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Coordination Silver Polymer with the Bridging Anion of Oxadiazolylacrylic Acid: Synthesis, Crystal Structure, and Luminescence Properties

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Abstract—Metal complex [AgL] (**I**) is synthesized by the reaction of $AgNO_3$ with 3-(5-furyl-1,3,4-oxadiazol-2-yl)acrylic acid (HL, $C_9H_6N_2O_4$), and its crystal structure is determined (CIF file CCDC no. 1426528). The crystals are monoclinic, space group $P2_1/n$, $a = 4.946(1)$, $b = 20.084(1)$, $c = 9.015(1)$ Å, $\beta = 92.32(1)°$, $V = 894.482$ Å^3, $\rho_{calcd} = 2.442$ g/cm^3, $Z = 4$. In structure **I**, pairs of centrosymmetric silver atoms are bound by bidentate-bridging oxygen atoms of two anions L into dimeric blocks. The Ag–Ag distance in the dimer is 2.854(1) Å. The coordination sphere of Ag^+ contains two oxygen atoms, one silver atom, and one nitrogen atom of the diazolyl fragment of the adjacent anion. The coordination polyhedron of Ag^+ is a strongly distorted tetrahedron. The molecular packing of crystal **I** is built of infinite ribbons $(AgL)_n$ extended along the direction [001]. The photoluminescence spectrum of compound **I** contains intense bands about 550 nm corresponding to the green spectral range and less intense bands at 425 and 485 nm.

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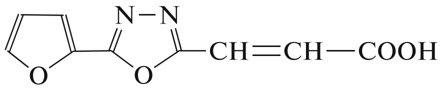
INTRODUCTION

Coordination compounds of metals with carboxylic acids (carboxylates) form a large class of organometallic compounds that find wide use in various areas of science and technology [1, 2]. Their structures depend on both the nature of the metal and acid and the synthesis conditions [3, 4]. The metal complexes based on unsaturated carboxylic acids are of great interest in the recent time [5, 6]. These compounds find use in catalysis [7, 8], in the production of photoactive materials [9–11] and molecular magnets, and in the simulation of bioactive molecules. Many monomeric and polymeric carboxylates are used as precursors for the preparation of nanocomposite and hybrid materials [12–15] applied in optoelectronics, cosmic technique, etc. In addition, an unsaturated acid molecule contains heterocyclic fragments, which extends the range of possible structures of the complexes due to the additional coordination of the heterocycle atoms. Several donor centers in the molecule allows the complexing metal to form bonds. In this work, the new substituted acrylic acid containing the 1,3,4-oxadiazolyl fragment was chosen as a ligand. It is known that this fragment is photoactive and can be in some electroluminescent devices named OLEDs [16–20].

The silver ions are bound to each other by carboxylate bridges in the dimeric silver carboxylates $Ag_2(RCO_2)_2$, which are used as secondary building blocks for the formation of coordination polymers with N-containing ligands [21, 22]. The d^{10}–d^{10} interactions with short metal–metal contacts are observed in several bi- and polynuclear coordination compounds of d^{10} metals with carboxyl anions. The Ag–Ag distances in the binuclear silver complexes range from 2.89 to 3.09 Å, and the Ag–Ag distance in metallic silver is 2.89 Å [23]. Similar metal–metal contacts were observed in the binuclear Cu(I) and Au(I) complexes. Therefore, the terms argentophilicity, cuprophilicity, and aurophilicity designating short metal–metal contacts appeared in the literature. Similar Ag–Ag contacts were found in a series of works devoted to the study of the structures of silver coordination compounds with different bridging acidic anions [24–27].

A new ligand system, 3-(5-furyl-1,3,4-oxadiazol-2-yl)acrylic acid (HL, $C_9H_6N_2O_4$), was synthesized as an unsaturated acid for the preparation of the coordination silver compound.



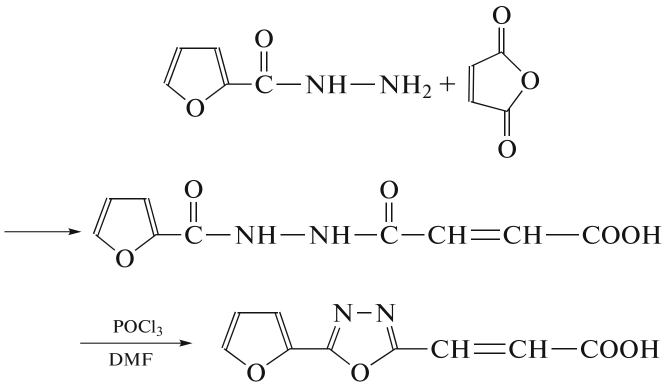
(HL)

This acid contains the carboxyl group capable of forming dimeric blocks and the diazolyl fragment with two nitrogen atoms. Therefore, the coordination of the nitrogen atom to the silver ion with the formation of coordination polymer compounds of unusual structure can be expected.

In this work, we synthesized oxadiazolylacrylic acid and the new coordination polymer compound [AgL] (**I**), determined the structure of the latter, and studied the photoluminescence (PL) spectra of HL and compound **I**.

EXPERIMENTAL

Synthesis of HL was carried out via the scheme



A solution of maleic anhydride (0.02 mol) in CH_3COOH (4 mL) was added to a solution of 2-furancarboxylic acid hydrazide (0.02 mol) in CH_3COOH (5 mL). The formation of a white precipitate and heating of the mixture were observed immediately. The mixture was stirred for 1.5 h at room temperature. The precipitate was separated and washed two times with CH_3COOH and C_2H_5OH. The obtained acyl hydrazide was introduced without additional purification into the reaction with $POCl_3$ in DMF (7 mL). The formed solution was stirred for 2 h at room temperature and poured to H_2O (50 mL). The precipitate formed was separated, washed two times with H_2O, and recrystallized from C_2H_5OH. The yield of colorless crystals of the product was 72% ($T_m \approx$ 205–206°C). According to the elemental analysis data, the product corresponds to the composition $C_9H_6N_2O_4$.

For $C_9H_6N_2O_4$			
anal. calcd., %:	C, 52.43;	H, 2.93;	N, 13.59.
Found, %:	C, 52.07;	H, 3.00;	N, 13.36.

^{1}H NMR (DMSO-d_6), δ, ppm: 6.78 (s, 1 H, fur.), 6.84 (d, 1 H, CH=CH, $^3J_{HH}$ = 5.5 Hz), 7.42 (s, 1 H, fur.), 7.48 (d, 1 H, CH=CH, $^3J_{HH}$ = 5.6 Hz), 8.11 (s, 1 H, fur.), 13.24 (s, 1 H, OH).

Synthesis of compound I. A 0.1 M solution of NBu_4OH in methanol was added dropwise with stirring to a suspension of HL (0.29 g, 1.44 mmol) in acetonitrile (7 mL) at ~40°C until the dissolution of the acid. A solution of $AgNO_3$ (reagent grade, 0.24 g, 1.44 mmol) in acetonitrile (5 mL) was added to the obtained solution. A finely crystalline precipitate that formed was filtered off, washed with a small amount of acetonitrile, and dried in air. The dried precipitate was recrystallized at ~40°C from an acetonitrile–ethanol (6 : 1) mixture with the addition of an aqueous solution of NH_4OH. The obtained solution was filtered and stored in the dark at room temperature under the conditions of the slow evaporation of the solvents. The formed prismatic crystals were separated from the solution, washed with a small amount of acetonitrile, and dried in air. According to the elemental analysis data, the compound corresponds to the composition $Ag(C_9H_5N_2O_4)$ (**I**).

For $C_9H_5AgN_2O_4$

anal. calcd, %:	C, 34.63;	H, 1.60;	N, 8.97.
Found, %:	C, 34.60;	H, 1.90;	N, 8.70.

X-ray diffraction analysis of I. The experimental material was obtained on an Enraf-Nonius CAD-4 automated diffractometer. The structure was solved by a direct method and refined by least squares in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [28]. Positions of the hydrogen atoms were calculated geometrically and included into the refinement by the riding model. The unit cell parameters and selected experimental characteristics are presented in the table. The full crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC 1426528; http://www.ccdc.cam.ac.uk/deposit/).

The PL spectra were recorded at room temperature on a PerkinElmer LS-55 spectrometer (λ_{exc} = 200–800 nm, λ_{em} = 200–900 nm, instrument resolution 0.5 nm, slit d = 10–12 nm). An attachment for solid-state samples was used.

RESULTS AND DISCUSSION

In structure **I**, the pairs of the centrosymmetric silver atoms are bound by the bidentate- bridging oxygen atoms of the carboxyl group of two anions L into dimeric blocks. The Ag–Ag distance in the dimer is 2.854(1) Å. The coordination polyhedron of the Ag^+ ion contains two oxygen atoms, one silver atom, and one nitrogen atom of the diazolyl fragment of the adjacent anion (Fig. 1). The coordination polyhedron of Ag^+ is a strongly distorted tetrahedron (Ag(1)–O(1) 2.220(3), Ag(1)–O(2)$^{\#1}$ 2.211(3), Ag(1)–N(1)$^{\#2}$ 2.426(5), Ag(1)–Ag(1)$^{\#1}$ 2.854(1) Å, angles O(2)$^{\#1}$Ag(1)O(1) 162.9(2)°, N(1)$^{\#2}$Ag(1)Ag(1)$^{\#1}$ 167.8(1)°, other tetrahedral angles are in a range of 77.7(1)°–98.9(1)° (symmetry transforms of the atoms:

Selected crystallographic data and experimental characteristics for structure **I**

Parameter	Value
FW	313.02
Color, habitus	Colorless, block
Crystal size, mm	0.16 × 0.08 × 0.05
Crystal system	Monoclinic
Space group	$P2_1/n$
Cell parameters:	
a, Å	4.946(1)
b, Å	20.084(1)
c, Å	9.015(1)
β, deg	92.32(1)
V, Å^3	894.8(2)
Z, ρ_{calcd}, g/cm^3	4, 2.323
μ_{Mo}, mm^{-1}	2.251
F(000)	608
Temperature, K	293
Radiation (λ, Å)	MoK_α (0.71073), graphite monochromator
Scan mode	ω
Range of θ, deg	2.0–29.97
Index range	$0 \leqslant h \leqslant 6$, $-28 \leqslant k \leqslant 28$, $-12 \leqslant l \leqslant 2$
Total number of reflections/independent	3639/1807 (R_{int} = 0.0449)
Number of reflections with $I \geqslant 2\sigma(I)$	1119
Number of refined parameters	145
GOOF for F^2	0.712
R ($I \geqslant 2\sigma(I)$)	R_1 = 0.0272, wR_2 = 0.0741
R (all data)	R_1 = 0.0798, wR_2 = 0.1064
Residual electron density (max/min), e/Å^3	0.384/–0.535

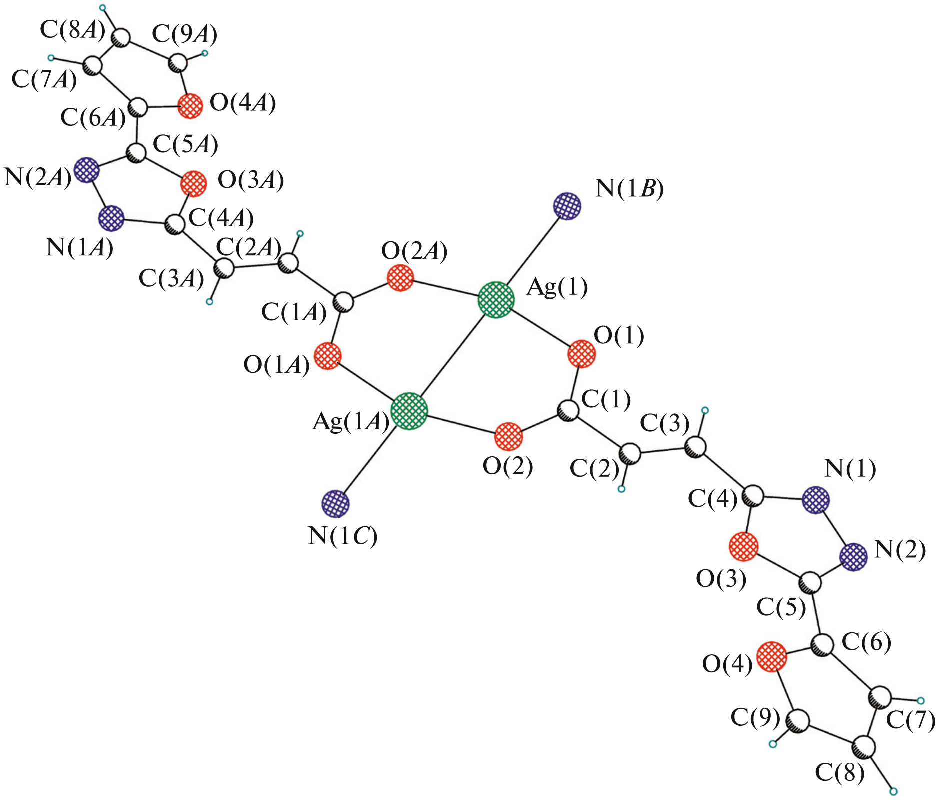


Fig. 1. Coordination environment of the silver atoms in structure **I**.

$^{\#1}\,-x, -y, -z$; $^{\#2}\,1-x, -y, -z$)). In addition to the carboxyl group resulting in the formation of the dimeric blocks, anion L^-contains the diazolyl fragment with two nitrogen atoms, one of which, N(1), as shown above, is coordinated to the silver ion. Due to this, anions L^- perform the bridging function between the adjacent dimeric blocks and join them into infinite ribbons $[AgL]_n$. The molecular packing (Fig. 2) represents infinite ribbons extended along the direction [001] and alternating along the direction [010] with an interval of 1/2*b* and different orientations of the dimeric blocks. The orientation of the latter is clearly shown in the projection of the structure along the *z* axis (Fig. 3). Thus, the above presented data confirm the argentophilicity of the obtained metal complex **I**.

The electronic absorption spectra and PL spectra were recorded (Fig. 4) to study the photochemical properties of the synthesized compounds. The both spectra are characterized by an intense band at 550 nm corresponding to the green spectral range and less intense bands at 425 and 485 nm. In the case of compound **I** (curve *2*), the intensity of the bands is substantially lower than that for HL (curve *1*). This indicates that the Ag^+ ion does not act as a sensitizer for the coordination of the acid, but an opposite effect is observed and is manifested as luminescence "quenching." It is considered that the intensity of the luminescence bands increased because of a decrease in the nonradiative energy loss upon the coordination of the luminescing ligand to the metal (especially in the case of chelation). In this case, we can believe that a more rigid structure than that in coordination compound **I** is formed in the solid state in acid HL due to a system of hydrogen bonds O–H···O and O–H···N. This can result in an increase in the band intensity in the spectrum of HL compared to that of the silver salt. The absence of shifts of the bands in the PL spectra of the acid and compound **I** means that the replacement of H^+ by Ag^+ does not affect the luminescence of the oxadiazolyl fragment. A similar effect (the same position of the luminophore band for the ligand and the compound with silver ions) has previously been observed for the complexes with the imidazole derivatives [29].

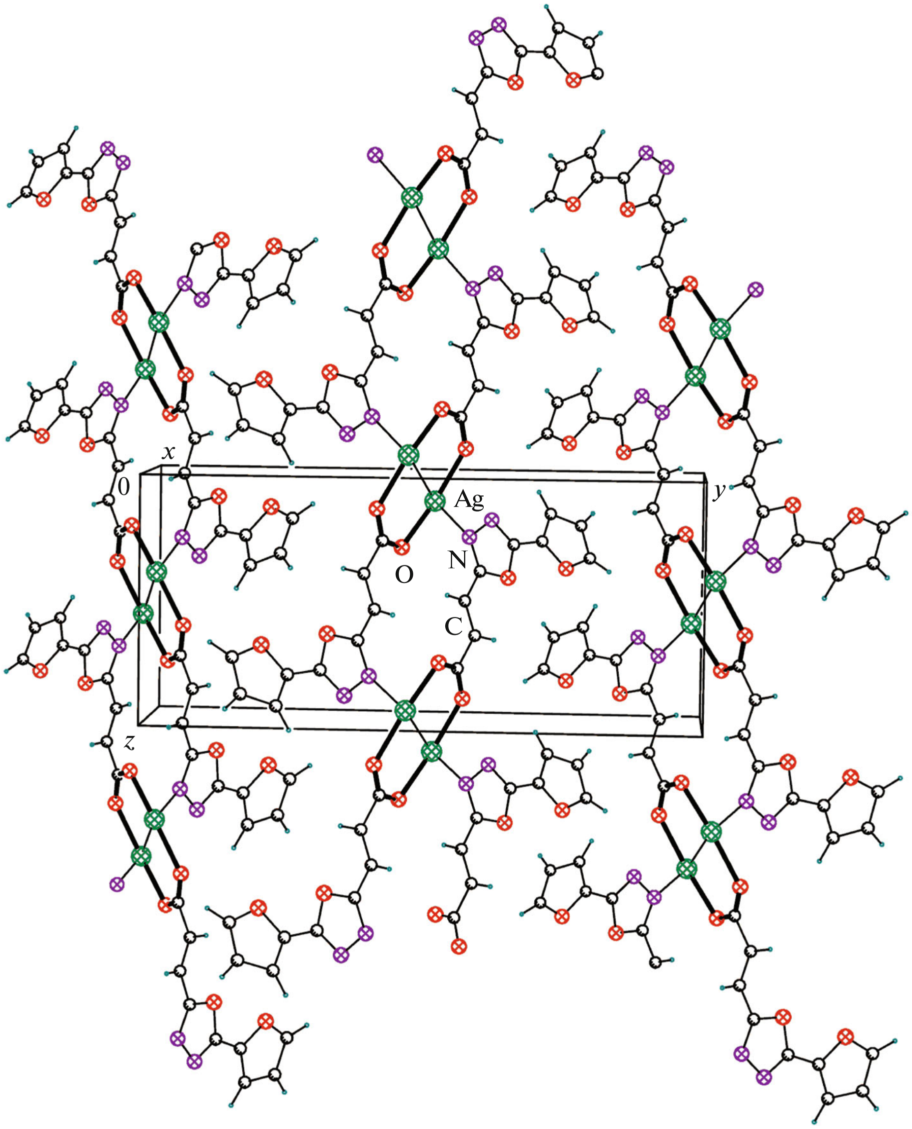


Fig. 2. Infinite ribbons $[AgL]_n$ with dimeric blocks (the latter are shown by solid).

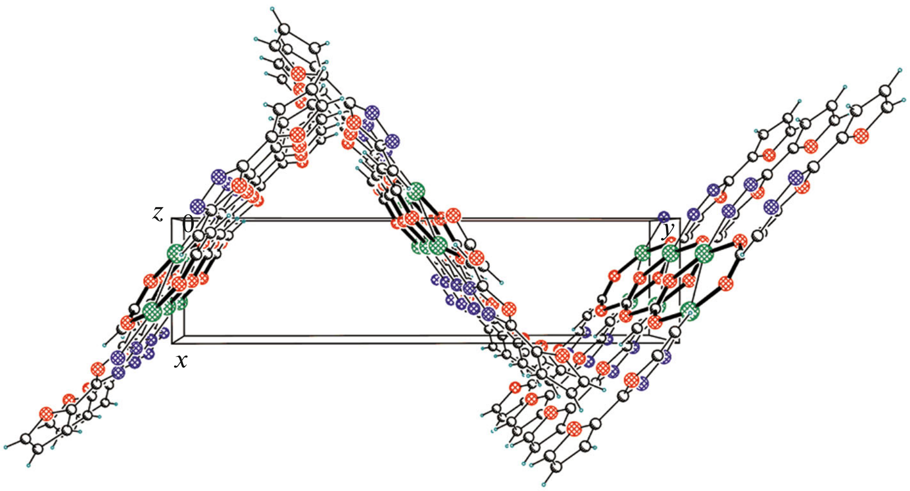


Fig. 3. Molecular structure of compound **I** along the direction [001].

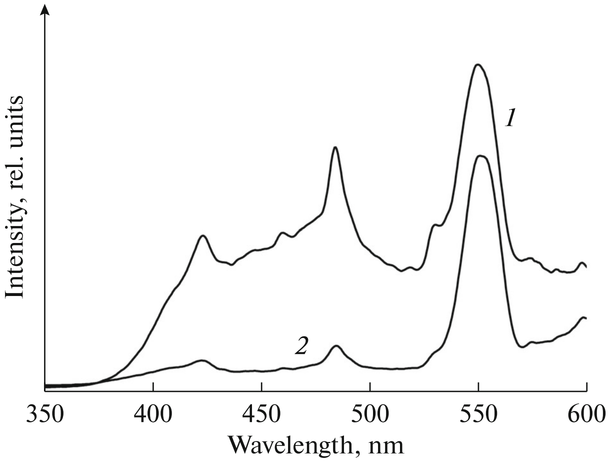


Fig. 4. Photoluminescence spectra of acid LH (curve *1*) and compound **I** (curve *2*). Excitation wavelength λ_{exc} = 270 nm.

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