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COORDINATION COMPOUNDS

Four- and Five-Coordinate Metal Atoms in a Supramolecular Polymeric Assembly of Silver(I) with (4-Methyl-2-quinolylthio)acetate

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Abstract—The coordination compound $[Ag_2L_2(H_2O)_2] \cdot 2H_2O$ (**I**), L = $C_{12}H_{10}NO_2S$ has been synthesized by the reaction of $AgNO_3$ with 4-methyl-2-quinolylthioacetic acid (HL) preliminarily neutralized with an equimolar amount of NBu_4OH. Its crystal structure has been determined, and luminescence properties have been studied. Crystals of **I** are monoclinic, space group $C2/c$, $a = 31.239(6)$ Å, $b = 12.056(2)$ Å, $c = 16.846(3)$ Å, $\beta = 122.17(3)°$, $V = 5370.4(2)$ Å^3, $\rho_{calc} = 1.861$ g/cm^3, $Z = 16$. The structure is formed by two crystallographically nonequivalent silver atoms Ag(1) and Ag(2) and two tridentate bridging ligands L coordinated through the S, N, and O atoms. These atoms, together with water molecules, form the coordination environments of the metal atoms with CN = 5 and 4, respectively. The Ag^+ ions and the tridentate ligands form infinite $[Ag_4L_4]_n$ bands extended in the [001] direction. The presence of outer-sphere water molecules involved in O–H···O hydrogen bonding is responsible for the formation of a supramolecular framework structure. The photoluminescence spectrum of compound **I** shows two bands at ~450 and ~485 nm corresponding to the blue spectral range.

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The development of the chemistry of coordination polymers calls for studying different factors that have an effect on structure formation, such as coordination properties of metals, the polyfunctionality of ligands, and their steric properties. Carboxylic acids are widely used for synthesis of various metal complexes [1, 2]. Carboxylates are of interest not only as objects for basic research but also as candidates for use as secondary blocks in synthesis of coordination polymers as well as precursors of nanocomposite and hybrid materials [3, 4].

The introduction of donor atoms (N or S) into a carboxylic acid chain can afford coordination polymers of higher dimensions (2D, 3D) and unusual structural compositions. Previously [5], we have shown that in the coordination polymer of silver oxodiazolylacrylate, pairs of centrosymmetric silver atoms are bound by bidentate bridging oxygen atoms of the carboxylate group of two anions to form dimeric blocks with the Ag–Ag distance of 2.854(1) Å. Each of the Ag^+ ions has a distorted tetrahedral environment formed by two carboxylate oxygen atoms and the silver atom and the diazolyl nitrogen atom of the neighboring anion. There are numerous examples of square coordination of Ag^+ ions [6]. Five-coordinate Ag(I) complexes are very rare [6]. The coordination sphere of Ag^+ is mainly composed of halide ions and O- and N-containing ligands. Known examples of coordination of S-containing organic ligands are few in number [7, 8]. It has been shown in [9] that weak silver–ligand interactions and crystal lattice forces (energy) have a large effect on the structure of the resulting compounds.

In this paper, we report the synthesis, crystal structure, and photoluminescence spectra of the silver coordination polymer $[Ag_2L_2(H_2O)_2] \cdot 2H_2O$ (**I**).

EXPERIMENTAL

Synthesis of HL (4-methyl-2-quinolylthioacetic acid) was carried out as described in [10] by the scheme:

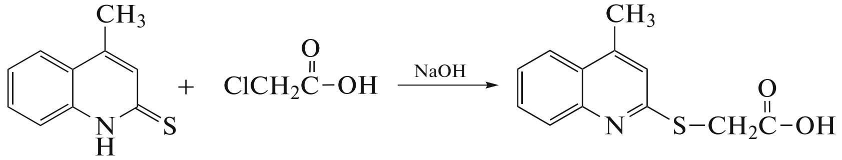

Table 1. Crystallographic data and experimental details for structure **I**

FW	367.17
Color, shape	Colorless, prism
Crystal size, mm	0.20 × 0.11 × 0.09
Symmetry system, space group	Monoclinic, *C*2/*c*
Unit cell parameters:	
a, Å	31.239(6)
b, Å	12.056(2)
c, Å	16.846(3)
β, deg	122.17(3)
V, $Å^3$	5370.4(2)
Z	16
ρ_{calc}, g/cm^3	1.861
μ_{Mo}, mm^{-1}	1.665
F(000)	3008
T, K	293(2)
Radiation, (λ, Å)	MoK_α (0.71073), graphite monochromator
Scan mode	ω
θ range, deg	2.08–27.96
Index ranges	$-41 \le h \le 35$, $-1 \le k \le 15$, $-1 \le l \le 22$
Total number of reflections/unique	7757/6465 [*R*(int) = 0.0610]
Completeness to θ = 27.96°	100%
Number of reflections with $I \ge 2\sigma(I)$	2463
Correction for absorption	Semiempirical from equivalents
Transmission (T_{min}/T_{max})	0.3251/0.5430
Data/discarded/parameters	3290/0/334
GOOF on F^2	0.867
R [$I \ge 2\sigma(I)$]	$R1 = 0.0427$, $wR2 = 0.1081$
R (all data)	$R1 = 0.2095$, $wR2 = 0.1683$
Residual electron density (max/min), e/$Å^3$	1.392/–0.979

A mixture of 0.8 g (20 mmol) NaOH in 4 mL of water, 0.875 g (5 mmol) 4-methyl-2-thioxo-1*H*-quinoline, and 0.59 g (6.25 mmol) of chloroacetic acid was heated in a water bath for 2 h. Then, the mixture was cooled, diluted with 20 mL of water, filtered, and acidified with hydrochloric acid to pH 5. The precipitate was filtered off and washed with water. Yield, 97% (1.13 g, mp 115–116°C).

IR, ν, cm^{-1}: 2600–3200 (OH); 1714 (C=O); 1598, 1553 (C=N and C=C).

^1H NMR (DMSO-d_6), δ, ppm: 2.80 (s, 3H, CH_3), 5.03 (s, 2H, CH_2), 6.51 (s, 1H, CH arom.), 7.38–8.27 (m, 4H, arom.).

Synthesis of I. Reagent grade $AgNO_3$, 1 M BuN_4OH solution in methanol, and 4-methyl-2-quinolylthioacetic acid were used. To a suspension of 0.23 g (0.98 mmol) of the acid in 10 mL of acetonitrile, 1 mL of the BuN_4OH solution was added, and the reaction mixture was heated for 0.5 h at ~40–45°C. The resulting transparent solution was introduced, with stirring, into a solution of 0.17 g (1 mmol) of silver nitrate in 5 mL of MeCN, which was accompanied by the formation of an amorphous and nonsettleable light yellow reaction product with a brown admixture of silver oxide. To the resulting suspension, an NH_4OH solution was added until the major portion of the amorphous phase was dissolved and its residue coagulated. Then, the liquid phase was decanted and filtered, and the filtrate was kept in the dark at room temperature for slow evaporation of the solvent. The deposited light yellow prismatic crystals was separated from the solution, washed with a small amount of acetonitrile, and dried in air. For $C_{12}H_{14}AgNO_4S$ (**I**) anal. calcd. (%): N, 3.73; C, 38.40; H, 3.73; S, 8.53. Found (%): N, 4.42; C, 39.18; H, 4.35; S, 7.89.

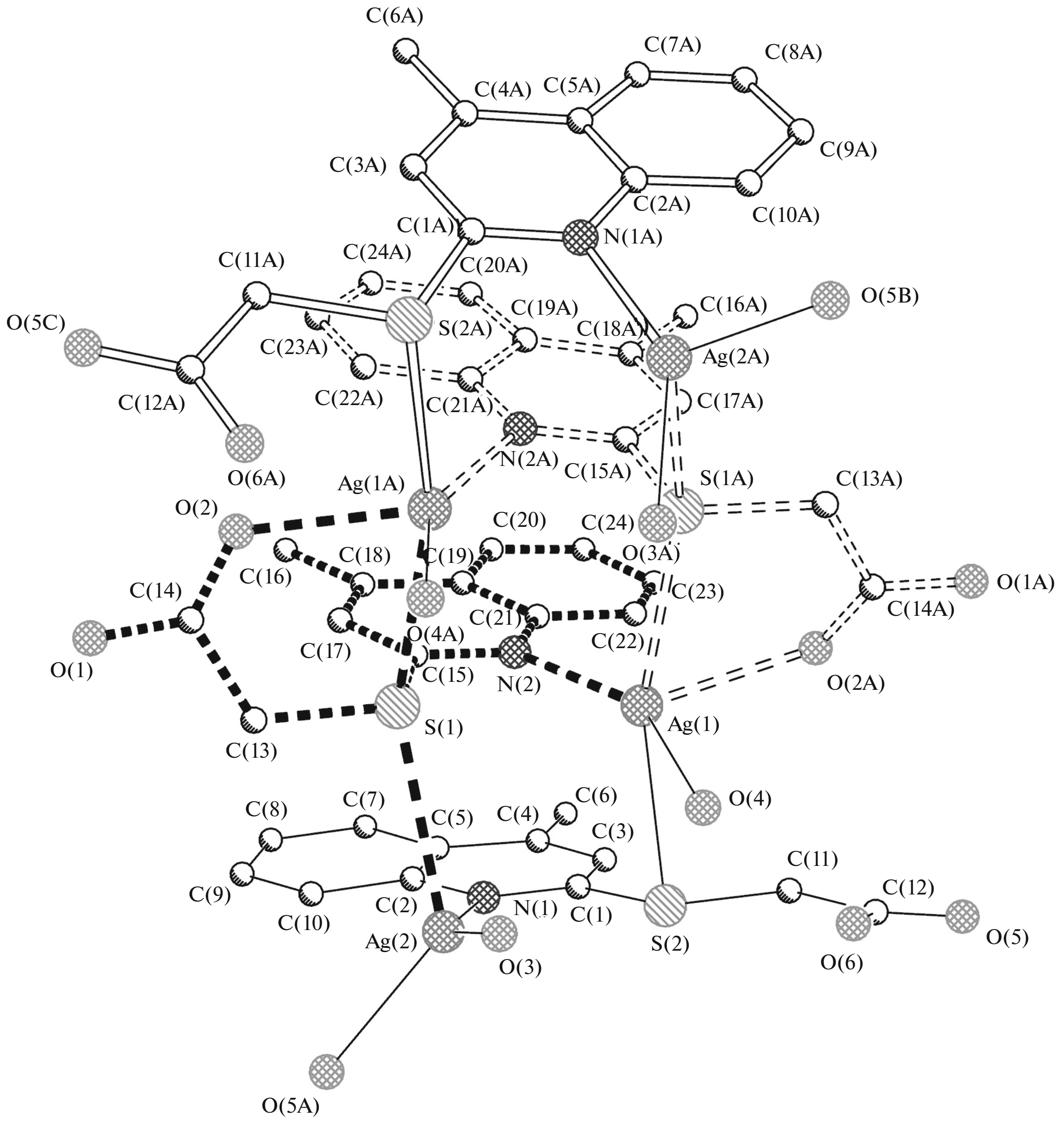

Fig. 1. A fragment of structure **I**: the coordination environments of the Ag(1) and Ag(2) atoms.

When kept in air, the crystals are stable for 2 weeks; on further storage, they gradually lose transparency, while retaining their shape.

X-ray crystallography. Experimental reflection intensities from a crystal of **I** were collected on an Enraf-Nonius CAD-4 automated diffractometer. The structure was solved by direct methods and refined by least-squares calculations in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [11]. Hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. The water protons were located from a difference Fourier synthesis. Unit cell parameters and selected experimental details are presented in Table 1.

Complete crystal data were deposited with the Cambridge Structural Database (no. 1475753; http://www.ccdc.cam.ac.uk/deposit/).

Photoluminescence spectra were recorded at room temperature on a Perkin Elmer LS-55 spectrometer (λ_{ex} = 200–800 nm, λ_{em} = 200–900 nm, instrumental resolution 0.5 nm, slit width d = 10–12 nm, a solid state attachment was used).

RESULTS AND DISCUSSION

Structure **I** is built by two crystallographically nonequivalent silver atoms, two independent tridentate bridging (due to the S, N, and O atoms) ligands L, and two independent H_2O molecules. The ligand donor

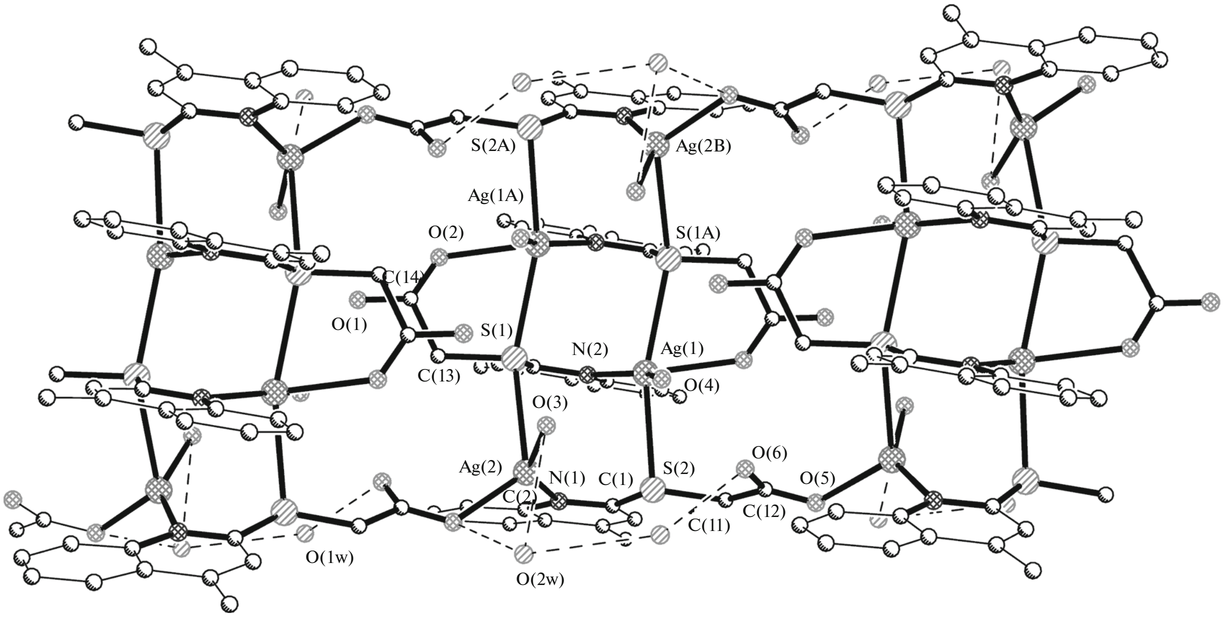

Fig. 2. Character of bonding of the independent $[Ag_4L_4]$ unit into infinite bands running in the [001] direction.

atoms and water molecules form the coordination environment of the Ag^+ ions (Fig. 1). In the distorted trigonal-bipyramidal polyhedron of Ag(1), the axial vertices are occupied by the sulfur atoms of two independent ligands L (Ag(1)–S(1A), 2.770(3) Å; Ag(1)–S(2), 2.780(2) Å; angle S(1A)Ag(1)S(2), 162.15(6)°). The equatorial plane is formed by the N(2) atom, the O(4) atom of the water molecule, and the O(2A) atom of the carboxylate moiety of ligand L (Ag(1)–N(2), 2.327(6) Å; Ag(1)–O(4), 2.484(6) Å; Ag(1)–O(2A), 2.425(6) Å; N(2)Ag(1)O(2A), 115.0(2)°; N(2)Ag(1)O(4), 150.8(2)°; O(2A)Ag(1)O(4), 94.2(2)°). This coordination mode of the donor atoms to the Ag^+ ion leads to the formation of the five-membered chelate ring $[AgO_2C_2]$, which is presumably responsible for a noticeable distortion of the Ag(1) coordination polyhedron. The second crystallographically nonequivalent silver atom Ag(2) (Fig. 1) has an irregular tetragonal coordination environment formed by the S(1), N(1), water O(3), and carboxylate O(5A) atoms (Ag(2)–S(1), 2.915(2) Å; Ag(2)–N(1), 2.216(6) Å; Ag(2)–O(3), 2.312(7) Å; Ag(2)–O(5A), 2.314(7) Å; N(1)Ag(2)O(3), 147.4(2)°; N(1)Ag(2)O(5A), 121.3(3)°; O(5A)Ag(2)S(1), 124.0(2)°; the other angles, in the range 85.2(2)°–90.2(3)°).

The interaction of Ag^+ with the ligands containing three donor sites leads to the formation of infinite $[Ag_4L_4]_n$ bands extended in the [001] direction. The

Table 2. Hydrogen bond geometry in structure **I**

A–H···B bond	A···B, Å	A–H, Å	H···B, Å	AHB angle, deg	B atom position
O(1w)–H(1)···O(2w)	2.852(8)	0.87	1.98	178	$-x - 1/2, y + 1/2, -z - 1/2$
O(1w)–H(2)···O(6)	3.112(8)	0.88	2.33	149	$x, -y + 2, z - 1/2$
O(2w)–H(3)···O(5)	2.825(7)	0.87	1.96	178	$x, -y + 1, z - 1/2$
O(2w)–H(4)···O(1w)	3.085(8)	0.92	2.37	135	$x, -y + 1, z + 1/2$
O(2w)–H(4)···O(3)	3.189(9)	0.92	2.64	119	$x, y - 1, z$
O(3)–H(5)···O(2w)	3.189(9)	0.96	2.31	133	$x, y + 1, z$
O(3)–H(6)···O(4)	2.907(8)	1.26	1.68	166	x, y, z
O(4)–H(7)···O(1)	2.715(7)	0.86	1.86	179	$x, -y + 2, z + 1/2$
O(4)–H(8)···O(6)	2.842(8)	0.94	2.12	132	x, y, z

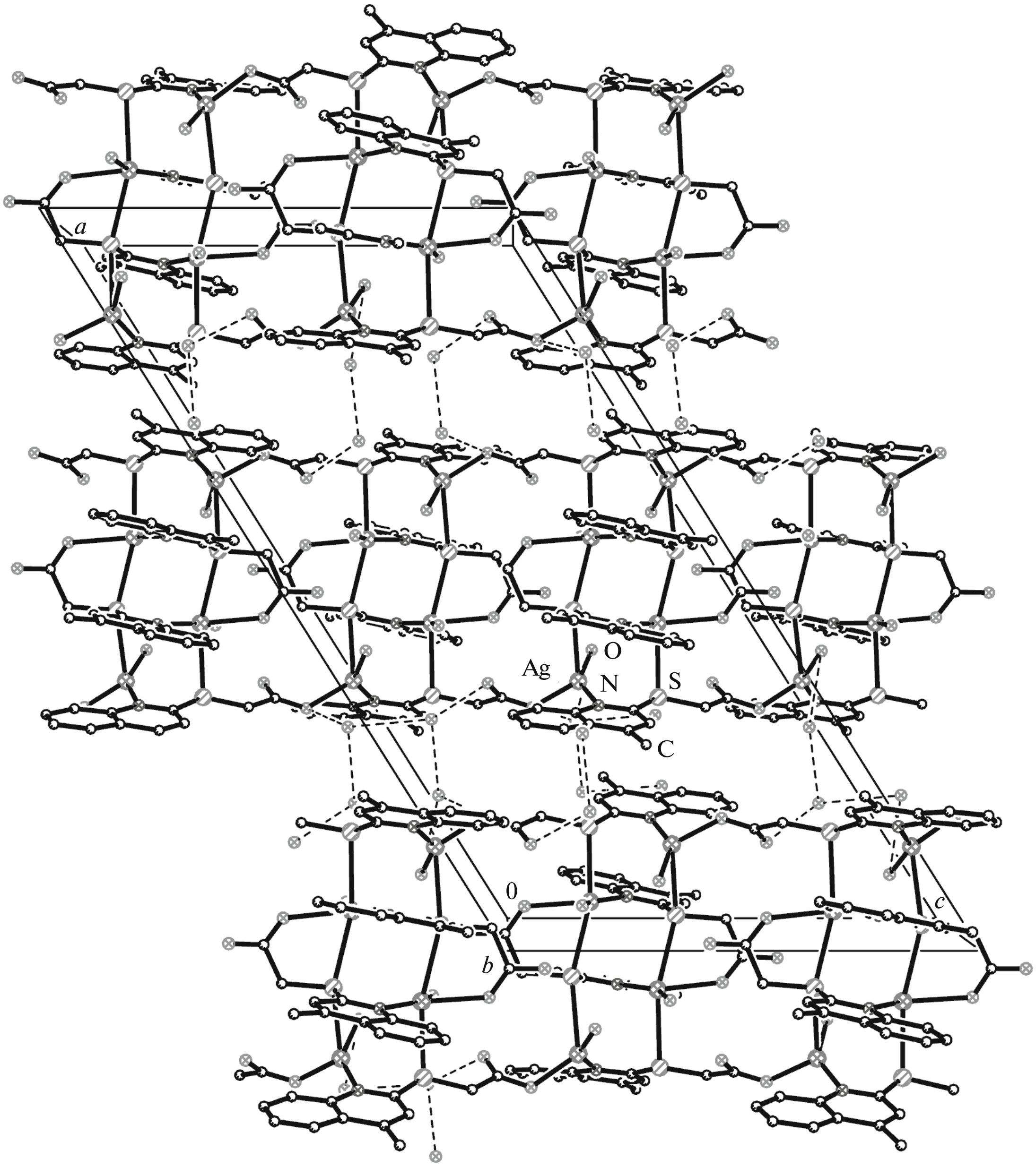

Fig. 3. Molecular packing of structure **I** from infinite bands alternating along the *a* axis at 1/2*a* intervals.

character of bonding of the independent [Ag_4L_4] unit into infinite [Ag_4L_4]$_n$ bands is shown in Fig. 2. The "width" of the [Ag_4L_4] band is 8.12 Å (the Ag(2)···S(2A) distance). The molecular packing of structure **I** consists of infinite bands alternating along the *a* axis at intervals of 1/2*a*. The bands are combined by an O–H···O hydrogen bond, which leads to a supramolecular framework structure (Fig. 3). Noteworthy is the presence of two types of water molecules in the structure—inner- and outer-sphere—involved in hydrogen bonding (Table 2) both as proton donors and proton acceptors.

Figure 4 shows the photoluminescence spectra of 4-methyl-2-quinolylthioacetic acid and its silver complex **I**. The spectrum of **I** shows two bands in the blue spectral range at ~450 and ~485 nm, which are lacking in the spectrum of the acid. They can be explained by ligand-to-metal charge transfer (LMCT mechanism) and electronic transitions (*ds*/*dp*) in the silver ion. Previously, we have observed an analogous effect for the $AgReO_4$ complex with quinoxaline [11]. The set of nearly

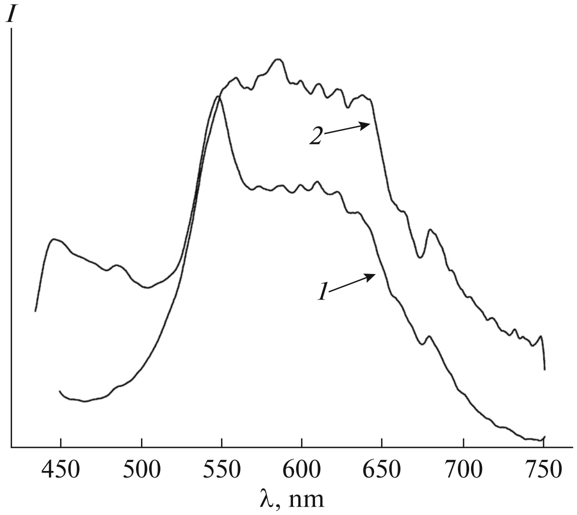

Fig. 4. Photoluminescence spectra of (*1*) compound **I** and (*2*) the acid at $\lambda_{ex} = 403$ nm and room temperature.

identical bands in the range 550–700 nm is associated with intraligand π → π* transitions in the acid.

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