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Unique Ag–C bonds, thermal, fluorescence, structural and solution studies of two-dimensional silver(I) coordination polymer

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Abstract

A 2D polymer with unique Ag–C bonds, $[Ag(\mu_4-DPOAc)]_n$ (1) [DPOAc = diphenylacetate], has been synthesized and characterized and its structure was determined by X-ray crystallography. In addition to the coordination to the O atoms of DPOAc the Ag atoms also form strong η^1 Ag–C π bonds and exhibit weak Ag–Ag interactions, resulting in the formation of O₃CAg···AgO₃C moieties. The thermal stabilities of 1 and of its thallium(I) analogue, $[Tl(\mu_3-DPOAc)]_n$ (2), were studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The ligand and compounds 1–2 are luminescent in the solution state, with emission maxima at 370, 383 and 360 nm, respectively. The results of studies of the stoichiometry and formation of complexes of 1 and 2 in DMF solution were found to be in support of their solid state stoichiometry.

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Keywords: Silver(I); Diphenyl acetic acid; AgI-C bond; Coordination polymer; Fluorescence; Thermal; Solution study

1. Introduction

Metal-organic coordination polymers are attracting a great deal of attention because of their potential as functional materials [1]. In metal-organic crystal engineering, one takes advantage of the coordinating ability of metal centers and organic ligands in order to build new coordination polymers. The main goal in metal-organic crystal engineering is to predict the topology of supramolecular architectures in order to synthesize extended solid-state materials with desired properties. However, there still remain many problems to overcome before the synthesis of coordination polymers with a desired topology is possible. Many parameters are involved in the formation of the metal-organic framework (MOF), such as the metal and its possibilities of coordination, the nature of the counteranion, the metal-to-ligand ratio, the flexibility of the organic building blocks, the number and orientation of the coordinating sites in the organic spacers, and the solvent of recrystallization, among others [2]. Silver(I) ions are regarded as soft acids favoring coordination to soft bases, and give rise to an interesting array of stereochemistries and geometric configurations with the coordination numbers of two to six all occurring. Previous related work on silver(I) coordination polymers has concentrated on the use of nitrogen-donor ligands [3] or oxygen-donor ligands [4] or a combination with both donors [5,6], but the use of a combination of oxygen and carbon-donor ligands are rare [7-11]. Up to now, metalheteroatom, metalcarbon and metal-metal interactions are three of the most important interactions in the construction of Ag polymeric networks in the solid state [12-14]. A search in the Cambridge Structural Database shows only 32 silver(I) complexes with Ag(I)-C_{phenyl} bonds [15] and the most of these silver(I) complexes are monomeric structures and coordination polymers type are rare.

In our last work, we reported the coordination polymer of $DPOAc^-$ with thallium(I) [16]. In the present study, we

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Table 1

report on the synthesis and crystal structure determination of a silver(I) coordination polymer with DPOAc⁻, and we also compare thermal resistance, emission properties and formation constants of these two coordination polymers with each other.



2. Experimental

2.1. Materials and physical techniques

All chemicals were of reagent grade and were used as commercially obtained without further purification. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The thermal behaviour was measured with a PL-STA 1500 apparatus. The luminescent properties were investigated with a Shimadzu RF-5000 spectrofluorophotometer. All UV-Vis spectra were recorded on a computerized double-beam Shimadzu 2550 spectrophotometer, using two matched 10-mm quartz cells. Conductometric measurements were carried out with a Metrohm 712 conductometer equipped with a Julabo F12-MB circulator. Crystallographic measurements were made at 100(2) K using a Bruker AXS SMART APEX CCD diffractometer. The intensity data were collected within the range $2.49 \le \theta \le 30.51^\circ$ using graphite monochromated Mo K α radiation (λ = 0.71073 Å). Accurate unit cell parameters and the orientation matrix were obtained from least-squares refinement using the programs SMART [17] and SAINT [18], and the data were integrated using SAINT [18]. The structure has been solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL [19]. The molecular structure plots were prepared using ORTEP and Mercury [20]. Crystallographic data and details of the data collection and structure refinements are listed in Table 1. The observed anisotropic thermal parameters, the calculated structure factors, and full lists of bond distances, bond angles and torsion angles are given in the supplementary material (see Table 2).

Crystal data and structure refinement for compound 1			
Identification code	1		
Empirical formula	$C_{14}H_{11}AgO_2$		
Formula weight	319.10		
Temperature (K)	100(2)		
Wavelength (Å)	0.71073		
Crystal system	Monoclinic		
Space group	$P2_{1}/c$		
Unit cell dimensions			
$a(\dot{\mathbf{A}})$	11.9677(10)		
$b(\mathbf{A})$	5.6277(5)		
c (Å)	16.6468(13)		
α (°)	90.00		
β (°)	100.2890(10)		
γ (°)	90.00		
Volume (A ³)	1103.14(16)		
Z	4		
Density (calculated) $(g \text{ cm}^{-3})$	1.921		
Absorption coefficient (mm ⁻¹)	1.810		
F(000)	632		
Crystal size (mm ³)	$0.16 \times 0.22 \times 0.31$		
θ Range for data collection (°)	2.49-30.51		
Index ranges	$-15 \leqslant h \leqslant 15, -7 \leqslant k \leqslant 7,$		
	$-21 \leq l \leq 22$		
Reflections collected	2737		
Independent reflections	2675		
Absorption correction	Multi-scan		
Maximum and minimum	0.749 and 0.573		
transmission			
Refinement method	Full-matrix		
	Least-squares on F^{2}		
Data/restraints/parameters	2737/0/154		
Goodness-of-fit on F^2	1.232		
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0294, wR_2 = 0.0642$		
<i>R</i> Indices (all data)	$K_1 = 0.0304, wK_2 = 0.0647$		
Largest difference and peak, hole $(e \text{ Å}^{-3})$	0.753 and -0.440		

2.2. Synthesis of $[Ag(\mu_4-DPOAc)]_n$ (1)

In 20 ml CH₃CN 0.212 g (1 mmol) 2,2-diphenylacetic acid were mixed and stirred with a solution of 0.057 g (1 mmol) KOH in 3 ml H₂O to form a clear solution. Addition of 0.170 g (1 mmol) AgNO₃ in 5 ml H₂O produced a clear solution. The resulting solution was stirred and then allowed to stand in darkness at room temperature to evaporate for several days to obtain suitable crystals. The crystals were washed with acetone and air dried, m.p. = 235 °C. Yield: 0.112 g (35%). IR (selected bands;

Table 2 Selected bond lengths (Å) and angles (°) for compound 1

		() 1	
Ag(1)–O(1)	2.2063(17)	O(1)-Ag(1)-C(5)	113.18(7)
Ag(1)–O(2)	2.2519(17)	O(2) - Ag(1) - C(5)	87.87(7)
Ag(1)–O(2)	2.4872(18)	O(2)-Ag(1)-C(5)	75.12(7)
Ag(1)-C(5)	2.710(3)	O(1) - Ag(1) - Ag(1)	85.19(5)
Ag(1)-Ag(1)	2.8463(4)	O(2) - Ag(1) - Ag(1)	77.25(5)
O(1)-Ag(1)-O(2)	157.11(7)	O(2) - Ag(1) - Ag(1)	149.80(4)
O(1)-Ag(1)-O(2)	117.77(6)	C(5)-Ag(1)-Ag(1)	115.56(6)
O(2)-Ag(1)-O(2)	74.97(7)		

in cm⁻¹): 554m, 637m, 691s, 723s, 752m, 1023w, 1068w, 1267w, 1328w, 1374vs, 1437w, 1479m, 1531vs and 1589m. Anal. Calc. for $C_{14}H_{11}AgO_2$: C, 52.64; H, 3.45; Ag, 33.84. Found: C, 52.50; H, 3.34; Ag, 33.60%.

2.3. Synthesis of $[Tl(\mu_3-DPOAc)]_n$ (2)

Compound **2** was prepared using a reported method [16] for evaluation of other data such as thermal stability, luminescent properties and solution study, m.p. = 157 °C. IR (selected bands): 642m, 694s, 734s, 1361s, 1484m, 1532vs, 1563s, 1587s, 2885w, 3050w. Anal. Calc. for $C_{14}H_{11}O_2TI$: C, 40.42; H, 2.64, Tl, 49.10. Found: C, 40.82; H, 2.56; Tl, 50.10%.

3. Results and discussion

3.1. Structure description

The reaction between diphenylacetate (DPOAc⁻) and Ag(NO₃) provided a crystalline material of the general formula $[Ag(\mu_4-DPOAc)]_n$ (1). Determination of the structure of 1 by X-ray crystallography showed the complex to be a novel two-dimensional polymer (Figs. 1 and 2). The silver atoms can be considered to be three-coordinate. The carboxylate groups of the DPOAc⁻ ligand act as a bridging group where each oxygen atom of the carboxylate group coordinates to a silver(I) ion, and one of these oxygen atoms also bridges to one other silver atom (Figs. 1 and 2).

With a low coordination number of 3 for the large silver(I) ions in 1, one tends to look for secondary interactions that could possibly relieve this coordinative unsaturation. A search was made generally for Ag···Ag and Ag···C approaches and it appears that Ag in 1 may also be involved in both Ag···Ag and Ag···C (η^1) interactions with the silver atoms and phenyl groups of neighboring molecules (Figs. 1 and 2).

The Ag–Ag interactions in compound 1, Ag1–Ag1 = 2.8463(4) Å, (Table 2) are longer than the Ag–Ag distances in similar dinuclear complexes (i.e., 2.704(2), 2.669(1), and 2.726(1) Å) [21–25] and slightly shorter than those in the polymeric structure [26–29]. The relatively short Ag–Ag bonds found here may thus be considered to be only $d^{10} \cdots d^{10}$ noncovalent interactions [21–29].

A general search was made for Ag–C approaches in compound 1 and it appears that the Ag atoms may unexpectedly be involved in an η^1 interaction with the C_{phenyl} atom of neighboring molecules with a Ag(1)–C(5) distance of 2.710(3) Å, thus augmenting the Ag¹ Ag₁O₃ coordination spheres and compound 1 can be considered to contain silver atoms with fourfold coordination and a O₃CAg···AgO₃C environment. In compounds with similar bonds the Ag–C distances are in the range of 2.40–2.70 Å [30–33], in [Ag(benzene)ClO₄] for example they are 2.496 and 2.634 Å [24]. Some other Ag(I) polymeric complexes with Ag–C(sp²) bonded polycyclic aromatic ligands have been reported to have mean Ag–arene distances of 2.82– 3.37 Å [34–39]. Thus, strong monohapto aromatic coordination of Ag atoms in the compound 1 can be considered and appears to be yet another factor which can make varying contributions to the construction of an organic–inorganic coordination polymer.

The structure of compound 1 may also be considered as a coordination polymer of Ag(I) consisting of one-dimensional linear chains constructed of carboxylate group bridging, running parallel to the *b*-axis and the individual polymeric chains are almost parallel to each other and further bridged by Ag–C bonds, resulting in a two-dimensional framework as shown in Fig. 2.

The structure of compound $[Tl(\mu_3-DPOAc)]_n$ (2) has recently been reported [16]. The single-crystal X-ray data of compound 2 show the coordination number in the Tl^I ions to be five, the thallium atoms have an irregular coordination sphere with a stereo-chemically active lone pair and hexa-hapto (η^6) interactions, thus attaining a total hapticity of 11 in a C₆O₅Tl coordination environment.

A striking difference between compound 1 and 2 is that the DPOAc⁻ anion in compound 1 acts as a fourfold donating bridging ligand, connecting four Ag^I ions in a μ -4,3 mode (Fig. 1b and Scheme 1a), whereas each DPOAc⁻ anion in compound 2 acts as a pentadentate ligand, connecting three Tl^I ions. The carboxylate groups of the DPOAc⁻ ligand in compound 2 act as both a bidentate chelating and a bridging group in a μ -3,2 mode (Fig. 1b and Scheme 1a). Another difference between compound 1 and 2 is that the phenyl rings in compound 1 involve in a strong η^1 interaction with Ag^I whereas the phenyl rings in compound 2 take part in a weak hexa-hapto (η^6) interactions with Tl^I.

3.2. Thermogravimetric analysis

To examine the thermal stability of the two new compounds, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 700 °C in a static atmosphere of air (Figs. 3 and 4). Compound **1** is stable up to 235 °C. The TG curve exhibits a distinct decomposition stage between 235 and 480 °C with a mass loss of 63.0% (calcd. 63.6% for the formation of Ag₂O). DTA curve displays three distinct exothermic peaks at 240, 300 and 450 °C and a endothermic peak at 600 °C. Compound **2** is stable up to 181 °C. TG curve exhibits a distinct decomposition stage between 193 and 550 °C with a mass loss of 48.5%(calcd. 48.9% for the formation of Tl₂O). The DTA curve displays a distinct endothermic peak at 181 °C and two exothermic peaks at 227 and 339 °C (see Figs. 3 and 4).

3.3. Luminescent properties

The fluorescence spectra of compounds 1 and 2 have been studied in DMF solution. The compounds show broad emission bands with the maximum intensities at 383 and 360 nm upon excitation at 300 nm, respectively (Fig. 5). These fluorescent emissions can be tentatively



Fig. 1. (a) ORTEP diagram, (b) view of the Ag environment; the phenyl groups have been omitted for clarity, (c) space-filling representations of compound 1, close approaches of Ag to the one of carbon atoms of phenyl rings can be seen. (Ag = violet, O = red, C = gray) i: -x, y + 1/2, -z + 1/2; ii: -x, -y, -z; iii: x, -y + 1/2, z + 1/2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

assigned to the intraligand fluorescence emission as similar emissions at 370 nm upon the same excitation at 300 nm (Fig. 5) can also be observed for the free ligand HDPOAc. The strong interactions of Ag^{I} with the ligand $DPOAc^{-}$ probably also cause this difference in the luminescent properties of the two compounds.

01

01ⁱⁱ



Fig. 2. A fragment of the two-dimensional layer in compound 1, showing the Ag-C and Ag-Ag interactions. H atoms are omitted for clarity.



Scheme 1. The coordination mode of ligand $DPOAc^-$ (a) in the compound 1 and (b) in the compound 2.



Fig. 3. Thermal behaviour of compound $[Ag(\mu_4-DPOAc)]_n$ (1).

3.4. Solution studies

The formation and stoichiometry of the compounds 1 and 2 in DMF solution was investigated by both conductometric and spectrophotometric methods. The conductivity of a 5.0×10^{-5} M solution of silver(I) nitrate and thallium(I) nitrate in DMF were monitored as a function of [DPOAc⁻]/[Ag^I] and [DPOAc⁻]/[Tl^I] mole ratio, respectively at 25.00 ± 0.05 °C and the resulting plot is shown in Fig. 6. As it is seen, the initial conductivity is relatively



Fig. 4. Thermal behaviour of compound $[Tl(\mu_3-DPOAc)]_n$ (2).



Fig. 5. The fluorescence spectra of ligand HDPOAc and compounds 1–2 in DMF solution. Bands 1 for $[Ag(\mu_4-DPOAc)]_n$ (2) for compound $[Tl(\mu_3-DPOAc)]_n$, room temperature, $\lambda_{exc} = 300$ nm.

low, probably due to some degree of ion pairing which is common in solvents like DMF. Addition of the ligand to the metal salt solution then causes an increase in the solution conductivity possessing a distinct inflection point at a molar ratio of about one, indicating the formation of 1:1



Fig. 6. Conductivity vs. [HDPOAc]/[M^+] mole ratio plot DMF solution for compounds 1 and 2.

complexes in solution. The electronic absorption spectra of the ligand (DPOAc⁻) in the presence of increasing concentration of silver(I) and thallium(I) ion in DMF at room temperature is shown in Figs. 7 and 8, respectively. As is obvious, the strong absorption of the ligand at 264 nm increases with increasing concentration of the metal ion. The resulting absorbance against $[Ag^+]/[DPOAc^-]$ and $[TI^+]/[DPOAc^-]$ mole ratio plots, shown in the inset of Figs. 7 and 8, respectively, revealed an indistinct inflection point at metal-to-ligand molar ratios of about 1, emphasizing the formation of a 1:1 complex in solution.

For evaluation of the conditional formation constants, the mole ratio data obtained by the two different physicochemical methods employed were fitted to the previously



Fig. 7. (a) Electronic absorption spectra of ligand HDPOAc in DMF $(1.4 \times 10^{-4} \text{ M})$ in the presence of increasing concentration of silver(I) ion at room temperature. (b) Corresponding mole ratio plot at 264 nm.



Fig. 8. (a) Electronic absorption spectra of ligand HDPOAc in DMF $(1.4 \times 10^{-4} \text{ M})$ in the presence of increasing concentration of thallium(I) ion at room temperature. (b) Corresponding mole ratio plot at 264 nm.

reported equations [40,41] using a non-linear least-squares curve fitting program KINFIT [42]. The conditional formation constants were evaluated as $\log K = 2.66 \pm 0.13$ and $\log K = 2.55 \pm 0.004$ compound for 1 and $\log K = 0.35 \pm 0.04$ and $\log K = 0.38 \pm 0.01$ for compound 2 from the conductometric and spectrophotometric methods, respectively. These results show that the silver(I) tendency to coordinate ligand DPOAc⁻ is more than thallium(I) in solution, probably due to more positive charge density of Ag⁺ compared with Tl⁺ ion. The strong interactions of Ag^I with the ligand DPOAc⁻, probably also cause the higher thermal stability of compound 1 as compared to compound 2 in the solid sate.

4. Conclusions

A organosilver(I) complex with an aromatic carboxylate ligands based coordination network was synthesized and characterized. The aromatic carboxylate ligand in this complex exhibits a less-common η^1 -coordination mode of the phenyl rings, in addition to the normal carboxylate coordination modes. The complex shows interesting properties analogous to those of silver(I) complexes of polycyclic aromatic compounds reported previously [43]. The results of studies of the stoichiometry and formation of 1 and 2 in DMF solution were found to be in support of their solid state stoichiometry and show that the formation constant of the silver(I) compound is much larger when compared with the thallium(I) one. Compounds 1-2 and ligand HDPOAc have shown luminescent properties in DMF solution. On this perspective, further systematic study of the Ag(I) coordination chemistry of this type of ligands is ongoing.

5. Supplementary material

CCDC 639612 contain the supplementary crystallographic data for 1. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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