

Crystal Structure of Poly[(μ_3 -iodo)(2-ethylpyrazine-N)-silver(I)] Containing a Novel AgX 6³ Net

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Reaction of silver(I) iodide with 2-ethylpyrazine yields crystals of the new coordination polymer poly[(μ_3 -iodo)(2-ethylpyrazine-N)-silver(I)]. In the crystal structure a novel AgI substructure has been found which consists of a 6³ net of alternating Ag and I atoms forming layers which are parallel to the *a-b*-plane. The 2-ethylpyrazine ligands are located above and below each layer and are coordinated only with one nitrogen atom to the silver atoms. The layers are stacked perpendicular to the *c*-axis and are connected only by weak van der Waals interactions. On heating the compound loses all ligands and transforms directly into AgI without the formation of a ligand poor intermediate compound.

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

Introduction

We are interested in the synthesis, structures and properties of coordination polymers based on copper(I) halides or pseudohalides and N-donor ligands, because we have recently found that such ligand rich compounds can be transformed into new ligand poor intermediate compounds by controlled thermal decomposition [1–8]. Because the intermediate compounds were obtained in very pure form and in almost 100% yield, this method is an adequate alternative to the synthesis in solution, in which very often mixtures of different compounds are observed or certain compounds are overlooked or cannot be prepared. These coordination polymers are built up of different CuX substructures (*X* = Cl, Br, I) like *e. g.* 4- and 6-membered rings, or single and double chains, which are connected into one-, two- or three-dimensional coordination polymers by the N-donor ligands. Similar compounds can also be prepared with silver(I) halides and selected examples can be found in references [9–14]. Thus, a similar reactivity can be expected and therefore, we have started investigations on the synthesis, structures and thermal properties of the corresponding AgX (*X* = Cl, Br, I) coordination polymers [15–17]. During these investigations we have reacted AgI with 2-ethylpyrazine and obtained a new AgI coordination compound which consists of a novel AgX substructure,

observed previously in copper(I) halide coordination polymers.

Experimental Section

Synthesis of poly[(μ_3 -iodo)(2-ethylpyrazine-N)-silver(I)]

131.72 mg (0.56 mmol) of AgI were reacted with 244.0 μ l (2.2 mmol) of 2-ethylpyrazine at r. t. in the dark. After 4 d colourless crystals had formed which were suitable for single crystal structure analysis without any further purification. The crystals must be stored in the dark because otherwise they decompose slowly. The compound is obtained phase pure which was proved by X-ray powder diffraction. C₆H₈N₂AgI (342.91): calcd. C 21.02, H 2.35, N 8.17; found C 20.92, H 2.27, N 8.09.

Single crystal structure analysis

All data were measured using an Imaging Plate Diffraction System from STOE & CIE and were corrected for absorption using X-Shape [18]. Structure solutions were performed with direct methods using SHELXS-97 [19], and structure refinement was carried out against *F*² using SHELXL-97 [19]. All non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms were positioned with idealised geometry and refined with isotropic displacement parameters using a riding model. The crystal was racemically twinned and therefore, a twin refinement was performed using SHELXL-97 (BASF parameter: 0.42(4)). A second crystal investigated also showed racemic

Table 1. Crystal data and results of the structure refinement for poly[(μ_3 -iodo)(2-ethylpyrazine-N)-silver(I)].

Empirical formula	C ₆ H ₈ N ₂ AgI
MW [g·mol ⁻¹]	342.91
Crystal colour	colourless
Crystal size [mm ⁻¹]	0.11 × 0.10 × 0.08
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	4.5101(3)
<i>b</i> [Å]	7.3272(5)
<i>c</i> [Å]	26.728 (2)
<i>V</i> [Å ³]	883.3 (1)
Temperature [K]	170
<i>Z</i>	4
<i>D</i> _{calc.} g·cm ⁻³	2.579
2 θ -Range [°]	6–50
<i>h</i> / <i>k</i> / <i>l</i> ranges	–5/5 / –8/8 / –27/31
μ (Mo-K α) [mm ⁻¹]	5.71
Absorption corr.	numerical
Min./max. transmission	0.3537 / 0.4729
Measured reflections	5244
<i>R</i> _{int}	0.0419
Independent refl.	1531
Refl. with <i>I</i> > 2 σ (<i>I</i>)	1435
Parameters	92
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0225
<i>wR</i> ₂ [all data]	0.0540
BASF-parameter	0.42(4)
Goof	1.006
Residual electron density [e·Å ⁻³]	0.58 / –0.47

Table 2. Atomic coordinates [$\cdot 10^4$] and equivalent isotropic displacement parameters [Å² · 10³] for poly[(μ_3 -iodo)(2-ethylpyrazine-N)-silver(I)].

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ag(1)	4 <i>a</i>	7049 (1)	2176 (1)	2324 (1)	29 (1)
I(1)	4 <i>a</i>	7974 (1)	–1634 (1)	2139 (1)	22 (1)
N(1)	4 <i>a</i>	4558 (11)	3931 (6)	500 (2)	25 (1)
C(1)	4 <i>a</i>	3339 (13)	4850 (7)	887 (2)	21 (1)
C(2)	4 <i>a</i>	4064 (12)	4409 (7)	1382 (2)	21 (1)
N(2)	4 <i>a</i>	6019 (10)	3087 (6)	1493 (2)	23 (1)
C(3)	4 <i>a</i>	7219 (13)	2175 (6)	1106 (2)	25 (1)
C(4)	4 <i>a</i>	6497 (14)	2612 (7)	619 (2)	27 (1)
C(5)	4 <i>a</i>	1293 (12)	6397 (8)	767 (2)	29 (1)
C(6)	4 <i>a</i>	2955 (17)	8179 (8)	688 (3)	42 (2)

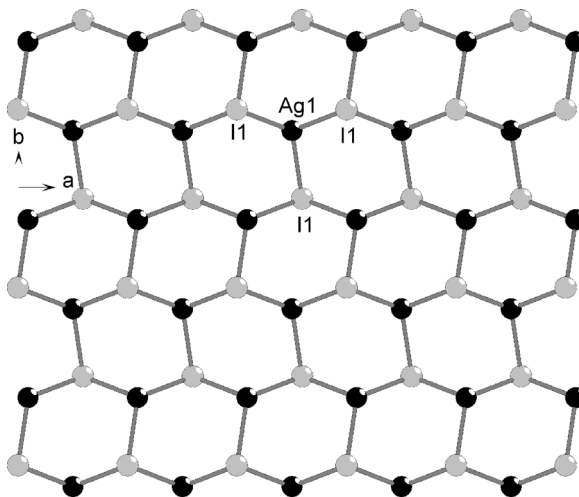
Equivalent isotropic *U* calculated as a third of the trace of the orthogonalized *U*_{ij} tensors.

twinning (BASF parameter: 0.19(5)) but slightly poorer reliability factors. Selected crystal data and results of the structure refinement are shown in Table 1, atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-600156. Copies of the data can be obtained, free of charge,

Table 3. Selected bond lengths (Å) and angles (°) for poly[(μ_3 -iodo)(2-ethylpyrazine-N)-silver(I)].

Ag(1) – I(1)	2.804 (1)	Ag(1) – I(1)	2.821 (1)
Ag(1) – I(1)	2.865 (1)	Ag(1) – N(2)	2.364 (5)
N(2) – Ag(1) – I(1)	123.4 (1)	N(2) – Ag(1) – I(1)	103.5 (2)
N(2) – Ag(1) – I(1)	98.1 (1)	I(1) – Ag(1) – I(1)	106.60 (2)
I(1) – Ag(1) – I(1)	105.97 (2)	I(1A) – Ag(1) – I(1)	120.41 (2)

Fig. 1. Crystal structure of poly[(μ_3 -iodo)(2-ethylpyrazine-N)-silver(I)] with labelling showing the infinite 6³ net parallel to the *a*-*b*-plane (the N-donor ligands are omitted for clarity).

on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk).

Results and Discussion

The 1 : 1 compound poly[(μ_3 -iodo)(2-ethylpyrazine-N)-silver(I)] crystallizes in the orthorhombic space group *P*2₁2₁2₁ with four formula units in the cell and all atoms in general positions. Each Ag atom is coordinated by three I atoms and one N atom of one 2-ethylpyrazine ligand within a strongly distorted tetrahedron (Table 3). The AgI bond lengths which are between 2.804(1) and 2.865(1) Å and the Ag–N bond length of 2.364(5) Å are in the range observed in other AgX coordination polymers (Table 3). The AgX substructure consists of layers which are parallel to the *a*-*b*-plane (Figs. 1 and 2). These layers are built up of six-membered AgI rings which consist of alternating Ag and I atoms and are condensed into a 6³ net. The 2-ethylpyrazine ligands are coordinated to the Ag atoms only with their nitrogen atom which is not

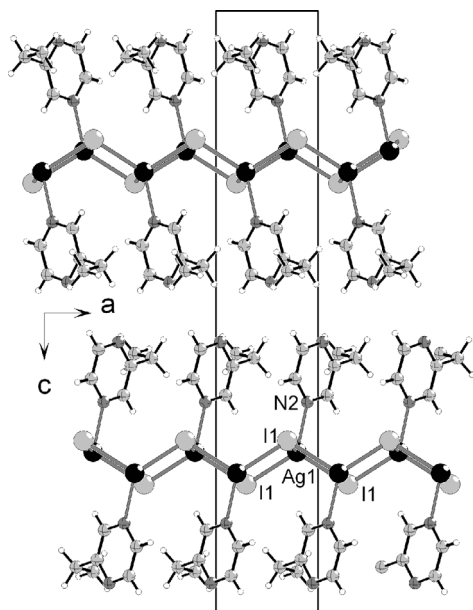


Fig. 2. Crystal structure of poly[(μ_3 -iodo)(2-ethylpyrazine-N)-silver(I)] with labelling viewed in the direction of the *b*-axis.

neighbouring to the ethyl group. This selectivity can be attributed to steric crowding of the substituent. The AgI-2-ethylpyrazine layers are stacked in the direction of the crystallographic *c*-axis and are connected only by weak Van der Waals interactions (Fig. 2). The mean distance between the layers is about 13.4 Å.

To the best of our knowledge the AgI substructure observed in the title compound is unique in silver(I) halide coordination polymers. In most of such compounds only dimers, or single and double chains

are found [9–14]. There are some AgX compounds reported in literature which also consist of more condensed AgX networks, but in all of these compounds the networks are charged and no layers are observed [20–22]. However, a network with identical topology of the metal halide substructure is found in the copper(I) compound catena[tetrakis(μ_3 -chloro)-bis(μ_2 -fumaronitrile)-tetra-copper(I)] [23]. In contrast to the title compound, in this coordination polymer the CuCl layers are connected by the fumaronitrile ligands into a three-dimensional coordination network.

The thermal reactivity was investigated by DTA-TG-MS measurements, in order to prove if a ligand poor intermediate can be observed. This would be of special interest because a structure can be expected in which the inorganic layers are pillared by the 2-ethylpyrazine ligand. However, on heating the compound in a thermobalance all ligands were emitted in one step without the formation of a ligand poor intermediate compound. Even heating rate dependent measurements gave no hints for a multistep process. It might be that the nitrogen atom which is not involved in the Ag coordination is protected by the bulky ethyl group and therefore bridging of the layers *via* μ_2 -N,N' coordination is not favourable.

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