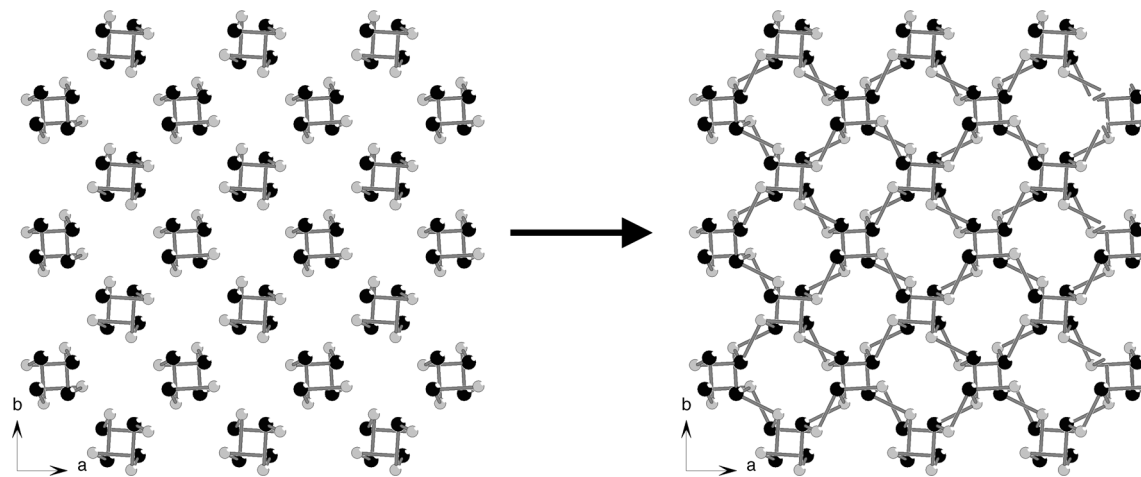
The thermal properties of compounds **I** and **II** were investigated by differential thermoanalysis, thermogravimetry and mass spectroscopy. On heating the ligand rich compound **I** in a helium atmosphere a first decomposition is observed at a peak temperature of about 80 °C. On further heating the sample mass drops slowly until a plateau is reached at about 220 °C (Fig. 6). The experimental mass loss up to this plateau of 24.4% is in

Fig. 4. AgBr substructure in compound **II** showing the connection of the helical chains (left) into the three-dimensional AgBr network (right).
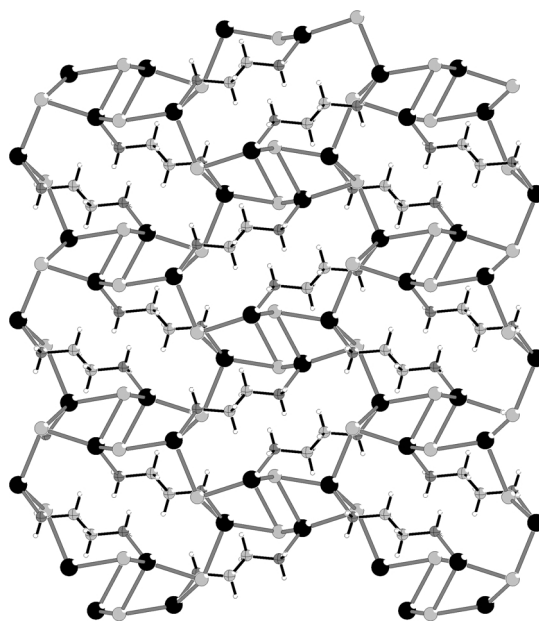
good agreement with that calculated for the complete loss of the organic ligands (Δm_{theo}: $-en = 24.25\%$. This is in agreement with mass spectrometric data, which show that the emission of the en is completed at about 220 °C (Fig. 6). The residue isolated at this temperature was identified as AgBr by X-ray powder diffraction. Above 230 °C decomposition of the AgBr intermediate is observed.

The DTG curve shows clearly that several mass steps are involved in this decomposition, which cannot be fully resolved (Fig. 6). Two additional endothermic events are observed at peak temperatures of about 113 and 210 °C (Fig. 6). The experimental mass loss of 12.1% at about 115 °C, where the TG curve shows a point of inflection corresponds to the loss of half of the en ligands (Δm_{theo}: $-1/2$ en $= 12.1\%$.

To get further insight into the thermal decomposition, additional TG experiments were performed in which the residues isolated at different temperatures were investigated with X-ray powder diffraction. These investigations have shown, that the ligand rich compound **I** decomposes at about 120 °C into a new phase which is yet unidentified. In this temperature range only traces of compound **II** are detected by X-ray powder diffraction. Compound **I**, **II** and the unknown intermediate coexist over a large temperature range before decomposition into AgBr is observed. Therefore, compound **II** cannot be prepared in pure form by thermal decomposition.

Conclusion

In the present work two silver(I) halide coordination polymers with aliphatic amine ligands were prepared for the first time. The silver(I) halide dimers observed in compound **I** are also found in several copper(I) halide compounds. In contrast, in the ligand poorer compound **II** a completely new three-dimensional AgX substructure has been found which is unprecedented in silver(I) or copper(I) halide coordination polymer chemistry. The preparation of pure silver(I) halide coordination polymers with N-donor ligands is more difficult to achieve than the preparation of the copper(I) halide counterparts. This is due to the low reactivity of silver(I) halides and their sensitivity against visible light. Whereas the ligand rich AgBr compound **I** can be prepared in a very pure form using an excess of ethylenediamine the ligand poorer compound **II** cannot be prepared pure from solution. This is in agreement with our findings for the copper(I) halide
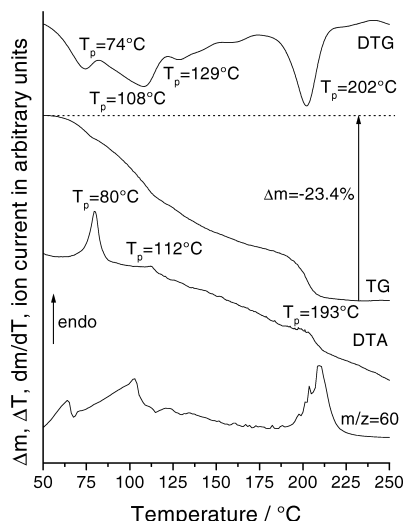

Fig. 6. DTA, TG, DTG and MS trend scan curves for poly[AgBr(μ_2-en-N,N')] (**I**) (weight: 32.04 mg; heating rate: 4 °C/min.; m/z = 60 (en).

coordination polymers, which show that the stability of the ligand rich coordination polymers decreases from chloride to iodide, whereas the stability of the ligand poorer compounds increases in the same order.

The thermal degradation of the ligand rich compound **I** is a complicated process. Only traces of compound **II** can be verified as an intermediate but the major intermediate phase could not yet be identified. Clearly, compound **II** cannot be prepared by thermal decomposition of compound **I**. In future studies systematic investigations of the thermal behaviour of silver(I) halide coordination polymers will be carried out.

Experimental Section

Synthesis of poly[AgBr(μ_2-en,N,N')] (**I**)

104 mg (0.55 mmol) of AgBr and 2 ml (29.9 mmol) of en were stirred in a glass container at room-temperature and in the dark for about 3 d. Subsequently the colourless microcrystalline precipitate was filtered off. Yield: 45% based on AgBr. Because of its sensitivity against visible light the compound must be stored in the dark. The homogeneity of the product was confirmed by comparison of the experimental and calculated X-ray powder patterns. Elemental analysis: calcd. C 9.7; N 11.3, H 3.2; found: C 9.9, N 11.1, H 3.3.

Single crystals of this compound were prepared by the reaction of 111.4 mg (0.59 mmol) of AgBr with 1.8 ml (26.9 mmol) en at room-temperature and in the dark. After 10 d colourless single crystals could be isolated.

Table 3. Selected crystal data and results of the structure refinements for compounds **I** and **II**.

Compound	**I**	**II**
Formula	$C_2H_8N_2AgBr$	$C_2H_8N_2Ag_2Br_2$
MW [g·mol^{-1}]	247.88	435.66
Crystal colour	colourless	colourless
Crystal size [mm^{-1}]	$0.06 \times 0.10 \times 0.12$	$0.04 \times 0.05 \times 0.06$
Crystal system	monoclinic	tetragonal
Space group	$P2_1/c$	$P4_12_12$
a [Å]	6.6261(7)	7.4979(6)
b [Å]	7.6673(6)	–
c [Å]	11.708(1)	14.209(1)
β [°]	92.28(1)	–
V [Å^3]	590.01 (9)	798.8 (1)
Temperature [K]	170	170
Z	4	4
$D_{calc.}$ [g·cm^{-3}]	2.791	3.623
2θ-Range [°]	$5-56$	$5-54$
$h/k/l$ Ranges	$-8/8$	$-8/9$
	$-10/8$	$-9/8$
	$-13/15$	$-17/18$
μ(Mo-K$_\alpha$) [mm^{-1}]	9.97	14.82
Absorption corr.	numerical	–
min./max. Trasmission	0.1796/0.3753	–
Measured reflections	4620	3996
$R_{int.}$	0.0268	0.0581
Independent refl.	1415	892
Refl. with $I > 2\sigma(I)$	1239	819
Parameters	56	37
$R_1 [I > 2\sigma(I)]$	0.0246	0.0273
wR_2 [all data]	0.0556	0.0613
Goof	1.067	1.037
Residual electron density /e·Å^{-3}	$0.78/-0.74$	$0.62/-0.78$

Table 4. Atomic coordinates [$\cdot 10^4$] and isotropic displacement parameters [Å$^2 \cdot 10^3$] for compound **I**.

Atom		X	Y	Z	U_{eq}
Ag(1)	4e	3741(1)	4606(1)	3825(1)	19(1)
Br(1)	4e	2990(1)	7605(1)	4880(1)	14(1)
N(1)	4e	5795(4)	5290(4)	2448(2)	15(1)
C(1)	4e	7712(5)	6185(5)	2911(3)	16(1)
C(2)	4e	9240(5)	6366(5)	2052(3)	15(1)
N(2)	4e	8333(4)	7291(4)	992(3)	14(1)

Table 5. Atomic coordinates [$\cdot 10^4$] and isotropic displacement parameters [Å$^2 \cdot 10^3$] for compound **II**.

Atom		X	Y	Z	U_{eq}
Ag(1)	8b	3981(1)	8649(1)	7066(1)	33(1)
Br(1)	8b	2910(1)	9194(1)	8820(1)	23(1)
N(1)	8b	5831(7)	6707(7)	6319(3)	22(1)
C(1)	8b	5632(9)	6861(9)	5279(4)	22(1)

Equivalent isotropic U calculated as a third of the trace of the orthogonalized U_{ij} tensors.

For compound **I** a numerical absorption correction was performed using X-RED and X-SHAPE [51]. The absolute structure for compound **II** was determined and is in agreement with the selected setting (Flack-x-parameter = 0.01(2). In addition, refinement of the inverted structure leads to significantly poorer reliability factors ($R1$ for 819 $Fo > 4\sigma(Fo) = 0.0514$ $wR2$ for all 892 reflections = 0.1321, Flack-x-parameter = 0.99 (5)). Selected crystal data and results of the structure refinement are shown in Table 3, atomic coordinates and equivalent isotropic displacement parameters are given in Tables 4 and 5.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- 246491 (**I**), CCDC- 246492 (**II**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

*Synthesis of poly[(AgBr)$_2$(μ_2-en-N,N')] (**II**)*

The ligand poorer compound **II** cannot be prepared pure in solution. Independent of the stoichiometry, the temperature and additional solvent always compound **I** has formed as the major phase. However, if an excess of AgBr (208 mg; 1.1 mmol) is reacted with 33 μl (0.5 mmol) of ethylenediamine in 3 ml of acetonitrile in a glass container for 8 d the product consist of compound **I** as the major phase and a few crystals of compound **II** as the minor phase which are suitable for single crystal structure analysis.

Single crystal structure analysis

All data were measured using an Imaging Plate Diffraction System from STOE & CIE. Structure solutions were performed with direct methods using SHELXS-97 [49]. Structure refinement was carried out against F^2 using SHELXL-97 [50]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C-H hydrogen atoms were positioned with idealised geometry and were refined with isotropic displacement parameters using the riding model.

X-ray powder diffraction

X-Ray powder diffraction experiments were performed using a STOE STADI P transmission powder diffractometer equipped with a 4° PSD (position sensitive detector) using Cu-K$_\alpha$ radiation ($\lambda = 1.540598$ Å). For the temperature dependent X-ray powder measurements a 45° PSD and a graphite furnace from STOE & CIE were used. These measurements were carried out in glass capillaries under static air atmosphere.

Differential thermal analysis, thermogravimetry and mass spectrometry

DTA-TG-MS measurements were performed using the STA-409CD with Skimmer coupling from Netzsch, which

is equipped with a quadrupole mass spectrometer QMA 400 (max. 512 amu) from Balzers. The MS measurements were performed in analog and trend scan mode, in Al_2O_3 crucibles under helium atmosphere (purity: 4.6) using heating rates of 4 °C/min. The heating rate dependent measurements were performed with the same instrument and a Pt-Rh furnace in flowing nitrogen (purity: 5.0). All measurements were performed with a flow rate of 75 ml/min and were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

Elemental analysis

C, H, N analysis was performed using a CHN-O-RAPID combustion analyser from Heraeus and EDAX were performed using a Philips XL30 Environmental Scanning Electron Microscope (ESEM) which is equipped with an EDAX system from Philips.

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